PREUSSAG

SEIBERSDORF

Recycling Technologies, Treatment of Waste and Contaminated Sites

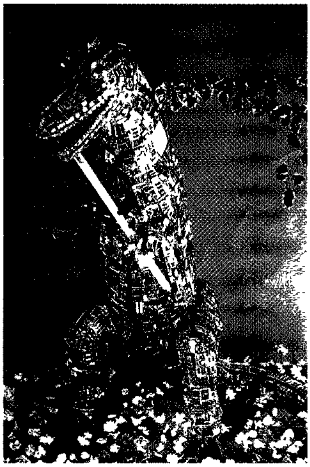
Workshop co-organized by

The Environment and Climate Programme
of the European Commission,
DG XII/D-1

and

Preussag AG

Report 15



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20 - 24 May 1996
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Editors:
J. Barton, B. Bilitewski, J. Büsing, D.V. Jackson, J. Jager,
M. Jauzein, P. Krejsa, K.H. Ujma

20 - 24 May 1996
Hannover, Germany

ISBN-3-9500255-5-3

Published by the

European Commission
Directorate-General XII
Science, Research and Development - Joint Research Centre
B-1049 Brussels

and the

Austrian Research Centre Seibersdorf
A-2444 Seibersdorf

ISBN-3-9500255-5-3

Printed in Austria

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European Workshop
on
Technologies for Environmental Protection:

Recycling Technologies, Treatment of Waste, and Remediation of Contaminated Sites

Hannover, 20 - 24 May 1996

Executive Summary

The workshop was jointly organized by the Environment and Climate Programme of the European Commission (DG XII/D-1) and the PREUSSAG AG in Hannover, Germany and is a continuation in the series of workshops held in previous years *) However, in contrast to earlier events, this workshop established for the first time the links between scientists working in the interrelated research areas with partly overlapping interests, i.e. life-cycle assessment, recycling, treatment of waste and problems related to contaminated sites.

The workshop was opened with welcoming speeches, by Mr. J. Rohde, member of the Executive Board of PREUSSAG AG, the host organisation, , by Secretary of State Dr Reinhardt from the Lower Saxony Ministry for Science and Cultural Affairs and by Dr. P. Reiniger, acting Head of Unit of Directorate General XII/D-1of the European Commission.

On the occasion of a reception hosted by the Lower Saxony Ministry of Economy, Technology and Transport, speeches were given by the Secretary of State Dr A. Tacke and Dr. M Frenzel, Head of the Executive Board of PREUSSAG, presenting Lower Saxony's and in particular PREUSSAG's R&D activities in a European context.

Lower Saxony is renowned for R&D in material science, particularly metallurgical engineering so the first technical paper was by Prof. Leschonski from the Technical University of Clausthal and also Managing Director of Clausthal Environmental Institute, who reviewed research in progress within these organisations

This presentation was followed by critical reviews of waste management policies and strategies in the United States and in the European Union, presented by Dr. H Alter from the U.S Chamber of Commerce and by Mr. J Arribas-Quintana from the European Commission, Directorate General XI/ E-3.

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*) European Workshop on Technologies for Environmental Protection, Bilbao, Spain, 31 January - 3 February 1995, Report 7, EUR 16200 EN,
Recycling, Waste Management, Remediation of Contaminated Sites 1995, Technologies for Environmental Protection, Report 8, ISBN-3-9500255-7

The EC Institute for Prospective Technological Studies, Sevilla, Spain and its work in the area of environment, recycling and LCA was described by Dr D Papameletiou. Impartial studies, for example into LCA relating to plastic wastes, the European recycling industries and the proposed directive on integrated pollution and prevention control (IPPC), should promote greater technical and economic realism in environmental planning and policy making.

Reports on 37 shared cost research projects were presented and these are summarized separately under the three title subjects of the workshop Many projects were approaching completion, some were being continued or extended and some new new projects had been initiated only this year

Concerted actions can be cost effective in promoting and exploiting R&D within the European Union and also insuring international collaboration particularly in the environmental protection field. The following three new concerted actions were presented at the workshop:

LCANET has been set up to establish a European network for strategic life cycle assessment research and development The main objective is the publication of an encompassing document describing the state-of-the-art of present LCA methodology and applications and a coherent strategic LCA research programme establishing the links to the research area "Environmental Technologies". Coordination in this field is essential for harmonisation and to ensure that LCA is developed for effective use.
NICOLE, a Network for Industrially Contaminated Land in Europe, is an industry initiative aimed at providing a forum for discussion and exchange of scientific and technological ideas and for coordination of collaborative R&D in this field.
CARACAS, a Concerted Action on Risk Assessment for Contaminated Sites, is oriented towards the development of guidelines and recommendations in this area

A specific task of the concerted actions is the identification of future research priorities The short-term priorities identified by the individual concerted actions are annexed to this report

During the course of the workshop three separate one hour sessions were devoted to open discussions and debate, led by Dr Harvey Alter, on the subject of thematic networks. The aim was to explore how future R&D work can be organised in order to achieve optimum results through coordination and collaboration among multidisciplinary team throughout the EU, and internationally where appropriate Although no final conclusions were reached many ideas and concepts were discussed which will undoubtedly facilitate further research planning

In addition to the technical session two most interesting visits were arranged: to the PREUSSAG subsidiary Electrocycling GmbH, dealing with the recycling of electronic scrap and to a pyrolysis plant in Salzgitter.

The week was an undoubted success and full credit must be given to the PREUSSAG AG for excellent organisation and generous hosting of the workshop.

The Steering Committee

PREUSSAG

Presse-Information

Speech by:

Dr. Michael Frenzel

at the Lower Saxony government reception at the opening of the European Workshop on

"Recycling Technologies, Treatment of Waste and Contaminated Sites"

20 May 1996, 5.30 pm, Medical Park Hannover

Actual speech may differ slightly from this text.

Permanent Secretary Tacke,
Ladies and Gentlemen,

The European Commission and Preussag AG are this year's hosts for the 4th European Workshop on Recycling Technologies, Treatment of Waste and Contaminated Sites. I would again like to warmly welcome all workshop participants who have travelled to Hannover with the purpose of reporting on their EU Environment and Climate Programme research projects, and to share their knowledge and experience.

I would also like to welcome to this evening's event, all guests, who by coming here, have expressed their interest in the scientific, economic and political significance of the environmental technologies being discussed.

The government of Lower Saxony has energetically supported the preparations for the workshop and the programme organisation, for which I would again like to give special thanks to permanent secretary Tacke. Tonight's event is an excellent example of successful collaboration between the European Union, the Lower Saxony government and business.

German companies are advocates and pioneers of European integration Naturally, this also includes the international commodities and technology Group, Preussag. We recognise that the potential for growth in our core businesses of steel, energy trading and logistics, plant engineering and building engineering, will increasingly lie in international markets. At the same time, the EU countries remain very important markets for our products and services. This is particularly true against the background of eastward expansion and the EU's new pro-active Mediterranean policies.

Brussels is setting the agenda for the future development of the European Union and the internal marked. We have therefore made it our objective to further strengthen our dialogue with the European Commission. Preussag considers this to be a vital factor in the Group's international realignment.

I am therefore delighted that by organising the 4th European recycling workshop we have been able to make an important contribution to enhancing the close exchange of ideas in an important field of European integration, namely, in research and development. For this I would like to thank the European Commission representatives, who I would again also like to warmly welcome to this evening's event.

Research and development have become a crucial factor in global competitiveness. Preussag therefore invests a great deal of time and effort in innovations. This amounted to more than DM 600 million in the previous financial year. Many of the innovations we have developed are in the field of plant engineering, building engineering and environmental technology. And we intend to continue to invest heavily in important research areas.

Particularly against the background of global competition, it is vital that there is a favourable framework in place to nurture innovation. And there is still room for improvement here. I am thinking in particular of the approval procedures and the, as yet, unforthcoming corporate tax relief for investment in R&D. Technology and research policies as a whole need to be more strongly aimed at enabling companies to establish their new products and processes in the market.

I therefore warmly welcome the European Commission's statement that their research and technology policies will be more clearly oriented to market requirements. This is a vital step, as is the continuous critical evaluation of the application procedures for the research programmes - which, in the interests of the matter in hand, are clearly still not sufficiently unbureaucratic.

Preussag is participating successfully in the EU research programmes and will continue to make use of these collaboration opportunities in future.

The above mentioned focus environmental technology within our research and development programme shows that Preussag is intimately involved in the subjects of this European research event. Our Group companies are equipped with well proven environmental technologies for use in national and international markets. We can provide complete service packages from waste treatment, through recycling, to clean-air measures, water treatment and soil remediation. In addition, our first class technical solutions are complemented by a comprehensive service spectrum encompassing advice, complete responsibility for plant operation, and financing.

On the one hand, Preussag manufactures environmental technology plant and equipment. On the other hand, we also operate our own environmental technology installations, such as recycling facilities. The Group companies, Preussag Recycling GmbH and Elektrocycling GmbH, are leaders in the recycling of vehicles and electronic scrap respectively. The recycling, utilisation, and disposal carried out by these companies meet the highest ecological policy requirements for comprehensive recycling and proper disposal. Our technologies enable valuable materials to be efficiently recycled.

The participants at this workshop will have the opportunity of visiting the Elektrocycling plant in Goslar, and to see the state-of-the-art recycling of objects ranging in size from telephones, through televisions and PCs to large main frame computers.

Business has invested a great deal of time and effort in complying with environmental legislation. And in the area of recycling, our technical solutions have even exceeded the legislative and political demands. I therefore very much hope, that in the field of electronic recycling in particular, prudent legislation will be enacted to guarantee comprehensive, environmentally-compatible recycling.

Another example of Preussag's range of environmental technologies is waste treatment. Despite waste minimisation policies and recycling, a significant amount of waste still requires proper disposal. At this point I would like to point out that for many years now Preussag has maintained its commitment to thermal utilisation processes - where these make technical, economic and ecological sense. We did not allow ourselves to be swayed by a public opinion at the time, which was predominantly critical of this type of technology. However, public opinion has recently swung into our side. The advantages of thermal utilisation are now widely recognised - justifying our determined stance on this issue.

For instance, the Noell Conversion Process is an effective solution for the clean disposal of residual waste. This process combines pyrolysis with entrained-bed gasification to produce a range of marketable products such as systhesis gas for the chemical industry, ferrous and non-ferrous metals, electric power, heat and granulate. The conversion process generates no waste water and a minimum amount of residuals. This technology gives us a sophisticated marketable solution which also meets the highest standards of environmental protection.

Let us not forget that in addition to these new technologies developed by the Preussag Group, Preussag also has a long tradition of commitment to recycling. I am thinking in particular here of the various recycling methods incorporated in our production processes. For instance, we are among the world leaders in the use of recycled materials for non-ferrous metal production. Our steel production also embraces many aspects of recycling. The virtues of steel itself as an extremely environmentally-compatible material - with unmatched recyclability - are well known. The conversion of the Peine Steel Works to electric steel metallurgy will allow us to use considerable volumes of scrap in the production cycle and thus make another important contribution to recycling and the efficient use of resources. The new electric furnace in Peine will be officially commissioned in a few days on 24 May. This will be another milestone for the recycling industry in Lower Saxony.

The 4th European Workshop for Recycling Technologies, Treatment of Waste and Contaminated Sites is concerned with transparency, information, coordination, cooperation and synergy - in short, all of the factors which must be embraced in all areas by competitive companies. The environment for a substantive exchange of ideas and experience is therefore in place! I wish the workshop participants a successful meeting, and everybody a pleasant evening of stimulating discussions.

Waste management policies and strategies in the United States

H. Alter

Resources Policy Department
U.S. Chamber of Commerce
USA - Washington, D.C. 20062
Tel: +1-202.463.5531
Fax: +1-202.887.3445

WASTE MANAGEMENT POLICIES AND STRATEGIES IN THE UNITED STATES[1]

Harvey Alter, Ph.D.
U.S. Chamber of Commerce
Washington, D.C. 20062 U.S.A.

Introduction

The United States established a national solid waste policy in 1965 with the passage of the Solid Waste Act, which was directed at closure of open dumps (open, burning pits of garbage), comprehensive solid waste planning at the state level, and establishing an R&D function. There have been several amendments to the law since then, which has increased its scope considerably. Many policy developments are at the state and municipal levels of government and generally beyond the scope of this paper.[2]

Solid wastes are classified by current U.S. federal law (the Resources Recovery and Conservation Act, or RCRA) as hazardous or non-hazardous. The latter includes municipal solid wastes (MSW) and industrial wastes. Mining and some other large volume, low toxicity wastes are an additional classification (named Bevill wastes after the Congressman who devised the scheme). Agricultural wastes are generally not regulated with the notable exception of large volume animal wastes (*e.g.* from feedlots), which are managed in accordance with the Clean Water Act.

The definition of solid and hazardous wastes under U.S. law is vague and controversial. RCRA defines solid waste as garbage, refuse, sludge, liquid, semi-solid, or contained gaseous material, or that "solid waste" can be gas, liquid, or solid. This accounts partially for the seemingly disproportionate generation of wastes in the Untied States compared to other countries.

A hazardous waste is a solid waste that, because of quantity, concentration, or physical, chemical, or infectious characteristics contributes to an increase in mortality or serious irreversible, or incapacitating reversible illness, or poses a substantial hazard to human health or the environment when improperly managed. The inclusion of mismanagement in the statutory definition has driven a great deal of the national policy on control of hazardous waste management.

National policy is to assure management of hazardous wastes from "the cradle to the grave" and with great assurance (some would argue over-assurance) of protection of human health and the environment. The law addresses management in great detail, as will be summarized below. There is some delegation of authority to states but only after they qualify. At the same time, federal law makes little mention of non-hazardous wastes much beyond prescribing sanitary landfill siting and design criteria. There is a small federal presence in medical wastes programs, prescribing that ring

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[1] Paper prepared for the European Workshop on "Environmental Technologies": Recycling, Waste Management and Remediation of Contaminated Sites. 20-24 May 1996. Hanover, Germany. Sponsored by the European Commission, Directorate General for Science, Research and Development, DG XII-D-1. Environmental Technologies.

[2] For an excellent history of municipal waste management in the United States, see: M. V. Melosi. 1981. *Garbage in the Cities. Refuse, Reform, and the Environment. 1880-1980.* Texas A&M Press. College Station.

connectors for beverage cans must be photodegradeable,[3] and for the cleanup of leaky underground storage tanks. Most of the management of non-hazardous wastes is overseen by the states.

For about the past decade there has been great emphasis on waste reduction programs (notably most successful with industrial hazardous and non-hazardous wastes) and with MSW recycling. Industrial recycling, which is a very large activity,[4] has long been difficult to define and regulate.

Hazardous Wastes

RCRA regulations comprehensively elaborate on the statutory definitions of a solid waste as any discarded material, abandoned, recycled or considered "inherently waste-like"; spent materials that can no longer serve, sludges, by-products ("a material ...not solely or separately produced by the production process ... slags or distillation column bottoms"), and discarded commercial chemical products. Further, materials are solid wastes if managed in a manner constituting disposal, burned for energy recovery, speculatively accumulated, or reclaimed prior to be recycled. Other notable exemptions are materials that are recycled by being used, reused, or returned to their original production process and domestic sewage sludge. Scrap metals are excluded, which assists recycling. However, the inclusion of by-products and reclamation prior to recycling discourages recycling. Many argue that reclamation is a manufacturing process, beyond the reach of RCRA, and not waste treatment. Discussions of the distinction between a hazardous substance and a hazardous waste are as long as they are fruitless.

A solid waste may be a hazardous waste if it possesses certain characteristics or is listed. The characteristics are corrosivity ($10 \leq \text{pH} \leq 1$); ignitabilty (flammable liquids are defined by flash point and combustible solids by ignition temperature); reactivity (*e.g.*, oxidizing agents, including explosives); and toxicity. Toxicity is measured by preparing an extract of the waste (finely ground) using a buffered acid. The extract is analyzed for approximately 400 constituents. The quantities found, divided by a dilution and attenuation factor (DAF), are compared to the regulatory levels. If any of the latter are exceeded, the waste is characteristically hazardous.

This Toxicity Characteristic Leach Procedure (TCLP) is intended to simulate, and thus protect against leachate leaking from a landfill into the soil, being diluted and attenuated (hence the DAF), and reaching an underground aquifer. The value of the DAF is a subject of some controversy. Some models have shows the $\text{DAF} \approx 140$ but the regulators conservatively lowered this to 100. Some investigators have considered the entire fate and transport of leachate plumes through different kinds of soil. The leachate may ion exchange with the soil, hydrolyze, physically or chemically adsorb, become diluted, anaerobically decomposed, or simply not move. Site and material specific DAF values may be 10,000 or more, but such values are not used in regulatory determinations.

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[3] Obviously this applies to a minuscule portion of the waste stream. The requirement was imposed because of marine littering, the careless discard of the connectors (and some other items) into the water. There is no agreement exactly what "photodegradeable" means or whether the polymers used (*e.g.*, poly(ethylene-co-carbon monoxide) photodegrade in the water.

[4] It is possible to account for more than 260 million tonnes of material recycled annually at the industrial level as a minimum. Much is recycled in-house and, because of absence of a commercial transaction, is not always included in the statistics. See: H. Alter. 1996. Industrial Recycling and the Basel Convention. Submitted to ***Waste Management & Research***. Also: H. Alter. 1995. The Recycling of Industrial Materials. Paper presented at R'95-Recovery, Recycling, Re-integration. ***Proceedings***, vol. II, pp. 59-65.

In spite of the RCRA emphasis on mismanagement, federal law prescribes detailed management and design standards for hazardous wastes. For example, a landfill must be double-lined (to a specified low permeability), be equipped for leachate collection, and have leachate monitoring wells installed. The TCLP (using a buffered acid) and monitoring are based on a mismanagement scenario of hazardous waste being mixed with biodegradable organic wastes (such as MSW), which is illegal. Hazardous waste incinerators are also carefully regulated including specifying the temperature, residence time, and destruction (typically 99.99+%). The management system includes tracking of the waste from point of origin to point of disposal, with transportation by specially certified carriers.

Many hazardous wastes are prohibited from being placed on the land (including in a landfill) until after they have been treated by the Best Demonstrated Available Technology (BDAT). This technology driven standard is to insure that no liquids (or other mobile moieties) are disposed of in landfills and that everything is treated to minimize the threat to human health and the environment. These well-sounding words have been the subject of different interpretations and court cases.

The United States generates approximately 276 million tonnes of hazardous waste annually, far more than that reported by other countries. The reason is that the U.S. system includes the total of dilute aqueous solutions as hazardous waste. Some 95% of all U.S. hazardous waste is water and approximately 96% of all hazardous waste is treated on-site. The destiny of these wastes are shown in Table 1.

Recycling of Hazardous Wastes

Many hazardous wastes, such as those with high contents of metals, are valuable resources. For example, the air pollution control dusts from electric arc furnaces and the water pollution control sludges from metal finishing, are listed hazardous wastes and rich in metals (Fe, Zn, Cr, Pb, Cu, etc.). For the most part, the recycling of such wastes is regulated the same as the treatment and storage of hazardous wastes. This raises the cost of recycling considerably. More troublesome is that under U.S. regulations any material derived from the treatment of a listed hazardous waste is hazardous. Thus, something like the slag from the pyrometallurgical recovery of metals from furnace dusts are defined as hazardous — independent of their characteristics or properties. There are some current regulatory proposals to "fix" this.

Table 1
Disposal of Hazardous Waste in the U.S.[5]
1991

Management System	Percent Managed
aqueous physico-chemical	76
deep well injection	~ 8.5
landfill	~ 0.5
incineration	1.1
recovery	2.2

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[5] OECD. 1996. *Environmental Performance Reviews. United States.* Organization for Economic Cooperation and Development. Paris.

Any discussion of the regulation of recycling invariably becomes entangled in two controversies. One is over the definition of what is a solid waste and the word "discard". The other is the confusion over sham recycling or the illegal disposal of wastes masquerading as recycling. Legitimate recycling (the opposite of sham) has been defined, which should assist regulators.[6]

There have been proposals to regulate the recycling of hazardous reclaimable materials, those that would be a hazardous waste if sent for final disposal. In several respects the regulations would be the same for the hazardous reclaimable materials and their counterpart wastes — such as for transportation, storage and handling. This should give regulators and the public confidence that human health and the environment are being protected while achieving the benefits of recycling and without the stigma or confusion with waste treatment.

A material becomes a waste when it is discarded, meaning no one has any further interest in the waste other than final disposal. The same "waste" is a secondary raw material when it is sent for recycling, reuse, or returned to the same process. The destination should determine the definition, which is a difficult concept in a regulatory system. Discussions of this approach have begun in the United States.

High Volume - Low Toxicity Wastes

Very large quantities of low toxicity wastes are generated, such as from mining, oil and gas exploration, coal-fired power plants and cement kilns. In 1984, one of the amendments to RCRA called for a study of such "Bevill" wastes and a determination how they should be managed. The general consensus of the studies done so far is that the toxicity of these wastes does not justify their management as hazardous wastes. The U.S. EPA has raised questions whether special management is needed for cement kiln dusts (independent of whether hazardous wastes were burned as part of the fuel) and has recently proposed special rules for mining wastes.

Municipal Solid Waste

MSW is defined in the United States differently than elsewhere. MSW includes the arisings from households, institutions (such as offices and universities), and commercial establishments. Approximately 45 to 50% of U.S. MSW is household waste.

In most OECD countries, MSW is loosely defined as that which the municipality collects, which is mostly from households. When the U.S. generation of MSW is divided by half, the *per capita* generation is about the same as other developed countries. This is shown in Table 2. In comparing such data, it must be kept in mind that the definition of MSW and the survey methods may vary from country to country. The differences in the values in Table 2 are not likely statistically significant.

The average rate of growth (tonnes/year) of the amount of MSW disposed of over the past 20 years or so has been greater than the rate of growth of population, which has been 1.1% per year. Moreover, the rates of growth of major categories of MSW disposed of are higher than the rate of growth of population — except for packaging. This is shown in Table 3. Nonetheless, packaging has its critics in the United States, the same as in the European Union. The only major packaging restriction is in the nine states that have some sort of beverage container deposit or other control system. For more than a decade, no additional states have passed such laws and no state has repealed

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[6] See footnote 4. The 1996 paper cited discusses a definition of legitimate recycling and offers an outline of how to achieve environmentally sound management.

its law. Such deposits and recycling are not always compatible.[7]

Table 2
Comparative Generation of MSW in
OECD Countries, 1992[8]
kg/capita/y

Country	**Generation**
USA (corrected)	365
Japan	410
France	470
Germany	360
United Kingdom	350
Italy	350

Table 3
Average Increase in Amounts of MSW
and its Major Categories Disposed
U.S., 1970-1993[9]

Waste Category	**Avg. Increase %/y**
all MSW	1.7
durable goods	2.8
non-durable goods	3.3
packaging	0.9

The amounts of MSW managed by landfilling, waste-to-energy, composting and recycling in the United States are shown in Table 4 for 1993. (Materials recovery for previous years was 16.6% in 1990 and 9.6% in 1980.) This recycling includes that from all portions of U.S. MSW. Calculations show that the greatest opportunities for increasing the recycling are with the non-household portion.[10] The same studies concluded that recycling much over 25% will require more effort and cost and reaching some stated goals of as much as 40%, will require tremendous effort, cost, and new infrastructure.

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[7] H. Alter. 1993. Cost of Recycling Solid Waste with and without a Concurrent Beverage Container Deposit Law. *The J. Consumer Affairs* 27(1) 166-186.

[8] OECD, *op. cit.*

[9] Derived from Franklin Associates, Ltd. 1993. Characterization of Municipal Solid Waste in the United States. 1993 Update. Prairie Village, KS.

[10] Franklin Associates, Ltd. "The Role of Recycling in Integrated Solid Waste Management to the Year 2000." Prepared for Keep America Beautiful, Inc., Stamford, CT.

Table 4
MSW Management in the U.S.
% of Generation, 1993[11]

Management Method	Percent
materials recovery	21.7
composting (not backyard)	18.6
combustion with energy recovery	14.8
combustion, no energy recovery	1.1
sanitary landfill	62.4

Some states have set very high goals, such as 40% recycling and 10% waste reduction, and some local governments even more, as much as 60%. Few, if any, have any mechanism to achieve these goals. One state set even higher goals and nearly achieves them by re-defining MSW to include heavy iron, shredded automobiles,[12] and crushed discarded concrete and asphalt from construction and demolition.

The Basel Convention

No discussion of waste management policies would be complete without a discussion of the Basel Convention on the Transboundary Movement of Hazardous Wastes and their Disposal and the U.S. position. This U.N. Convention was signed in 1989 and came in force in 1992 when 20 countries ratified it. Approximately 100 countries have ratified the Convention, not including the United States.

The Convention was negotiated to stop the egregious final disposal of hazardous wastes in developing countries, particularly by developed countries. This has virtually stopped. However, the Convention defines disposal so as to include recycling. It addresses the intrinsic hazard of wastes, independent of the way they are managed. Hazardous wastes are defined as something from a listed waste stream or containing a listed constituent and exhibiting one of the characteristics in another list of the Convention. The characteristics are given generally without test methods or numerical limits. Further, the Convention is worded so that whether a waste contains one of the listed constituents, or whether it exhibits the characteristic, are rebuttable presumptions. This means the proving of two negative hypotheses, something impossible in science or logic.[13]

The Basel Convention establishes a systems management regime for the control of "Basel" wastes (not to be confused with *e.g.*, U.S. hazardous wastes or the E.U. waste catalog) including: prior informed consent, shipment only to facilities with environmentally sound management, using the U.N. Code on Transport of Dangerous Goods, and ultimately there will be training programs and a liability protocol. The contracting parties to the Convention (*i.e.*, the countries ratifying) instead of stressing this control regime have elected to impose an export ban on some countries (mostly

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[11] Franklin Associates, Ltd. *op. cit.*

[12] More than 95% of end-of-life vehicles are recycled in the United States with about a 75% yield.

[13] For a more detailed discussion of the Basel Convention, see footnote 4 or K. Kummer. 1995. *International Management of Hazardous Wastes*. Claredon Press. Oxford.

OECD) of wastes for either final disposal or recycling. The latter denies importing countries needed raw materials because of the ambiguities in the definition of hazardous wastes. The recycling ban decision (subject to ratification and not effective before 1998) substitutes a political ban, and disposal in the generating countries, instead of recycling as a major waste management method.

The United States government, with the strong support of U.S. industry, has chosen not to ratify the Convention at this time because it is not in the national interest. The U.S. has an annual net positive trade balance of approximately $6 billion in recyclable commodities, much of that to non-OECD countries.[14] As long as the definition of a hazardous waste is ambiguous, that entire amount is potentially at risk. Prohibiting emerging economies from receiving needed raw materials relegates them to mercantilistic and possible neocolonialistic status, which is also contrary to U.S. national interests. At the present time, the Basel Convention is not good waste management.

The Future of Solid Waste Management

There is a growing trend among municipalities to charge for MSW collection by volume or mass. Containers are coded, sometimes weighed, and other schemes are used. In some instances, containers of material for recycling are collected "free" in order to encourage the practice. Of course the cost of such collection is included elsewhere. It is not yet decided if such methods reduce waste generation. The marginal cost of collection is very low.

Other trends are to very large, privately owned landfills (which put an end to claims that the country was running out of landfill capacity), privatization of collection services, and promotion of recycling. The limit to the amount of material that can be recycled has been described, but is not accepted by enthusiasts.[15] The composition of MSW is changing (particularly the amount of packaging for recycling), which makes household separation and subsequent recycling more problematical in the future.[16] Like elsewhere, myths of municipal solid waste persist.[17]

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[14] The total world trade in just scrap metals and metal-bearing materials has been estimated at $36 billion a year. See: U. Hoffman. 1995. *A Statistical Review of International Trade in Metal Scrap and Residues.* United Nations Commission on Trade and Development. Printed by the International Council on Metals and the Environment. Ottawa.

[15] See footnotes 10 and 16.

[16] H. Alter. 1991. The Future Course of Solid Waste Management in the U.S. *Waste Management & Research* 9(1) 3-20.

[17] H. Alter. 1992. The Myths of Municipal Solid Waste. *Solid Waste & Power* July/August. pp. 46-55.

The community strategy for waste management

J. Arribas-Quintana

European Commission
DG XI/E-3
B - 1049 Brussels
Tel: +32-2.296.23.14
Fax: +32-2.299.10.68

THE COMMUNITY STRATEGY FOR WASTE MANAGEMENT

Javier Arribas-Quintana
European Commission, Directorate General XI, E-3

Executive summary

Waste management policy is one of the key sectors identified by the 5th Environmental Action Programme whose primary goal is the achievement of sustainable development. Community waste legislation started in 1975. In 1996, twenty years later, a complete legal framework is in place: Directive 75/442/EEC on waste, Directive 91/689/EEC on hazardous waste and Regulation (EEC) 259/93 on shipment of waste, contain the basic definitions, rules and principles of the Community waste policy. This three pillar framework is completed by specific legislation, already adopted (packaging, batteries, hazardous waste incineration), or in the last stages prior to final adoption (landfill, PCBs/PCTs). Furthermore the Community Strategy for waste management, adopted in 1989 and currently being reviewed, establishes the guidelines for the Community waste policy, namely, priority to prevention, promotion of recovery, minimization of final disposal and regulation of waste shipments. Future Community actions will have to concentrate on appropriate implementation and enforcement of existing legislation, promotion and use of a broad range of non-legislative instruments and exploration of other fields for actions such as promotion of market recycling, minimization and prevention of specific waste streams, etc..

Résumé

La politique de gestion des déchets est reconnu comme un secteur clé par le 5ème Programme d'Action Environnemental, dont le but principal consiste en la réalisation d'un développement durable. La législation communautaire en matière de déchets est née en 1975. Vingt ans plus tard, en 1996, un cadre législatif est en place: les directives 75/442/CEE relative aux déchets et 91/689/CEE relative aux déchets dangereux, et le règlement (CEE) 259/93 sur le transfert des déchets contiennent les définitions, les règles et les principes de base de la politique communautaire dans le domaine des déchets. Cet encadrement, qui repose sur les trois piliers mentionnés ci-dessus, est complété par une législation plus spécifique, déjà adoptée (emballages, piles, incinération de déchets dangereux) ou aux stades ultimes précédant l'adoption (décharges, PCB/PCT). Par ailleurs, la Stratégie Communautaire pour la gestion des déchets, adoptée en 1989 et en cours de réexamen, établit les lignes directrices de la politique communautaire de gestion

des déchets: priorité à la prévention, promotion de la valorisation, minimization de l'élimination finale, et réglementation du transfert de déchets. Les actions communautaires à venir devront donc se focaliser sur la mise en oeuvre effective de la législation existante, la promotion et l'usage d'un large éventail d'instruments non législatifs et l'exploration de possibles actions dans des domaines, tels que la promotion des marchés des produits recyclés, la prévention et la réduction de certains flux spécifiques de déchets etc..

Zusammenfassung

Abfallwirtschaftspolitik ist einer der vom fünften Umweltaktionsprogramm herausgestellten Kernbereiche, dessen Hauptziel in der Erhaltung einer nachhaltigen Entwicklung besteht. Gemeinschaftliche Abfallgesetzgebung gibt es seit 1975. Im Jahre 1996, 20 Jahre später, ist ein abschließender rechtlicher Rahmen in Kraft: Die Richtlinien 75/442/EWG über Abfälle, 91/689/EWG über gefährliche Abfälle und die Verordnung (EWG) Nr. 259/93 über die Verbringung von Abfälle, die die wesentlichen Definitionen, Prinzipien und Grundlagen der Gemeinschaftsgesetzgebung im Abfallbereich enthalten. Dieser auf drei Eckpfeiler gestützte Rahmen ist vervollständigt durch spezifische Gesetzgebung, die bereits verabschiedet (Verpackungen, Batterien, Verbrennung von gefährlichem Abfall) oder im letzten Stadium vor der endgültigen Verabschiedung (Deponien, PCB/PCT) ist. Ferner legt die 1989 verabschiedete Gemeinschaftsstrategie für die Abfallwirtschaft, die derzeit überarbeitet wird, die Leitlinien der Abfallpolitik der Gemeinschaft fest, namentlich den Vorrang der Vermeidung, die Förderung der Wiederverwertung und die Minimierung der endgültigen Beseitigung sowie die Regelung von Abfallverbringungen. Künftige Gemeinschaftsaktionen werden sich darauf konzentrieren, bestehende Gesetzgebung in geeigneter Weise umzusetzen und zur Geltung zu bringen, eine breite Palette nicht-legislativer Instrumente zu fördern und zu nutzen sowie andere Aktionsbereiche zu untersuchen, etwa die Förderung von Märkten im Recyclingbereich und der Minimierung und Vermeidung spezifischer Abfallströme.

I. INTRODUCTION

Pollution has been with us since the beginning of time. However, only with industrialisation and increasing congestion has it become a real problem. This problem is now urgent. Our task - a task which we have already begun - is to find a coherent and effective response to the problem.

The Community environmental policy was initiated in the early 1970's. At that time, there was no clear legal basis in the Treaty of Rome to establish such a policy. In 1973 the Community adopted its first environmental action programme (EAP); since then, another four programmes have followed and more than 200 pieces of legislation on environmental matters have been adopted at Community level. During this period, (more than 20 years), Community policy has moved from a philosophy based on remedial actions to a completely different one focused on a preventive approach. This approach has been concretised in the 5th EAP adopted in 1992, and recently revised, for which sustainable development is the key concept and the primary goal to be achieved.

With the entering into force of the Single European Act in July 1987, and the Maastricht Treaty on the European Union, in November 1993, the Community policy on environment has been formally included in the Treaty. Its Article 130r spells out the principal objectives of this policy: precaution and prevention are to the fore; environmental damage, as a priority should be rectified at source and the polluter should pay. Furthermore, environmental requirements must be integrated into the definition and implementation of other Community policies.

Since its inception in the early 1970's, Community Environment Policy has moved from an approach emphasising remedial actions to a clear focus on prevention. This development of the basic philosophy is reflected in the Community's Waste Policy.

II. THE WASTE MANAGEMENT POLICY IN THE EUROPEAN UNION

The 5th EAP identified waste management as one of the key sectors of the Community environmental policy. Although legislation on this sector started in 1975 with the adoption of Council Directives 75/339/EEC[1] on waste oils and 75/442/EEC[2] on waste, a concentrated effort to create a coherent and complete legislative framework on waste has been made in the last seven years, since the first **Community Strategy for Waste Management**[3] was adopted in September 1989. Six years later the Commission submitted a **Report to the Council and Parliament on waste management**[4] presenting its results towards setting up a comprehensive policy to deal with all waste in the Community. Since the Strategy was adopted, action in this field has been developed in the following five areas:

- prevention,
- promotion of recovery,
- minimization of final disposal,
- regulation of transport,
- remedial action.

These major themes have inspired both the legislation adopted since 1989 and the programming of future Community action.

The strategy called for a consistent approach to waste management in the Community, an important precondition of which was the establishment of a suitable legal framework of basic definitions and concepts. This has been promoted through the following three pieces of legislation, which currently constitute the backbone of the waste management policy:

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[1] OJ 1975, L 194, p. 23

[2] OJ 1975, L 194, p. 39

[3] SEC (89) 934 final, 18.9.89

[4] COM (95) 522 final, 8.11.95

- **Council Directive 91/156/EEC**[5], amending **Directive 75/442/EEC on waste,** is the key legislative instrument of the EU waste policy. It provides for a definition of waste, further developed by the European waste catalogue. It lays down the principles of proximity and self sufficiency regarding final disposal operations, requires the establishment of waste management plans by the relevant competent authorities and foresees a permit and registration system for final disposal and recovery operations carried out by establishments and undertakings.

- **Council Directive 91/689/EEC on hazardous waste**[6], which replaces **Directive 78/319/EEC on toxic and dangerous waste,**[7] falls within the general framework of Directive 75/442/EEC on waste, as amended by Directive 91/156/EEC. It lays down additional, more stringent rules to take account of the special nature of hazardous waste. The Directive is designed to make the management of hazardous waste in the Community more effective, to use a precise and uniform definition of hazardous waste and to ensure that the disposal and recovery of hazardous waste is monitored as closely as possible. This precise and uniform definition had to be in the form of a list, the compilation of which proved very difficult. The Council adopted the list[8] on 15 December 1994.

- **Council Regulation 259/93/EEC on the supervision and control of shipments of waste within, into and out of the European Community**[9], replacing **Directive 84/631/EEC on the supervision and control within the European Community of the transfrontier shipment of hazardous waste.**[10] The Regulation is adapted to the new context of the single market and transposes into EC law the relevant international agreements, such as the Lomé IV Convention, the Basel Convention on the control of transboundary movements of hazardous waste and their disposal and the OECD decision on the control of transfrontier movements of waste destined for recovery.

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[5] OJ 1991, L 78, p.32.

[6] OJ 1991 L 377, p. 20.

[7] OJ 1978 L 84, p. 43.

[8] OJ 1994, L 356, p. 14

[9] OJ 1993 L 30, p. 1.

[10] OJ 1984 L 326.

Amongst other decisions taken under these international agreements, the Regulation bans the export of hazardous waste from the European Union to ACP countries. The Regulation takes account of the new approach of limiting movements of waste intended for disposal, in accordance with the principles of self-sufficiency and proximity, and regulates the control of movement of waste intended for recovery in order to promote recovery.

Furthermore, the Commission has proposed other, more specific measures to deal with waste disposal operations (incineration) or particular types of waste (batteries and accumulators, packaging), which have already been adopted by the Council. Further measures are in the last stages prior to final adoption (PCBs, landfill).

- After the Council adopted the **Directives on new** (89/369/EEC)[11] **and existing** (89/429/EEC)[12] **municipal waste incineration plants**, the Commission presented a proposal for a **Directive on the incineration of hazardous waste.** This Directive was adopted on 15 December 1994[13]. In view of the rapid development of technology in this area, the Commission is preparing a proposal for a directive on the incineration of non-hazardous waste to replace the two Directives on the incineration of municipal waste and to include non-hazardous industrial waste.

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[11] OJ 1989 L 163, p. 32.

[12] OJ 1989 L 163, p. 50.

[13] OJ 1994 L 365, p. 34

- The Commission has presented to the Council a proposal for a **Directive on the landfill of waste.**[14] The proposal introduces a horizontal framework imposing a specific authorization procedure for landfills and acceptability criteria for different types of waste for specific and appropriately prepared categories of landfill. It intends to prevent or reduce adverse effects on the environment as far as possible, and especially the pollution of surface water, groundwater, soil and air and the risks this can pose to human health. It lays down environmental and technical standards for the operation of landfills, based on a high level of environmental protection. It also lays down monitoring and control procedures for when landfills are closed down. Following favourable opinions from the European Parliament and the Economic and Social Committee, the Council adopted a common position on the proposal and the directive is expected to be adopted in 1996.

- With the aim of harmonizing disparate national laws, the European Parliament and the Council adopted a **Directive on packaging and packaging waste**[15] in December 1994. The Directive covers all packaging and packaging waste placed on the Community market and aims to harmonize national management measures so as to provide a high level of environmental protection and ensure the functioning of the internal market.The Directive sets the following targets: for Recovery, between 50 % and 65 % of all packaging waste, and for Recycling, between 25 % and 45 % of all packaging materials, with a minimum of 15 % for each individual material.To allow for particular situations, it includes a clause enabling Member States to pursue higher targets, provided they comply with a number of conditions, and in particular that their policies should not hinder the introduction of similar policies in other Member States. Member States must take the necessary steps to set up return, collection and recovery systems so as to attain the objectives of the Directive. In accordance with the principle of subsidiarity, Member States are free to develop their own management systems according to their national requirements and in accordance with the Treaty.

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[14] OJ 1991 C 190, p. 1.

[15] OJ L 365, 31.12.1994.

- On 18 March 1991 the Council adopted **Directive 91/157/EEC on batteries and accumulators containing certain dangerous substances**[16] (mercury, cadmium and lead). The Directive establishes that Member States must draw up prevention programmes and programmes to collect the batteries and accumulators and bans the marketing of batteries and accumulators with a high heavy metal content .

- To counter the risks posed to the environment by the elimination of PCBs and PCTs, a new proposal for a **Directive on the disposal of polychlorobiphenyls and polychloroterphenyls (PCB/PCT)**[17] will replace **Directive 76/403/EEC**[18] on the same subject. It promotes better control of the management of PCBs and PCTs and improves the way they are disposed of and replaced. Furthermore it is foreseen to eliminate all PCBs and PCTs contained in existing products by the year 2010. The Council has adopted a common position on the proposal and the directive is expected to be adopted in 1996.

- Other specific legislative works have been tackled in the framework of the so-called **Priority waste streams programme**, following the Council resolution of 7 May 1990, which asked for EC-wide actions for particular types of waste. The action concentrated on used tyres, end-of-life vehicles, healthcare waste, construction and demolition waste and waste from electrical and electronic equipment. The Commission is now working on a proposal for a Council directive on end-of-life vehicles. The appropriate follow-up for the other four projects is currently being examined by the Commission.

The legislative work has been completed with measures and proposals for the management of specific waste streams, the development of waste statistics and exploration of the application of new economic and technical instruments to help achieve the ultimate objective of turning waste management into a generally accepted, necessary, environmentally sound, and economically viable practice.

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[16] OJ 1991 L 78, p. 38.

[17] OJ 1988, C 319, p. 57.

[18] OJ 1976 L 108, p. 41.

III. FUTURE PERSPECTIVES FOR EU WASTE POLICY

The Commission is currently reviewing the Community Strategy for waste management of 1989. It intends to inform the European Parliament, the Council, the Economic and Social Committee and the Committee of the Regions by means of a communication which should be adopted in June this year.

The review should confirm the hierarchy of principles established by the strategy document of 1989 that **prevention** of waste shall remain the first priority, followed by the **recovery** and finally by the **safe disposal** of waste. The choice between these different options has to be founded on the basis of the principle of the best environmental option, although economic costs are also to be taken into consideration.

- As regards the prevention option, the following measures should be particularly developed: promotion of clean technologies and products, the establishment of technical standards and eventually EC-wide rules to limit the presence of certain dangerous substances in products, the promotion of reuse and recycling schemes, the appropriate use of economic instruments, eco-balances, eco-audit schemes, life cycle analysis, and actions on consumer information and education as well as further development of the european eco-label system.

- Within the recovery option, preference should be given to material recycling over energy recovery operations, as is already the case in Directive 94/62/EC on packaging and packaging waste. Reasons for this option are, on the one hand, the fact that recycling implies the separation of waste at source involving end-users and consumers in the waste management chain making them more aware of the necessity to reduce waste generation, and on the other hand, the undesirability of establishing energy strategies relying heavily on waste supplies.

- Concerning final disposal, particular care should be taken to avoid as much as possible incineration operations without energy recovery. Uncontrolled landfilling and contaminated sites are two problems requiring special and strong actions at different levels.

The reviewed strategy will address the question of **producer's responsibility**. Considering the life cycle of a product from manufacture until the end of its useful life, material suppliers, traders, consumers and public authorities all share specific waste management responsibilities. However it is the product manufacturer who has a predominant role since he makes the key decisions concerning his product before marketing it. Furthermore, his active involvement in the product's sound treatment once it becomes waste should not be excluded. This approach is compatible with the concept of "shared responsibility" as proposed in the 5th EAP. Indeed, this concept underlines that progress in environmental policies can only be achieved when action is taken by all actors involved in a coherent way.

The Commission intends to integrate and practically implement the above-mentioned principles in all future measures, on a case by case basis, which it suggests or undertakes in the waste area, taken into account the specific responsibilities of the different economic operators.

The reviewed strategy on the priority waste streams programme may suggest that the approach has not been sufficiently successful to replace the traditional preparatory stage of the institutional decision making process and that, therefore, in principle, no new specific projects would be initiated. Rather, waste streams should be examined on a case by case basis.

The strategy will reaffirm the need of appropriate control of shipment of waste within the legal framework set up by Regulation 259/93. Particular attention is to be paid to achieve the double objective of ensuring a high level of environmental protection without distorting the functioning of the internal market. Appropriate application of the proximity and self-sufficiency principles is needed. These principles entail that waste must be disposed of in one of the nearest appropriate installations and that waste which is generated within the Community should not be disposed of elsewhere. In this context the Community goes even further by also prohibiting hazardous waste for recovery operations to be exported to non-OECD countries. This has been initiated at the request of developing countries in the framework of the Basel Convention since they don't have the necessary treatment facilities nor adequate control capacity.

The new document will include a chapter on the instruments to be used, at all different levels, in order to achieve the objectives fixed by the strategy, namely regulatory and economic instruments, reliable and comparable statistics on waste and other management instruments such as waste management plans, appropriate enforcement of legislation and impartial use of life cycle analysis and eco-balances.

The above objectives cannot be achieved without the participation of all economic operators namely, public authorities, private and public companies, environmental organizations and, in particular, individuals as citizens and consumers.

IV. FINAL REMARKS

The Community policy on the environment focuses on the achievement and maintenance of high environmental standards, sharing of responsibilities ensuring that the polluter pays and reinforcement of compliance with adopted legislation. The Commission is giving special attention to the principle of subsidiarity but avoiding the undermining of Community environmental action.

Management of waste generated within the Community will be a key task of the next few years. The Community strategy for waste management is to be pursued and reinforced in a new stage that will entail the development, implementation and follow up of all measures contained in existing legislation.

This general legal framework is to be complemented by other actions dealing with the management of specific waste streams and the use of a broader range of instruments including, not only the traditional legislative ones, but also market based instruments. Horizontal supporting instruments and financial support mechanisms should be encouraged.

This implies the implementation of the hierarchy established in the Community strategy, with special emphasis on prevention of production of waste and solving waste problems at source. It has to be taken into account the need of an appropriate flexibility to adapt to different local situations, and this on the basis of evaluation techniques such as life-cycle analysis and ecobalances.

Recycling is a priority in the Community strategy. The creation of markets for recyclables in fair competition conditions in relation to primary raw materials should be a priority for all waste management policies throughout the Community. This could be enhanced by the application of specific economic instruments to products which are to be recycled. The recently adopted Directive on packaging and packaging waste sets, for the first time, targets on recovery and recycling. From an environmental point of view recycling should be regarded as an important part of recovery with a particular view to reducing the consumption of energy and of primary raw materials and the final disposal of waste.

On-going actions on a number of priority waste streams might conclude on similar proposals intended to encourage recycling activities.

It cannot be denied that, in spite of the considerable distrust of local populations of any form of incineration, waste incineration is a management option which plays an important role in a number of national waste policies in the Community. Nevertheless there are good reasons not to promote incineration without energy recovery, as this type of incineration is generally not cost efficient, and while it may reduce the volume of waste, it does not contribute to saving resources. Furthermore, strict monitoring of incineration installations will continue to be necessary in order to ensure that emission of pollutants is minimized.

Waste landfilling is another management option which requires important efforts to prevent and minimize the quantity of waste that goes into landfill. The Commission will have to ensure that the future landfill directive is fully put into operation. Moreover, particular attention is to be paid to uncontrolled and old landfill sites.

Waste dumping at sea has also been, until now, considered as an acceptable waste management option. In conformity with several international conventions, the Commission is of the opinion that the discharge of waste into the sea or onto the seabed is not a desirable option and should be avoided. This applies to all forms of waste, including end-of-life ships and other bulky wastes. Furthermore, wastes from ships continue to be one of the major pollution sources of the seas surrounding the Community, particularly when cleaning operations, changes of motor oil etc. are included in this notion. Until now, the Community has paid little attention to this problem and has left initiatives to international conventions. However, since progress is extremely slow in international bodies, the Commission might explore, at a later stage, possible actions that could be initiated in order to reduce pollution of the Community seas.

It is estimated that about 16 million tons of plastic waste are generated annually in the EC, with important growth rates for the next coming years. At present, almost 80 percent of that waste is put to incineration or to landfill; recycling counts for some five percent and incineration with energy recovery for some 15 percent. Efforts to increase the quantity of recycled waste should be made.

The drawing up by Member States of waste management plans, such as it is required by the framework Directive on waste, is the essential precondition for successful action in this field and the Commission attaches very special attention to them. These management plans should be a major tool, in particular for an effective and environmentally sound network of recovery and recycling installations.

Concerning radioactive wastes, particular care will have to be taken in order to ensure they undergo at least the same measures of precaution and control during storage, shipment and incineration as other dangerous wastes, especially as regards the principles of proximity and self-sufficiency.

Last but not least, a supplementary effort is still to be made by Community institutions in order to increase public awareness, transparency and better access to information. This is particularly important in the waste sector due to the special sensitivity citizens have in relation to this problem which is present in every day life. Strengthening dialogue with industry, public and social partners should enable all these operators to get more actively involved in the development and practical implementation of policies.

A European network for strategic life-cycle assessment research and development (LCANET)

ENV4-CT95-0153

Coordinator: H.A. Udo de Haes / N. Wrisberg

CML
NL - 2300 RA Leiden
Tel: +31-71.5277.488
Fax: +31-71.5277.496

Title: European Network for Startegic Life-Cycle Assessment Research and Development (LCANET)

Project number: ENV4-CT95-0153

Starting date: 1 March 1996

Duration: 15 month

Addresses of participants:

coordinator:
Prof.dr. H.A. Udo de Haes
CML
P.O. Box 9518
2300 RA Leiden
The Netherlands
tel. 31 71 5277 488
fax. 31 71 5277 496

partners:
Dr. A.A. Jensen
dK-Teknik
Gladsaxe Møllevej 15
DK-2860 Søborg
Denmark
tel. 45 39 696 511
fax 45 39 696 002

Dr. L.G. Lindfors
IVL
P.O. Box 21060
S-10031 Stockholm
Sweden
tel. 46 8 729 1500
fax. 46 8 318 516

Prof.dr. R. Clift
Centre for Environmental Strategy
University of Surrey
Guildford Surrey GU2 5XH
United Kingdom
tel. 44 1483 259 271
fax. 44 1483 259 394

Prof.dr. F. Schmidt-Bleek
Wuppertal Institute
Döppersberg 19
D-42103 Wuppertal
Germany
tel. 49 202 2492 132
fax. 49 202 2492 138

Dr. P. Hofstetter
ETH-Zentrum UNL
CH-8092 Zürich
Switzerland
tel. 41 1 632 49 78
fax. 41 1 632 12 832
E-mail: hofstetter@iet.mavt.ethz.ch

Dr. L. Grisel
Ecobilan
13-15 rue Buffon
F-75005 Paris
France
tel. 33 1 433 14141
fax. 33 1 433 14400

Main objectives:

1. The building of a European Network for Life-Cycle Assessment Research and Development (LCANET).
2. The identification of the state-of-the-art of LCA methodology and applications and of research needs.
3. The publication of an encompassing document, containing the state-of-the-art of present LCA methodology and applications and a coherent strategic LCA research programme.

Main results:

1. Definition Document, describing the scope and general direction of four theme research lines.
2. Four theme reports, describing the research strategies of the four themes.
3. Final report, bringing together the results of the theme reports.

European Network for Strategic Life-Cycle Assessment Research and Development (LCANET)

1. Introduction

Life-Cycle Assessment is a new environmental management tool of increasing importance. It aims to provide the basis for decisions which will promote sustainable development of our economies. In an LCA study all extractions of resources from the environment and emissions to the environment are determined throughout the whole life cycle (from cradle to grave) of a product or other object. Based on these data the potential impacts posed to natural resources, to the environment and to human health are assessed.

There is a number of ongoing national and international activities (e.g. SETAC, ISO, Groupe des Sages, OECD, Nordic Council) related to the development of the LCA methodology and its standardization. However, these are insufficiently being harmonised, while coordinated research is mainly lacking. Given this situation there is a strong need for a network for LCA research and development, which acts as a well structured scientific platform for discussions on LCA methodology. **LCANET** is a Concerted Action in the Environment and Climate programme for establishing a network for LCA research and development.

Objectives

1. The building of a European Network for Life-Cycle Assessment Research and Development (LCANET). This network will be a platform for discussion on LCA research and development by regular and rapid exchange of information between European universities, research institutes, companies, non governmental organisations and the European Commission.

2. The identification of the state-of-the-art of LCA methodology and applications (agreement points within the LCA community), present research needs and future research perspectives on core topics of LCA through a broadly-based interactive process.

3. The publication of an encompassing document, containing the state-of-the-art of present LCA methodology and applications and a coherent strategic LCA research programme, including developments needed to employ LCA effectively as a policy support tool.

2. Approach

2.1 Work programme

A network for LCA research and development will be built, to act as a well structured scientific platform for discussion about LCA methodology. The first phase of LCANET consist of three stages as indicated in figure 1. Opinions of experts on desirable research and development lines will be collected during one network meeting and seven expert meetings. Proposed research lines will be discussed in workshops, one for each theme. The results will be published in the form of a definition document, theme reports and a final document.

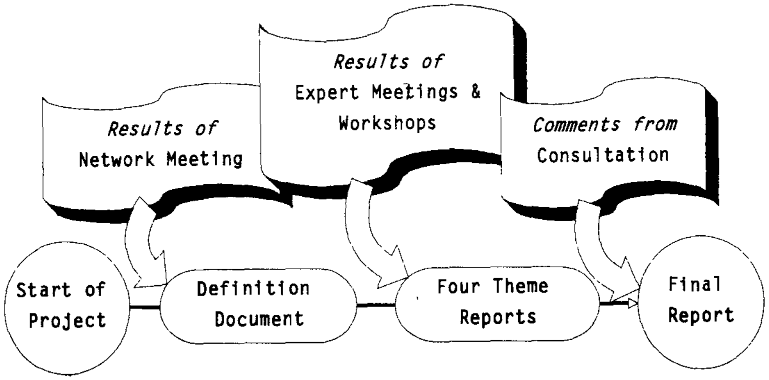

Figure 1: Three stages of the first phase of LCANET.

In the first stage of the project a Network meeting will be held, to arrive at a stricter formulation of the state-of-the-art and of the research questions. The results of this meeting will be published in a Definition Document. The Definition Document will act as a guiding text and agenda for the rest of the project.

The main activity in the second stage will be the organisation of four workshops on core areas of the LCA working field to make a more detailed inventory of the state of the art, the existing knowledge and experience and the open research questions together with their priority. Each workshop will be prepared during one or two expert meetings. The results of each workshop will be published in a Theme report.

In the third stage a final report will be prepared and published based on the four theme reports from the workshops, including the state-of-the-art of LCA methodology, the identified gaps in the knowledge and data, and an encompassing research programme.
During the preparation of this report, there will be further consultation with the members of LCANET. If any substantive differences of view emerge, they will be identified in the report. Clearly differing opinions will be included in an annex of the report. A principle priority of this part of the programme will be to establish relative priorities between the

different research tasks.

The responsibility for the whole process lies with the LCANET Board with 7 members from different European Institutes (CML, Centre for Environmental Strategy, dK-Teknik, Ecobilan, ETH-Zentrum UNL, IVL, Wuppertal Institute). CML acts as coordinator and chairman of the board and is responsible for the total of the project. CML is directly responsible for the publication of the Definition Document and the Final Report.
One Board member is responsible for the organization of the network meeting. Each of the other Board members is responsible for the organization of one or two expert meetings, one workshop and the publication of one theme report.

2.2 Problem areas

LCA is a methodology under development with quite a few gaps. However, gradually a consensus is developing on what the gaps are and which questions will have to be answered to make LCA into a robust tool. There are four fields for which a development line will have to be formulated and which will be subject of LCANET workshops:

Workshop 1: Positioning and Applications of LCA
One of the main purposes of this theme is to dispel the confusion which has arisen from the development of a number of different but related tools (e.g. Material Intensity Par Unit Service, Substance Flow Analysis, Risk Assessment, Environmental Impact Assessment and Environmental Audit), so that appropriate areas of application and hence of future development can be identified.

Workshop 2: Issues related to Goal and Scope Definition and to Inventory Analysis
The Goal and Scope Definition component establishes the purpose and scope of the study; the functional unit, as a central measure of the service delivered; the main delineation of the product system boundaries; the level of detail required for the application in question; and a procedure for ensuring the quality of the study.

The most important aspect of this component is the definition of the functional unit. The key issue is to determine the functional unit in such a way that it covers all representative product alternatives that may usefully be compared.

The Inventory Analysis identifies and, where possible, quantifies the inputs from the environment and the outputs from the system to the environment of the product system investigated, together known as the environmental burdens, loadings or interventions of the system resulting in the inventory table. Core research questions include the definition of system boundaries and the development of a consistent approach to allocating borders between different functional outputs of a multi-function system.

Workshop 3: Issues related to Impact Assessment and Interpretation
Impact Assessment identifies, characterises and assesses the effects on the environment of the loadings identified in the Inventory Analysis. Three consecutive elements are defined:

classification, characterisation and valuation.

Classification is the element in which the relevant impact categories are identified and in which the loadings of the inventory table are assigned to each of the problem themes to which they may contribute. The main issue is a consistent, standard default list of impact categories.

Characterisation is the element in which the effects of the loadings are specified, where possible quantified, and aggregated within the defined impact categories.
The way in which the characterisation step should be carried out is still a matter for debate. However, in Europe most LCA experts are of the opinion that the use of equivalency factors seems most appropriate for LCA, but the application of this approach needs to be defined more precisely. These factors have been sufficiently developed for a few impact categories only; for others, particularly for regional and local impacts, they are in the process of development or are still missing.

The last element valuation, is a normative element, based on social values which, by their nature, cannot be defined purely in a natural science framework. In this step the different impact categories are weighed against each other in order to arrive at an overall environmental comparison of the given alternatives. This valuation step may take the form of a structured weighting procedure or it may be performed on an ad hoc basis. A number of options are present for comparison and weighting of the different impact categories, resulting in a further aggregation of the results.

Workshop 4: Issues related to databases and software

Data gathering is a core issue in LCA, in particular in the inventory analysis. The availability and quality of the data may greatly influence the credibility of the LCA. In order to save time and money in carrying out LCAs, a public database, is needed to provide the inventory data-sets, at least those describing generic utilities and commodities which are always required in LCA studies. Apart from the availability of the data there are also methodological choices to be made, in particular in relation to the data about generic utilities and commodities such as electricity, transportation, the different types of waste management processes (including landfill, incineration, composting, etc.) and basic materials production (e.g. fuels and bulk materials including those for packaging). A last point concerns the development of public multi-use software for LCA.

2.3 Application oriented research

The LCA issues will be discussed in relation to actual applications in order to make the specification of research needs application oriented. The main applications which might be dealt with include the following:

* Waste management:This topic deals with the assessment of the environmental burdens of a number of different strategies for the recovery of materials and energy from solid waste. Attention has to be paid to direct, indirect and avoided burdens of the different waste management systems.
* Ecolabelling: Here LCA can play an important role in underpinning of the procedure

for setting criteria. Different types of criteria can be distinguished and be compared with respect to their validity and usefulness.

* Product stewardship: This issue includes product improvement and design, taking into account processes of the whole product system. A specific point of attention is the role of LCA software, and the way in which both simple and detailed information can be applied in this context.

* Food, agriculture and forestry: LCA has been developed for industrial production. It is important that its scope will be widened to biotic materials. This in turn will also require further methodology development, building on a current concerted action programme exploring the implications of different approaches for a single agricultural product. An issue of specific importance is the assessment of the (avoided) environmental burdens of the production of biomass as an energy source.

* Transportation: A systematic comparison of the environmental burdens of different transportation systems is of high relevance. This should not be limited to the choice between public and automotive transport, but also include other transportation modes and particularly the transport of freight.

3. Results and future perspectives

3.1 Preliminary results

The project only started on March 1 1996. The first activity is to develop and strengthen the existing network, with more effective administrative procedures and a coordinated schedule of meetings. More than 200 people has been approached in relation to the Network meeting in Copenhagen held March 14 1996. About 80 LCA experts/practitioners/users attended the meeting, during which the structure and membership of the network was discussed. A draft definition document addressing the position of LCA in relation to other tools and the state-of-the-art of LCA methodology and the most important gaps in the methodology was input for discussions.

3.2 Future perspectives

The first stage of the project will end with a definition document, describing the scope and general direction of the four theme research lines. The second stage will entail seven expert meetings, four workshops and end with four theme reports, describing the research strategies of the four themes. The third and final stage of the project will end with the publication of a final report, bringing together the results of the theme reports.

The building of a network will be continued throughout the project's first phase. About 100 people have indicated their interest in becoming a member (active contributing) or agenda member (receiving only information) of the LCANET.

Following the first phase it is envisaged that LCANET could remain a discussion platform for research and development issues as well as consensus on principles.

Postconsumer plastics recycling from waste streams: on-line pick-up, on-line analysis - on-line sorting - SIRIUS

EVWA-CT92-0001

Coordinator: L. Buydens

Koninklijke Universiteit Nijmegen
NL - 6525 ED Nijmegen
Tel.: +31-24.3653192
Fax: +31-24.3652653

Post-consumer Plastics Recycling: On-line Pick Up, On-line Analysis, On-line Sorting (EEC project SIRIUS, EVWA- CT92-001)

Wienke D., Broek v.d. W., Melssen W., Buydens L. (all Nijmegen, NL)*
Huth-Fehre T., Feldhoff R., Kantimm T., Winter F., Cammann K. (all Münster, D)**

* Lab. for Analytical Chemistry, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands, tel: +314-24.3653192; fax: +31-24.3652653.
** Inst. für Chemo-und Biosensorik, Universität Münster, Wilhem-Klemm-Strasse 8, 4400 Münster, Germany, tel: +49-251.9802801; fax: +49-251.982802.

The joint EEC-financed research project SIRIUS (Sensors and Artificial Intelligence for Recognition and Identification of Used PlasticS between the Laboratory for Analytical Chemistry of the Catholic University of Nijmegen (The Netherlands, coordinator, partner 1) and the Institute for Chemical and Biochemical Sensors Research (Münster, Germany, partner 2) dealt with analytical sensors for rapid sorting of post-consumer waste. The project run under the program ENVIRONMENT of the EEC from 1 May 1993 to 30 April 1996. SIRIUS concerned three main parts: evaluation of sensor principles for application in a pre-sorter for waste, sensor principles for a fine-sorter for post-consumer plastics and artificial intelligence algorithms for control and adaption of pre-sorter and fine-sorter.

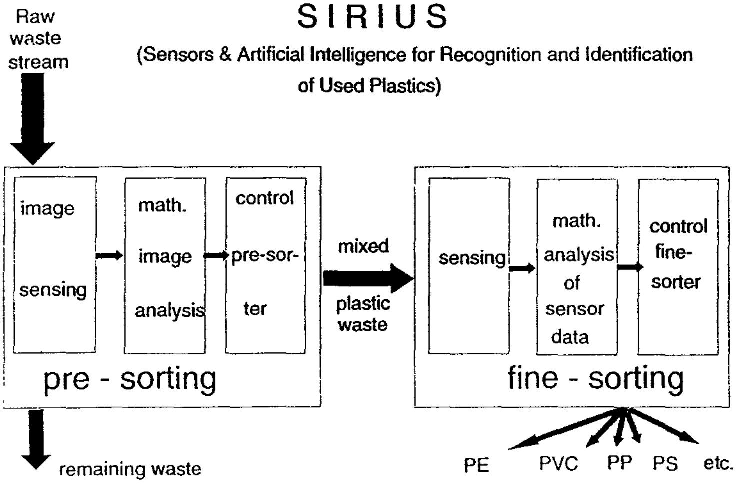

Figure 1: Experimental flowchart of the SIRIUS project

Spectroscopic (near)-infrared imaging has been studied as method for discrimination of plastics and non-plastics in a pre-sorter. An experimental laboratory set-up has been built up in Nijmegen to demonstrate the proof-of-principle. The output of this pre-sorter is a concentrated pure sub-stream of mixed plastics.

The sub-stream of mixed plastics is divided into pure plastics by remote optical sensing combined with rapid sorting. Among several spectroscopic sensor principles such as NIR, MIR, FIR and RAMAN it has been found that rapid parallel NIR spectroscopy is the method of choice.

The PERT diagram (Figure 2) illustrates the working program of the entire SIRIUS project.

Major Results of the SIRIUS project

In the last year since our report in Vienna 1995 both hardware parts (pre-sorter, fine-sorter) have been optimized, tested and validated. The same has been done for the software modules developed for both parts of hardware. The main result of the last year was the successful finishing of both laboratory set-ups. Real-world samples from waste can be presented now to the sensors and are classified by 'remote sensing' with a high rate of correct identification.

Parts of the hardware (collimation optics, multiplexer, parallel spectrometer) and parts of the software (parallelized artificial neural network) were successful installed in commercial large-scale facility for automated waste sortation nearby Hamburg (Germany). Since 1 January 1996, the plant produces sorted household waste.

Both research groups produced about 13 publications, 2 patents and 15 lectures and posters.

Parts of the SIRIUS project were presented at several fairs to industry.

Two PhD Thesis (1 German, 1 Dutch) and one German Habilitation Thesis are in preparation based one results of the SIRIUS project.

Results of the SIRIUS project have been recognized by four awards.

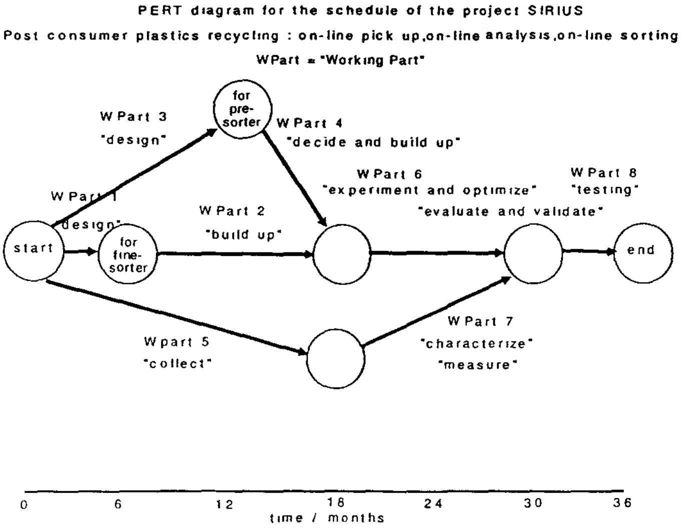

Figure 2: Time schedule (PERT diagram) of the SIRIUS project

Post-Consumer Plastics Recycling: On-line Pick Up, On-line Analysis, On-line Sorting (EEC project SIRIUS, EVWA- CT92-001) Extended Scientific Abstract (partner 1 and coordinator : Catholic University of Nijmegen (NL), partner 2: ICB Münster (D))

Wienke D., Broek v.d. W., Melssen W., Buydens L. (all Nijmegen, NL)
Huth-Fehre T., Feldhoff R., Kantimm T., Winter F., Cammann K. (all Münster, D)

Design and application of analytical sensors for rapid sorting of post-consumer waste have been the aims of a joint EC-financed research project SIRIUS (Sensors and Artificial Intelligence for Recognition and Identification of Used PlasticS).

A bilateral project consortium between the Laboratory for Analytical Chemistry of the Catholic University of Nijmegen (The Netherlands, participant 1 and coordinator) and the Institute for Chemical and Biochemical Sensors Research Münster (Germany, participant 2) has been formed for the period between 5/1993 - 5/1996 within the EC's 3rd frame program.

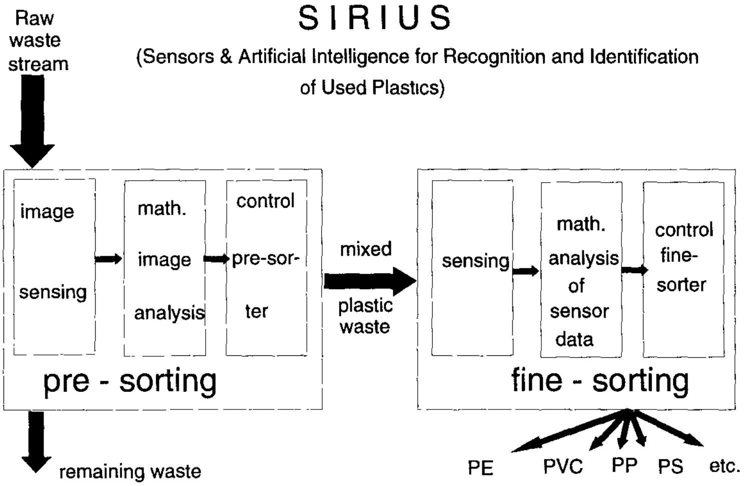

Figure 1: Experimental flowchart of the SIRIUS project

This extended abstract lists results, reached in the third and last project year and within SIRIUS in general. Further detailed results of the SIRIUS project are documented by three EC internal scientific and financial reports [1] – [3]. Two patent applications [4], [5], numerous publications, lectures, posters and exhibitions [6] – [21] and four awards [22] – [25] provide further information about this project.

Based on the recognized results of SIRIUS, a project in succession has been dedicated to an extended consortium where both partners contribute again (EC project AUTOSORT, 4th frame program BRITE-EURAM, no. BRPR-CT95-0013). This follow up project studies since January, 1st 1996 the feasibility of automated sorting of demolition waste.

Pre-sorter : final results

An experimental laboratory set up for a pre-sorter has been developed which is based on spectroscopic information. Typical plastics such as PP, PE, PVC, PET and PS show characteristic reflectance peaks in the optical NIR/MIR wavelength region (Figure 2).

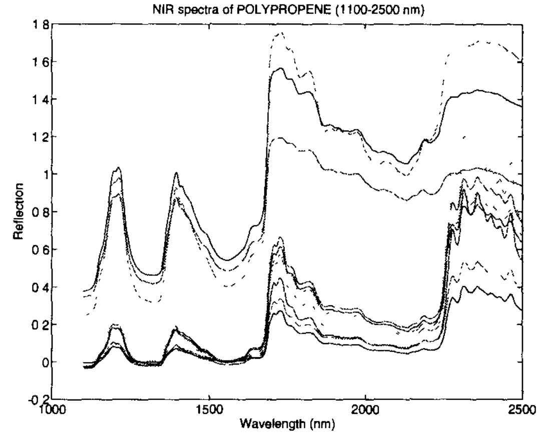

Figure 2: NIR spectra of several grades of polypropene

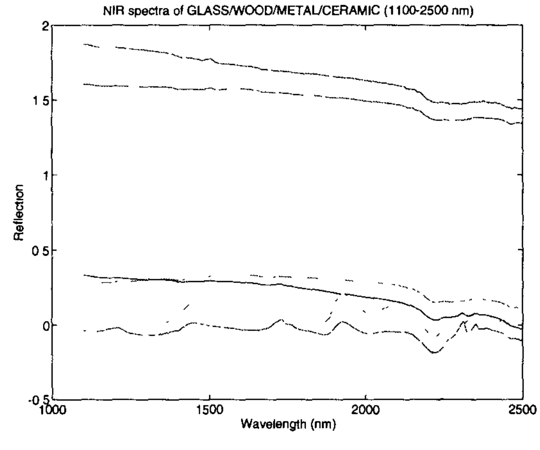

Figure 3: NIR spectra of several types of non-plastics

Non-plastics such as metals, wood, paper, ceramics and glass show less characteristic spectral patterns (Figure 3). Based on these spectral differences, both classes of materials (plastics, non-plastics) can be identified using computer-assisted mathematical "pattern recognition methods". Several of these methods were tested and implemented during the SIRIUS project. Best performing meth-

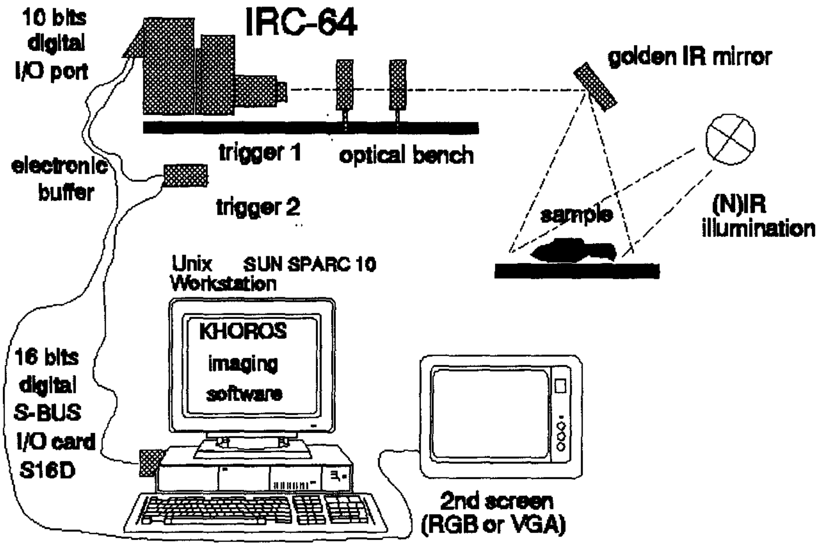

Figure 4: Laboratory set up for a pre-sorter for post-consumer waste

ods will be discussed below.

Pre-sorter : final hardware results

The experimental laboratory set-up for a pre-sorter (Figure 4), developed by partner 1, concerns a computer controlled infrared camera, equipped with spectral filters, monitoring a conveyor belt carrying separated single waste samples. A sequence of digital infrared images is taken from each illuminated waste sample and processed by pattern recognition software. The images are analyzed in real time to determine whether the sample is a piece of plastic or not.

The advantage of simultaneous imaging and spectroscopy (NIRIS = "near infrared imaging spectroscopy") over near infrared spectroscopy is the gain in additional information about sample location, size, shape, blends and mixtures. In contrast to NIRIS, classical NIR spectroscopy integrates over a sample part, yielding only an averaged material information.

Pre-sorter : final software results

The following example presents an original infrared image of a real plastic waste sample (Figure 5), classified image regions (Figure 6), and results obtained from using different pattern recognition methods (Table 1).

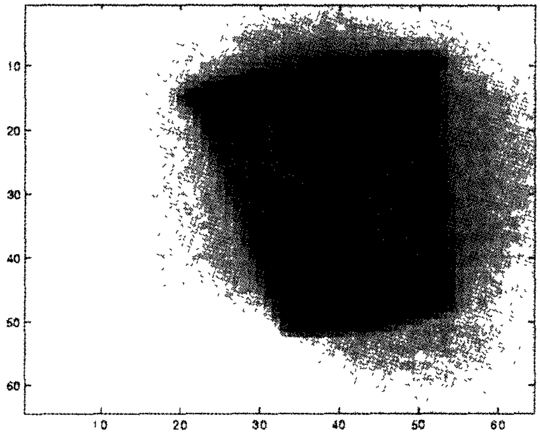

Figure 5: Infrared image of a plastic beaker (polystyrene) at the conveyor belt.

Table 1: The table lists percentages of correct pixel classification obtained for images of real-world samples by the pre-sorter set-up (Figure 4) with different pattern recognition methods [10].

tested and implemented classification method	plastic	non-plastic	back-ground	total
MLF neural network	99	100	98	99
KohonenLVQ-network	98	98	100	99
radial base network	93	98	100	97
Fuzzyartmap network	87	99	99	95
PLS regression	97	95	95	96
linear discrim. analysis	95	96	96	96

During the third (and last) project period between 5/1995 - 5/1996 the pre-sorter has been optimized with respect to illumination, optics, background and software. This optimized set-up has been validated with a large sample data set taken from the metropolitan area Hamburg (Germany) and from two Dutch large-scale waste processing plants (VAM Wijster, AVRN Nijmegen). The sample collection concerns plastic bottles, beakers, cans, card board, metals, paper, glass waste, and stone.

Summary pre-sorter

An experimental pre-sorter set-up based on near-infrared imaging spectroscopy and combined with neural network classification software has been built up, optimized, validated and tested within the SIRIUS project. This set-up is able to substitute the human eye for identification of plastic waste at a conveyor belt. A recognition rate of better than 80 % has been reached so far with a recognition speed of 1 sample per 10 seconds for arbitrary sized, shaped, located and colored real-world waste samples. In this way, the proof-of-principle has been carried out that plastics can be identified and sorted out from

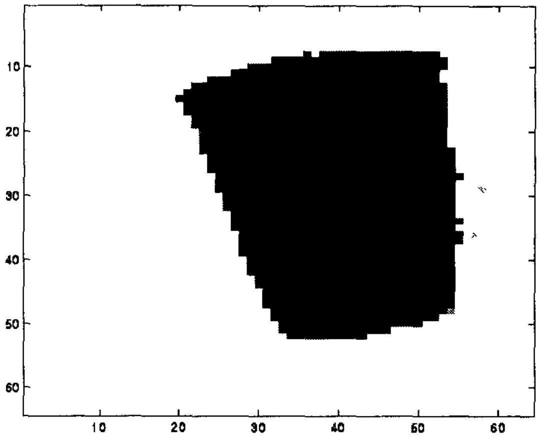

Figure 6: On-line discrimination between the plastic beaker (black) and the background (conveyor belt, white) obtained by the implemented automatic working pattern recognition software. Shape, size and location as well material type (see also Table 1) were correctly recognized (compare with Figure 5).

mixed waste stream into sub-stream of plastics for future fine-sorting into different types of plastics. For future industrial applications the developed pre-sorter set-up needs to be speeded up in its optical hardware components which, however, was beyond the financial budget of the present project.

Fine-Sorter: final results

Within the project period 5/1993 - 5/1996, a fine-sorting device for a sub-stream of plastic waste has been designed and developed at laboratory scale. This technical solution is based on remote near-infrared fingerprint spectroscopy combined with advanced and flexible pattern recognition software.

In the third and last project year the set-up has been optimized, extended, tested and validated under industrial real-world circumstances.

Presently the first implemented commercial system is working in a large-scale plant in German under full production conditions.

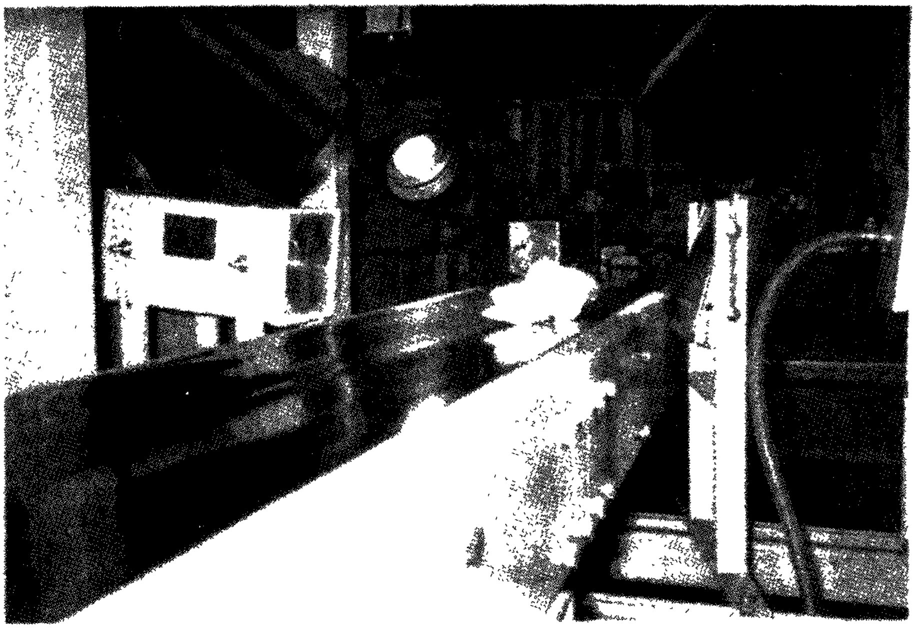

Figure 7: Automated fine-sorting of post-consumer packaging waste as developed by the SIRIUS project and installed, optimized and tested in a large-scale production plant in Hamburg-Glinde (Germany). This photograph shows the sensor system with a piece of plastic waste at the spot of measurement: The camera for image analysis is located straight above the belt , whereas coupling optics and reflector are 'looking' across the belt.

Fine-Sorter: final hardware results

The laboratory setup as described in Report 2, was presented to the public at the trade fair for environmental technology 'ENVITEC' in June 95. In addition it could be tested at an industrial sorting system that was under construction at that time at TZN Unterlüß GmbH (Hannover, Germany). The optical setup consisting of coupling optics, 500 W halogen lamp and aluminum reflector was installed at a 20 meter long and 30 cm wide conveyor belt. The belt moved at a speed of 1 meter per second and was fed with original and heavily soiled DSD-plastic waste automatically at an average rate of 1 object per meter. The spectrometer is triggered by a light barrier and spectra are taken and stored from more than 300 objects.

In a second step these spectra were off-line classified with a correctness of more than 97

From these measurements and discussions with TZN we learned, that 1 meter per second was the upper speed limit for transporting such light goods as for example yoghurt beakers on conveyor belts without having the objects rolling around or flying away. In order to make full use of the systems high theoretical measurement speed of 150 identifications per second, an optical multiplexer was developed to connect the coupling optics of up to eight conveyor lines subsequently with the fast diode array spectrometer. For this whole optical system an international patent application was filed [4], [5].

The sample collection as described in report 2 was further enlarged by sets of PE/PP foils, dif-

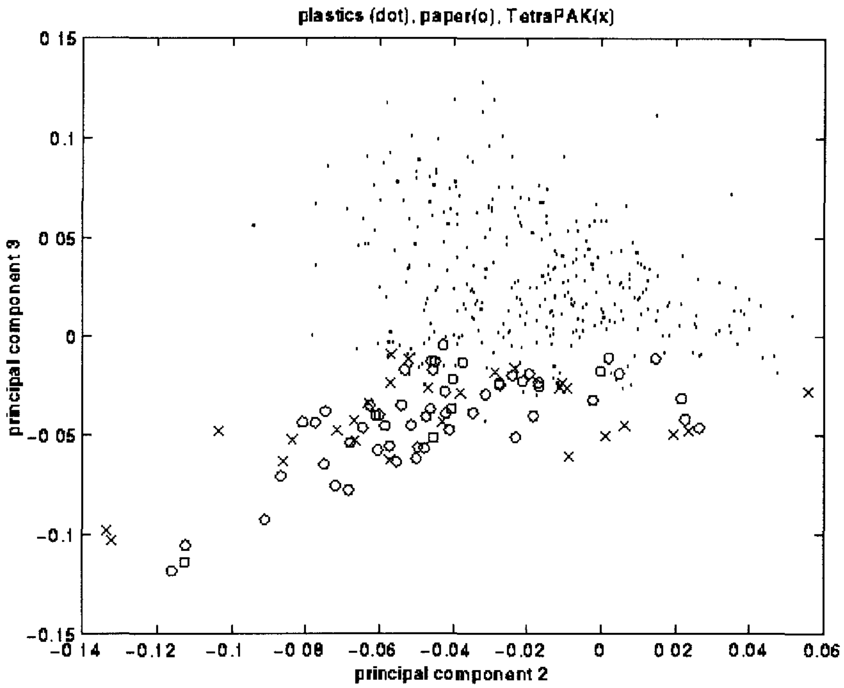

Figure 8: Spectral dissimilarity of plastics (dots), paper waste (o) and cardboard material (x), shown by a principal component plot. On-line separation of plastics (dots) is possible with excellent quality (see Table 2). A separation of cardboard (x) from paper (o) seems to be possible till a certain extend (see Table 2), but needs further optimization of hardware and software

ferent kinds of paper, cardboard and waxed papers. From these objects spectra were taken in the wavelength range between 800 nm and 1700 nm and were added to the database.

For the fine sorter this whole part of the project could be performed in the world's first fully automatic sorting plant for post consumer packaging waste in the city of Reinbek, close to Hamburg. In this plant one ton of DSD waste per hour is sieved in different steps and then distributed on 16 sorting lines, each being equipped with an image recognition system (TZN) and a set of the above mentioned lamps and coupling optics. These optics were redesigned into dust tight housings according to industry standard IP 54. Two spectrometer - multiplexer systems are serving 8 lines each for material recognition. Data evaluation is done in standard industrial personal computers, as described below. The computers, spectrometers and multiplexers are situated in a temperature stabilized remote control room and are connected to the coupling optics by optical fibers of up to 30 meters length.

In this installation a new dataset consisting of the classes PE, PP, PS, PET, plain paper, waxed paper and Tetra was measured off line. Based on this database the on line version of the networks were trained (see below). The on line performance of the whole system is very promising, although the optimization is not yet completed. More than 80 % of all objects, including non- DSD material as for example filled diapers, motor oil containers or TV sets, are given a material classification with more

Table 2: Validation results for automated on-line sortation of 680 real-world waste samples concerning six classes of packaging materials (PET, PE, PP, PS, TetraPAK and paper) by an artificial neural network. 'Empty' corresponds to the empty conveyor belt. Results were obtained by the combination of fine-sorter software and hardware developed in the project SIRIUS and installed in the large-scale waste sortation plant at Hamburg-Glinde (Germany).

samples of packaging material	outside all classes	PET	PE	PP	PS	TetraPAK^{TM}	Paper	Empty
PET (106)	0	97	0	0	0	1	5	3
PE (116)	0	0	111	2	0	2	1	0
PP (91)	0	0	1	86	0	2	1	1
PS (62)	0	0	0	0	55	0	3	4
TetraPAK^{TM}(105)	0	0	0	0	0	83	11	11
Paper (118)	0	0	0	0	0	18	74	26
Empty (82)	0	0	0	0	0	0	6	76

than 95 % correctness (Figure 8, Table 2). The identification proved to be very robust towards food residues or other heavy soiling. On two of the lines a large amount of foils is passing the sensors. Although foils were not used for obtaining the calibration, they could be identified quite well after installing additional illumination. For the long term stability of these results, cleaning the optics once a week proved to be sufficient. The complete installation is commercially available now.

Fine-Sorter: final software results

An intelligent and flexible data analysis strategy for automated on-line classification of highly correlated and overlapping NIR spectra of different plastics has been developed (Figure 9 - 10).

Several pattern recognition methods were implemented and validated for the classification of the NIR spectra. The goal has been to achieve a complete separation of plastics with zero overlap between the distinct classes. It was found that artificial neural networks provide the best classification results.

An advanced type of artificial neural networks (FuzzyARTMAP, Figure 9) has been combined with some data pre-treatment techniques (Figure 10) to reach maximum correctness of waste identification (Table 2).

The algorithms were additionally parallelized and embedded in a commercial software package for an industrial PC running the WINDOWS operating system. The software has been tested, optimized, and validated in the final project period 5/1995 - 5/1996 under industrial circumstances in a large-scale plant for automated waste sortation (Figure 7, Table 2) as described in detail in the hardware part of the fine-sorter (see above).

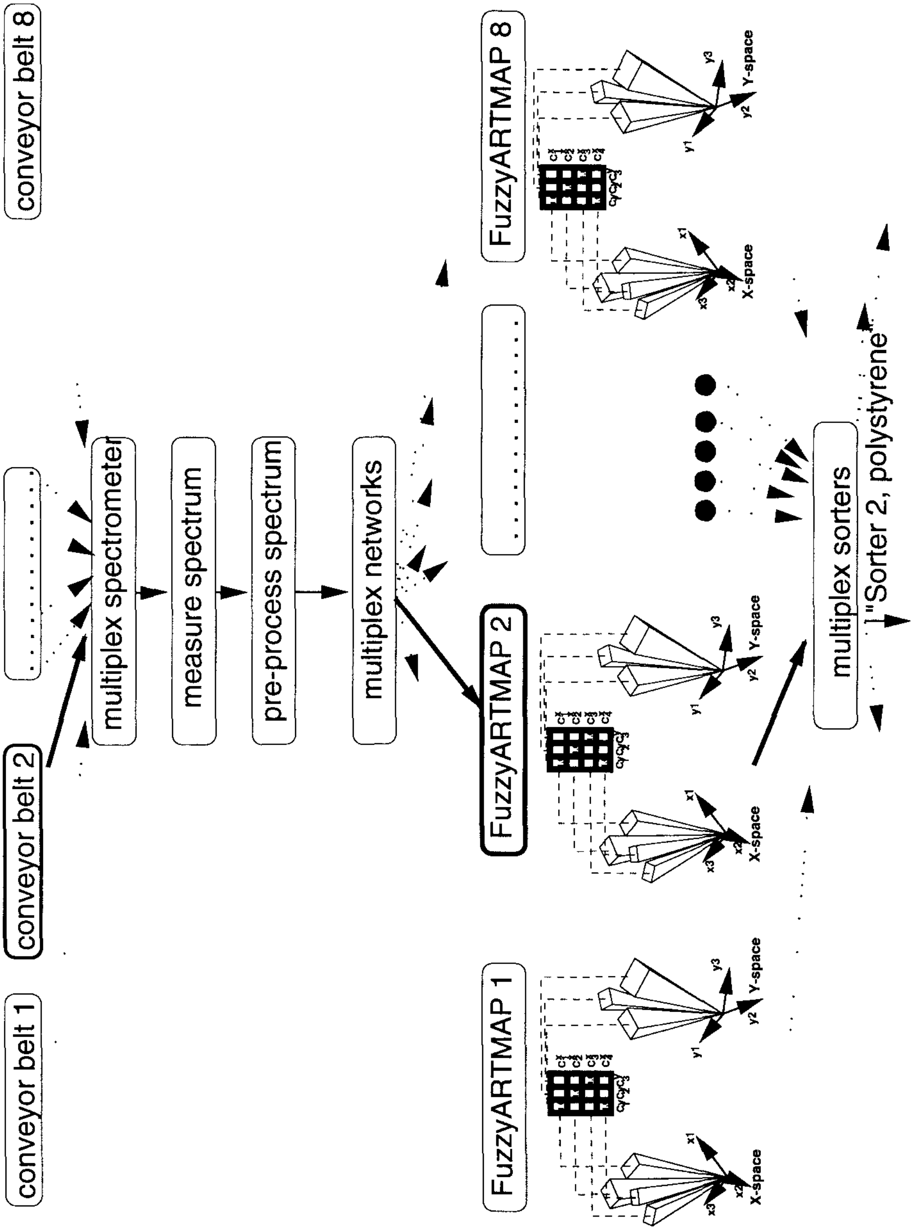

Figure 9: Semi-parallel calculation flow for on-line classification of NIR spectra during automated sorting of post-consumer waste. Software has been implemented in a large-scale facility in Hamburg-Glinde (Germany)

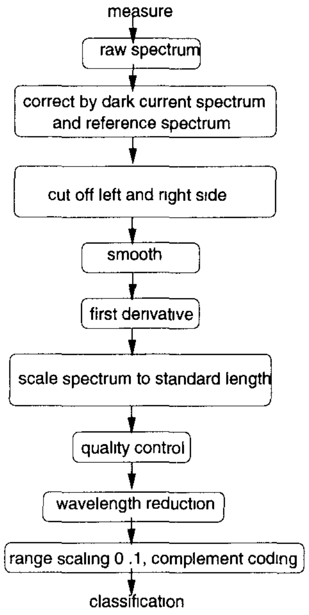

Figure 10: Flow scheme representing data pre-processing of measured NIR spectra

Summary fine-sorter

A hardware solution has been developed on basis of remote NIR spectroscopy which enables automated on-line sorting of post-consumer household plastics including a non-plastic compound material. After a laboratory test phase, the solution has been parallelized in its optical and in its software compartments. This distributed technology has been implemented as important sensor part in one of the most advanced sorting plants for post-consumer waste in Hamburg-Glinde. Presently a sorting purity of about 95 % for plastic waste and about 70 % for compound material and card board/paper has been reached under industrial circumstances. A smaller laboratory version can be seen at the laboratory of Partner 2 (ICB Münster).

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Valorisation of municipal solid waste using a clean technology which associates pressing, aerobic and anaerobic digestion and wet air oxidation

REWA-CT92-0015

Coordinator: C. Massiani

Laboratoire de Chimie et Environnement
Université de Provence
F - 13331 Marseille
Tel: +33-91.10.63.74
Fax: +33-91.10.63.77

VALORIZATION OF MUNICIPAL SOLID WASTE USING A CLEAN TECHNOLOGY WHICH ASSOCIATES PRESSING, AEROBIC OR ANAEROBIC DIGESTION AND WET AIR OXIDATION

REWA-CT92-0015

Summary Report

Coordinators : C. MASSIANI, A. PRONE.
Partners, Scientific directors
J.L. PINEAU, U. BIANCHI, P. LESSART

OBJECTIVES

The originality of the proposed scheme for the treatment of municipal solid waste (M.S.W.) consists in the association of a hydraulic press for "phase" separation with wet air oxidation for the treatment of specific constituents. In the first stage of the process, waste is introduced into the cylindrical compression chamber of the press in which various pressures can be applied. These can reach 1300 bar with the prototype used. The "phase" separation leads to an organic fraction, obtained by the extrusion of organic matter through the small pores of the die (a few millimetres) and called "pulp" because of its physical aspect, and to a "dry" fraction called "pancake" because of its shape given by the compression chamber. In wet air oxidation processes, combustible compounds are oxidized by air or pure oxygen in the presence of liquid water. Operating conditions can be varied from low oxidation, 2 MPa, 200°C, to high oxidation, 20 MPa, 350°C.

The principal expected results are :

- for the press
    - to separate, in a one stage process, the easily biodegradable fraction of the waste, fraction which may be valorized in agriculture after biological treatment,
    - to reduce the volume of the waste,
    - to obtain chemically and biologically stable "pancakes", which makes their storage possible and facilitates their sorting by usual industrial techniques,
- for wet air oxidation, proposed as an alternative to conventional combustion,
    - to improve control of the quality of aqueous and gaseous effluents,
    - to minimize air pollution since the reactions take place in a confined reactor (for example gaseous pollutants such as acidic gases may be transferred to the aqueous phase).

The aim of this work was to demonstrate the feasibility of such a proposal. The major points to be considered were :

1- definition of a sampling strategy
2- characterization of the performances of the press
3- determination of the optimum working pressure,
4- quality of the "pulp" : concentrations of macro-contaminants such as glass and plastics, concentrations of trace metals, and capacity of the "pulp" to undergo aerobic treatment or anaerobic digestion,
5- agronomic value of the biologically treated pulp,
6- quantities and qualities of valorizable compounds which can be obtained by sorting the "pancakes" and determination of the more appropriate sorting techniques,
7- adaptation of wet air oxidation to the destruction of solid waste and mixtures of solid waste, determination of the kinetics of reactions, and verification of the quality of the effluents,

RESULTS

Results about pressing homogeneous reconstituted samples of M.S.W. at various pressures, show that a pressure of 800 bar is not sufficient to optimize the extraction of the biodegradable organic matter and to have a non liable to putrefy "dry fraction" even if the volume reduction ratio is almost the same than with higher pressures (coefficient of volume reduction from 6.5 to 8 according to the composition of the waste). When pressure is risen from 1080 to 1300 bar, the density of the dry fraction decreases and the concentration of low biodegradable organic compounds of pulp increases. The increase of low biodegradable compounds of pulp causes a decrease in the performances of ulterior biological treatments and particularly a decrease of methane yields during anaerobic digestion. A pressure of 1080 bar makes it possible to meet one part of the requirements i.e. obtaining a good pulp-extraction rate and a stable dry fraction with a high density. Consequently, a pressure of 1000 bar is chosen as the optimal pressure for "phase" separation.

Results of this first set of experiments are compared with results obtained with a direct feeding of the press with unsorted M.S.W. (except monster and cardboard). It demonstrates that an important parameter in pressing is the method of loading the press. Sacks containing M.S.W. should not be opened, the M.S.W. should not be homogenized but loaded directly into the press to maintain the diversity of distribution of the organic matter in particular and to lose not more than 20% maximum of pulp. The composition of the pulp is comparable to the composition of pulp obtained by pressing reconstituted waste at 1000 bar. Percentages of plastics, nitrogen and phosphorus are only slightly lowered. However, if a heavy rain dampens paper to an important degree, it will be extracted by the press. The paper thus present in the pulp will modify the amount of nitrogen, reducing it with reference to carbon and consequently raising the C/N ratio.

Anaerobic and composting processes may be applied to pulps obtained by pressing M.S.V. at 1000 bar. Direct methanization of 1000-bar pulp is possible without dilution. It is reasonable not to exceed a feeding of 18 kg / m^3 of reactor. Methane production reaches around 430 l / kg of dry matter. However, at an industrial scale, problems of mass or gas transfer might appears. The destruction of the structure of organic matter improves the immediate biodegradability but makes it more difficult to keep this two processes under control. Less reactive waste or bulking agent may be added.

Gross mature compost is naturally granule-shaped. However, the quantity of small fragments of plastics is too high to consider a direct marketing. Refining is possible by the mean of attrition and sieving using a 3 mm cut. Refined compost may be granule-shaped again by adjusting moisture. The trace metal concentrations are within the European label except for Cadmium, the concentration of which is slightly above the limit value. It may be used to renew the humic substances of soil. It brings nitrogen essentially as organic nitrogen but is poor in phosphorus. Thanks to its physical properties i.e. permeability, water-holding capacity, high structural stability and granulometry, compost from pulp obtained by pressing M.S.W. may be considered as a good organic amendment.

The dry part obtained after pressing M.S.W. takes the form of pancakes. Pancakes might be incinerated without any treatment. In such conditions, incinerating the pancakes gives the same ultimate waste as direct domestic waste incineration. The advantages of incinerating pancakes compared to rough domestic waste are the higher "lower combustion heat" of pancakes and the possibility of seasonal storage (in order to burn them only when the energy demand is high).

The valorization of pancakes has been studied. It begins with breaking down followed by sifting at 2.5 cm. The fraction larger than this mesh is made up mostly of paper, plastics, textiles and metals. The techniques of separation are magnetism and Foucault currents for the metals. The use of pneumatic tabling makes it possible to separate heavy plastics (mainly PVC). This makes easier the incineration of the fraction constituted of plastics (except PVC), paper and wood and which may be considered as a refuse derived fuel. The fraction smaller than 2.5 cm is largely made up of glass and inert. A pneumatic tabling enables glass to be extracted. Glass may be valorized as abrasive.

However, the different fractions obtained remain as mixtures which would necessitate a new refining by complementary exhaustive stages before envisaging recycling.

Wet air oxidation may be used for the destruction of particular constituents such as PVC, the risks of air pollution being lower than with other conventional destruction techniques. It is demonstrated that wet air oxidation of solid polymers is possible. The process may also be applied to the destruction of chemically or biologically contaminated materials. The destruction of polymeric material, synthetic as well as natural, is complete at the relatively low temperature of 280°C. After this step, the problem is the degradation of soluble intermediaries of reaction, such as acetic and benzoic acids, which have been more extensively studied. Oxidation of organic compounds containing chlorine or sulphur causes the formation of strong mineral acids which must be neutralized. Addition of $CaCO_3$ is a good solution to it. At the end of the process, halogens are found in the aqueous effluent in the anionic form. One of the advantages of wet air oxidation is that some constituents of M.S.W. could be simultaneously treated with industrial waste.

The various results makes it possible to propose a general diagram for M.S.W. treatment. It is economically viable, enables the recycling of organic matter, energetic valorization and takes into account environmental problems. The choice of one of the variants depends on the size of the conurbation.

VALORIZATION OF MUNICIPAL SOLID WASTE USING A CLEAN TECHNOLOGY WHICH ASSOCIATES PRESSING, AEROBIC OR ANAEROBIC DIGESTION AND WET AIR OXIDATION

REWA-CT92-0015

Coordinator : **Laboratoire de Chimie et Environnement** (LCE),
Université de Provence, 3 Place Victor Hugo, 13331 Marseille Cedex 3, France.
Tel : 33 91 10 63 74 or 33 91 10 63 77
Fax : 33 91 10 63 77

C. Massiani, A. Prone, M. Ambrosio, Domeizel, N. Valentin, E. Krisner, Tech. J.L. Da Prato

The staff is composed of 9 research workers and one engineer, 8 PhD students and 3 technicians. The main activities of the laboratory are related to the treatment and valorization of solid wastes and to the development of analytical methods. The research work deals more particularly with the following aspects : composting and agricultural valorization of organic wastes, electrodepollution, wet air oxidation, speciation and mechanisms of micropollutant transfers in treatment chains and in environment, metrology of water quality, study of the UV spectroscopic characteristics of fresh waters and effluents. LCE has a co-responsibility in the organization of a PhD and is involved in national and international programmes.

Institut Polytechnique de Lorraine (INPL-LEM)
Rue du doyen M. Roubault, 54 500 Vandoeuvre, France
Tel : 33 83 50 30 38
Fax : 33 83 55 21 53

J.L. Pineau,

The "Laboratoire Environnement et Minéralurgie" (LEM) is a part of the Institute National Polytechnique de Lorraine. The LEM is also associated with the CNRS (CNRS-URA 235). The laboratory consists of 36 members of staff and about 40 students. The LEM is divided into six scientific and technical departments : mineralogical and physico-chemical research, mineral processing engineering, chemical treatment, pyrometallurgical treatment, chemical laboratory, and infrared spectrometry department. The major problems we are currently working on are : characterization, modification and utilisation of natural minerals, physico-chemistry of selective flotation and flocculation, water treatment, industrial and municipal waste treatment, stabilization-solidification processes, purification of solid and liquid waste. The LEM is involved in many national and international projects.

Istituto di Chimica Industriale,
Universita di Genova, Corso Europa 30, 16132 Genova, Italia.
Tel : 39 10 353 61 99
Fax : 39 10 353 61 96

U. Bianchi, P. Marchese, L. Musi, A. Panaro, S. Penco, E. Piovano

The Istituto di Chimica Industriale which is a part of the Faculty of Science of the University of Genoa, consists of a staff of 18 professors and researchers, and 18 technicians. In 40 years of activity, competence has been developed in the field of both natural and synthetic macromolecules. About 10 years ago, a group on environmental chemistry was constituted. It deals with the interactions, at a global level, between production processes and environment. In this field, specific research have been done on plastics and environment, conservation of non renewable resource, and management of industrial and urban waste. Recently, a research project was concluded with DGXII/H2 within the framework of programme SAST, project n° 7 on "Non oil-based polymers" and "The substitution of virgin plastics by recycled material".

Génie Chimique en Biotechnologie, DCC/DESD/SEP/SEATN
Centre d'Etudes nucléaires de Cadarache, 13108 Saint Paul Lez Durance Cedex, France.
Tel : 33 42 25 71 72
Fax : 33 42 25 42 74

P. Lessart

DESD/SEP/SEATN in Cadarache is a laboratory specialised in the transfer of technologies developed for the nuclear industry to non nuclear applications and particularly the environment. For the latter field, this laboratory works on 3 techniques :

- membrane separation of particles or molecules with or without previous specific adsorption, and/or surface membrane pre-treatment (micro or ultra or nano filtration),
- industrial waste water depollution using microbial properties (sorption, degradation) with application to metal removal and nitrate degradation, and the dissolving and complexing capacities of micro-organisms (treatment of soils polluted by metals or HAP),
- thermal treatment of waste with high temperature gas filtration, pyrolysis under controlled atmosphere, and wet air oxidation.

The laboratory also has some proficiency in chemical engineering.

MAIN OBJECTIVES OF THE PROJECT

The originality of the proposed scheme for the treatment of municipal solid waste (M.S.W.) consists in the association of a hydraulic press for "phase" separation with wet air oxidation for the treatment of specific constituents.

The principal expected results are :

- for the press
    - to separate, in a one stage process, the easily biodegradable fraction of the waste from the other constituents, fraction which may be valorized in agriculture after biological treatment,
    - to reduce the volume of the waste,
    - to obtain chemically and biologically stable "dry constituents", which makes their storage possible and facilitates their sorting by usual industrial techniques,
- for wet air oxidation, proposed as an alternative to conventional combustion for particular constituents such as PVC,
    - to improve control of the quality of aqueous and gaseous effluents,
    - to minimize air pollution since the reactions take place in a confined reactor (for example gaseous pollutants such as acidic gases may be transferred to the aqueous phase).

Recycling of mass consumer products

EV5V-CT92-0241

Coordinator: A.M.M. Ansems

TNO-MEP
NL - 7300 AH Apeldoorn
Tel: +31-55.5493937
Fax: +31-55.5493287

The recycling of mass consumer products

Environment project EV5V-CT92-0241

Starting date 1-1-1993
Duration 42 months

Project partners

TNO-MEP (Coordinator)
Mr. A.M.M. Ansems
P.O. Box 501
7300 AH Apeldoorn
The Netherlands
Tel: +31.55.5493937
Fax: +31.55.5493287

Forschungs Zentrum Seibersdorf Ges.m.b.H
Mr. N. Schwarz
A-2444 Seibersdorf
Austria
Tel: +43.2254.7802216
Fax: +43.2254.74060

Fraunhofer Gesellschaft
FHG-ICT
Mr. N. Eisenreich
Joseph von Fraunhofer Strasse 7
D-76327 Pfinztal 1 (Berghausen)
Germany
Tel: +49.721.4640.138
Fax: +49.721.4640.111

General Electric Plastics BV
Mr. S. Verbraak
P.O. Box 117
4600 AC Bergen op Zoom
The Netherlands
Tel: +31.164.231575
fax: +31.164.232327

Sony Deutschland International
Mr. J.M. Ludwig
Stuttgarter Strasse 106
D-70736 Fellbach
Germany
Tel: +49.711.5858.476
Fax: +49.711.5789.833

Skoda Research
Mr. V. Kanta
Tylova 57
316 00 Plzen
Czech Republic
Tel: +4219.221967
Fax: +4219.7733889

Main objectives

- The development of processing routes for the recycling of the plastics from mass consumer goods as brown and grey goods (TV-sets, Computers, etc.)
- Focusing on dismantling, materials recovery and upgrading, bulk recycling, materials recognition and degradation of plastics containing hazardous components.

Main results

- Model for the analysis of disassembly of mass consumer goods,
- Automatized robot cell for the disassembly of components like keyboards,
- Hybrid system for the disassembly of TV-sets
- Processing route for the re-use of plastics from the disassembled housings of . keyboards,
- Processing route for the re-use of plastics from bulk recycled housings of TV-sets,
- On-line recognition system for non-black plastics
- Batch-process for the degradation of plastics and hazardous materials like flame retardants by means of critical water oxidation.
- Development of improved components for a continuous process for the degradation of plastics by critical water oxidation.
- Risk Assesment on the processing and granulation of mixtures of plastics, adhesives and coatings.

The recycling of mass consumer products
Environment project EV5V-CT92-0241

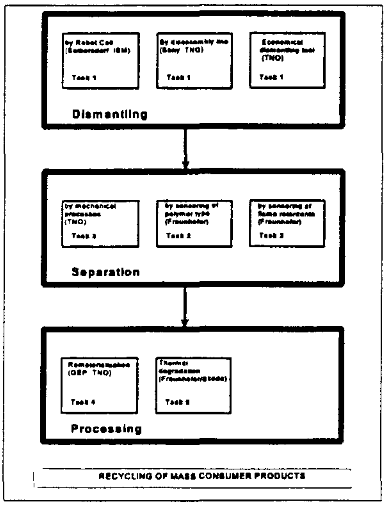
Edwin Langerak,
TNO Institute of Environmental Sciences, Energy Research and Process Innovation
Apeldoorn, The Netherlands

Objectives of the project

In totally 7 partners: TNO-MEP (Coordinator, The Netherlands), Forschungs Zentrum Seibersdorf (Austria), Fraunhofer Gesellschaft (FHG-ICT,Germany), General Electric Plastics BV(The Netherlands), IBM UK, (United Kingdom), Sony Deutschland International (Germany), Skoda Research (Czech Republic) have combined their forces to develop solutions for the recycling of the plastics from from mass consumer goods as brown and grey goods (TV-sets, Computers, etc.). The scope of the project was focused on different technologies, like dismantling, materials recovery and upgrading, bulk recycling, materials recognition and degradation of plastics that contain hazardous components. The project started on January 1993 and has a duration of 42 months.

Main results of the project

During the last 36 months the results of the project have been integrated in the development of an overall processing route, as shown on the following figure:



The general route for a recycling process consists of 3 steps:

- Dismantling
- Separation
- Processing

This figure shows that, depending on the composition of the product and the objectives of the process, various routes can be followed to reach the final goal. Depending on the route, for example disassembly could be achieved by manual labour or automated recognition and disassembly, or could even be skipped in the favour of mechanical bulk recycling. The processing can consist of rematerialization of the recyclate by blending and reextrusion, or degradation of the material in non-hazardous components.

Model for the analysis of disassembly of mass consumer goods

The main advantage of disassembly of a product is that the remaining materials are defined very well. The disadvantage is that it can be very time consuming.

The disassembly of a product must be carried out cost-effective, and at the same time various processing routes exist. In order to be able to define the most promising routes, a model has been developed that can be used to determine the best processing route available. A software prototype, *ERIS: Electronics Recycling Information System*, has been set up as a tool for economial evaluation and optimization of the recycling process, and to facilitate communication between the manufacturers and recyclers of products.

Automatized robot cell for the disassembly of components

The dismantling of electronic devices into clean fractions (e.g. plastics) is to be preferred to a shreddering procedure where the generated mix of materials is of a lower quality. In addition to manual dismantling activities, the aim was to show that there is an automatic alternative, which is adaptable to changing environmental parameters and flexible enough to handle a manifold of different variatons of a technical product.

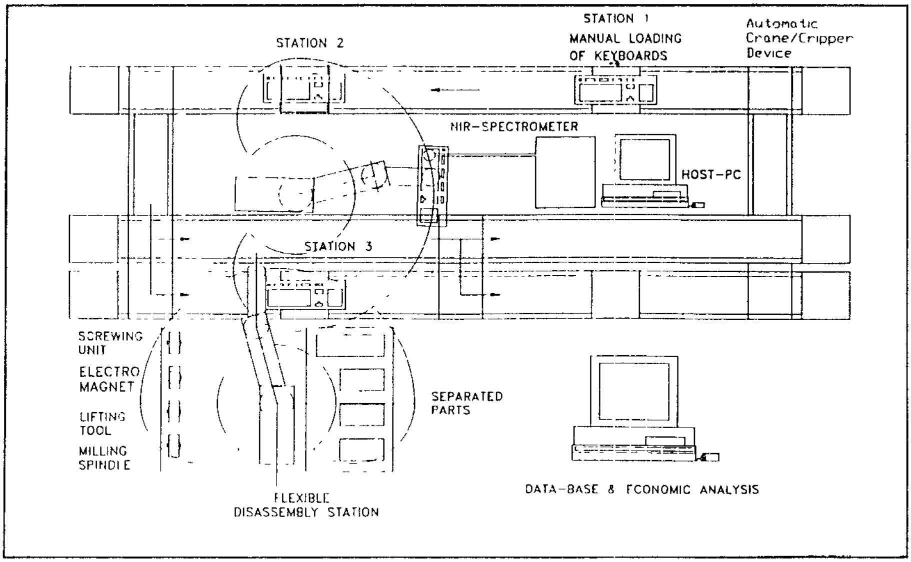
To make things not too complicated, a computer keyboard has been chosen for a representative consumer product which is complex enough to merit the application of an automated robotaided disassembling process, has a high plastic fraction by weight, has been produced in sufficient numbers to expect the necessary backflow in the near future.

The processing cycle of the system is as follows (see also figure on next page). From a waiting position, Station 1, the keyboards are transported automatically to a Station 2. The first robot transfers the keyboard from here to Station 3, where it is exactly positioned for the following disassembling procedures.

On demand, there is the possibility to perform a fast material identification step with the NIR-Spectrometer between Station 2 and 3. This step can be activated by the information given to the robot after the product data base has been searched for relevant information during the waiting position on Station 1. Although the connection between data base information and robot working decisions have not been part of the project, some ideas about their possible interaction have been discussed. The disassembling procedure starts with the pneumatic fixation of the keyboard. The following working steps are then performed sequentially.

The last step is the removal of the base plate and an optional cleaning of the working position by a vacuum cleaner. Meanwhile the first robot starts the next working cycle.

Layout of Disassembly Cell for Computer–Keyboards



Hybrid system for the disassembly of TV-sets

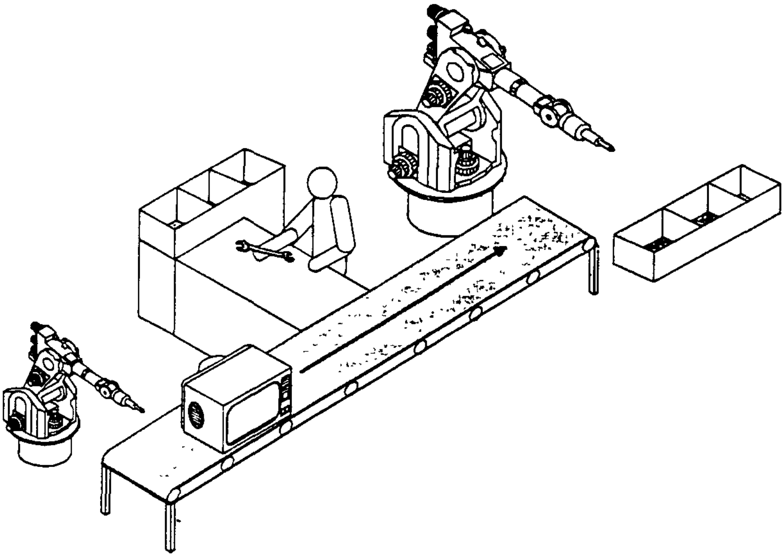
In this project, disassembly for recycling has been examined with a focus on TV sets. Manufacturers become more aware of recycling problems, and they feel more responsible for their products even after their life cycle. German legislation, for example, puts responsibility for the whole product to the person or company developing, producing, manufacturing, or distributing a product.

SONY takes its responsibility and, together with the University of Karlsruhe and also TNO, has developed a concept for a well planned semi-manual disassembly line. In parallel, automation possibilities for TV disassembly have been evaluated. The design and the construction of an experimental setup has been realized. The different tasks required for disassembly were examined and automation possibilities considered.

The value of the used products in general is very low, enforcing a quick, cheap disposal. To be able to re-use and re-utilize the materials and components, separation of the hazardous and valuable materials, and thus disassembly is necessary. Only with proper disassembly, high quality materials that can replace raw materials can be obtained.

Therefore, the main argument for a well-planned disassembly is a material purity of the fractions, which cannot be obtained by today's material separation processes, which start with shredding processes at a very early stage. Especially for TV sets which consists of a high number of different substances and elements.

A modern disassembly facility has to focus the following items: the technical and organizational system-flexibility, the advanced disassembly technology and distribution on future technology developments, the fields of safety provisions for workers, the demand for low-cost and the environmental acceptability.



The developed concept focuses mainly on a well-planned work organization and an half-automated material stream This is added by mechanical equipment, which supports workers by carrying heavy loads, and protection provisions.

Processing route for the rematerialization of disassembled plastics
The degree to which an end-of-life piece of electronic equipment has to be dismantled for recycling depends largely on the economical value of the resulting fractions. Without going into details for engineering thermoplastics the general rule holds that these materials should be sorted to complete purity within this material class, and should also be free of non-plastic contaminants. However in practice this can never been achieved for the full 100% so for each case realistic guidelines and specifications have to be designed.

Aimed at gaining relevant practical experience it was decided to take the IBM PS/2 keyboard as the subject of study. Dismantled IBM PS/2 keyboards as received from Seibersdorf were subjected to the following process steps:
1. Inspection
2. Identification
3. Separation (where needed)
4. Grinding
5. Direct injection moulding
6. Characterization

It was felt that the results from this study would create a perfect benchmark for quality standards in future, larger scale commercial recycling. Results of both characterization efforts together with the above mentioned reference values are presented in tables 1 and 2 for PBT and PC regrind, respectively.

	Standard	Unit	PBT regrind	VALOX® 325
MVR 250°C/2 16 kg	ISO 1133	cc/10'	24	14
Izod notched impact @ 23°C	ISO 180	kJ/m	5	5
Izod unnotched impact @ 23°C	ISO 180	kJ/m	NB	NB
Vicat B/120	ISO 306	°C	175	175
Flexural modulus	ISO 178	MPa	2300	2400
Flexural strength	ISO 178	MPa	79	80
Tensile modulus	ISO 527	MPa	2600	2400
Tensile stress @ yield	ISO 527	MPa	58	55
Tensile strain @ break	ISO 527	%	23	60

Table 1: Results for PBT regrind vs. VALOX© 325 reference

Property	Standard	Unit	PC regrind	Mann sample
MVR 300°C/1 2 kg	ISO 1133	cc/10'	22	20
Izod notched impact @ 23°C	ISO 180	kJ/m	16	15
Izod unnotched impact @ 23°C	ISO 180	kJ/m	NB	NB
Vicat B/120	ISO 306	°C	144	148
Flexural modulus	ISO 178	MPa	2300	2200
Flexural strength	ISO 178	MPa	87	76
Tensile modulus	ISO 527	MPa	2300	2300
Tensile stress @ yield	ISO 527	MPa	60	54
Tensile strain @ break	ISO 527	%	18	84

Table 2. Results for PC regrind vs. Mann Organisation sample reference

From the results as presented in tables 1 and 2 some important conclusions can be drawn.

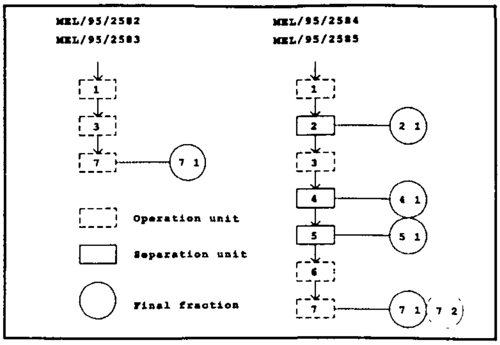
- First of all it has to be emphasized that - as a result of the fact that extreme attention has been given to the inspection, identification and separation steps - the quality of the starting material of this study should be considered as the best one could ever get. Furthermore all following steps were taken using small lab-scale machinery, again paying extra attention to processing conditions. It should be clear that, in terms of the resulting property profiles, we are looking at a best case scenario and that these results should at most only be used as a benchmark and not as a direct quality reference.
- After dismantling of the keyboards according to the Seibersdorf development some extra attention has to be given to metal separation. This can be done either before or after grinding but should in principle be no issue whatsoever.
- The rubber parts, whether they be thermoset butadiene based or of polyurethane nature, should be removed. Even the smallest level of residual contamination will undoubtedly lead to reduced residual properties. There is also a potential health risk involved in the form of isocyanate fume emissions during melt processing resulting from the polyurethane rubber parts.
- For as far as can be judged by comparing with the references and also based on our experience it can be stated that the residual properties of the tested materials reflect the effect of multiple melt processing (molecular weight breakdown leading to higher flowability, MVR and lower ductility, tensile strain at break) ands potentially also low levels of residual contaminations (lower ductility, tensile strain at break).
- Overall it can be concluded that material of this or equivalent quality represent a valuable feedstock for post-consumer recycle based products, such as GE Plastics REMEX® product line. This can be taken as very encouraging in view of future recycling opportunities.

Processing route for the rematerialization of bulk recycled plastics

The activities that have been carried out have been focused to determine the quality of the endfractions with different ways of treatment. A number of experiments have been carried out to determine the effectiveness of dismantling compared to bulk recycling techniques. A series of frontcovers and backcovers of one of the latest Sony models have been treated in various ways:

Method a: dismantling of the cover to remove all components (inserts, connectors, etc.)
Method b. shredding of the covers and separation of polluting materials.

The resulting endfractions have been tested subsequently on material properties and applicability.



Operation units	Separation units	Final fractions
1. Shredder 3. Knife mill 6. Dryer 7 Knife mill	2. Drum magnet 4 Sink/float-cell 5. Sink/float-cell	2 1 Iron fraction 4.1 Sink fraction 5 1 Float fraction 7 1 End product 7 2 Dust fraction

Figure 1: Flow diagrams of recycling routes

The results of these separation experiments are described in the following tables:

Sample	**Composition**							
MEL 95/2584	**Al (kg)**	**Fe (kg)**	**Felt (kg)**	**Paper (kg)**	**PS-HI (kg)**	**SAN (kg)**	**Plastics (kg)**	**Total (kg)**
2.1	-	0.040					0.432	0.472
4.1	0 024	0.001					0.049	0.074
5.1								6.033
7.1								32.496
7.2								0.002
Feed								39 722

Sample	**Composition**							
MEL 95/2585	**Al (kg)**	**Fe (kg)**	**Felt (kg)**	**Paper (kg)**	**PPE+PS (kg)**	**SAN (kg)**	**Plastics (kg)**	**Total (kg)**
2.1	-	0.216					0.042	0.258
4.1								22.057
5 1								0.020
7 1								27.245
Feed								50.253

As can be seen instantly, the material losses are of a far larger magnitude than with manual disassembly. The yield of the samples is in the range of 82% to 54% (compared to more than 98% when dismantling the fractions). This occurs because of the inevitable loss of materials due to the characteristics of the separation process. This is clearly illustrated by the example that air holes in the material can reduce the apparent density, so that more material is sieved out of the process than strictly necessary.

Comparing the bulk process with the disassembly process, the following can be concluded:
- the costs of the bulk process is caused by the grinding step and the sink-float steps. When carried out on a sufficient high scale, the unit price is appr. 0.25 ECU/kg. For disassembly, the unit price will be approximately 0.50 ECU/kg.
- the disassembly process has a better yield. With the bulk process a number of adaptations could result in improved yield, but costs will not permit too many processing steps.

On-line recognition system for non-black plastics

In order to reuse the polymeric materials from mass consumer products and to minimize the amount of chemical waste their identification and the analysis of additives is required.

The economic aspects demand fast response times (parts of a second), easy handling and its integration in on-line automated systems.

The need for a diagnostic tools arises from the fact that the physical methods e.g. based on the density do not allow a separation of polymers especially of technical plastics with sufficient purity. Various standard methods of chemical analysis have been discussed in the past. First results have been obtained using x-ray fluorescence, mass spectrometry and FTIR-spectroscopy, but have not yet lead to industrial applications.
Possibly, a combination of methods has to be applied. The following methods have been studied at the Fraunhofer-Institut ICT:

laser break down spectroscopy (LBDS)

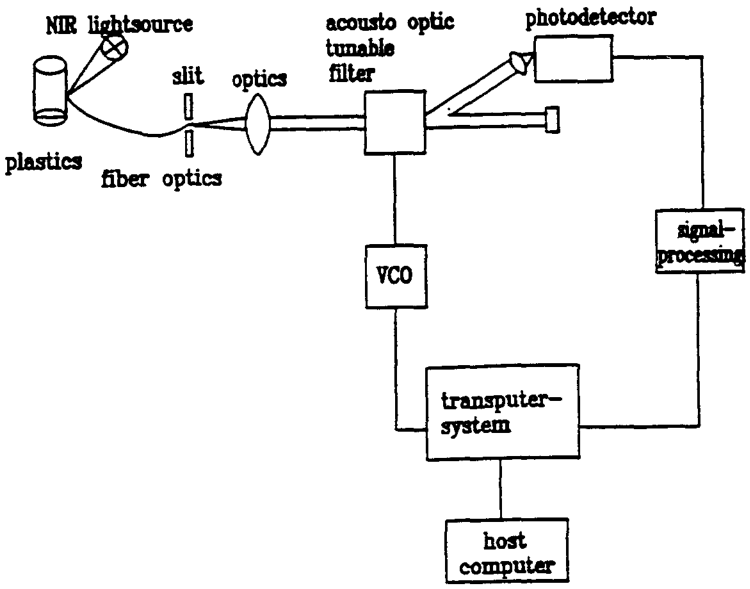
- near infrared spectroscopy (NIRS)

According to the work program of this project, the NIRS will be developed to identify the polymers of mass consumer products which are not dyed black and the LBDS to identify heavy metals and flame retardents.

During the project a dismantling robot of keyboards was developed. It was decided to adapt the identification unit not to a conveyor belt but to this robot.

The identification unit was linked by a communication interface to the robot and synchronized to its dismantling activity. So the keyboard was moved by the robot past the detector head of the NIR-spectrometer to identify the plastic material of the keys and case of the keyboard in two steps.

A demonstration was arranged at Seibersdorf to demonstrate this adaption. The identification unit fullfilled its task as expected.



The LBDS was tested independently at Fraunhofer Institute. The results were:
- heavy metals (Ba) were identified clearly
- brominated flame retardent showed no signature in LBD-spectroscopy, but the synergistic antimony trioxide could be detected, so that there is an indirect prove for their presence
- the LBD-signal could be coupled into an optical fibre
- the present version of the low-cost-spectrometersystem failed in resolution and sensitivity
- the peak power densities of a pulsed laser damaged the optical fibre

The conclusion are, that the irradiation laser must hit the sample without use of an optical fibre, but for the LBD-signal an optical fibre could be used.

Degradation of hazardous plastics by supercritical water oxidation

Supercritical fluids have attracted a great attention as potential extraction agents and reaction media in waste disposal. The use of supercritical water as a reaction medium for the disposal of halogenated hydrocarbons offers an attractive alternative to the commonly used disposal techniques. Below the critical point of water (T_c= 374 °C, p = 22.1 MPa) reactions of organic substances normally take place in a two-phase region as a consequence of the low miscibility with water. However, near and above the critical point the properties of water change drastically. As a result of the decreasing density and dielectric constant supercritical water acts like a dense gas, and the solvation properties are comparable to those of a low polarify organic solvent. Hydrocarbons and also permanent gases like oxygen and carbon dioxide dissolve completely in supercritical water. Contrary to the solubility of organic compounds the solubility of inorganic salts decreases drastically as a consequence of the decreased dielectric constant of water. These properties make supercritical water very attractive for use as a reaction medium.

The tests have led to the concept of a continuous flow reactor
The idea is to feed the waste or a waste/water-mixture and the oxidizer under supercritical conditions separately to the reactor. So the reaction starts under fixed conditions. After the reactor the product stream is cooled down depressurized so that the products can be analyzed. With this concept the reaction mechanism, reaction kinetics and several reactor types can be studied. Some components of the continuos working facility were provided in cooperation with Skoda Research.

Main hazardous materials for disposal are halogenated compounds. These compounds induce strong corrosion effects in supercritical water. The following experiments have been started in cooperation with Skoda research:
Autoclaves which were used in experiments were cut and investigated by photografic and microscopic methods to obtained some insight in the corrosion mechanisms. Typical effects of propagation of cracks in crazes and cracks were found. Several high temperature corrosion resistant materials were chosen. Corrosion effects were investigated under SCWO conditions and analyzed.

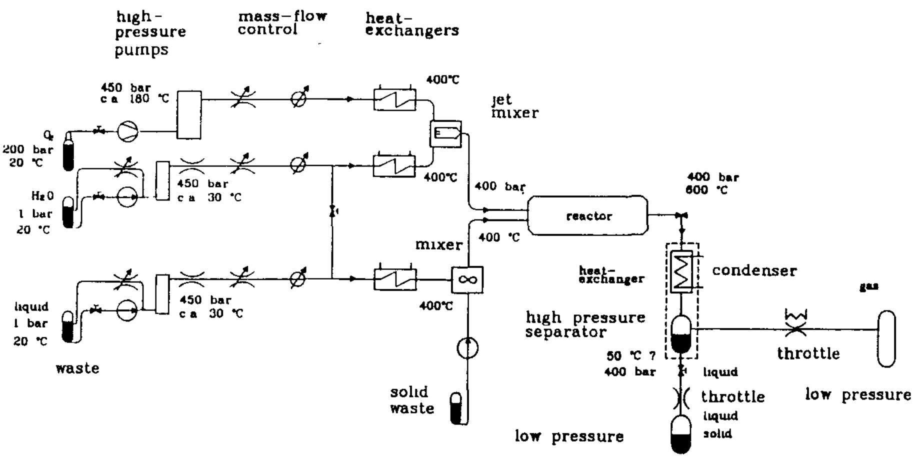


figure: continuous SCWO facility

Risk Assesment on mixtures of plastics, adhesives and coatings

It is commonly known that polymers can degrade at certain relatively high temperatures, which are usually higher than their processing temperature. This is true for both virgin and recycled polymers, but despite this, it can be recommended to consider the thermal stability of the polymer before processing any polymer. It is important to know how stable it is at elevated temperatures with oxygen absent or present and what degradation products, if any, are given off. For recycling of post-consumer products more things have to be known, like the presence of coatings, stickers and labels on the recycled product, as well as the thermal stability of these materials. These materials can consist of components which degrade at temperatures the basic polymer does not, leading to unknown emissions during reprocessing and unknown health risks.

The goal of this study is to determine the risks which can occur during reprocessing of contaminated, ground plastic material obtained from the recycling of electronic products. An example of such a health risk is the forming of the very toxic isocyanates when reprocessing ground plastic parts coated with polyurethane as in car bumpers. The determination of these kinds of risks is mostly a matter of coincidence. A structural approach could lead to the decision to change, or even to stop, a recycling process for these specific products. From the research up to now it can be concluded, however, that still not much is known about specific combinations of recycling plastics. In general not much emissions during reprocessing under normal conditions will be detected because of short period at high tempertaures. When also proper stabilization has been taken care of, there won't be much risks, besides some cases that have been reported. Laboratory analysis can be necessary in case problems are expected.

Redesign of electromechanic products for reuse and recyclability with special attention to the Cu-problem

ENV4-CT95-0148

Coordinator: N. Schwarz

Österreichisches Forschungszentrum Seibersdorf
AT - 2444 Seibersdorf
Tel: 43-2254.780 Ext.2736
Fax: 43-2254.74060

REDESIGN OF ELECTROMECHANIC PRODUCTS FOR REUSE AND RECYCLABILITY WITH SPECIAL ATTENTION TO THE COPPER PROBLEM
ACRONYM: REMPRODUSE-Cu

Contract: Nr. ENV4-CT95-0148 Starting Date: February 1996 Duration: 36 months

Coordinator: Austrian Research Centre Seibersdorf, Seibersdorf/AT
A-2444 Seibersdorf
Schwarz Norbert Dipl. Ing. Dr. tech
Tel: +02254-780
Fax: +02254-74060
Tel. Ext: 2736
E-Mail: schwarz@zdfzs.arcs.ac.at

Partners:

ABB Corporate Research,
ABB/SE
S-72178 Västeras
Ashkin Alena Dr.
Tel:+ 46 21 32 3108
Fax: +46 21 32 30 90
E-Mail: alas@secrc.abb.se

Centre for Impact Assessment, CIMA/IT
I-39012-Meran, A-1030 Wien
Via delle Corse 23, Salesianergasse 11
Alber Sebastian Dipl. Ing Dr.techn. Ass. Prof.
Tel: +39 473 210007 +43 1 713 60 84
Fax: +39 473 210304 +43 1 712 71 83
E-Mail: alber@magnet.at

Department of Physics and Measurement
Technology, Linköping Univ., LIU/IFM/SE
S 58183 Linköping,
Norrthon Petter, M. Sc.
Tel: +46 13 28 27 85
Fax: +46 13 12 25 87
E-Mail: pno@ifm.liu.se

Institute of Manufacturing Engineering,
Techn. Univ. of Denmark, DTU/DK
DK-2800 Lyngby Building 425
Gregersen Johan Christian M. Sc. ME
Tel: +45 45 25 46 06
Fax: 45 45 88 25 25
E-Mail: iputek@ipv.dtu.dk

Swedish Institute of Product Engineering
Research, IVF/SE
S 583 30 Linköping Teknikringen 1
Lundgren Jonas Tekn. Lic.M.Sc.ME
Tel: +46 13 21 25 75
Fax: +46 13 21 25 05
E-Mail: jl@ivf.se

Assembly Technology, Department of Mechan.
Engineering, Linköping Univ., LIU/IKP/SE
S 581 83 Linköping
Björkman Mats Ph.D., Mech.Eng.
Tel: +46 13 28 11 36
Fax: +46 1328 27 98
E-Mail: matbj@ikp.liu.se

Objective:

The project's main goal is to reduce significantly the environmental burdens by reducing the flow of resources and by recycling valuable materials during the product life cycle. This will be achieved by a complementary strategy of redesign, reuse, recycling and disassembly options with LCA as a guiding instrument for environmentally sound decisions.

Brief Description of the Research Project:
The following research tasks will be carried out during the project
(1) Detailed analysis of the present technical situation. Identification of the most relevant Cu-containing product.
(2) LCA for selected product. Reference basis for later investigations.
(3) Develop a first design-methodology, including disassembly, reuse and life extension.
(4) Develop multisensory systems for functionality check to support automated disassembly.
(5) Design of functional unit using new methodology and functionality check. LCA elaborations.
(6) Evaluation of technical feasibility. Choice of fabrication procedure with respect to economic considerations.
(7) Mechanical and software adaptation of robot-aided disassembly line.Test of procedures on laboratory scale.
(8) Test of improved sensor systems and integration with disassembly line.
(9) Final LCA of developed product line.
(10) Improved design methodology, elaboration of guidelines and design tools based on experiences gained during sensor-controlled disassembly demonstration.

REDESIGN OF ELECTROMECHANIC PRODUCTS FOR REUSE AND RECYCLABILITY WITH SPECIAL ATTENTION TO THE COPPER PROBLEM

ACRONYM: REMPRODUSE-Cu

Objective of the Research Programme

The objective of the research work is to contribute to the elimination or mitigation of priority environmental problems by developing solutions of wide-ranging and general applicability. This will be realised by using and further developing a consistent methodology for life-cycle analysis to be used for developing cleaner products and production methods and to find solutions for a significant reduction of overall environmental impacts.

Most of to-day's mass-products are characterised by a linear flow of materials through the technosphere, from the mining of the resources until the products are thrown away Although it is technical standard to shredder products or part of products at the end of their life, this procedure needs a high energy input and results in the mixing of materials. The necessary sorting, in most cases, will not give the needed purity of materials required for the fabrication of new products. The resulting downcycling or quality loss of materials will therefore not reduce the necessary flow of resources in the product life cycle and will only decelerate the flow of material to landfills

An essential improvement of this situation can be realised by the following measures:

- Design for disassembly and recycling to generate clean materials at the end of the product life and to realise a closed material cycle.
- Design for reuse of products or part of it to reduce the input of new resources.

To demonstrate the viability of this approach, electromechanic devices which have a high copper content are chosen as an example of a more complex industrial product.

Special attention is given to copper because it is a heavy metal and hence a potential menace to the environment. Primary smeltering and refining of copper belongs to the most intensive industry sectors for toxic emissions and electricity consumptions. In addition, copper can be an irritating impurity, e g. in steel scrap to be reused for steel production. Problems with copper can also be seen in a resource perspective. It is expensive and causes great material flows during mining. There should be no doubt that copper has to be handled in closed cycles in a future sustainable society.

The results of the project activities will be of importance for product designers, production- and recycling industries and education organisations and comprise the following items:

- Information generated about the present situation of products in relation to environmental issues, by performing LCA with emphasis on copper recycling.
- Information on redesign with a model example by increasing life-time and recyclability, with the aim to protect the environment and at the same time save money.
- Investigation and demonstration of the feasibility of recycling and reuse options in the production industries, thereby reducing mass-flows and energy-consumption.
- Creation of design-tools and process management tools to improve future product development decisions.

Overall effects of the project can be seen in the reduction of necessary energy and labour input for the requalification of materials, in the increase of the residence time of materials in the technosphere, the closing of material cycles and a better and safe handling of copper resources. A further aim is to implement a change in design strategy for new product lines and a contribution to the knowledge and general concern for creating a sustainable society in the foreseeable future.

Outline of Project Methodology and Work Plan

With LCA as a guiding instrument for sound economic and environmental decisions, the feasibility of new design and fabrication models, the improvements in the disassembly procedure, and the economic validity of automated, robot-aided disassembly techniques will be investigated.
By applying these strategies to a selected representative electromechanic component (e.g. motor or transformer) improvements in the following areas will be demonstrated.

Reduction of the flow of resources:
    by reducing ore-mining and accompanying mass flow and transport activities
    by increasing the efficiency of copper-use, thereby reducing the flow of Cu through the technosphere and reducing Cu concentration in the environment and in landfills
Reduction of energy use:
    by reducing ore-mining, thereby avoiding Cu smeltering and refining processes
    by using added value in products through the reuse of functional units
Reduction of environmental impacts:
    by reducing mass flows for energy and material production and their accompanying side-effects (e.g. landscape demolition, dust production, transport infrastructure)
    by reducing the production of secondary toxic substances like greenhouse gases.
Reduction of handling problems during recycling:
    by designing products for disassembly
    by using automated disassembly techniques with multisensor technology to avoid human contact with poisonous materials and dusts

The overall structure of the project is the following:

- Analysis of the present technical situation, the role of copper products and production systems, recycling options by performing a LCA-analysis
- Selection of the most promising product for redesign
- Development of new tools for reuse and recycling strategies, focusing on copper problems
- Design of adapted sensor systems and performance of laboratory tests for improved material recycling
- Design and test of automated robot-aided recycling technologies using new sensor systems
- Development of product prototype with new reuse and recycling options
- LCA of prototype, considering the new design strategies
- Construction of prototype (rapid prototyping or similar method) and demonstration of reuse, disassembly and recycling
- Documentation and publication of improved guidelines and design tools for learning and educational purposes

Description of the First Working Periode, Task 1

Since the Project is in its starting phase, only the work content without discussion of the preliminary results can be described:

During this Task, the problem areas of possible redesign for life-extension, reuse, Cu-recycling, and implications to the production process will be analysed and an electromechanic product will be identified and used as a test case for further investigation.
Since this Task has a kind of kickoff effect, it is thought desirable that all partners are engaged in the process of understanding each others' problems and learn to know the available problem solution capacities.

The ongoing different activities in the sub-tasks which finally will be summarised in a Task-report, are the following:

Identification of problem areas with respect to reuse and recycling of electromechanic products (technological, societal, cultural...) with special focus on copper. Description of present situation.

- The flow of copper through individual economies is analysed for two test-cases, Austria and Sweden
- The use of typical materials in E-motors is investigated (actual dismantling of different motor types) and analysed with respect to environmental implications
- Description of recycling paths for E-motors used to-day
- Evaluation of new data (field tests in Austria) about collection, dismantling and deposition of consumer- and electromechanic products

Selection of representative electromechanic product and description of present environmental implications.

- Quantitative description of size, design and production numbers of motors in different product groups (e.g. household appliances and motorcars)
- Screening of representative products focused on household washing machines and a ventillation system, which will be further analysed
- Analysis of two preliminary life cycle cases with the the washing machine. One with full recycling into a new washing machine, and one with steel and copper recycling into products with less severe metal quality requirements. Subsequent parameter variations to find optimum improvements
- General description of the toxicity of copper in the environment and implications to the life cycle of copper containing products

First choice of adaptable guidelines.

- Critical evaluation of the state of the art of support methods being used for all aspects of redesign of products, with special focus on EM-containing products
- Preliminary application of a first choice of guidelines for redesigning the production process of a selected product, e.g. household washing machines

The removal and recovery of cadmium by biosorption, flotation and electrolysis

EVWA-CT92-0003

Coordinator: I.C. Hancock

Microbial Technology Group
Department of Microbiology
Newcastle University
UK - NE2 4HH Newcastle upon Tyne
Tel: +44-191.222.7704
Fax: +44-191.222.7736

REMOVAL AND RECOVERY OF CADMIUM BY BIOSORPTION, FLOTATION AND ELECTROLYSIS

Contract no. EVWA-CT92-0003

STARTING DATE JANUARY 1st, 1993, DURATION 2 YEARS

COORDINATOR:
Microbial Technology Group, Department of Microbiology, Newcastle University
Dr I C Hancock Department of Microbiology, The Medical School, University of Newcastle upon Tyne, Framlington Place, Newcastle upon Tyne NE2 4HH, UK.
Telephone +44 191 222 7704
Fax +44 191 222 7736
E-mail I.C.Hancock@ncl.ac.uk

PARTNERS:

Environmental Engineering Laboratory, Department of Civil Engineering, Newcastle University
Ms L M Evison Department of Civil Engineering, Cassie Building, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK.
Telephone +44 191 222 7931
Fax +44 191 222 6669

Department of Chemistry, Aristotle University, Thessaloniki, Greece.
K.A. Matis Chemistry Department - Chemical technology Division, BOX114, Aristotle University, Thessaloniki 54006, Greece.
Telephone +3031 997794
FAX +3031 206138

Electrochemical Techniques Limited, Stockport, Cheshire, UK (ETL)
Dr F.S. Holland Electrochemical Techniques Limited, 5 Castleton Road, Hazel Grove, Stockport SK7 6LB, Cheshire, UK
Telephone +44 161 483 6665
Fax +44 161 456 8542

OBJECTIVES

The aims and objectives of the 24 month programme were as follows:

(a) To develop a highly innovative total cadmium removal and recovery process involving biosorptive removal of the metal ions from dilute aqueous solution, recovery of the metal-loaded bacteria by flotation techniques, and electrolytic recovery of cadmium metal from the biomass.

(b) To develop an equally innovative multidisciplinary approach to solving cadmium removal involving microbiology, reactor design, flotation technology and electrochemistry.

(c) To enable cadmium to be removed down to 10 parts per billion (ppb) and below, from industrial effluents (including the liquid effluent from ion-flotation processes), landfill leachates, mine drainage waters, and other dilute solutions and recover the cadmium as elemental metal so that there is no cadmium waste disposal hazard.

(d) To develop a cadmium removal process which can be exploited commercially after further development. The focal point for this commercialisation will be the SME associated with this project, with the technical support of the other proposers.

RESULTS AND ACHIEVEMENTS

The two-year project ran to programme throughout, and in general met the expectations of the original plan. In one respect the work achieved an unexpected success. The development of a simple technique for recovering cadmium-loaded biomass on a filter and eluting cadmium from it *in situ* had not been planned, but followed from small-scale experiments early in the project. This process has the potential to effectively eliminate a more expensive phase-separation step in the overall process, with potentially considerable savings in cost.

As proposed in the original programme, a joint experiment of the project research groups was conducted in the Environmental Engineering Laboratories of Newcastle University during January, 1995. Flow rates from 100 to 400 cm^3/minute were tested in six separate experiments, with two different ratios of biomass to filter-aid material. Phase separation by both flotation and flocculation-sedimentation were examined. The process was successful, giving a reduction in cadmium concentration of dilute aqueous solutions from 5 mg/litre to about 10 μg/litre. Elution from the biomass with a sodium sulphate-containing electrolyte solution achieved sifficient concentration of Cd to facilitate metal recovery by electrolysis. The process was very rapid, taking about 40 minutes to complete, starting with 40 litres of dilute cadmium solution and finishing with 0.8 litre of concentrated eluate for electrolysis. Flotation recovery of cadmium-loaded biomass showed some reduction in efficiency due to excessive foaming after several cycles, but batch studies suggest that this can be readily remedied by a reduction in surfactant addition during later cycles. No problems were encountered with the flocculation technique.

The project successfully achieved its aim of designing and demonstrating the effectiveness of a strategy for the removal of cadmium from dilute aqueous solution using bacteria biosorption with dead biomass of waste commercial origin, flotation for phase separation and electrolysis for recovery from the eluted cadmium sulphate of metallic cadmium powder. In the process a simple and very effective phase separation and elution technique using flocculation and sedimentation of the biomass in the presence of mineral filter aids has been developed and successfully applied in the process.

The process has considerable commercial potential and this is now being pursued through a variety of channels.

PUBLICATION

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REMOVAL AND RECOVERY OF CADMIUM BY BIOSORPTION, FLOTATION AND ELECTROLYSIS

Contract no. EVWA-CT92-0003

PARTNERS:

Department of Microbiology, University of Newcastle, UK
Responsible scientist: I. C. Hancock
Researcher: A. Phillipson

Department of Civil Engineering, Newcastle University
Responsible scientist : L. Evison
Researcher: T. Butter

Department of Chemistry, Aristotle University, Thessaloniki, Greece.
Responsible Scientist: K.A. Matis
Researcher: N. Lazaridis

ETL. Ltd, Stockport, Cheshire, U.K.
Electrochemical Techniques Ltd (ETL), Stockport, UK
Responsible Scientist: F. Holland
Researcher: A. I. Sheikh

INTRODUCTION

The process under investigation is the removal by biosorption of cadmium ions (nominally Cd^{2+}) from dilute aqueous solutions by biosorption, separation of the biomass by flotation, elution of sorbed cadmium ions at a high concentration and their recovery as cadmium metal powder by electrolysis in a commercially available rotating cathode electrolytic cell.

The biomass selected for this project consists of dead actinomycete bacteria of the genus*Streptomyces*. These bacteria grow as a branched, filamentous, flocculent biomass and we and others have shown that most of their bivalent metal cation-binding capacity can be attributed to anionic groups in the cell wall. Thus, biosorption occurs with either dead or living material. Over the course of one biosorption/elution cycle the biomass is challenged with two extreme environments. Firstly, cadmium itself is a very toxic element (growth of the majority of *Streptomyces* strains examined was inhibited by 10 ppm added cadmium in the standard culture medium) and is frequently associated in industrial discharges with additional toxins such as cyanide and other heavy metals, as well as extremes of pH. Secondly, at the elution stage the biomass is subjected to a very high ionic strength which would adversely affect the osmotic balance of living bacteria. For these reasons dead biomass has been preferred in the present work. *Streptomyces clavuligerus* biomass, a by-product of an industrial antibiotic fermentation process, has been the chosen biomass for the majority of the work as it is cheap, available in large quantities and exhibits a high loading capacity and high affinity for cadmium. The process flow diagram is shown in the Appendix

PART I. Department of Microbiology, Newcastle University

Selection of *Streptomyces* strain for process development

The cadmium binding properties of dead biomass from a range of strains of branched, filamentous *Streptomyces* bacteria isolated from cadmium-polluted sites have been compared with the properties of a strain of *Streptomyces clavuligerus* that is a waste product of the commercial fermentation producing the antibiotic, clavulanic acid. Detailed examination of strains isolated from cadmium-polluted sites has revealed a sub-set of strains (A312, A403, A702, A801) that exhibit both high capacity and high affinity for cadmium-binding.

We have compared the Cd-binding properties of these strains, together with one (A101) that had exceptionally low affinity, with the performance of industrial *S. clavuligerus* biomass (**Figure 1**). Langmuir anlaysis of the equilibrium binding data provides a measure of maximum binding capacity (Bmax) and binding affinity (K). While *S. clavuligerus* exhibited a higher capacity for binding Cd than the other strains, its apparent affinity was very much lower than most of the others, and indeed not much higher than strain A101. In this form it would not be useful for biosorption at low cadmium concentrations. However, we have determined that conversion of the biomass to an appropriate initial ionic form achieves a dramatic improvement in performance. The protonated form had decreased capacity and affinity for Cd , but the sodium form of the biomass showed a slight increase in capacity and an order of magnitude increase in apparent affinity for Cd (**Table 1**). Similar treatment of other strains exhibiting low affinity also produced increases in affinity but had little effect on several strains that initially exhibited high affinity. Thus by converting the *S. clavuligerus* biomass to the sodium form its performance could be improved to approach that of the best of the new isolates. Recycled biomass from which Cd had been eluted with a sodium salt would thus be expected to exhibit excellent performance in a subsequent biosorption cycle.

On this basis, industrial *S. clavuligerus* biomass was chosen for subsequent work.

Optimisation of cadmium biosorption to *S. clavuligerus*

Cd-binding capacity increased progressively with increasing pH from 3 to 8. The binding affinity was maximal at pH5 (**Figure 2**). Above pH 8 apparent binding capacity and affinity rose steeply, probably due to changes in speciation of Cd. Above about pH 10 it is likely that precipitation would occur. Cd biosorption was extremely rapid, reaching at least 85% of saturation in the first 30 sec of mixing (**Figure 3**). The biosorption of metals from equimolar mixtures of cadmium, copper, lead and zinc nitrates is shown in **Figure 4**. The relative affinities are those predicted on simple ion-exchange theory. Comparison with 20 other strains of *Streptomyces* from cadmium-polluted soils showed no dramatic variation in metal selectivity between the strains at the lower concentration (each metal initially at 0.1mM, i.e 11.2 ppm cadmium, total metal bound 0.28 mmol/g biomass) but selectivity was more pronounced at the higher (saturating) concentration (total metal bound, 0.54 mmol/g biomass), when cadmium and zinc competed less effectively with , in particular, lead. The basis of this concentration-dependent selectivity is currently under investigation.

Summary

After appropriate treatment, waste *Streptomyces clavuligerus* biomass from an industrial antibiotic fermentation process exhibits cadmium biosorption properties close to the best performance identified in a wide range of new isolates. The biosorption properties of this biomass are unchanged when it is mixed with filter aid materials. Metal binding to the biomass is extremely rapid, and is effective over a range of pH between 5 and 8. The biomass binds a range of metal cations as predicted from ion-exchange theory. It is concluded that because of its availability in large quantities as a by-product of an industrial process *S. clavuligerus* is an appropriate choice for the proposed process.

PART II. Department of Civil Engineering, Newcastle University

Biosorption of cadmium

A simple stirred tank reactor containing a free cell suspension is used for biosorption. This facilitates a high mass transfer rate between metal ions in solution and the bacterial cell walls. The filamentous morphology of the *Streptomyces* biomass aids floc formation and phase separation. For biosorption/elution work in this part of the project the biomass as supplied was mixed with filter aids which were of additional benefit during separation steps. Using this biomass cadmium concentrations can be reduced from 5mg/litre (0.45 x 10^{-4}M) down to about 10µg/litre (greater than 99% removal). For high initial cadmium concentrations a multiple step biosorption is required to meet the target discharge levels. As shown in Part I above, other heavy metals compete with cadmium for binding sites in the cell wall but Group I and II metals will not interfere except at very high concentrations. The biomass has been taken through eight complete cycles of biosorption and elution with no reduction in cadmium uptake performance.

Phase separation

Three methods for the recovery of biomass from the waste liquor after biosorption have been examined.

Flotation. Analysis of this technique is presented in Part III. Dispersed air flotation was very effective over several cycles but accumulation of surfactant and/or frother on the biomass appeared to cause excessive frothing after 4 or 5 cycles, and a reduction in the biosorptive capacity of the biomass (**Table 2**). Dissolved air flotation appears to offer improved performance.

Filtration. Filtration did not prove satisfactory on its own, since the flow rate of liquor through the filter decreased over time through a combination of blinding of the filter membrane (45 μm nylon mesh) and compaction of the filter bed.

Sedimentation. The addition of a cationic polyelectrolyte (Zetag 64, Allied Colloids) accelerated the flocculation and settlement of the biomass. The solids were concentrated at the bottom of a conical sedimentation tank and then collected for subsequent elution. This method of phase separation was very effective (>95% recovery of biomass), fast (at the 40 litre scale sedimentation time is 10-15 minutes) and the apparatus is simple and cheap. The polyelectrolyte did not affect biosorption of cadmium by the biomass in subsequent cycles (see **Table 1**). This combination of factors results in sedimentation being an attractive method of phase separation.

Elution

The elution stage has two main functions: to strip biosorbed cadmium from the biomass, which is thus regenerated for a subsequent biosorption step; and to generate an electrolyte for final cadmium recovery by electrolysis using the Rotating Cathode Cell (RCC). The eluant / electrolyte system which has been successfully tested consists of sodium sulphate and ethylenediamine in boric acid. The latter two components aid electrolysis, while the high sodium concentration displaces bound cadmium by ion exchange and ensures that the biomass is in the optimum sodium form for the next cycle of biosorption (see Part I and **Table 1**).

Initial experiments using a stirred tank proved unsuccessful, giving poor removal of bound cadmium. However, when the solids (including the filter aids) from the biosorption stage were immobilised on a filter, the biomass could be eluted rapidly and efficiently by drawing the eluant through the filter bed under a slight vacuum (< 0.17 bar vacuum). 95-100% removal of cadmium was routinely achieved if the eluant was drawn through the filter at a linear flow rate of 12.5-25 cm.h^{-1}. The biomass/filter-aid mix was rehomogenised and used for a further biosorption step (**Table 1**).

To minimise the volume of eluant to achieve a cadmium concentration sufficiently high for efficient electrolytic recovery, the cadmium-loaded solids from the 40 litre rig were eluted on a 500 mm diameter Nütsche filter with 800 ml of eluant to give a 50-fold increase in cadmium concentration from the original 0.5 x 10^{-4} M test solution. For cost-effective electrolysis the RCC does not recover all the cadmium presented to it in this eluate (see Part IV). As the concentration of cadmium in the electrolyte drops, metal recovery becomes increasingly ineficient in terms of plant utilisation. Consequently, depleted eluate returned for the next cycle contains some Cd^{2+} . The presence of 1mM Cd in the eluant slightly reduced elution efficiency in subsequent cycles, but there was no detrimental effect on biosorption (**Table 3**). In addition, the concentration of Cd in the eluate/electrolyte returning to the RCC was higher in the subsequent cycles, improving the efficiency of the electrolysis process.

Summary

Through a combination of biosorption using a free cell suspension, phase separation by sedimentation, and elution on a filter, the cadmium concentration of dilute aqueous solutions can be reduced from 5 mg/litre to about 10 μg/litre, then concentrated by elution in an electrolyte salt solution to facilitate metal recovery by electrolysis. The process is very rapid, taking about 40 minutes to complete, starting with 40 litres of dilute cadmium solution and finishing with 0.8 litre of concentrated eluate for electrolysis. The simplicity, low cost and short timescale for the complete operation suggests that the process will readily scale up for industrial use.

PART III. Department of Chemistry, Aristotle University, Thessaloniki, Greece.

Flotation recovery of cadmium-loaded biomass

A continuous dissolved air flotation rig has been constructed and tested, and some results are presented below. In addition an electrolytic flotation technique was briefly tested, with rather similar results.

Optimisation of flotation collector and other additives

Efficient flotation of biomass and biomass/filter-aid requires addition of a surface-active collector to create the appropriate surface properties on the biomass. It was found that the flotation collector cetyltrimethylammonium bromide (CTMA-Br) affected cadmium biosorption at high concentrations. At 10^{-4} M CTMA-Br, a cadmium removal from a 10^{-4}M solution of 92.8% was achieved. **Table 1** summarises the performance of a single cycle, using *S. clavuligerus* biomass without filter-aid. The presence of filter-aid material did not affect the performance of the flotation cell at an equivalent total solids weight. However, at 10^{-3} M CTMA-Br the cadmium removal was reduced by 27.5% and at 10^{-2} M CTMA-Br it fell by 82%. Dissolved air flotation gave good cadmium and biomass recovery at lower CTMA-Br concentrations (10^{-4}M) and in the absence of ethanol.The effect of other additives that might be present in the process (borate, formaldehyde, electroplating brightener) was investigated. In some cases an effect on flotation was observed, which could be minimised by an increase in collector concentration.

Test of continuous biosorption/flotation on the 40 litre scale

A joint experiment of the project research groups was conducted in the Environmental Engineering Laboratories of Newcastle University during January, 1995. The results are summarised in **Table 2.** Flow rates from 100 to 400 cm^3/minute were tested in six separate experiments, with two different ratios of biomass to filter aid.

Summary

Conditions for efficient continuous flotation of *Streptomyces* biomass with residence times as low as 4 minutes have been determined. The process provides a satisfactory and fast method of recovering both metal-free and metal-loaded biomass and permits excellent recovery of biosorbed cadmium. Work is continuing to find a solution to the problem of foaming during repeated recycling.

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PART IV. Electrochemical Techniques Ltd (ETL), Stockport, UK
Responsible Scientist: F. Holland
Researcher: A. I. Sheikh

RECOVERY OF CADMIUM METAL POWDER FROM BIOMASS ELUATES BY ELECTROLYSIS

Electrolysis is the final recovery step of the multistage process for cadmium metal abstraction from dilute aqueous solutions. Because the stages are interlinked the conditions used in the electrolysis stage can have significant implications for the elution and biosorption stages. Electrolysis aims to produce metallic cadmium powder and cadmium-depleted electrolyte for re-use as eluant for cadmium loaded biomass.

The Rotating Cathode Cell (RCC) is one of the most successful 2-dimensional cathode geometries of electrochemical reactor designs. This is a continuous flow cell operating at very high rates of mass transport, recovering the metal automatically outside the cell. Important experimental conditions are described below, and the design of the unit is shown in **diagram 1**.

Composition of electrolyte

The criteria for selecting the electrolyte are quite restrictive. The electrolyte must be capable of eluting the cadmium ions from the biomass and compatible with the production of powdered cadmium rather than smooth plate enabling metal to be removed easily from the cell. The catholyte system in use is sodium sulphate salt solution, boric acid for buffer capacity and ethylenediamine as a chelating agent to improve the overall stability of the electrolyte system. This facilitates electrolysis at higher pH values of 8.5-9.5 enhancing powder formation.

Electrolysis cell

Peripheral velocity of rotating cathode. A peripheral velocity of between 300 and 600cm/s provides the turbulent flow conditions required, while a catholyte flow of 300-900l/h allows high intensity mass transfer in the cell.

Current density. Current densities between 0.04-0.29A/cm^2 and optimum current efficiencies of 22-54% are conducive to metal powder production at higher cadmium feed concentrations of 650mg/l down to 10 mg/l. Electrolysis power consumption of the order of 8 KWH/kg of cadmium was utilized. Controlled cathode potential experiments were conducted as this affects current efficiency and thus the nature of the metal deposit.

Metal deposition

Electrolysis conducted on an initially hydrodynamically smooth electrode resulted in fine powder formation, thus facilitating continuous product removal from the cell and recovery in the metal collection area of the reactor.

Ratios of metal remaining on the electrode post-run to the total amount of cadmium deposited during a run were tabulated. Lower ratios of 0.12-0.2 were repeatedly observed with ethylenediamine/cadmium ratios of 1.2-0.7.

Conclusions

Experimental work on conditioning the electrolyte and the optimization of the electrochemical parameters has been satisfactory and the technique for production of continuous metal powder as the final stage of the multi -step process has been well-researched. The effectiveness of the technique as part of the overall process of biosorption, elution and metal recovery has been demonstrated.

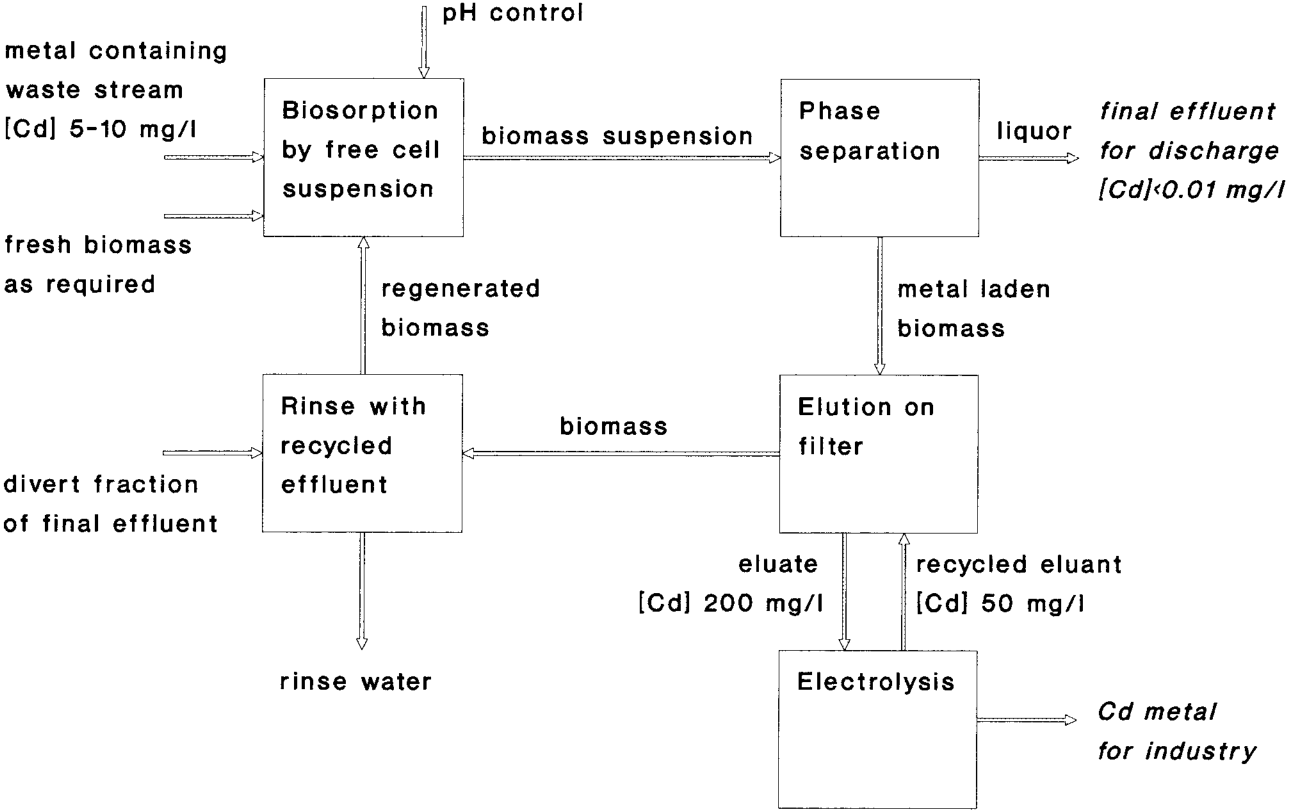

Figure 1. Schematic flow diagram of overall process

PART I

TABLE 1. Langmuir constants B_{max} (maximum binding capacity) and K (affinity constant) for biosorption of cadmium by *S. clavuligerus* with different counter-ion forms of initial biomass.

Form	**B_{max}**		**K**	
	mg/g biomass	μmol/g biomass	l/mg	mM^{-1}
untreated	52.8	470	0.38	43.0
sodium	66.7	593	2.50	281.0
protonated	30.3	270	0.13	14.7

PART II

Table 1. Biosorption and elution performance over 5 complete cycles using the 40 litre rig, sedimentation for phase separation, and elution on the Nütsche filter.

CYCLE	1	2	3	4	5
Initial [Cd] (mg/l)	5.13	4.66	4.65	4.73	4.57
Final [Cd] (mg/l)	0.34	0.03	0.06	0.01	0.00
% of Cd biosorbed	93	99	99	100	100
% of biosorbed Cd eluted	77	95	83	74	94

NOTES TO TABLE 1:

1) The final and initial cadmium concentrations referred to in the table are those in the test waste solution.

2) Note that biosorption efficiency improves as the biomass is taken through more recycles.

3) The variable elution results are believed to be due to the speed with which the eluant passes through the filter bed, which in itself is a result of slight variations in the vacuum pressure applied to the Nütsche filter.

Table 2. Biosorption and elution performance over 5 complete cycles using flotation for phase separation.

CYCLE	1	2	3	4	5
% of initial Cd biosorbed	96	87	50	32	25
CTMA added to give X molar conc	1.0x10^{-4}	0.5x10^{-4}	0.5x10^{-4}	0.5x10^{-4}	0.5x10^{-4}
% of biosorbed Cd eluted	95	89	98	92	–

NOTES TO TABLE 2:

1) Experiments performed on a 20 litre batch scale, the biomass being challenged with a 4.5 mg Cd/l test solution.

2) Biosorbed Cd eluted on a 240 mm diameter Buchner filter using 500 mls of eluant. Biomass then re-homogenised and reused for biosorption.

3) CTMA-Br was added at every flotation step in sufficient quantity to give the concentrations described above. The actual concentration of CTMA-Br was probably higher due to it moving from one step onto the next on the biomass.

4) At the end of Cycle 5 the biomass was too frothy to handle so no elution was performed.

Table 3. Biosorption and elution performance over 3 complete cycles comparing the effects of elution with and without 100 mg Cd/l in the eluant on subsequent biosorptions and elutions.

CYCLE	1A	1B	2A	2B	3A	3B
Initial [Cd] (mg/l)	4.84	4.84	5.37	5.37	5.06	5.06
Final [Cd] (mg/l)	0.01	0.01	0.00	0.00	0.01	0.01
% biosorbed Cd eluted	97	82	100	106	98	78

NOTES TO TABLE 3:

1) Sample A eluted with eluant containing no extra Cd. Sample B eluted with eluant containing 100 mg/l Cd.

2) Experiments performed as 400 ml batches with sedimentation for phase separation. Elution on a 48 mm diameter Buchner filter using 70 mls of eluant.

PART III

TABLE 1. Laboratory dissolved-air flotation experiments with cadmium-loaded biomass (unwashed*S. clavuligerus*, pH 7, 41% solubility; CTMA-Br 10^{-4}M, ethanol 0.5%). A 5 litre feed was used, with a retention time of 10 minutes)

Biomass addition (g/L)	Initial cadmium concentration (x 10^4) M	Recycle ratio	Removal of cadmium (%)	Biomass recovery (%)	
				turbidim.	gravim.
1	1	30	90.8	96.7	98.0
1	1	10	82.6	54.6	61.6
2	1	30	94.4	75.3	74.1
1	0.5	30	92.8	77.3	79.7

European Workshop on Recycling Technologies,
Treatment of Waste and Contaminated Sites
Hannover, 20-24 May 1996
POSTER

RECOVERY OF HEAVY METALS FROM EFFLUENTS BY SORPTION (OR BIOSORPTION) AND FLOTATION

K. A. Matis and A. I. Zouboulis

Chem. Technol. Div., Chemistry Dept.,
Aristotle Univ., GR-540 06 Thessaloniki

Abstract

Sorption and flotation have been extensively studied in the laboratory applied, among others, to toxic metals recovery from effluents. The various parameters of the process were investigated in-depth, including the reuse of sorbent. The latter could also well be a biosorbent, i.e. biomass produced as an industrial by-product.

Many inorganic sorbents were proved to be effective for metal ions removal from dilute aqueous solutions. Synthetic sorbents (hydroxyapatite, goethite, etc.) are often produced in particulate form and after metal sorption in a CSTR-type equipment, solid/liquid separation is necessary, for instance by flotation. Promising results were obtained from the point of view both of metal removal and solids recovery.

The removal of toxic metals from water and their selective recovery by biosorption, elution and electrolysis

ENV4-CT95-0068

Coordinator: I.C. Hancock

Microbial Technology Group
Department of Microbiology
Newcastle University
UK - NE2 4HH Newcastle upon Tyne
Tel: +44-191.222.7704
Fax: +44-191.222.7736

THE REMOVAL OF TOXIC METALS FROM WATER AND THEIR SELECTIVE RECOVERY BY BIOSORPTION, ELUTION AND ELECTROLYSIS (BioElecDetox) ENV4-CT95-0068

STARTING DATE MARCH 1st, 1996, DURATION 3 YEARS.

COORDINATOR:
Microbial Technology Group, Department of Microbiology, Newcastle University
Dr I C Hancock Department of Microbiology, The Medical School, University of Newcastle upon Tyne, Framlington Place, Newcastle upon Tyne NE2 4HH, UK.
Telephone +44 191 222 7704
Fax +44 191 222 7736
E-mail I.C.Hancock@ncl.ac.uk

PARTNERS:
Environmental Engineering Laboratory, Department of Civil Engineering, Newcastle University
Ms L M Evison Department of Civil Engineering, Cassie Building, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK.
Telephone +44 191 222 7931
Fax +44 191 222 6669

Departamento de Engenharia Quimica, Instituto Superior Tecnico , Lisbon, Portugal (IST).
Professor Jorge M. Rodrigues Carvalho Departamento de Engenharia Quimica, Instituto Superior Tecnico , Av. Rovisco Pais 1, 1096 Lisboa Codex, Portugal.
Telephone +3511 841 7311
Fax +3511 849 9242

Department of Chemistry, Aristotle University Thessaloniki, Greece (AUT).
Dr A I Zouboulis Chemistry Department-Chemical Technology Division, BOX 116, Aristotle University, Thessaloniki 54006, Greece
Telephone +3031 997794
Fax +3031 206138

Nucleo de Hydraulica Sanitaria, Laboratorio Nacional de Engenharia Civil, Lisbon, Portugal (LNEC)
Dr M. Mesquita Hydraulics Department- Division of Sanitary Engineering, Laboratório Nacional de Engenharia Civil, Avenida do Brasil 101, 1799 Lisboa Codex, Portugal.
Telephone +3511 846 3439
Fax +3511 847 8614
E-mail mmesquita@lnec.pt

IMP Metals Department, Instituto Nacional de Engenharia e Tecnologia Industrial, Lisbon, Portugal (INETI)
Dr Francisco Rodrigues IMP Metals Department, Instituto Nacional de Engenharia e Tecnologia Industrial, Estrado do Paço do Lumiar, 1699 Lisboa Codex, Portugal.
Telephone +3511 716 5141
Fax +3511 716 6568

Electrochemical Techniques Limited, Stockport, Cheshire, UK (ETL)
Dr F.S. Holland Electrochemical Techniques Limited, 5 Castleton Road, Hazel Grove, Stockport SK7 6LB, Cheshire, UK
Telephone +44 161 483 6665
Fax +44 161 456 8542

1. OBJECTIVES and EXPECTED ACHIEVEMENT

The project takes a multidisciplinary approach involving the combination of microbiology, environmental engineering, chemical engineering, chemistry and electrochemistry to remove, separate and recycle toxic metals from wastewater. It aims to develop a process involving the following steps:

(a) absorption of metal ions on dead bacteria , yeasts or fungi or mixtures thereof, obtaining partial selection/absorption
(b) selective or partially selective elution of the metal ions from the separated biomass
(c) controlled potential electrolysis of the eluates to give the individual metals.

The successful project would economically:-

- reduce toxic metal ion concentrations in aqueous wastes down to 10 µg/L
- enable the European Union to meet its own water quality directives
- recover and recycle clean water for reuse within industry
- recover the metals as separate metals for industrial use

Thus there will be no toxic metal waste disposal hazards.

Expertise has been assembled in the following areas:
Microbial metal biosorption - University of Newcastle upon Tyne (bacteria and fungi) and IST, Lisbon (yeasts)
Biomass-liquid separation by flotation - Aristotle University, Thessaloniki
Biomass-liquid separation by flocculation - LNEC, Lisbon
Metal elution and hydrometallurgy - INETI, Lisbon
Controlled potential electrolysis - ETL, Stockport

In addition, a continuous techno-economic assessment of the data and its significance for the overall process will be carried out by the Solid and Hazardous Waste Research Unit (SHWRU), Newcastle upon Tyne, as a sub-contract within the the Newcastle component of the project.

At the time of preparation of this abstract work industrial sources of bacterial, fungal and yeast biomass have been identified, and the initial project meeting has been held. Laboratory work will commence on April 1st, 1996.

1. OBJECTIVES and EXPECTED ACHIEVEMENT

The project takes a multidisciplinary approach involving the combination of microbiology, environmental engineering, chemical engineering, chemistry and electrochemistry.

The successful project would economically:-

- reduce the metal ion concentrations down to 10 μg/L
- enable the European Union to meet its own water quality directives
- recover and recycle clean water for reuse within industry
- recover the metals as separate metals for industrial use

Thus there will be no toxic metal waste disposal hazards.

2. TECHNICAL APPROACH

Several of the present consortium came together in the last framework (EVWA-CT92-003) and have developed a successful, very specific, almost total, removal of cadmium (down to 10 g/litre) with the metal being recovered as virtually pure cadmium for reuse. This process will have limitations when applied to the mixed metal situation of commonly occurring contaminated waters. Such mixtures could be Cu, Ni, Zn with Cd, Hg, Pb, and a total removal of these would be advantageous in giving clear water, but if the metals were recovered as a mixture then this would be of low value and require further refining. This refining would in turn generate more pollution hazards.

To overcome these limitations we propose to:

(a) absorb the metal ions on dead bacteria or fungi or mixtures thereof, obtaining partial selection/absorption
(b) selective or partially selective elution of the metal ions from the separated biomass
(c) controlled potential electrolysis of the eluates to give the individual metals

This is novel and we believe we are combining the best aspects of novel biosorption technology with the best aspects of chemistry, chemical engineering and electrochemistry to produce a low energy consuming highly efficient process to give clean water, recover separate metals with a good space time yield and low environmental impact and cost.

This approach to removing and safely recycling mixtures of toxic metals as separate metals envisages a process involving repeated re-use of the microbial sorbant. Bacterial, yeast and fungal biomass will be used together, or in succession, to achieve maximum removal of the widest range of mixed metals. A degree of selectivity will be achieved (a) at the biosorption step by the use of bacterial and fungal biomass exhibiting different biosortion properties, (b) at the elution step by selective elution, (c) at the electrolysis stage by controlled potential electrolysis.

The overall process will contain the following steps:

(a) obtaining metal- binding bacteria and fungi for initial plant charge and much smaller make-up;
(b) contacting contaminated water with biomass, leading to absorption of metal cations onto the biomass;
(c) separating the metal-loaded bacteria by flotation or flocculation and filtration;
(d) sending the liquid effluent (containing tracesof the metal-loaded biomass) to a suitable polisher to remove remaining traces of microbes and give metal-free water. Periodically the polisher is back-washed and the biomass returned to the system;
(e) eluting the metals from the flocculated and settled biomass by filter elution;
(f) electrolysing the dilute aqueous metal eluant to give metal and regenerate elution liquor for re-use;
(g) selling the metal powder for industrial use.

Steps (a), (b), (c), (e) and (f) are the subject of this research project .

Measurable Objectives

* metal removal from contaminated water to 10 g/Litre
* metals recovered as nearly pure and separately

- relatively small, efficient plant with low running costs
- no toxic metal containing waste for disposal

3. OVERVIEW OF THE TECHNICAL PROGRAMME

The scientific and technical background.

Fundamental processes of biosorption

The biosorption of toxic metal cations by microorganisms, including bacteria, cyanobacteria, yeasts, fungi and algae has become well established in the last decade. Biosorption by dead microbes involves binding by ionic and covalent complexation mechanisms to the surface matrix of the microbial cell (the cell wall and capsule). Cell-surface binding and deposition of bivalent metal cations in the thick, porous, anionic matrix of the cell walls of Gram-positive bacteria, particularly the filamentous actinomycetes, exhibits considerable variations in extent and selectivity depending on the nature and amount of the anionic cell wall components (teichoic acids and acidic polysaccharides). Actinomycete bacteria are attractive because of their wide commercial use and the favourable morphological characteristics that they display for use in waste-treatment processes. In these Gram-positive bacteria, there is a strong correlation between the amount of teichoic acid in purified cell walls and the metal-binding capacity of walls and whole biomass. Metal binding is generally an electrostatic process of the kind found for conventional ion-exchange resins. "Hard" metal cations that form predominantly ionic interactions (such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}) are favoured in this type of process.

Yeasts exhibit substantial biosorption of "soft" metals that form principally covalent metal-ligand bonds (such as Cu^+, Pb^{2+}, Tl^+, Hg^{2+}) , and this form of biosorption is even more pronounced in some filamentous fungi such as *Rhizopus* and *Penicillium* . Metal cations of intermediate "hardness" (such as Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+},Cd^{2+} exhibit some interactions of both kinds. The different metal selectivity of the fungi is due to the very different chemistry of the metal-binding sites on their surfaces. In most of these microbes, the wall consists of interwoven chitin microfibrils embedded in a protein/polysaccharide matrix, and the formation of covalent complexes with the chitin N and O is believed to be the basis of soft metal binding. These differences in properties lead to significant differences in metal selectivity between bacteria and yeast/fungi , with soft/intermediate metals favouring ligands such as -SH, $-NH_2$, imidazole, and hard metals favouring anionic ligands such as phosphate and carboxylate . The precise geometry of the ligand groups can also be important - Ni^{2+} complexation favours octahedral, over tetrahedral, geometry for binding, for example, while the possibility of phosphodiester groups in close proximity to one another acting as bidentate ligands adds an additional degree of selectivity to hard metal cation binding .

An important feature of the type of biosorption discussed above is that the microbes bind the metals of interest primarily in the stable cell wall, outside the biochemically active cell membrane and cytoplasm, and so can be used in processes as live or dead biomass with good biosorptive capacities. This feature has three particular advantages:

(i) since the metal is extracellular, mass transfer for both absorption and elution is improved;

(ii) since the microbes need not be alive, the toxic effects of the metal of interest, and of other metals in the environment, need not be a problem.

(iii) since dead biomass can be used, waste biomass from commercially sensitive manufacturing processes, and from processes that result in partial microbial death, such as brewing, is available. Tens of thousands of tonnes of these by-product biomasses are produced in each European country each year.

Biosorption and elution for biomass-process design

For many existing biosorption techniques, the biomass has to be immobilised as small, porous, stable beads with good hydrodynamic properties. Immobilisation in this form requires the development of specific protocols for individual species of microbe. It may be expensive and result in poor mass transfer kinetics due to diffusional limitation. Methods of contacting using microbes in their native forms offer considerable advantages in these respects, if suitable cheap, efficient solid-liquid separation techniques are available. Such separation techniques are already in widespread use in sludge processes, but have received relatively little attention in the field of metal biosorption, possibly due to the perceived difficulty of subsequently eluting the metals for recycling.

We have investigated the removal by biosorption of cadmium ions from dilute aqueous solutions on dead filamentous bacterial biomass in free suspension. A simple stirred tank reactor containing a free cell suspension was used for biosorption. This facilitated a high mass transfer rate between metal ions in solution and the bacterial cell walls. The filamentous morphology of the *Streptomyces* biomass aided floc formation and phase separation. For biosorption/elution work in this part of the project the biomass was mixed with filter aids which were of additional benefit during separation steps. Using this biomass, cadmium concentrations could be reduced from 5 ppm (0.45 x 10^{-4}M) down to about 10 ppb (greater than 99% removal). For high initial cadmium concentrations a multiple step biosorption was devised to meet the target discharge levels. Methods for recovery of metal-loaded biomass wereeither flotation with a surfactant, or sedimentation following the addition of a cationic polyelectrolyte flocculant. Both were successful for the recovery of biomass from the waste liquor after biosorption.

The possibility of selective elution of metals from biosorbent loaded with mixed metals has not been widely studied. However, ion exchange theory and the concept of "hard" and "soft" metals predicts that gradations of ionic strength and pH should result in partial separation of metals during the elution process, while further selectivity might be obtained by the use of specific complexation agents, such as the use of bicarbonate for elution of actinide elements and "soft" anions such as thiosulphate and water-soluble organic complexing agents for soft metals.

A particular advantage of the use of free biomass and the solid recovery and elution techniques described above is the small volume occupied by the sedimented biosorbent. Total biosorption of metals from solution requires a high biomass/metal ratio, but for economical metal recovery costs the eluate must have the highest possible metal concentration. By minimising the volume occupied by the biosorbent, the use of free biomass offers much greater efficiency in comparison with immobilised biosorbents in which the inert support material forms a very substantial proportion of the total volume.

The electrolytic recovery of metals

Disposal of metal-loaded biomass simply creates a further environmental hazard - one which has recognised in connection with the accumulation of heavy metals in sludge from activated sludge sewage-treatment processes. However biosorbed metals can be eluted from biomass and the bacteria re-used. Though the concentration of metal ions in the eluate is still dilute (10-100ppm), specialised electrolysis techniques are available to abstract metals from these solutions to give the metallic elements and reusable elution liquors.

We have demonstrated that cadmium can be extracted from biosorption eluates using a Rotating Cathode Cell (the RC-Cell). The RC-Cell is a major advance in the technique of recovering dissolved metals from effluents and other dilute solutions, offering considerable advantages over existing systems. It means that, for the first time metals, including cadmium, copper, zinc, nickel, cobalt and tin can be extracted efficiently from liquids, even very dirty effluents, by a continuous process at comparatively low cost.

Impure and dilute solutions of metal are treated in a cell incorporating a rotating cathode. The metal is reduced by a continuous electrolysis process forming dendrytic crystals of the metal onto the cathode. These crystals are broken off in a turbulant boundary flow and are separated from the liquid by conventional liquid-solid separation techniques. Due to very high mass transfer levels, a high rate of deposition is achieved, and in many cases most of the metal is extracted. The products of the cell are metal powder and metal-depleted liquor.

Dilute solutions containing from 10 ppm to 200 ppm of metal can be reduced in soluble metal concentration down to as little as 2ppm.

The Tasks of the Programme

The roles of the participant groups are shown diagramatically in the Figure

TASK 1: SELECTION OF MICROORGANISMS AND ASSESSMENT OF THEIR BIOSORPTION PROPERTIES.

TASK 2: MICROBIAL PROCESS DEVELOPMENT FOR BIOSORPTION.

TASK 3: BIOMASS-LIQUID SEPARATION BY FLOCCULATION AND SETTLING

TASK 4: BIOMASS-LIQUID SEPARATION BY FLOTATION

TASK 5: ELUTION OF METALS AND RECYCLING OF BIOMASS.

TASK 6: ELECTROLYTIC RECOVERY OF METALS FROM ELUATES OF BACTERIA.

TASK 7: TESTING OF THE OVERALL PROCESS.

The aim of the final task will be to assess the performance of the components of the system in an integrated form at the 40 litre scale.

The work will comprize:

(a) a large scale (40 litre reactor) experiment, binding mixed metals from synthetic and real wastewatersonto the selected biomasses;

(b) recovery of the metal-biomass by flotation and flocculation/sedimentation;

(c) elution of the metals using the best elution techniques to achieve some separation of metals in the process streams;

(d) electrolytic recovery of the metals, with metal separation achieved by controlled potential electrolysis.

All the parameters of the process described for **Tasks 1-5** will be monitored during the tests.

Some of the required equipment, including the RCC electrolysis unit, is already available in the Environmental Engineering Laboratory at Newcastle. Further non-standard equipment will be fabricated in the workshops there.

TASK 8: TECHNO-ECONOMIC ASSESSMENT

The overall objectives of this task are to evaluate the technical and economic potential of the project as an ongoing task through the project, and to ensure that we are taking the correct options at every stage. This will amount to an ongoing feasibility study assessing each task and its results against the criteria: does it work and at what eventual cost?

During the project potential end users will be approached and the feasibility of our processes assessed against their requirements with the aim of stimulating interest towards collaboration and justifying the building of a prototype pilot plant.

Process technology for the recovery and recycling of chromium from leather waste and sludge

EV5V-CT94-0542

Coordinator: M. van Vliet

BLC The Leather Technology Centre
Leather Trade House
UK - NN3 6JD Northampton
Tel: +44-1604.494131
Fax: +44-1604.648220

Project: Process technology for the recovery and recycling of chromium form leather waste and sludge.

Project No.: EV5V-CT94-0542

Start Date: 01.07.1994

End Date: 01.11.1996

Duration: 28 Months

Project Co-ordinator:

Dr. M. van Vliet
BLC The Leather Technology Centre
Leather Trade House
Kings Park Road
Moulton Park
NORTHAMPTON
NN3 6JD
U.K.
Tel. +44 1604 494131
Fax. +44 1604 648220

Partners:

Dr. S. Rydin
Danish Technological Institute
Postbox 141
DK-2630 Taastrup
Tel. +45 4350 4350
Fax. +45 4350 7150

Dr. Ing.habil. Hans-Jurgen Kellert
Westdeutsche Gerberschule Reutlingen
72764 Reutlingen
Erwin-Seiz-Str. 9
GERMANY
Tel. +49 7121 1623-0
Fax. +49 7121 1623-11

Mr. R. Tumer
SATRA Footwear Technology Centre
SATRA House
Rockingham Road
Kettering
Northamptonshire
NN16 9JH
U.K.
Tel. +44 1536 410000
Fax. +44 1536 410626

Main Objectives:

To recover chromium from solid wastes produced by the tanning industry.

To recover chromium from discarded leather items such as worn out footwear, upholstery and clothing

To recycle the chromium as a tanning agent

Main Results:

Development of chemical processes for the recovery of chromium from blue shavings

Production of tanning agent from recovered chromium

Production of leather from recovered chromium

Production of chromium containing ash from tannery wastes

Publications:

Project presentation at the European Workshop on Environmental Technologies in the Leather Industry held in Bologna on 10 May 1995.

Project presentation at the second European Recycling Workshop held in Brussels 29-30 June 1994.

Project presentation from a workshop in Vienna on Recycling Technologies.

Recovery and Recycling of Chromium from Leather Waste and Tannery Sludge.
BLC Journal, August 1995.

Recovery and Recycling of Chromium from Leather Waste and Tannery Sludge - Part II
BLC Journal, November/December 1995.

PROCESS TECHNOLOGY FOR THE RECOVERY AND RECYCLING OF CHROMIUM FROM LEATHER WASTE AND SLUDGE

A research project supported by the European Commission

Presented by: Dr. Stefan Rydin, Danish Technological Institute, Denmark

Summary

The general objective of the project is to recover chromium from solid waste byproducts from the leather industry, mainly shavings and trimmings. Furthermore, the possibilities of recycling the recovered chromium as a tanning agent or as a raw material in the metallurgic industry have been investigated.

Two fundamentally different recycling routes have been investigated.

Thermal treatment has included trials with plasma pyrolysis, conventional incineration and gasification. Preliminary results indicate that gasification is a cost-effective and technically feasible method for the treatment of chrome waste.

Chemical treatment has included trials with alkaline hydrolysis, acid hydrolysis and enzymatic hydrolysis. Simple processes have been developed with both alkaline and acid hydrolysis. The addition of enzymes to the hydrolysis process only showed a limited improvement of the process. Successful tanning trials using recovered chromium from alkaline hydrolysis have been performed.

Introduction

Throughout the world approximately 90% of the produced leather is tanned with chromium. One of the major environmental problems of the leather industry is the generation of solid waste containing chromium. This waste is generated as chrome shavings, leather trimmings, buffing dust and sewage sludge.

In Europe, more than 100,000 tonnes of chrome shavings are generated every year as a waste product in connection with leather manufacturing. In addition, approximately 500,000 tonnes of chromium containing sludge with 1-5% chrome from waste water treatment are produced.

The leather waste material is considered to be a major problem because of:

1. Lack of depositing sites for waste
2. Waste of valuable resources that may have a potential value

Landfilling is currently the final destination of most chromium containing waste. A minor proportion of the total amount of chrome shavings is utilized in the production of "leatherboard", but this amount is decreasing.

In order to investigate different potential solutions to the problem with chromium containing leather waste, a consortium consisting of BLC The Leather Technology Centre (coordinator, UK), Danish Technological Institute (Denmark), Lederinstitut Gerberschule Reutlingen (Germany) and SATRA (UK) started a research project 1 July, 1994 which will end in November, 1996. The project has obtained financial support from the EC Environment and Climate Programme.

The general objectives of the project are to:

- Recover chromium from solid wastes produced by the tanning industry.
- Recycle chromium as a tanning agent

The objectives of the project can be summarized as in figure 1, where the relationship between the existing problem and the proposed solution is shown.

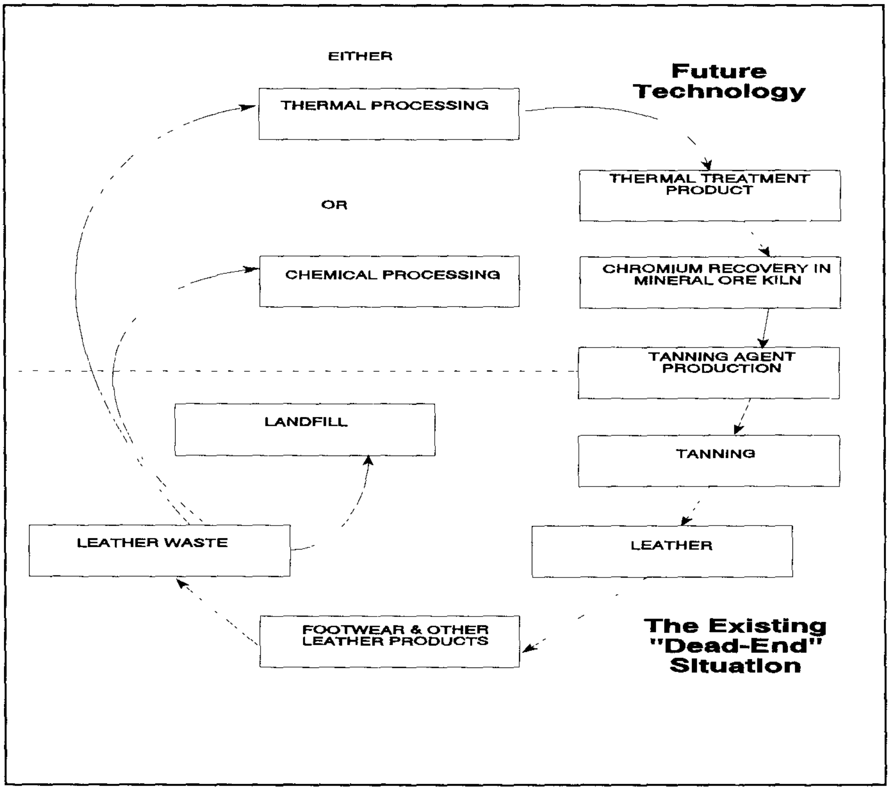

Figure 1 *Relationship between existing problem and proposed solution*

Work Programme

The research has been concentrated on two fundamentally different approaches to solve the problem with chromium containing waste from leather manufacturing. The two ways are thermal treatment and chemical treatment.

Thermal treatment

Plasma pyrolysis, incineration and thermal degradation have been investigated with emphasis on general performance, energy efficiency and environmental impact.

The ash produced has been analyzed and its suitability for use in the metallurgic industry or as a tanning agent has been evaluated.

Chemical treatment

Chemical processing represents a potential alternative or complement to thermal treatment, and the philosophy is that the system could be implemented using relatively simple equipment in the tannery. The main objectives are:

- To identify the most appropriate leather waste hydrolysis system in terms of practicality and efficiency.
- To optimize the process.
- To use the recovered chromium as a tanning agent.

Results

Chemical treatment

Three different ways of chemical hydrolysis have been investigated in the project. The different technologies are: alkaline hydrolysis, acid hydrolysis and enzymatic hydrolysis.

A simple chemical process to hydrolyse wet blue shavings has been developed. The principle is shown in figure 2.

A major problem has been the production of hexavalent chrome. It has been shown that this is due to the high pH of 12.4. The reaction from trivalent to hexavalent chrome is slow, and measurable concentrations have only been found after allowing the digest to stand for 24 hours. Hexavalent chrome formation has been overcome by reducing pH to 10.5 immediately after the digest is complete. At this time no hexavalent chrome can be detected.

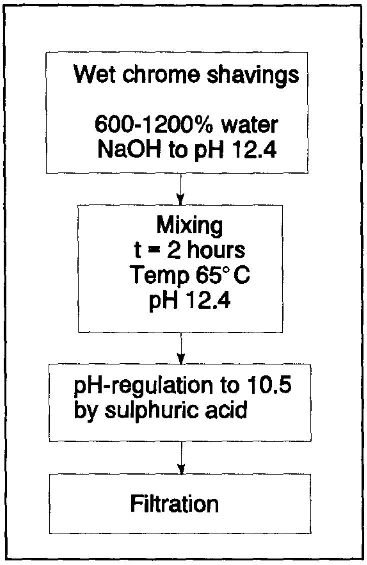

Figure 2 *Alkaline hydrolysis of wet chrome shavings*

The chrome sludge obtained from the alkaline digestion has been used to produce a chrome tanning liquor. This process includes an acidification using sulphuric acid at a temperature between 95-100°C. Small pieces of leather have successfully been tanned using 25% recycled chrome together with 75% conventional chrome tanning agent.

The effect of adding enzymes to the alkaline hydrolysis process has been studied. The effect of enzymes is low and it does not seem to be an economically feasible solution to add enzymes during the hydrolysis.

Another problem which occurred during the alkaline hydrolysis was poor filterability of the hydrolysate. This could be improved by an acid treatment followed by raising the pH to approximately 9.5 in order to achieve precipitation of the chromium.

Furthermore, trials with acid hydrolysis were carried out. These trials showed that it is possible to achieve a good hydrolysis using acid hydrolysis with sulphuric acid.

Chemical treatment has successfully been employed to recover the chrome from wet blue shavings. Buffing dust and finished leather were digested using the alkaline hydrolysis method previously employed, but without success. It is thought that the chemicals present in the leather inhibit the precipitation of the chromium in some way.

Thermal treatment

Thermal gasification can be described as an incomplete combustion, i.e. an understoichiometric combustion. During this process, solid fuel is converted into a combustible process gas.

Thermal gasification of chrome shavings has been tested at a pilot gasifier with a capacity of around 50 kg per hour of chrome leather waste (200 kW) at DTI Environmental Technology, Denmark. Chrome leather waste containing 60% water was dried and pressed to pellets. The produced pellets had a high density and was mixed with charcoal to obtain a stabile structure which is necessary to obtain a good gasification. The results have been very promising and the following conclusions have been made:

- Practically all chromium (>99.96%) was found in the ashes with a chromium content of approximately 25% and with a content of Cr^{6+} < 1%.
- No Cr^{6+} was found in the gas or in the particles from the filter units.
- A gas was produced with a composition suitable for heat production.

Plasma gasification is a novel process for thermally degrading waste products. A plasma is a gas in which some of the gas molecules are ionised to form positive ion and electron pairs. The simplest way to create a plasma in practice is to form an electrical discharge such as an arc discharge in a gas. In the plasma chamber the leather wastes are exposed to the high temperatures of the arc and are pyrolysed to a carbonaceous char, low molecular mass gases and inorganic ash. The technology has been investigated in England. The following results were obtained. Plasma arc gasification has a high initial capital cost and a relatively high energy consumption. The plasma torch electrode requires replacing after every fortnight continuous operation. This would suggest that this method of pyrolysis is not practicable to scale up.

Conventional incineration trials on chromium containing waste have been performed in Germany. The results showed that a combustion of shavings and sludge is possible without any technical problems. No Cr^{6+} could be traced in the gas.

Future research

The ashes which have been produced during the different thermal treatment methods will be analyzed and the possibilities for use of the chromium will be evaluated and tested.

Furthermore, an economic evaluation of the different technologies to threat chromium-containing waste from the leather industry will be carried out. This evaluation will be carried out on different amounts of waste depending on the size of the tanneries.

Development of a selective extractant for iron in hydrometallurgical process solutions in order to reduce the amount of ferric sludges to be dumped as chemical waste

EV5V-CT94-0568

Coordinator: K.H. Ujma

Preussag AG
D - 30625 Hannover
Tel: +49-511.566.1135
Fax: +49-511.566.1159

"DEVELOPMENT OF A SELECTIVE EXTRACTANT FOR IRON IN HYDROMETALLURGICAL PROCESS SOLUTIONS IN ORDER TO REDUCE THE AMOUNT OF FERRIC SLUDGES TO BE DUMPED AS CHEMICAL WASTE"

"IRONEX"

(contract No. EV5V-CT94-0568)

Start: 1 October 1994
Duration: 24 months

Dr. Karl-Heinz Ujma (coordinator)
Preussag AG
Karl-Wiechert-Allee 4
D-30625 HANNOVER
Germany
phone: +49.511.566-1135
fax: +49.511.566-1159

Dr. Michael Ehle
BASF AG
ZDH/S M 311
D-67056 LUDWIGSHAFEN
Germany
phone: +49.621.60-79232
fax: +49.621.60-79398

Ir. Ferdinand Lemmert
Budelco B. V.
Hoofdstraat 1
NL-6024 AA BUDEL-DORPLEIN
The Netherlands
phone: +31.4950.12529
fax: +31.4950.18285

Dr. Francisco Delmas
I.N.E.T.I.
Estrada do Paço do Lumiar
P-1699 LISBOA CODEX
phone: +351.1.7165141
fax: +351.1.7166568

Christian Plazanet
Metaleurop Recherche S. A.
1, av. Albert Einstein
F-78193 TRAPPES CEDEX
phone: +33.1.30662-849
fax: +33.1.30662-728

"IRONEX"

Main Objectives:

1. Development of a complexing agent or extraction system selective for iron, especially in the presence of zinc and free sulphuric acid.
2. Detailed investigation of phase relations, distribution equilibria, and stripping behaviour.
3. Application to industrial solutions based upon the data from laboratory experiments, and development of a continuous process.
4. Evaluation and testing of possible iron products, e.g. flocculants for effluent cleaning.
5. Creating new means for reducing the amount of iron sludges out of hydrometallurgical processes to be dumped as chemical waste.

Main Results:

(after ca. 12 months, i. e. half of planned project duration)

At least two of the newly developed extractants are very promising and quite better than substances available on the market which were used as reference material: concerning their extraction aptitude for iron, even in highly acidic media. The loading capacity of the best new substance at 80 g/l free acidity is around five times the equilibrium value for the reference material at the same conditions which constitutes an unusual good performance. At the same time, the phase disengagement seems sufficiently quick, the co-extraction of zinc is small enough, and the stripping behaviour is good. These results were obtained in batch experiments and on laboratory (small) scale. They will be checked within the remaining project time in continuously operated test facilities and at a somewhat bigger scale.

Publication:

Oral presentation at the International Solvent Extraction Conference ISEC '96, 19 - 23 March, 1996, Melbourne, Australia, Paper number: 267N (20 March, 1996),
Title: Development of a Selective Extractant for Iron in Hydrometallurgical Process Solutions in Order to Reduce the Amount of Ferric Sludges.
Authors: F. Delmas, M. Ehle, R. O. Koch, C. Nogueira, K. Oppenländer, C. Plazanet, K. H. Ujma (to whom correspondence should be addressed), V. Weigel

Development of a Selective Extractant for Iron in Hydrometallurgical Process Solutions in Order to Reduce the Amount of Ferric Sludges

F. Delmas, M. Ehle, R. O. Koch, C. Nogueira, K. Oppenländer, C. Plazanet, K.-H. Ujma, V. Weigel

Abstract

Subject of this work is the development, synthesis, prescreening, and testing of novel solvent extraction chemicals. These are acting as selective extractants for iron in highly acidic environment. The extraction of iron from aqueous solutions, having more than a threefold excess of zinc, and containing free sulphuric acid, is demonstrated. Results are given about phase disengagement, extraction capacity for iron, co-extraction of zinc, and the back stripping of iron from organic phase

Zusammenfassung

Gegenstand dieser Arbeit ist die Entwicklung, Synthese, Vorauswahl und Ermittlung der Eigenschaften von neuartigen Extraktionsmitteln für die Flussig-Flüssig-Extraktion. Diese Substanzen sind so beschaffen, daß sie als selektive Extraktionsmittel für Eisen in stark sauren Losungen arbeiten. Es wird gezeigt, daß die Extraktion von Eisen in schwefelsauren wassrigen Lösungen auch bei einem dreifachen Überschuß von Zink moglich ist. Erste Ergebnisse werden berichtet über das Phasenverhalten, die Beladungsfähigkeit für Eisen, die Koextraktion von Zink und das Verhalten von Eisen beim Strippen aus der organischen Phase.

Introduction

Hydrometallurgical Zinc Production

In hydrometallurgic zinc processes the basic steps for the production of zinc are the following: roasting, neutral leaching, hot acid leaching, solution purification and finally, electrolysis.

The undissolved solids separated after neutral leaching constitute the zinc plant residue. This residue contains several metals, the most important component being zinc ferrite. Without further treatment, this zinc is lost. Therefore, zinc ferrite must be dissolved through hot acid leaching giving a solution of zinc sulphate together with a high concentration of ferric sulphate, which constitutes a severe impurity and must be removed before electrolysis.

This iron removal from leach solutions is a problem in many hydrometallurgical processes. Several methods have been suggested to remove iron from process zinc solutions by precipitation as hematite or goethite, but in most existing electrolytic zinc plants, the method of iron removal adopted is a controlled hydrolytic precipitation of iron as a basic iron sulphate, called the Jarosite Process. The iron is removed from the hot acid leach liquor as (K, Na, NH_4) Fe_3 $(SO_4)_2(OH)_6$, the jarosite precipitate, in the presence of ammonium or alkali metal ions.

However, this precipitation method has economical disadvantages, due to the high cost of deposition of jarosite in controlled tailing ponds. Otherwise such residues contain heavy metals such as Se, In, Ge, Co, As, Te, and sulphur, causing environmental problems. Although insoluble, long-term stability of jarosite is not known.

As a result of these problems, solvent extraction is being investigated as an alternative process for the removal of iron from aqueous solutions, avoiding the generation of iron residues and producing marketable iron products.

Solvent Extraction of Iron

The extraction of iron (in the majority of cases in its trivalent state: Fe^{3+}) by different extractants, from sulphate or chloride media, has been investigated by many researchers. There exists a review of the numerous papers in this area [Dutrizac J E and Monhemius A J, 1986].

Several processes have been described to remove iron from sulphate media. Primary amines, secondary amines, alkylphosphoric acids and carboxylic acids have been used as extractants for iron removal. However, all these techniques have some drawbacks, such as:

- Leaching with the carboxylic acid will change the usual hydrometallurgical zinc processing;
- High organic losses in the hydrolytic stripping, once the precipitate contains solvent. Washing of the precipitate could be a solution, but high costs would be required;
- Iron precipitation occurs during exchange reaction, which can produce phase disengagement problems and contamination of the solutions;
- High energy consumption.

From chloride leach solutions, there has also been proposed a large number of processes, with TBP and amines as the main extractants.

Many methods have been developed and proposed but difficulties in the stripping of the iron from the organic loaded phase, the poor selectivity and other problems are not yet solved. Furthermore, existing extractants are not able to extract efficiently iron from highly acidic sulphate solutions.

A possible way to avoid these problems is to synthesize new tailor-made solvents for iron extraction, with high capacity and high selectivity for iron, even in highly acidic environments as is proposed in the IRONEX Project reported here.

Experimental Work

Synthesis of New Extractants

It is known that water-soluble aminomethylenephosphonic acids are good complexing agents for iron [Kobachnik M I, et al., 1968] These compounds can be seen as phosphorous compounds analogous to amino acids. Therefore the idea from the side of BASF was to synthesize and use oil-soluble derivatives of aminomethylenephosphonic acids as Fe(III) extractants for solvent extraction.

In varying the structural elements there are two different important aspects to be considered. Firstly, the oil solubility and phase behaviour of potential extractants might be influenced by the introduction of lipophilic groups such as alkyl substituents (branched, unbranched, saturated and unsaturated).

Secondly, the capacity for iron in the organic phase might be influenced by the introduction of more or less iron complexing groups such as, for example, the aminomethylenephosphono group. The high density of these substituents should lead to products with high capacities for iron but on the other hand the oil solubility might decrease and solubility in water might increase. Therefore a tradeoff in view of the desired properties has to be made.

Aminomethylenephosphonic acids were synthesized by a „Mannich-Type Reaction“ of amines, formaldehyde, and phosphorous acid [Moedritzer K and Irani R R, 1966]. The „Phosphonomethylation Reaction“ proceeds according to the equation given below which gives an example for the case of phosphonomethylated di-2-ethylhexylamine:

$$(C_8H_{17})_2NH \xrightarrow{HP(O)(OH)_2;CH_2O;H_3O^+} (C_8H_{17})_2N-CH_2-PO_3H_2$$

The hydrogen atom directly bonded to phosphorous in the phosphorous acid is the ‘acidic’ hydrogen required for the Mannich-type reaction.

The reaction proceeds almost quantitatively, depending on the starting amine, if an excess of formaldehyde and/or phosphorous acid is used. An acid is usually the catalyst. A side reaction takes place which produces methylation products (tertiary amines) as by-products. This means that the substituents are methyl instead of aminomethylenephophono groups.

Phosphonomethylation reactions are one-pot synthesis reactions which were carried out in glass apparatus with mechanical stirring at ~ 100°C for about 20 to 70 hours. The organic reaction products were separated from the aqueous phase (directly or by salting out) and purified by washing repeatedly with water. After separation of organic products and washings, residual water was removed under reduced pressure. The products obtained were characterized usually by elementary analysis, ^1H-, ^{31}P-NMR spectroscopy, and/or mass spectroscopy. From elementary analysis (P and N values) some information is obtained on the degree of conversion to phosphonomethylated products (P/N ratio).

Test Procedures

The prescreening evaluates the most effective extractants, judging by the following properties:

- oil solubility in a proper diluent
- phase behaviour (organic phase/highly acidic aqueous phase)
- extraction experiments (synthetic binary system Fe/Zn)
- washing/stripping tests

Extraction, washing and stripping tests are carried out in laboratory scale stirring batch experiments. The prescreening gives information about physical properties, Fe vs. Zn - selectivity, and loading capacity for Fe in the organic phase. Successfully tested chemical samples were selected for further examination.

The most promising candidates out of this prescreening procedure were until now:

EU2·	$(i-C_8H_{17})_2NCH_2PO(OH)_2$
EU4	$(i-C_{13}H_{27})_2NCH_2PO(OH)_2$
EU5/6	$(Oleyl-)(CH_2PO_3H_2)N-C_3H_6-N(CH_2PO_3H_2)_2$

The second stage of examination comprised:

- Comparative extraction and, partly, stripping tests on existing extractants, namely D2EHPA (di-2-ethylhexylphosphoric acid), Versatic 10, Primene JMT, and Amberlite LA2, and the influence of pH and several modifiers on iron extraction.
- Extraction and stripping tests on the new extractants synthesized by BASF (EU2, EU4, and EU5/6):
  - Influence of diluent (extractant EU2)
  - Influence of modifiers (extractant EU 2)
  - Influence of feed acidity (extractants EU2, EU4, and EU5/6)

The aqueous feed solutions considered in all the work were synthetic solutions similar to typical leach liquors coming from hot acid leaching of zinc ferrites, containing:

80g/l zinc; 25g/l iron; 40g/l free sulphuric acid.

In some tests, acidity was changed and so different quantities of H_2SO_4 were added. The solutions were prepared from the dissolution of the metal sulphates. The extractants used were D2EPHA, EU2, EU4 and EU5/6, together with a modifier and dissolved in the appropriate diluent. The units used were weight/volume percentages (% w/v). The modifiers used were

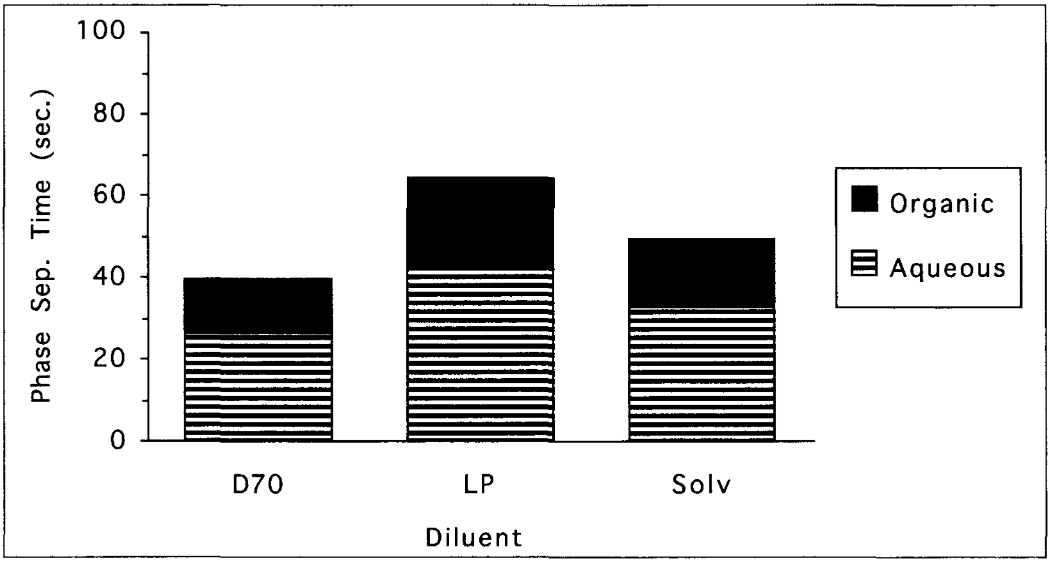

Figure 1. Influence of diluent on phase disengagement for EU2 extractant.

Abb 1· Einfluß des Diluenten auf die Phasentrennung beim Extraktionsmittel EU2.

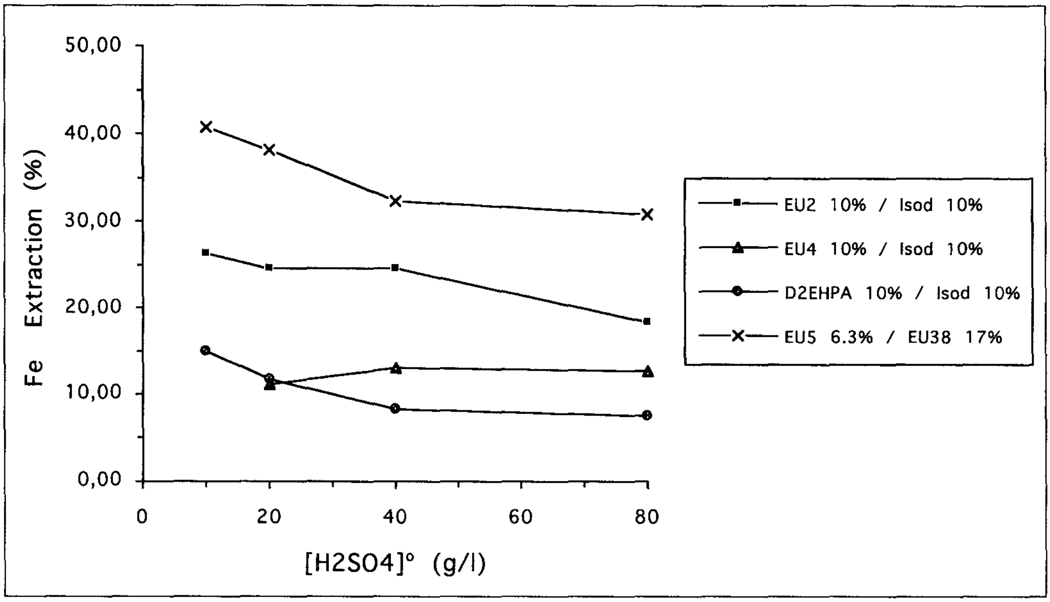

Figure 2. Influence of feed acidity on iron extraction with the new extractants and, for comparison, D2EHPA in LP, from sulphate solutionscontaining about 25 g/l Fe and 80 g/l Zn.

Abb 2: Extraktion von Eisen in Abhangigkeit vom Sauregehalt fur die neuentwickelten Extraktionsmittel im Vergleich mit D2EHPA (Diluent: Leuchtpetroleum); schwefelsaure Ausgangslosung enthalt etwa 25 g/l Eisen und 88 g/l Zink.

Isodecanol, Tributylphosphate (TBP), EU38 from BASF, and Trioctylphosphine oxide (TOPO). The diluents were D70 (Shell), LP („Leuchtpetroleum“, =EU37) from BASF, and Solvesso 150 (Exxon).

The extraction tests were performed in thermostatized mechanically stirred vessels, at 50° C, using an organic/ aqueous volume ratio of O/A=1/2 (usually 20 ml organic and 40 ml aqueous). The residence time used was 15 minutes and the stirring speed used was 600 rpm. When necessary, pH control by addition of small amounts of concentrated sodium hydroxide was achieved. After mixing the phases were settled and the separation time was measured. The phases were separated, filtered, and the final volumes were checked to evaluate possible volume changes during the test. For the stripping tests, separatory funnels were used and lower O/A ratio was considered (O/A=1/10). Temperature and time were the same referred for extraction.

Analysis of both metals in initial aqueous and equilibrated aqueous solutions were made by atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES). Zinc organic concentrations were determined after complete stripping with 2M-H_2SO_4 and subsequent analysis of the strip liquor containing all the zinc. In the case of iron, organic concentrations were determined by balance using both initial and final aqueous concentrations. When such balance was doubtful, confirmation was made using semiquantitative analysis of organic by X-ray fluorescence or by quantitative stripping of iron with NaOH (in the case of D2EHPA). The extraction or stripping percentages were calculated from metal concentrations taking into account, if necessary, the phase volume variations.

Results

The phase disengagement was in the range of 1 min (EU2) to 4 min (EU5/6), (see figure 1).

The tested diluents did not influence significantly the extraction of iron.

Even now, at an early time of the IRONEX project, it can be stated that the loading capacity for iron is, for at least two of the new extractants, markedly higher than that of the reference extractant D2EHPA; these new chemicals exhibiting a more powerful extraction behaviour than known ones (see figure 2).

- Zinc co-extraction values were in the range of 8 - 20 mg/l (EU2) to 200 - 300 mg/l (EU5/6), (see figure 3).
- The stripping behaviour for iron depends on the extraction power of the extractant; the lower this extraction power, the easier is the back-stripping of iron. Seemingly, this affects the more powerful extractants if judged by the relative stripping rate (see figure 4). However, if the absolute Fe concentration is considered, the new extractants EU2 and EU5/6 exhibit a higher overall transportation efficiency than D2EHPA.
- Some of the modifiers tested gave promising results; further investigations are needed.

Conclusions

At least two of the newly developed extractants are very promising and quite better than D2EHPA concerning their extraction aptitude for iron, even in highly acidic media. The EU5/6 loading capacity at 80 g/l free acidity is around five times the equilibrium value for D2EHPA at the same conditions which constitutes an unusual good performance. At the same time, the phase disengagement seems sufficiently quick, the co-extraction of zinc is small enough, and the

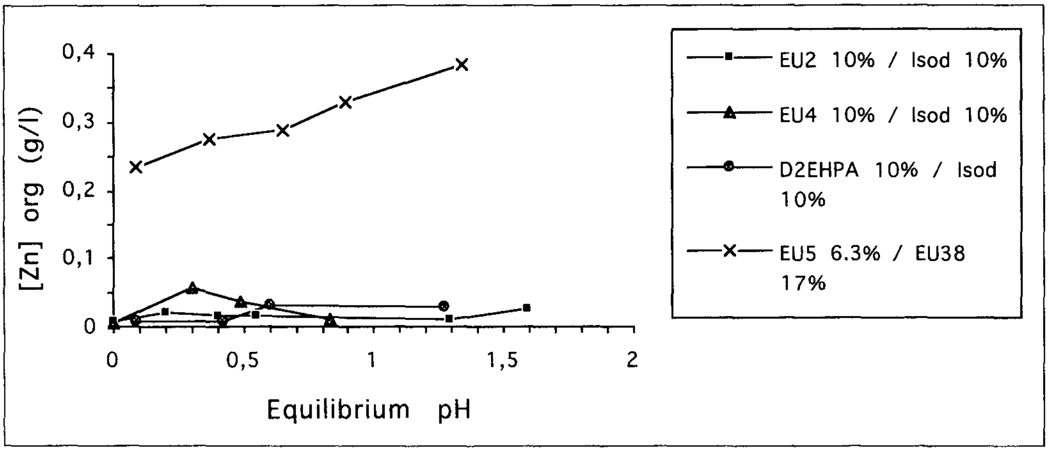

Figure 3: Influence of feed acidity on the co-extraction of zinc with the new extractants and, for comparison, D2EHPA, from sulphate solutions containing 25 g/l Fe and 80 g/l Zn.

Abb 3: Koextraktion von Zink in Abhangigkeit vom Gleichgewichts-pH-Wert für die neuen Extraktionsmittel im Vergleich mit D2EHPA; schwefelsaure Losung mit etwa 25g/l Eisen und 80 g/l Zink.

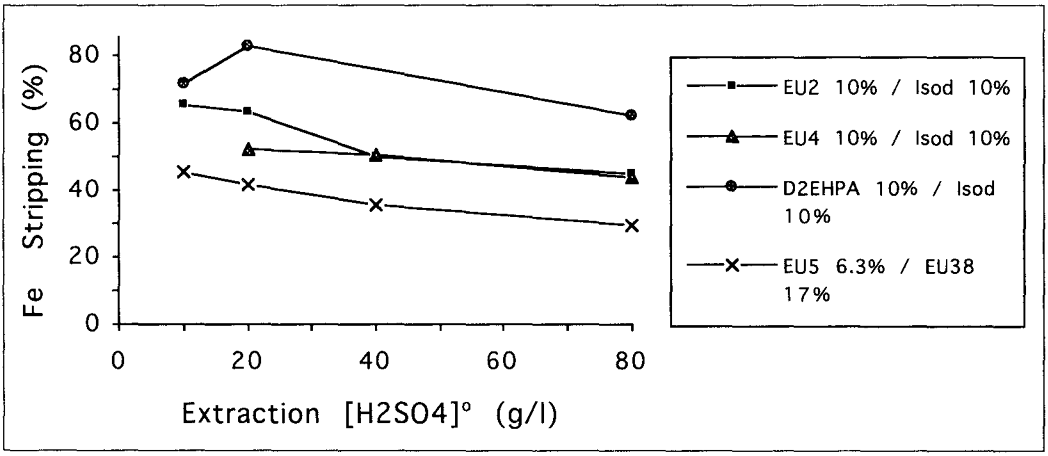

Figure 4 Influence of feed acidity in extraction on further stripping of iron from loaded organics. [Fe]org = 9-16 g/l (EU2); 5-12 g/l (EU4); 15-22 g/l (EU 5/6); 4-11 g/l (D2EHPA).

Abb. 4. Relativer Anteil von Eisen nach dem Strippen der beladenen organischen Phase; (Fe(org=9-16 g/l (EU2), 5-12 g/l (EU4); 15-22 g/l (EU5/6); 4-11 g/l (D2EHPA).

stripping behaviour is good. However, after only one half year of project duration many questions are open still, and a lot of investigations will have to follow.

Acknowledgements

The authors wish to thank all involved colleagues within the IRONEX consortium for their indispensable help. The work is supported in part by the Research and Technical Development Programme of the European Communities, European Commission, DG XII-D1, Brussels, Belgium, specific programme ENVIRONMENT AND CLIMATE. This funding is gratefully acknowledged.

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Authors: F. Delmas, Instituto Nacional de Engenharia e Tecnologia Industrial, Lisbon, Portugal; M. Ehle, BASF AG, Ludwigshafen, Germany; R. O. Koch, Budelco B.V., Budel-Dorplein, The Netherlands; C. Nogueira, Instituto Nacional de Engenharia e Tecnologia Industrial, Lisbon, Portugal; K. Oppenländer, BASF AG, Ludwigshafen, Germany; C. Plazanet, Metaleurop Recherche S.A., Trappes, France; K.-H. Ujma, Preussag AG, Hannover, Germany; V. Weigel, Metaleurop Recherche S.A., Trappes, France.

Presented at the ISEC '96 in Melbourne, Australia, 19 - 23 March, 1996.

Development of a procedure for the re-use of wash water required in photographic processes and for the recycling or destruction of the removed harmful compounds

EV5V-CT94-0552

Coordinator: U. Nickel

University of Erlangen-Nürnberg
Institute of Physical Chemistry
D - 91058 Erlangen
Tel: +49-9131.857334
Fax: +49-9131.858307

Development of a procedure for the re-use of wash water required in photographic processes and for the recycling or destruction of the removed harmful compounds

EV5V-CT94-0552

starting date 1. 7. 1994 duration 3 years

LAB no. 1

Ulrich Nickel (coordinator)
University of Erlangen-Nürnberg
Institute of Physical Chemistry
Egerlandstr. 3, 91058 Erlangen **(Germany)**
Tel: +49 9131 857334 FAX: +49 9131 858307

LAB no. 2

Nicholas Evrimidis
University of Ioannina
Laboratory of Analytical Chemistry
Dourouti Area 1186, 45110 Ioannina **(Greece)**
Tel: +30 651 92202 FAX: +30 651 44112

LAB no. 3

Dolores Pérez-Bendito
University of Córdoba
Department of Analytical Chemistry
San Alberto Magno S/N, 14071 Córdoba **(Spain)**
Tel: +34 57 218614 FAX: +34 57 218606

main objectives

- recycling of the wash water of photographic development processes
- recycling of photographic developers
- recycling on photographic chemicals
- conversion of harmful photographic chemicals in biodegradable compounds

main results

- analytical procedures for the determination of the components of developers
- 2-step adsorption of the components of the components present in the wash water
- oxidative destruction of developing agents

Development of a procedure for the re-use of wash water required in photographic processes and for the recycling or destruction of the removed harmful compounds

EV5V-CT94-0552

Ulrich Nickel (coordinator), University Erlangen-Nürnberg, DE-91058 Erlangen
Nicholas Evmiridis, University of Ioannina, GR-45110 Ioannina
Dolores Pérez-Bendito, University of Córdoba, SP-14004 Córdoba

Introduction

Photographic processes require a huge amount of clean water for rinsing the material during and after the different developing steps. Usually the wash water flows away without any cleaning. Sometimes, however, this weakly poisoned water is taken to dilute the overflow of the developing baths. Thus, the concentration of harmful photographic substances can most often be brought under the level fixed by the community, but, of course, the total amount of dangerous compounds released into the environment is not decreased by this simple dilution procedure.

Any procedure to decrease the demand for rinsing water therefore also has to take into account the removal of harmful compounds from the overflow of photographic processes, too, because the operator of a lab may loose the possiblity to dilute these solutions.

In the last years there have been undertaken many efforts to decrease the amount of water necessary to develop photographic materials. But most attempts to do photographic processes without any rinsing have failed. The second or third process solution may be poisoned too strongly by compounds from previous baths. Furthermore, the long time stability of photographic material not carefully rinsed in a final bath is not very high.

An effective procedure to save water is the multiple re-use of the wash water. For this purpose some of the compounds released from the process solutions as well as from the photographic material should be removed by adsorption at suitable adsorbents. Thus, the water can be used several times and only a small amount of fresh water has to be added continuously or discontinuously. Of course, the water which finally flows away should be free from toxic compounds. All these compounds should be collected at the adsorbing agent. The adsorbent may finally be burned, brought to a disposal or recovered by desorption. A recycling of compounds via the adsorbent is possible, but can not be carried out economically so far. The recycling of wash water therefore does not automatically include the recycling of chemicals.

The chemicals removed from the wash water have to be treated at a central station. The best way - except of the very difficult recycling - is their controlled conversion into harmless compounds. The adsorbent should partially or completely be recovered.

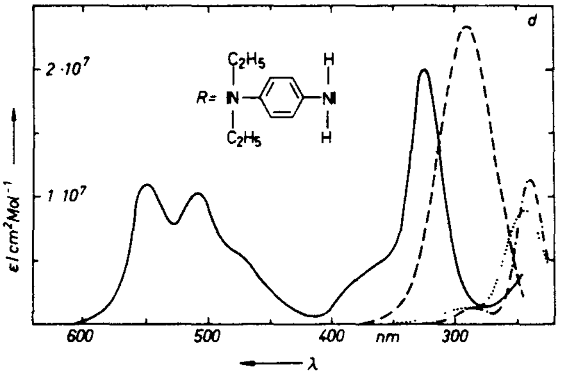


Fig. 3

UV-vis absorption spectra of N,N-diethyl-p-phenylendiamine (···) and its protonated forms as well as the semiquinoidic (___) and quinoidic (---) form

The quantitative determination of almost all organic compounds present in developers applying a diode array HPLC is now possible and yields reliable results. Reliable procedures have also been developed to determine some other compounds, e. g. EDTA and PDTA. For the determination of a small amount of the inorganic compound sulphite an electrochemical method was developed based on the reaction of sulphite with quinone diimine. A plot of the reciproke square root of the cathodic current of cyclic voltammograms recorded at a carbon electrode versus the concentration of sulphite yields a calibration line which allows the accurate determination of sulphite even in very low concentration. Fig. 4 shows some cyclic voltammograms obtained with CD4, Fig. 5 the derived calibration line.

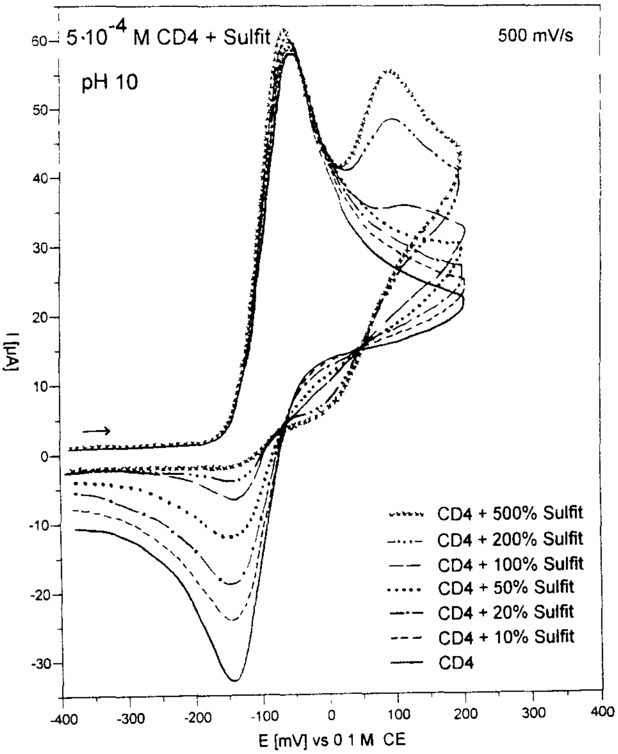


Fig. 4

Cyclic voltammogramms for CD4 (0.5 mM at pH 10) recorded at a carbon disc electrode (4 mm diameter) in the presence of a varying concentration of sulphite. Scan rate 500 mV/s

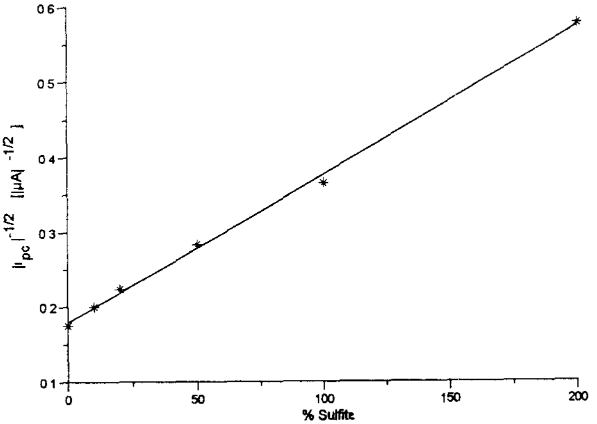


Fig. 5

Calibration line for the electrochemical determination of sulphite in the concentration range from 0.02mM to 1.0 mM.

Current-potential curves recorded at both the stationary and the rotated disc electrode have also been applied to characterize the most important components present in developers. Thus, besides of the more common photometric determination of the components present in photographic baths also an electrochemical procedure can now be applied.

Adsorption studies

For the adsorption of both inorganic and organic anions the most suitable ion exchange resins have been determined. Some of these resins were found to adsorb very specifically bromide. Thus, this substance can be separated from the other components present in the wash water and the overflow of the developing process as well as in exhausted developers. Most important is this selective adsorption for the recycling of developers, because here the adsorption of the developing compound is undesired.

On the other hand, most of the organic compounds should be removed from the wash water. For this purpose not only commercially resins were used but also special zeolites synthesized. Thus, the removal of all colour developing agents was successfully carried out. An example for this kind of adsorption is displayed in Fig. 6. There are still, however, some problems concerning the removal of black and white developing agents. At a pH > 8 some of these compounds are negatively charged and therefore the separation from bromide is difficult. Good results were obtained, however, after decreasing the pH by the addition of a small amount of acid.

Complexing agents could also removed from the process solutions. The results obtained so far show that the two-step adsorption of halide ions, EDTA, PDTA, ADA and the developing compounds can be carried out within a few minutes to a degree of more than 90 %. Thus the wash water as well as most developing solutions can be recycled. The recycling of the adsorbed material, however, is still difficult (except bromide). For this reason the controlled destruction is favoured.

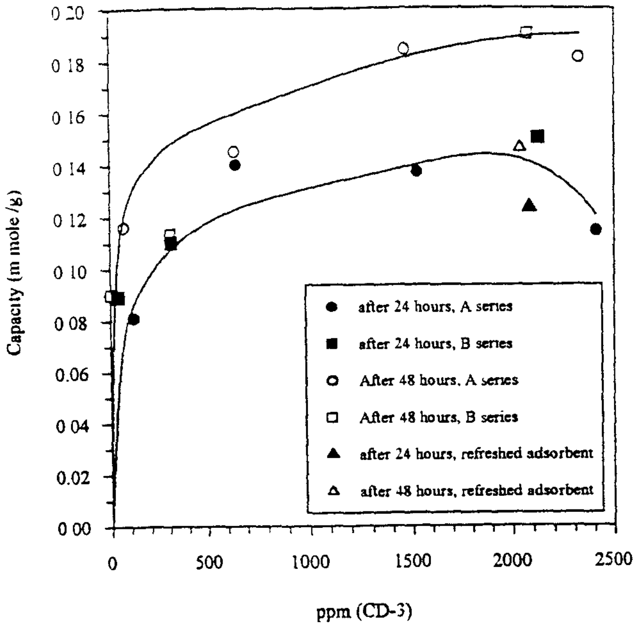


Fig. 6

Ion-exchange isotherms: CD3 and a synthesized mesopore material, ME, after special calcination up to 600 °C for one hour

Destruction of developing compounds

The destruction of photographic developers like CD3, CD4, metol, and hydroquinone was carried out by chemical oxidation with hydrogen peroxide in the presence of suitable catalysts. The course of the reaction was followed photometrically applying HPLC techniques. With a pretty high concentration of the oxidant a conversion to quinoidic compounds was found. Preliminary experiments have shown, however, that the oxidation may also result in the desired destruction of the aromatic ring. Under certain conditions the resin used to adsorb the developing compound could be recovered.

Conclusions

Both the recycling of the wash water of most developing processes and the recycling of colour developers can be carried out economically. The fundamental analytical problems have been resolved, too. But cheap sensors should be developed in order to avoid expensive analytical equipment. On the other hand, the recycling of most photographic chemicals still causes problems. Some problems have also to be resolved concerning the controlled conversion of harmful compound into biodegradable substances as well as the recovery of the adsorbent.

Immiscible solvent displacement process for the recovery and recycle of water soluble organic effluents

EV5V-CT94-0557

Coordinator: S.R. Tennison

MAST International Ltd
UK - KT15 3HR Addlestone
Tel: +44-1932.336892
Fax: +44-1932.336892

IMMISCIBLE SOLVENT DISPLACEMENT PROCESS FOR THE RECOVERY OF SOLUBLE ORGANICS FROM AQUEOUS WASTE STREAMS

EV5V-CT94-0557

Start date:-	1st September 1994
Finish Date	30th March 1996
Duration	19 months

PARTICIPANTS

Mr. S R Tennison , (project Co-ordinator)
MAST International Ltd, 62 Farleigh Road, New Haw, Addlestone, Surrey, KT15 3HR
Tel +44 1932 336892 Fax +44 1932 336892
e-mail 100545.3002@compuserve.com
Dr. D Watson'
Research and Development, BP Chemicals, Saltend, Heddon, Hull, HU12 8SX
Tel +44 89 1482 2927 Fax +44 89 1482 2191
Professor G Findenegg,
Iwan-N-Stranski Institut, Technical University of Berlin, Strasse des 17 Juni 112, D10623, Berlin
Tel +49 30 314 24171 Fax +49 30 314 26602
Dr. S Ragan
Sutcliffe Speakman Carbons Ltd, Antler House, Lockett Road, Ashton -in-Makerfield, Lancashire, WN4 8DE
Tel +44 1942 275400 Fax +44 1942 275603

MAIN OBJECTIVES

- The primary target of the project was to develop a novel process for the recovery of acetic and formic acids from dilute process aqueous effluent. The process was to be based on the immiscible solvent displacement principle already established by BP.
- In addition the programme was to establish the carbon adsorbent structural requirements for the process and to confirm whether the synthetic carbon adsorbent was critical.
- The final part of the work programme was to develop an understanding of the mechanism of the three stages to permit the design/development of improved adsorbents and displacers.

RESULTS

- PROCESS DEVELOPMENT
  The overall process has been shown to be feasible although the economics are seriously impacted by problems with the steam regeneration step. At present this requires ca. 250te of steam to recover 1 tonne of acid. This must be reduced to a maximum of 40 tonnes of steam if the process is to operate economically. Attempts to reduce the steam utilisation by the use of hydrocarbon displacers, in place of the di-isopropyl ether, failed probably due to the phase behaviour characteristics of the three component mixture (water-pentane-acid). Paper studies have indicated that it may be possible to reach the required targets, still using DIPE as the displacer, by reducing the degree of regeneration in the steam stage. However further tests would be required to confirm this.
- CARBON DEVELOPMENT
  The small scale and large scale tests have confirmed that the overall process is critically dependent upon the improved displacement and regeneration characteristics of the synthetic activated carbons. 100% displacement of the adsorbed acid by the DIPE, which is critical to the process, could not be achieved with the best available commercial carbon in under 20 bed volumes whereas the cycle was complete in <5 bed volumes with the synthetic carbon. Further improvements to the synthetic carbon may also be possible by modifying the carbon surface chemistry.
- MECHANISTIC STUDIES
  The small scale kinetics tests demonstrated that the acid adsorption stage of the process was fast and dominated by the adsorbate particle size and macropore structure. In contrast the DIPE displacement step was very slow and controlled by the micropore structure of the carbon. The method of preparation of the synthetic carbon allowed both aspects of the structure to be modified which permitted both of these steps to be

optimised. The use of displacers other than the DIPE has also confirmed the sensitivity of the process to the nature of the displacer, and also possibly the chemistry of the carbon surface ,although further work would be required to precisely identify the critical parameters. A major aspect is undoubtedly the phase behaviour of the three component mixtures - acid:displacer:water.

PATENTS AND PUBLICATIONS

Papers have been accepted for presentation at the following conferences:-
CARBON 96
CLEAN TECH 96
COPS III
The paper from Clean-Tech will be published in Journal of Chemical Technology and Biotechnology, whilst the COPSII paper will be published in the conference proceedings.

The patent on the Process has now been published :-
Process for separating components of a liquid mixture, EU 0 635 294 A1, 25/1/95, D Watson and S R Tennison

IMMISCIBLE SOLVENT DISPLACEMENT PROCESS FOR THE RECOVERY OF SOLUBLE ORGANICS FROM AQUEOUS WASTE STREAMS

O Dietsch[1], J Carey[4], G Findenegg[1], J Jones[4], S Ragan[2], M Roberts[4], H Sharrock[2], S R Tennison*[3] and D Watson[4]

(1) Iwan-N-Stranski Institut, Technical University of Berlin, Strasse des 17 Juni 112, D10623, Berlin
(2) Sutcliffe Speakman Carbons Ltd, Antler House, Lockett Road, Ashton -in-Makerfield, Lancashire, WN4 8DE
(3) MAST International Ltd, 62 Farleigh Road, New Haw, Addlestone, Surrey, KT15 3HR
(4) Research and Development, BP Chemicals, Saltend, Heddon, Hull, HU12 8SX

1. CURRENT STATUS

This project to develop a new process for treating aqueous process waste streams has now finished and this report summarises the final results. The economic recovery of water soluble organics from waste water by a conventional active carbon adsorption process is not usually possible. The high levels frequently found in process effluent streams combined with the low capacity of active carbons for these compounds would make it essential to use frequent insitu regeneration. However conventional steam regeneration cannot be used to recover the adsorbed materials as the condensate from the regeneration stage would simply be another dilute aqueous stream. This has been overcome by using a displacement solvent to remove the adsorbed organics that is immiscible with water and can therefore be recovered by steam regeneration - hence IMMISCIBLE SOLVENT DISPLACEMENT (ISD)[1]. This detailed study has demonstrated the feasibility of the process for the recovery of dilute acetic and formic acids but has also shown its dependence on adsorbates with greatly enhanced regeneration kinetics. It has also shown that compete removal of the DIPE displacer with steam is not economically possible. At the completion of this project the value of the steam required to achieve complete removal of the DIPE (ca.5 bed volumes) significantly exceeded the value of the recovered acids. A preliminary economic evaluation of the process demonstrated that the maximum amount of steam possible, if the recovery process was to pay for itself, would be less than 1 bed volume. Further work will be required to confirm whether an alternative process cycle, in which incomplete DIPE recovery is used, but which will require an increase in the adsorber bed volumes, is viable.

2. PROCESS DESCRIPTION

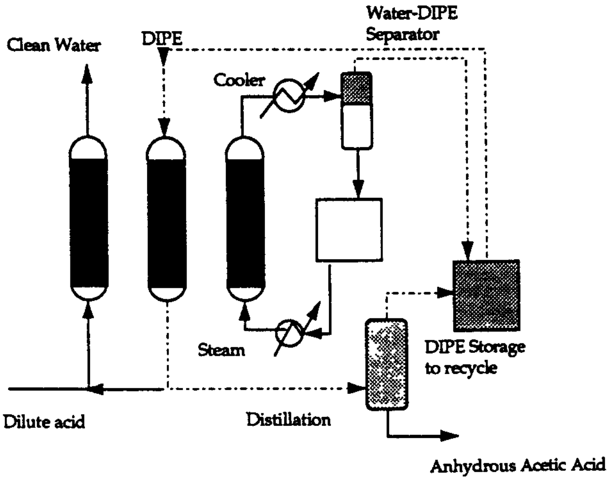
The process is shown schematically in Figure 1 and involves three adsorbent beds each undergoing a separate step in sequence:-

1. **Adsorption** The dilute acid stream containing approximately 10,000ppm (50:50 molar) of mixed acetic and formic acids is passed up through the adsorbent bed until acid breakthrough occurs
2. **Displacement.** This is the key stage in the process. Di-isopropyl ether (DIPE) is flowed down through the dilute acid saturated bed. This initially displaces the dilute acid in the bed free space which is returned to the feed tank. Subsequently the DIPE displaces the adsorbed acids from the carbon producing a DIPE/acid mixture that can be distilled to recover anhydrous acids.
3. **Steam regeneration.** Steam is then flowed up through the bed to remove the DIPE. As DIPE and water are immiscible the majority of the DIPE can be removed by phase separation although some stripping is required to remove residual traces from the condensate. After this step the bed is clean, but wet, and ready for the next adsorption cycle.

In this process the selection of the displacement solvent has been shown to be critical as it must be capable of displacing interstitial dilute acid without fingering, be able to displace the adsorbed acid from the carbon micropore structure and have a low solubility in water. The last point is important as a high solubility would tend to simply regenerate a dilute aqueous waste stream with the displacer as the contaminant rather than the original organic. Even so, the more detailed process design studies have shown that it will be necessary to include a small stripping column to reduce this to an acceptable level.

The performance of the carbon is also critical as it must exhibit a high acid capacity with good adsorption kinetics but more critically it must show good DIPE displacement and steam regeneration kinetics. The programme has shown that these requirements cannot be met by conventional active carbons but are possible using the synthetic active carbon based on phenolic resin.

Figure 1 : Schematic of 3 Bed ISD Process



3. MATERIALS

Preliminary screening of a wide selection of commercial active carbons demonstrated that an acid washed Sutcliffe Speakman coconut shell carbon , 607C, gave the best performance and this programme was therefore restricted to this material as the commercial baseline. The other material used was a synthetic activated carbon produced from phenolic resin (PRC)[2]. The route to this material allowed extruded carbons to be produced with a variety of macropore sizes[3] based on the different resin particle sizes produced in step 3(Figure 2). The majority of the carbons produced were used as ca. 1mm extrudates although some "spherical" materials were also used. After carbonisation to 800C the PRC's were activated at varying levels upto a 60% carbon loss using primarily steam at 850C although carbon dioxide was also examined. A material was also made by steam activation followed by air treatment at 300C. This introduces a large amount of carboxylic acid groups onto the carbon surface which it was anticipated would change the relative adsorption characteristics for formic and acetic acid. After activation the materials were characterised by nitrogen adsorption (BET area, micropore volume) and mercury porosimetry (macropore volume). During the course of the project 15 carbons have been evaluated either at the small scale (ca. 500ml) or the large scale (1L). Typical properties for the large scale materials, compared to the commercial carbon, 607C, are given in Table 1.

Figure 2 : PRC Production Route

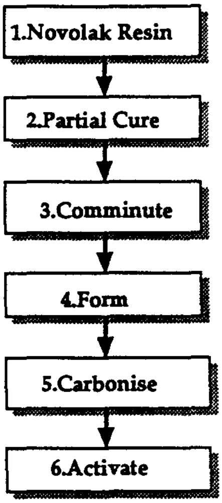


Table 1 Typical Characteristics of Synthetic Carbons

		Extruded Carbons		"Spherical" Carbons	
	607C	95-052 70μm	95-054 30μm	95-056 1-2mm	95-057 .35-.6mm
%w/w yield	50	36	31.6	38.8	45.6
BET area m2/g	1245	1454	1560	1560	1551
Micropore vol	0.55	0.68	0.76	0.74	0.720
B.density g/cc	0.49	0.416	0.420	0.447	0.505
macropore vol (Hg)	0.136	0.398	0.378	0.155	0.036

It can be seen that the extruded PRC's have a significantly higher macropore volume than either the commercial carbon (607C), or the spherical carbons whilst all of the PRC's have significantly higher areas and pore volumes than the 607C.

4. EXPERIMENTAL PROGRAMME

The experimental test programme comprised three main elements:-

1. **Equilibrium Adsorption.** The acetic and formic acid adsorption isotherms from aqueous solutions were determined at TUB by the "bottle" technique
2. **Small scale adsorption and DIPE displacement kinetics** were measured at TUB using a 30cmx1cm carbon bed and HPLC pumps and detectors.
3. **The complete process** cycle was carried out at BP Chemicals using a pilot plant with a 2m bed (ca. 1L of adsorbate). This was the minimum scale at which it was possible to fully evaluate the steam regeneration step and to carry out multiple adsorption/regeneration cycles.

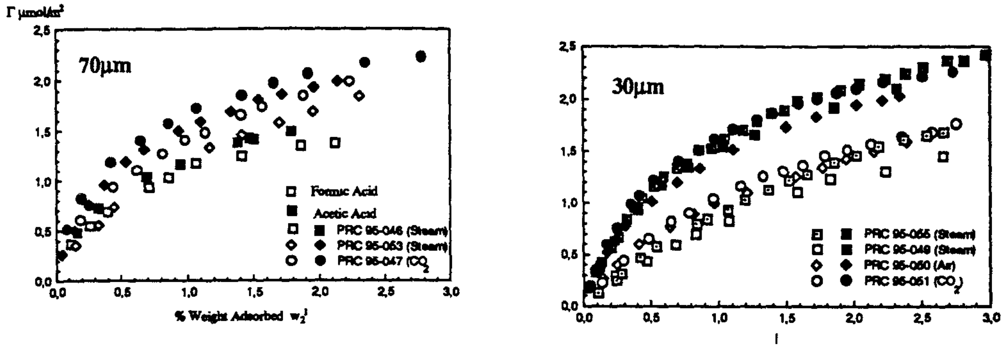
4.1 Equilibrium Data

The isotherms were determined by adding a fixed volume of acid of known concentration to a known weight of carbon and leaving this to stand for 24 hours. The residual acid concentration was then determined and from the initial and final acid concentrations the amount adsorbed was determined. Typical single component adsorption isotherms for acetic acid on the different carbons are shown in Figure 3 where the lines are the fit to the extended Langmuir equation (1):-

$$\frac{m_2}{m_s}=\frac{m_2^{\infty}}{m_s}\left[\frac{w_2^1}{K_{21}+w_2^1}\right]^k \qquad (1)$$

This expression was found to fit both the acetic and formic acid adsorption over a very wide concentration range (up to 5% wt.). In this expression m_2/m_s is the acid adsorption at solution concentration w^1_2 , m^{∞}_2/m_s is the infinite solution concentration uptake, K_{21} is related to the energy of adsorption and k is a term quantifying the adsorbent heterogeneity (1 = homogeneous). This can then be converted to Γ (μmol/m^2), which is the uptake normalised to the carbon surface area and the adsorbate molecular weight

Figure 3 Normalised Acetic and Formic Acid Adsorption on Various PRC's



The GL constants for a selection of the carbons tested are given in Table 2..

Table 2 Summary of the GL Parameters for Acetic and Formic Acids

	Acetic Acid				Formic Acid			
	k	K_{21} (wt%)	m_2/m_s	Γ ($\mu mol/m^2$)	*k*	K_{21} (wt%)	m_2/m_s	Γ ($\mu mol/m^2$)
70um Resin								
95-046 (steam)	0.6	2.1	22.6	2.4	0.60	1.9	15.1	2.1
95-047(CO2)	0.56	1.8	25.2	2.94	0.56	4.5	24.2	3.7
95-053(steam)	0.74	1.2	23.8	2.73	0.74	3.5	24.3	3.6
30um resin								
95-049 (steam)	0.79	1.4	28.1	3.04	0.79	6.4	27.6	3.9
95-050 (air)	0.71	2.1	29.5	3.18	0.71	4.7	24.2	3.4
95-051 (CO2)	0.83	1.0	29.0	2.93	0.83	2.6	22.9	3.0
607C	0.48	4.0	23.5	3.1	0.48	14.0	20.0	3.5

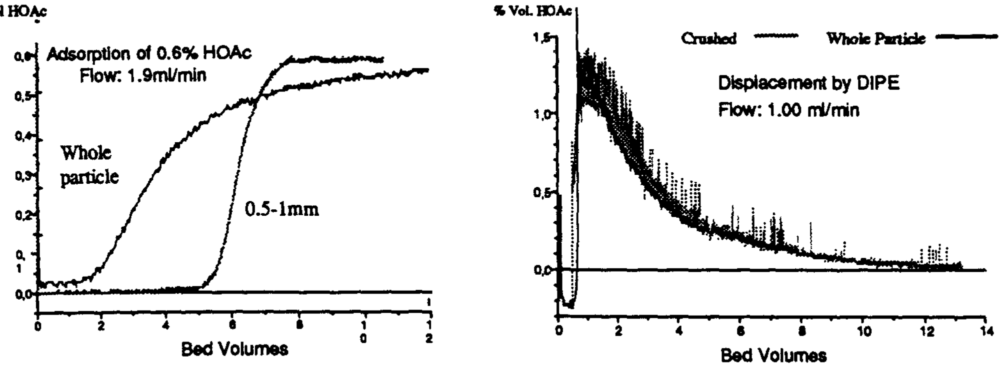
Several key points emerge from a consideration of the data in Figure 2 and Table 2:-

- The *k* value, which reflects the energetic homogeneity of the adsorbate is identical for acetic and formic as would be expected. It also shows that the phenolic resins are all more homogeneous than the 607C irrespective of preparative route
- The K_{21} value, which reflects energy of adsorption, shows a much higher value for the 607C than for all of the PRC's, which probably impacts on the inferior regenerability of the commercial material
- K_{21} is always higher for formic acid. This is also reflected in the regeneration where Formic is slower than acetic.
- There is little significant difference between the limiting (infinite concentration) normalised acetic and formic acid adsorption (Γ) in any of the carbons, synthetic or commercial.
- There is some evidence for a variation in adsorption efficiency for acetic acid as a function of resin particle size

4.2 Adsorption and Displacement Kinetics

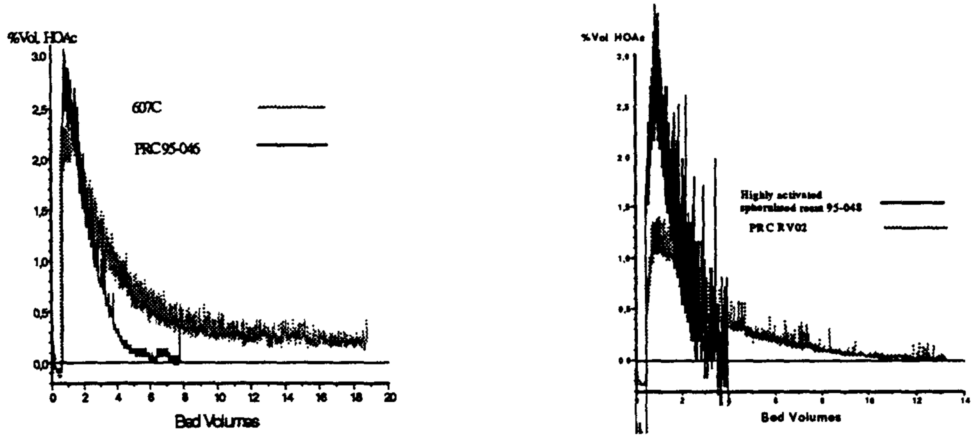
The kinetics of the aqueous acid adsorption and DIPE displacement steps were evaluated using a small laboratory HPLC rig described previously[4]. This used a small column (ca. 30cmx1cm) that necessitated the use of small particle size material (it is geneally recommended in liquid adsorption studies that the reactor diameter be at least 10 times the particle diameter) . For all of these tests the extrudate and spherical carbons were reduced to a 0.5-1mm mesh fraction. As steam regeneration was not possible on this scale the carbons were regenerated after the DIPE displacement using methanol which was then removed using a large amount of distilled water. This allowed the repeatability of the test cycles to be determined and the relative performance of acetic and formic acid to be compered without changing the adsorbate.

Figure 4: Adsorption and DIPE Displacement Kinetics



These results (Figure 4) show the impact of particle size on the kinetics. During the adsorption step the particle size has a major influence demonstrating that adsorption in the micropores is rapid and that the process is controlled by the macropore transport. During displacement particle size has no effect showing that the process is controlled by micropore transport. This has significant implications for the development of carbons for the process which the require both elements of the structure to be optimised. There is however little difference between the adsorption kinetics for the commercial and synthetic carbons for a similar particle size. The displacement kinetics, which depend on the nature of the micropore structure do however show major differences both as a function of the type of carbon and the degree of activation (Figure 5). In the latter case activation can be seen as removing constrictions within the micropore structure which inhibit diffusion.

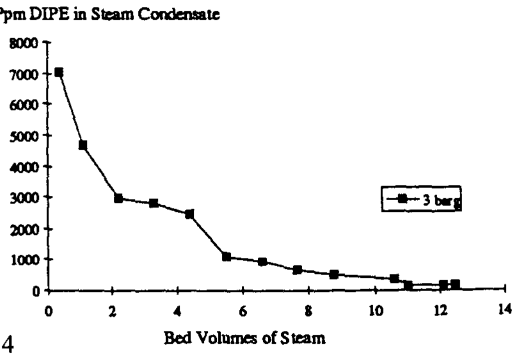
Figure 5 Effect of Carbon Type and Degree of Activation on DIPE Displacement



4.3 Steam Regeneration

The pilot plant facility allowed the steam regeneration step and the integration of the complete cycle to be evaluated using mixed acid effluent (3000ppm acetic acid/3000ppm formic acid). These tests confirmed the adsorption and DIPE displacement results from the small scale kinetics tests but also demonstrated that steam regeneration, using medium pressure steam, was the most difficult stage in the process. Typical results from the steam regeneration stage are shown in Figure 6. Comparison with Figure 5 shows that steam regen is much slower than the DIPE displacement stage. These are typical of all of the PRC materials although the commercial carbon, in line with the DIPE displacement results showed still slower regeneration..

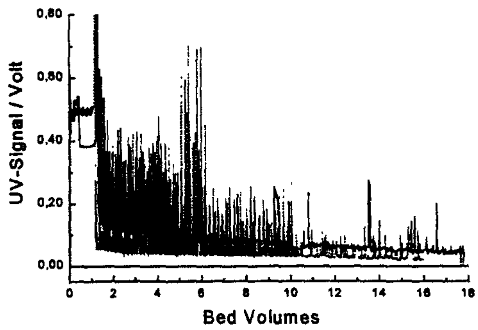
Figure 6 : Steam Regeneration of 95-052



An evaluation of the process economics based on an effluent flow of 7tonnes/hour of 1% mixed acetic/formic acid effluent, the steam regeneration shown in Figure 6(12 bed volumes of steam), and the acid adsorption (6 bed volumes) and DIPE regeneration (6 bed volumes) cycles also observed on the large scale plant showed that approximately 400te of steam would be required to generate 1 tonne of recovered acid based on three $1m^3$ carbon beds. The value of this steam then exceeded the value of the acid by around x10. The overall process costs were not very sensitive to the capital cost of the process which were £0.76million if a condensate DIPE stripper was included and £0.32million if a simple three bed adsorber was used.

Whilst modifications to the process cycle (lower LHSV's) have reduced the number of bed volumes of steam to around 6, it seems highly unlikely that the steam utilisation can be reduced to the 1 bed volume required by the acid value. In the light of these results, and on the basis of experience at BP Chemicals in steam regenerating pentane saturated beds, pentane was evaluated as a possible displacer. Preliminary results obtained in the HPLC facility at TUB, and subsequently confirmed in the large scale facility, demonstrated that pentane could NOT be used despite its much better steam regeneration characteristics.

Figure 7 : Pentane Displacement Kinetics



The results obtained in the two units are summarised in Figure 7. the initial high acid level reflected the displacement of the interparticle dilute acid phase by the pentane. The subsequent displacement from the micropores was however extremely inefficient with only trace levels of acid in the hydrocarbon stream and occasional slugs of aqueous acid. Significant acid was still present in the hydrocarbon even after 18 bed volumes

It seems likely that this reflects two different problems. The phase behaviour of the system water:pentane:acid means that the solubility of wet acetic acid in pentane is very low . Displaced acid cannot therefore be easily carried away by the pentane stream. There may also be a surface tension problem with the pentane unable penetrate the water saturated carbon macropores.

It is apparent from these tests that there are quire severe phase behaviour constraints imposed on the displacer solvent in addition to the requirement that it be immiscible with water. Whilst there are other solvents that may meet these requirements, and also be more readily removed by steam than DIPE, it has not been possible to evaluate these at the Hull facility for both time and logistic reasons. An alternative, and perhaps more realistic, approach will be to reduce the extent of steam regeneration to 1 bed volume, leaving some residual DIPE on the bed. It is possible that this will simply reduce the capacity of the bed for the acids during the subsequent adsorption steps which can be compensated for by increasing the bed volumes and the amount of carbon used. If this proves possible the economics of the process should still be viable although confirmation of the complete cycle efficiency will still be required

5. CONCLUSIONS.

The work has shown that the ISD process using the synthetic active carbons can treat dilute aqueous acid waste streams to give anhydrous organic products although at present the overall process economics are impacted by steam utilisation. This cannot be overcome by using a more readily removed, hydrocarbon, displacer. Further examination of the DIPE results has suggested that complete removal of the DIPE is not in fact necessary and that if the steam regeneration is reduced to 1 bed volume an increase in the carbon bed size by around 25% may be sufficient to compensate. If this can be confirmed the economical recovery of dilute aqueous organics should be possible.

6. REFERENCES

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[3] S B Bhowmik, S P Waldram, R McMurray and S R Tennison, in *"Characterisation of Porous Solids"*, Elsevier, 273 (1991)

[4] Proceedings of the Enviroment Programme meeting, Vienna, 1995

Recycling oriented strategies for the production of paper pulps and for paper manufacture

Contract CEE EV5V-CT94-0554; **Alain Cochqux**

1 Introduction

The project focusses on the influences of the vital processes and additives of papermaking on the value of the finished paper with regard to its suitability as a future raw material for the paper industry. These include above all those processes which directly or indirectly influence the fibre properties during pulp production (beating, bleaching) or during web forming (wet end chemistry) and drying as well as finishing (coating, calendering). In addition further effects are to be assessed which are expected to occur in the wake of intensified recycling, namely the accumulation of contraries in papers with high secondary fibre contents.

From the above, the principal objective of the project becomes evident. An investigation into the relations between papermaking processes and waste paper properties will yield the fundamentals of recycling-oriented paper manufacture. This term denotes a technology which takes waste paper recycling requirements into account at the early stage of paper manufacture from virgin fibre pulps. The use of these recycling-oriented manufacturing processes will be an essential prerequisite for an increasing waste paper recycling. An assessment of the influences causing an accumulation of contraries in the highly closed whitewater circuits of intensified paper recycling is intended to assist in the drafting of scenarios showing the quality developments of secondary fibre based new papers and of waste papers. These scenarios will allow a timely detection of critical trends.

This project for the first time studies the effects of processes and additives used in the manufacture of pulps and paper on the quality of the raw material 'waste paper' in terms of recyclability, cleanliness, brightness and strength. In addition it will ascertain to what extent the value of the finished products can be influenced in these processes with a view to subsequent reprocessing. Besides an assessment will be made of the increased contraries accumulation in secondary fibre based new papers which are inevitably encountered as a consequence of intensified recycling. From the findings obtained, recommendations will be derived for a recycling-oriented pulp and paper manufacture with a view to positively influencing - at this early stage - the value of the finished products with regard to their subsequent recycling, and to avoiding influences that might turn out negative for the product and the environment.

The different demands to be met by the various graphic papers are already taken into account in the selection of pulps and in the paper manufacturing and finishing processes. Accordingly the recycling-relevant influences are highly different for the various qualities. Planning of the project studies have taken these differences into account.

In view of the multitude of different effects to be studied, a selection had to be made. The project work is primarily restricted to the following tasks, which have been chosen by their assumed relevance:

1 influences associated with the manufacture of fibres (various mechanical and chemical pulps as well as recycled fibres treated with and without hot dispersion) (CTP,PTS)
2 influences of wet end chemicals and chemicals used in the waste paper treatment processes (STFI)
3 influences of drying techniques and operating conditions of the drying process (CTP, PTS)
4 influences of techniques used for the thermo-mechanical treatment of paper surfaces (calendering and supercalendering) (CTP,PTS)
5 influences of bleaching techniques (CTP)
6 influences of paper coatings (CTP)
7 influences of the accumulation of impurities (CTP,PTS)

Theoretical and experimental work performed up to now was dedicated to the items 1, 3, 4, 5 and 7 This presentation will primarily focus on the influences hot dispersing as well calendering

Influence of hot dispersing

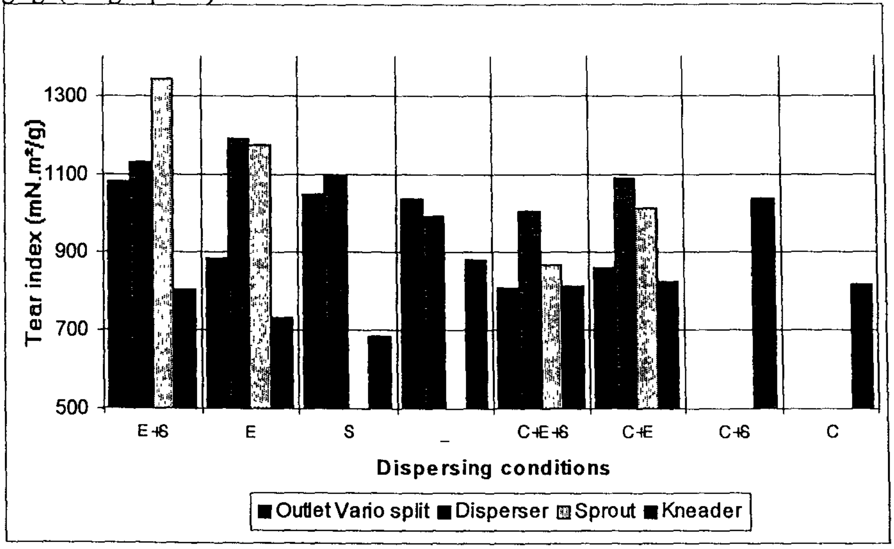
The so-called high speed dispersion is a technique derived by technology transfer from pulper-refiners for mechanical pulp with bar discs, followed by the adaptation of high-consistency deflakers. These techniques (disc or tooth type mechanical dispersion systems) are considered to be conventional.

Low speed dispersion is performed in finger dispersers comprising a single shaft or two shafts, particualrily developed for hot dispersion or resulting from technology transfer from mixers.

Trials were performed in a paper mill with an industrial high speed disperser (Disperger), a small scale kneader (a Lamort device) and a small scale high speed disperser (delivered by Sprout) which is available at theCTP pilot plant and installed in parallel with the industrial device. All the devices were fed with identical pulp compositions (Vario Split).

Various dispersing conditions combining two different energy input levels, two different temperature inputs both with and without addition of hydrogen peroxide were investigated. These variables are supposed to be the most relevant for hot dispersing.

The investigations so far have revealed that whatever the dispersion conditions are, breaking length usually decreases after kneading (low speed dispersing) while it increases after disperging (at high speeds).



The impact of dispersing conditions on the tear index

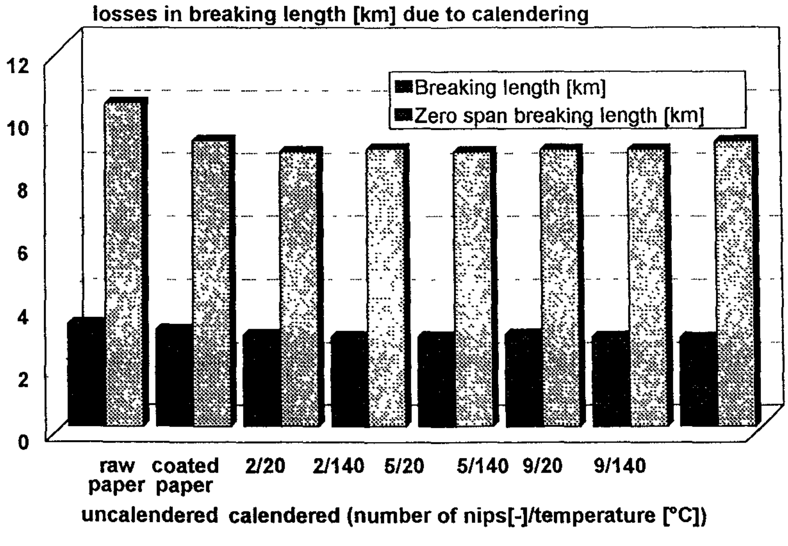
The decrease after kneading is significant and probably a consequence of a reduction in bonding ability. The residence time in the kneader screw is rather long, so that fibre curling might occur which to a certain extent can be irreversible The high temperature additionally contributes to the losses in bonding ability due to hornification and longitudinal forces lead to some fibre shortening.

The benefitial influence of high speed dispersion can be explained by the way the pulp is treated This treatment is basically comparable to the treatment in a beater, however at a much lower energy input. The result is a certain fibrillation of the fibre surface and - as a consequence - an increase in bonding ability.

The same trends have been observed for the development of tearing strength. This property decreases as well after kneading and increases after dispersing although the influences are less pronounced as for the breaking length. The influences of the addition of bleaching chemicals, of steam and the influence of the level of energy input can not yet be identified. But it can be stated, that the kneading is by far more detrimental than high speed dispersing. Mechanical property loss after kneading can however be restored to a certain extent by treating the pulp under alklaine conditions (latency treatment).

The influence of calendering

The processes by which the surface properties of paper are finally influenced within a paper mill are called calendering. Calendering thus aims at improving surface smoothness or gloss or both properties. Such improvements are typically associated with the application of high pressures in nips between metall and coated rolls Today there is quite a number of different calendering techniques available which have completely different impacts on the fibres. The main parameters which can be varied is the number of nips, the nip loads, the nip geometry the hardness of the steel rolls, the temperature oft the rolls and moisture content of the web.



The influence of calendering and temperature on strength properties of a coated wood-containing paper

Conventional calendering conditions i.e. calendering at elevated temperature and moderate nip loads usually causes only a moderate reduction of fibre properties wheras both increasing temperature and in particular increasing nip loads seem to be more detrimental. Trials with a so-called softcalender revealed that it is in the first place the temperature that contributes to property losses not so much the number of nips. Mechanical fibres performed better than chemical fibres in terms of strength loss, but of course the strength level of mechanical fibres is much lower.

Results concerning the influence of drying

Numerous paper properties are decisevly influenced by the drying techniques applied in the dry end of the paper machine. Traditionally contact drying is employed but other techniques are generally possible. In the frame of task 3 of the work programme PTS has conducted first trials with respect to the influence of this drying technique. In a series of experiments laboratory sheet consisting only of fibres of the same pulp without any other components were dried under varying temperatures. The temprature response over time was recorded both on the top and the bottom side of the sheet. The dried sheets were then tested in order to get information concerning differences in major mechanical or optical properties which depend upon the drying conditions.

Astonishingly, these rather preliminary tests revealed that a variation of the drying temperature has only a rather limited impact on the properties of the dried sheet. A summary of the responses found is given in table 1. Variations whenever they occured could be attributed to the various pulps.

Properties which were influenced were elongation, bending stiffness, air permeability and water retention. Optical properties on the other hand as well as breaking length or tear resistance were not influenced at all. From these results it can be concluded that there are no major restrictions with respect to the drying temperatures on the final sheet properties within the range studied. It however can not be concluded that more practice related furnishes will neither exhibit any sensitivity towards drying conditions.

	pulp					
	pine craft		spruce sulphite		ground-wood	
property	E	M	E	M	E	M
water retention	+	-	-	+	+	+
bulk density	-	-	-	-	-	-
breaking length	-	-	-	-	-	-
stretch at break	-	+	+	-	-	-
Young modulud	-	+	-	-	-	-
tear strength	-	-	-	-	-	-
bending stiffness	+	+	+	+	-	-
air permeability	-	+	+	-	+	+
capillary rise	+	+	+	+	+	-
brightness	-	-	-	-	-	-
opacity	-	-	-	-	-	-

E = one drying cycle; M = multiple drying cycles;
+ = significant influences; - = minor or no influences

Paper properties influenced by drying conditions

Additionally laboratory work was performed according to task 5 and 7, i.e. the influences of drying techniques and the operating conditions of the dry end, the bleachability of recycled fibres as well as the accumulation of impurities.

Ash Recycling technologies

EV5V-CT92-0196

Coordinator: B. Morgana

Conphoebus S.c.r.l.
Istituto di Ricerche per le Energie
IT - 95030 Catania - Piano d'Arci
Tel: +39-95.7489205
Fax: +39-95.291246

ASHREC
ASH RECYCLING TECHNOLOGIES

Contract n. : EV5V-CT92-0196
Title : Ash Recycling Technologies (ASHREC)
Starting date : January 1st 1993
Duration : 31 months
Project Coordinator :

CONPHOEBUS S.c.r.l. - Catania (Italy)
Istituto di Ricerche per le Energie
Rinnovabili e il Risparmio Energetico
Zona Industriale Passo Martino
IT - 95030 Catania - Piano d'Arci
Scientific responsible: *Beniamino MORGANA*
Tel.: 39 95 7489205 Fax: 39 95 291246

Partners:

ANSALDO RICERCHE S.r.l.
Società per lo Sviluppo di Nuove Tecnologie
Corso F.M. Perrone 25
IT - 16161 Genova
Scientific responsible: *Malgorzata DROZDZ*
Tel.: 39 10 6558342 Fax: 39 10 444666

C.E.B.T.P. (Centre Experimental de Recherches et d'Etudes du Bâtiment et des Travaux Publics)
Domaine de Saint Paul - B.P. 37 - 78470
St. Rémy lès Chevreuse - FRANCE
Scientific responsible: *André MOREL*
Tel.: 33 1 30852188 Fax: 33 1 30852314

G.H.I. (Institut für Gesteinshüttenkunde) - Aachen, GERMANY
Mauerstraße, 5 D-5100 Aachen
Scientific responsible: *Hans J. FEUERBORN*
Tel.: 49 241 804969 Fax: 49 241 8888271

PHYSIK+DATENTECHNIK
(Technologie und Innovations Service GmbH) Heroldsberger Weg 5 D-8500
Nürnberg 10 - GERMANY
Scientific responsible: *Kurt REUTER*
Tel.: 49 911 5216999 Fax: 49 911 5216998

CEBET (Research and Development Centre for the Concrete Industry)
Marywilska, 42b 03-042 Warszawa
(Poland) Tel.: 48 22 114425 Fax.: 48 22 112479
Scientific responsible: *Genowefa ZAPOTOCZNA SYTEK*

MINING & PROCESSING TECHNOLOGY INSTITUTE
Blokku "Vasil Shanto" Tirana (Albania)
Tel.: 355 42 26968 Fax.: 355 42 27885
Scientific responsible: *Genc MYFTIU*

UNIVERSITY "POLITEHNICA" OF BUCHAREST - Catedra SIMO
76206 Bucharest (Romania)
Scientific responsible: *Petru BALTÀ*
Tel.: 40 13 1296647 Fax.: 40 13 129647

WATER RESEARCH INSTITUTE
Nabr. Gen. Svobodu, 5
81249 Bratislava (Slovakia)
Scientific responsible: *Julia SUMNÀ*
Tel.: 42 7 343488 Fax.: 42 7 315743

OBJECTIVES OF THE PROJECT

The project objective is to supply decision making elements for the selection of the most suitable MSW fly ash recycling process, investigating on four different routes, assessing their relative advantages, considering technical, economic and social aspects. The final output from this project is a comparative technological assessment, performed by skilled companies, that will contribute to the addressing of industries and public bodies toward the best management process for the recycling of incineration fly ashes.

SUMMARY OF THE WORK DEVELOPED AND RESULTS OBTAINED

European MSW fly ash map - An investigation on quality and quantity of MSW fly ashes, concerning each involved countries, was carried out. For those countries not provided of incineration plants, the investigation was addressed to the waste production and management existing in the partner Country.

MSW fly ashes characterisation - The second phase of the project consisted in the characterisation of different types of MSW fly ashes. Samples, coming from different incinerators were characterised. On the basis of the characterisation results, the partners selected the fly ashes most suitable to each of the four processes to be developed.

Main results obtained - For each of the processes investigated, the conclusions of the testing laboratories, about the products obtained, are summarized hereinafter:

HYDRAULIC BINDING - Mechanical, chemical and environmental properties of the samples obtained with CPA cement and one French fly ashes show that 6 % of fly ashes (dry process) may be incorporated into cement paste without modification of the specimen durability. Blended cements containing MSW fly ashes as well as blast furnace slag or thermal station fly ash were also characterised and very significative results were obtained.

LIGHTWEIGHT GRANULATES PRODUCED BY THERMAL PROCESS - Mechanical properties of the aggregates produced by sinterisation process are good and corresponding to legal constraints. Only sulphates and chlorides constitute an hazard for the durability of the final product and the environmental behaviour. Future research has to be oriented to the stabilization of these elements to permit a re-use in building industry. Moreover, interesting results were reached with lightweight granulates (CEGRAN) obtained by low thermal treatment.

GLASS-FIBERS - The production and testing of fiber samples, obtained with the addition of MSW fly ashes to the usual components of the glass fibers, were carried out. They showed a good resistance to the alkaline ambient due to their surface coating reinforced with the heavy metals contained in MSW fly ashes.

FOAMGLASS LIGHTWEIGHT GRANULATES - Physical measures showed that water absorption and porosity are high and similar to lightweight granulates. Bulk density and mechanical resistance are better than the corresponding characteristics of foamglass from waste bottle glass.However, because of its leaching behaviour, this material is not suitable for use in cement matrix.

ASHREC
ASH RECYCLING TECHNOLOGIES

Contract n.	: EV5V-CT92-0196
Starting date	: January 1st 1993
Duration	: 31 months
Project Coordinator	: CONPHOEBUS S.c.r.l. - Catania (Italy)
Partners	: ANSALDO RICERCHE s.r.l. - Genova (Italy) C.E.B.T.P. - St. Rémy lès Chevreuse (France) G.H.I (Institut für Gesteinshüttenkunde) - Aachen (Germany) PHYSIK+DATENTECHNIK Nürnberg (Germany) CEBET - Warszawa (Poland) ITNPM - Tirana (Albania) POLYTECHNIC UNIVERSITY of BUCHAREST (Romania) WATER RESEARCH INSTITUTE - Bratislava (Slovakia)
Reference period	: from 1 January 1993 to 31 July 1995

OBJECTIVES OF THE PROJECT

The incineration of urban solid wastes produces large quantities of fly ashes, that need to be eliminated with care, due to the toxicity of high heavy metal concentration. The management of these hazardous wastes (containing heavy metals, chlorides, mercury, in widely variable concentrations) concerns all countries that utilise the incineration process for MSW management.

The problem is assuming increasing importance as the national legislation progressively limits the utilisation of landfill disposal for hazardous waste and the cost for pre-processing MSW fly ash (inertization), before their disposal in standard dumps, is very high. Moreover the public concern for the increased consumption of land for waste disposal is growing. The possibility of re-use of urban waste incineration fly ashes as construction industry materials is therefore very appealing, but has to face the severe environmental concerns related to the safe and stable behavior of the obtained components in their final use.

The project objective is to supply decision making elements for the selection of the most suitable recycling process, investigating on four different routes, assessing their relative advantages, considering technical, economic and social aspects. The final output from this project is a comparative technological assessment, performed by skilled companies, that will contribute to the addressing of industries and public bodies toward the best management process for incineration fly ashes. Moreover, the partners from Central and Eastern European Countries have the objective of :

- assessing the extent of this problem in Central and Eastern European Countries and identifying the present technologies and research perspectives;
- proposing new recycling technologies and characterising new materials;
- supporting Central and Eastern Public Authorities for decision making on MSW fly ash recycle.

Social benefits are clearly related to: a) the possibility of reducing the amount of disposed wastes, and consequent reduction of land consumption, b) the safe inertization of hazardous wastes, c) the independent and comparative assessment of the long term stability of the processed secondary materials by suitable laboratory test cycles.

SUMMARY OF THE WORK DEVELOPED AND RESULTS OBTAINED

European MSW fly ash map

The first phase of the project was addressed to the definition of the state of the art concerning quality and quantity of fly ashes from MSW incinerators. Data concerning the amount of waste treated each year in the involved countries were collected. Mass balance of MSW incineration unit with recognition of total gas amount and residuals was given. The distribution of toxic materials in residuals of municipal waste incineration fly ashes was also shown. Statistic data on chemical and mineralogical analyses of fly ashes, representing the average composition of those produced in each country, were supplied.

The chemical data show that the main constituents of fly ashes are silicate, aluminium oxides and calcium combinations. The metals Hg, Cd, Zn and Pb evaporate at temperatures of 800 - 1000°C and then very high contents of these metals are present in the fly ashes. In the case of mercury, Hg may evaporate from the captured fly ashes and migrate to other parts of the effluent gas cleaning equipment.

For those countries not provided of incineration plants, the investigation was addressed to the waste production and management existing in the partner Country. Special attention was devoted to comparing the European regulation on wastes (particularly fly ashes) with that of each partner Country from Central and Eastern Europe.

MSW fly ashes characterisation

The second phase of the project consisted in the characterisation of different types of MSW fly ashes. Before the characterisation work, the national and international procedures for the chemical, environmental and physical test methods were compared and standard levels were defined for the test sequences. For the environmental tests the leaching procedure were well described in schedules after selection by literature data. Seven fly ash samples, coming from different incinerators sited in France, Germany and Italy, were characterised by the two laboratories, C.E.B.T.P. and G.H.I. The analyses carried out were the following: Chemical (XRF, C_{org} , heavy metals), Mineralogical (XRD), Thermoanalysis (DTA/TG), Physical (grain size distribution by sieve and Laseranalysis), Hydraulic index, Pozzolanic index, Morphology. On the basis of the characterisation results, the partners selected the fly ashes most suitable to each of the four processes to be developed.

Participation of the partners from Central and Eastern European Countries

During the first year of the project, four Partners from Central and Eastern European Countries were selected, according to the provisions of the PECO programme, on the basis of their fruitful participation in the research. Their participation to the research work started with the acquirement of knowledges developed, during the first year of Ashrec Project, by the Western Partners. Therefore, each PECO Partner selected the line(s) in which he has the greatest interest; research stage periods in Western partners' laboratories were also spent.

Processes investigated

Hereinafter it is summarized the work carried out by the partners and the final assessment for each of the four ASHREC processes.

i) Hydraulic binders: ANSALDO RICERCHE carried out experiments on the inertization and recycling of MSW fly ashes with hydraulic binders and the addition of additives. Tests were performed to determine the metal concentration variations in eluate from mortar specimens made up with fly ashes and chemical additives, used to enhance the inertizing effect already verified in a first series of experimental tests. The MSW fly ashes employed were those coming from one Italian incinerator. The specimens have been tested using the EPA normative.

At the beginning it has been chosen to utilise the developed technology in the production of a tile. The results of the tests performed were quite good in terms of the eluate of the leaching test but some problems occurred concerning the freezing and carbonatation test mainly due to the surface porosity. To solve this problem, it was decided to produce rubble samples to substitute the crushed stones. A further product that has been considered is represented by the direct use of fly ashes, just after their inertization process, as sand.

C.E.B.T.P. and G.H.I. produced reference samples by standard building technologies to offer a comparison basis to the new products developed by ANSALDO RICERCHE.

One French and one German fly ash, that were more suitable to this process than that from Italy, were selected to be used in this phase after chemical and rheological analyses; these ashes were added to the concrete composition in substitution of calcareous filler at different rates. The characterisation for hydraulic binding material, as agreed by the partners, provided the following tests: Normal consistency, Setting time, Ambient stability, Compressive strength, Binding strength, Porosity, Water permeability, Accelerated carbonation, Frost resistance, Leaching test.

On the whole it can be said that the results obtained in this line are very interesting as it was determined that a certain amount of MSW fly ashes could be used in concrete preparation with no significative decrease of its mechanical properties and without polluting elements, over the law limits, in the leacheate. But, from the other hand, the "new hydraulic binders" proposed didn't allow the attainment of better results with respect to those reached without using any additive or special binders.

The WATER RESEARCH INSTITUTE investigated also this line with special attention to the leaching test application to the specimen containing MSW fly ashes.

The POLYTECHNIC UNIVERSITY of BUCHAREST characterised blended cements containing MSW fly ashes as well as blast furnace slag or thermal station fly ash. The results obtained confirm those reached by the western partners.

ii) Thermal process: CONPHOEBUS investigated the possibility of MSW fly ashes recycling by means of a sintering thermal process allowing the production of lightweight aggregates having a safe and stable behaviour with respect to the environment as well as physical and mechanical properties comparable with or better than the existing ones.

The first phase of this research consisted in the individuation of the best mixtures of MSW fly ashes and other components. Steel-works dust (toxic wastes containing heavy metals trapped in the electrofilters of the steel-making factories) and coal fly ashes, from electric power plant, were added to the MSW fly ashes. Several mixtures were formulated with different composition of the above mentioned wastes and secondary raw material. The produced pellets were then treated in a rotating kiln at temperatures of 1100 - 1200°C until the attainment of their sinterisation.

The main characteristics of ASHREC aggregates are:

Bulk density	1,21	t/m^3	(*)
Particle density	2,189	t/m^3	(*)
Water absorption coefficient	4,5	(NFP 18 554)	
Porosity(%)	15,6	(NFP 18 554)	
Crushing strength (MPa)	20	(NFP 18 576)	
Moisture content (%)	0	(NFP 18 554)	
Alkali silica reaction (Δl/l%)	<0.15	(NFP 18590)	
Leaching test	(**)		

(*) This value can be decreased by reducing the content of steel-works dust in the mixture.

(**) The last samples tested have only the chlorides content higher than the threshold value (Italian regulation:<1000 mg/l).

On the whole we can say that the results of this line seem to be very promising as aggregates, having very good mechanical properties, have been produced. In the leacheate only sulphates are still higher than the limits of European regulation. Another fact to consider is that the bulk density is still a little higher than 1000 kg/dm^3; therefore these aggregates couldn't be considered lightweight aggregates. However, this line seems to be the nearest to the fixed goals as the above mentioned problems could be easily solved in the next period. Moreover the economical and technical analysis pointed out very convenient applications of this new material in the building industry, with very low production costs. The purpose of recycling of MSW fly ashes seems to be reached in this line.

Also ITNPM carried out experiments on the sintering thermal process. Pellets made up by MSW fly ashes, coal fly ashes and different kinds of toxic wastes (dusts from copper, chromium, pyrite metallurgical plant and steelmaking industries) were produced and tested. Moreover, a feasibility study was performed and production costs were estimated.

Interesting results were obtained also by CEBET that investigated the possibility of MSW fly ash recycling by a low thermal treatment. Lightweight aggregates, containing 5% of MSW fly ashes, were produced and tested by using a patented technology (CEGRAN). Production costs were estimated by means of a feasibility study.

iii) Fibers - This line has been only partially investigated, as provided in the work-programme. The production and a partial testing of fiber samples, obtained with the addition of MSW fly ashes to the usual components of the glass fibers, were charged to CONPHOEBUS while further characterisation was charged to C.E.B.T.P. Very significative samples have been produced and tested. Different kinds of application could be envisaged for this material.

The main steps of the work carried out in this line can be summarized as follows:

a) Chemical analysis of wastes; b) Preparation of vitrifiable mixtures; c) Vitrification phase
d) Chemical analysis of mixtures; e) Spinning phase; f) Chemical analysis of the glass fibers;
g) Hydrolitic test in alkaline solution; f) Morphological analysis on fibers surface

Studies on glass fibers including MSW fly ashes were carried out by UPB too. Good results were obtained by using German and French fly ashes mixed with Romanian basalt.

iv) Foam glass - This line was charged to P+D. The recycling of MSW fly ashes together with exhaust fluorescent lamp glass has been investigated. At first, a procedure for the decomposition of fluorescent lamps and TV-tubes has been developed. After the characterisation of different European fly ashes a fly ash from one plant in Germany was chosen without residuals from the wet cleaning section. Crushed and milled glass from fluorescent lamps as well as mixtures of this glass with fly ash were formed to foamable pellets by adding a sodium silicate solution. The treatment of pure fluorescent lamp glass at temperatures of 850°C or of mixtures at 1100°C resulted in mechanically stable foamed granules. During the treatment of fluorescent lamp glass from the washing to the thermal treatment, the mercury content in the glass was reduced to about 20% in the foamglass. Most of the mercury vaporises during the treatment. Furthermore, the leaching behaviour of the granules of fluorescent lamp glass showed some critical contamination with zinc.

Foamglass aggregates obtained from a mixture of fly ash and fluorescent lamp glass in a ratio of 1:2 (w/w) have been introduced into a cement matrix. The leacheate of this product had a very high sulphate content. Due to this it is not applicable for the production of concrete because the sulphate leacheate would reduce the long term stability of the concrete.

ITNPM

INSTITUTI TEKNOLOGJISE
NXJERRESE DHE PERPUNUESE TE
MINERALEVE
General Director Genc MYFTIU

MINING & PROCESSING
TECHNOLOGY INSTITUTE

Blloku "Vasil Shanto", Tirana, ALBANIA
Tel 00355 42 26968
Tel &Fax 00355 42 27885

RECYCLING OF FLY ASHES FOR THE PRODUCTION OF CERAMIC MATERIALS

Authors
Genc **MYFTIU**
Sokol **MATI**

TIRANE MARCH 1996

RECYCLING OF FLY ASHES FOR THE PRODUCTION OF CERAMIC MATERIALS

1. INTRODUCTION

Fly ashes in Albania are waste which are produced from many processes in industries, as well as from the municipal solid wastes. MSW till now in Albania are disposed to the municipal dumping ground. MSW are dumped on disposal sites without any efficient system for the protection of environment and the negative effects of them. This problem discussed so much in nowadays is of a great importance for our cities. The fly ashes from copper metallurgy is mostly composed from copper and sulphur and is about 2 - 3 %. About 70 % of this quantity is caught by cyclones and filters. The other part now goes in atmosphere and created many problems in environment which obliges us to close one of them in Kukes. The same problem is for the fly ash of chromium metallurgy. Fly ashes from power station which are spreading in the whole country are also a great problem. Recycling of them for the production of constructin materials as well as ceramic products is of great interest. In these study are taken in consideration fly ashes from MSW, metallurgical industry and thermo power station.

2. EXPERIMENTS

In order to realise the production of pellets after some preliminary tests results that it is better that the whole material would be under 0.1 mm. At this size the process of pelletization is done fast and with good results. Also it is useful a good mixture of all materials use in their production as well as weighting of the quantities of materials used in the pelletization process.

Pelletization process itself is composed from these phases: The preparation of fly ashes samples (milling, drying), Mixture process (weighting, mixing), Drying Process, Pelletization process, Mixture process (weighting, mixing), Calcination process, Sinterization process, Test for pellets.

Mixture Process, Mixture of dust of water and preparing of pellets (we have prepared pellets manually)

Drying Process, Drying of pellets is done in temperature 105 °C for 4 hours. After this pellets in different dimension (10-20mm in diameter) goes in calcination process.

Calcination Process is done in two ways: First way, pellets arrived from drying process goes directly at 700 °C for 1 hour and remain at this temperature for 2 hours. Second way, pellets arrived from drying process goes first at 300 °C for 30 minutes and remain at this temperature for 1 hour, after this goes at 700 °C for other 30 minutes and remain 1 hour at this temperature.

Sinterization Process is done at two temperatures 1120 °C and 1140 °C. Pellets arrived from calcination process goes at these temperatures for 1 hour and remain at these temperatures for 30 minutes after this furnace is open and pellets are taken out.

Four types of mixtures are taken in consideration and them are distinguished from the type of metallurgical dust used. Different proportion in mixture as well as different temperature of sinterisation have realised different types of pellets.

The sample 1 includes pellets derived from the sinterisation cycle carried out by employing Tiru (France) MSW fly ashes, coal fly ashes of power station of Monfalcone (Italy) and steel work dusts of Udine (Italy).

Table 1. The results of the test for the first type of mixture {Tiru (France) MSW fly ashes, coal fly ashes of power station of Monfalcone (Italy) and steel work dusts of Udine (Italy)}

No	MSW %	Coal %	Dust %	Water %	Tmax (°C)	Weight after drying gr	Weight after sinterisation gr	Loss in weight %	Weight after 24 hour in water gr	Adsorption %
1	30 00	30 00	40 00	22 00	1120	3.59	2 75	23 20	3 83	39 32
2	30 00	30 00	40 00	22.00	1140	3 90	2 88	26 14	3 64	26 57
3	40 00	30 00	30.00	22 00	1120	3.37	2 59	22 90	3 63	40 27
4	40 00	30 00	30 00	22.00	1140	3 71	2 74	25 98	3 49	27.44
5	33 33	33 33	33 33	22 00	1120	3 96	3 16	20 13	4 45	41 13
6.	33 33	33 33	33 33	22 00	1140	4 32	3 29	23 80	4 21	27 98
7	40.00	20 00	40 00	22 00	1120	3 64	3.00	17 58	4 27	42 42
8	40 00	20 00	40 00	22 00	1140	3.49	2 79	19 90	3 59	28 62

The sample 2 includes pellets derived from the sinterisation cycle carried out by employing Tiru (France) MSW fly ashes, coal fly ashes of power station of Monfalcone (Italy) and dusts of pyrites from chemical plant of Lac (Albania).

Table 2. The results of the test for the first type of mixture {Tiru (France) MSW fly ashes, coal fly ashes of power station of Monfalcone (Italy) and dusts of pyrites from chemical plant of Lac (Albania)}

No	MSW %	Coal %	Dust %	Water %	Tmax (^{0}C)	Weight after drying gr	Weight after sinterisation gr	Loss in weight %	Weight after 24 hour in water	Adsorption %
1	33.33	33.33	33.33	22.00	1120	3.64	2.80	22.90	3.92	40.03
2	33.33	33.33	33.33	22.00	1140	3.49	2.58	25.80	3.24	25.67
3	40.00	20.00	40.00	22.00	1120	3.87	3.06	20.90	4.31	41.12
4.	40.00	20.00	40.00	22.00	1140	3.08	2.33	24.10	2.95	26.62

The sample 3 includes pellets derived from the sinterisation cycle carried out by employing Tiru (France) MSW fly ashes, coal fly ashes of power station of Monfalcone (Italy) and dusts of cooper metallurgical plant of Lac (Albania).

Table 3. The results of the test for the first type of mixture {Tiru (France) MSW fly ashes, coal fly ashes of power station of Monfalcone (Italy) and dusts of cooper metallurgical plant of Lac (Albania)}

No	MSW %	Coal %	Dust %	Water %	Tmax (^{0}C)	Weight after drying gr	Weight after sinterisation gr	Loss in weight %	Weight after 24 hour in water	Adsorption %
1	33.33	33.33	33.33	22.00	1120	3.12	2.25	27.60	3.08	36.97
2	33.33	33.33	33.33	22.00	1140	3.37	2.28	32.30	2.72	19.35
3	40.00	20.00	40.00	22.00	1120	3.22	2.45	23.90	3.35	36.78
4	40.00	20.00	40.00	22.00	1140	3.66	2.72	26.50	3.34	23.03

The sample 4 includes pellets derived from the sinterisation cycle carried out by employing Tiru (France) MSW fly ashes, coal fly ashes of power station of Monfalcone (Italy) and dusts of chromium metallurgical plant of Burrel (Albania).

Table 4. The results of the test for the first type of mixture {Tiru (France) MSW fly ashes, coal fly ashes of power station of Monfalcone (Italy) and dusts of chromium metallurgical plant of Burrel (Albania)}

No	MSW %	Coal %	Dust %	Water %	Tmax (^{0}C)	Weight after drying gr	Weight after sinterisation gr	Loss in weight %	Weight after 24 hour in water	Adsorption %
1	33.33	33.33	33.33	22.00	1120	3.16	2.45	22.20	3.40	38.77
2	33.33	33.33	33.33	22.00	1140	3.55	2.65	25.30	3.30	24.88
3	40.00	20.00	40.00	22.00	1120	3.36	2.73	18.70	3.82	40.01
4.	40.00	20.00	40.00	22.00	1140	3.19	2.52	20.90	3.26	29.43

3. COMPARISON OF DIFFERENT TECHNOLOGICAL FLOWSHEETS IN LABORATORY CONDITION

Our test with different type of cycles for calcination and sinterisation processes have take an importance in order to realise good pellets because in some test some of pellets are broken during the sinterisation process. In this context we have proposed two types of cycles with two and three steps in increasing of temperature. The two type of cycles are shown in figures 1.

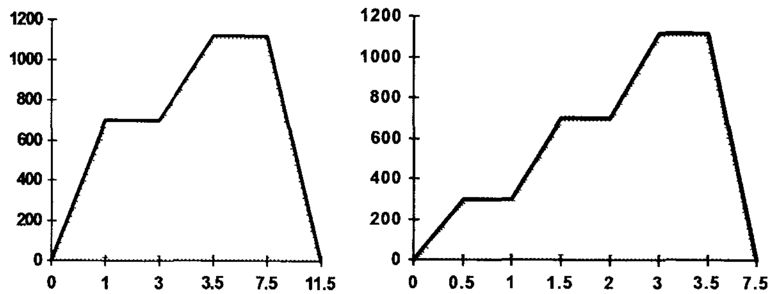


Figure 1. The cycle of sinterisation with two and three steps in increasing the temperature.

4. •TRANSFORMATION TYPE AND PROCESS PARAMETERS.

The most important parameters which are taken in consideration are:

4a. The determination of the quantity of water during balling process,

To impart sufficient strength to the balls, the correct amount of water must be available. Maximum strength, or integrity of a ball is obtained if all the capillaries are filled with water. A low water content causes closing of the air bubbles inside the ball, and this phenomenon is responsible for a restriction of the capillary action, conversely excessive causes a water film to be produces on the surface of the whole ball. This film destroyed the capillary forces and particle cohesiveness is then affected solely by the surface tension water. Taken in consideration this phenomenon we have tested with moisture from 16 % with step 1%. We see that at value 22 % of moisture the balling process goes very well and pellets produced are good in form and have sufficient strength for passing in other processes.. So for this parameter we have decided that the moisture in balling process must be 22 %.

4b. Determination of quantities of the constituents,

In order to realise pellets with good characteristics determination of the quantities of the constituents is another parameter which is needed to take in consideration for the production of pellets. In these context the mineralogical composition of constituent is also a factor decisive for the balling. From these point of view we have selected for producing balls three types of constituents for four types of pellets. With the first mixture we have tested with four different percentage participation of the constituents in the mixture. the two parameters measured are loss in weight during sinterisation process and the adsorption of water. The results are given in table 5.

Table 5. The results of weight loss and adsorption from the different percentage of quantity of the constituents.

No	MSW %	Coal %	Dust %	Tmax (^{0}C)	Loss in weight %	Adsorption %
1a	30 00	30.00	40.00	1120	23.20	39.32
2a	40.00	30.00	30.00	1120	22.90	40 27
3a	33.33	33.33	33.33	1120	20.13	41 13
4a	40.00	20.00	40.00	1120	17.58	42 42
1b	30.00	30.00	40.00	1140	26.14	26.57
2b	40.00	30.00	30.00	1140	25.98	27.44
3b	33.33	33.33	33.33	1140	23.80	27.98
4b	40.00	20.00	40.00	1140	19.90	28.62

From the results we have decided that the quantities of the constituents used in balling process must be 35 % from fly ash of MSW, 30 % fly ash from thermal power station and 35 % dust from metallurgical plant.

4c. Determination of the temperature of sinterisation,

The heat hardening is the process which we have used for strengthening of pellets and changing them is ceramics. The pellets are hardened owing to recrystallization of oxides which serves as nuclei in the formation of pellets and secondary components. These processes take place at high temperatures. Two are the most important reasons during this process. The undestroyed and fusion of pellets and the quantities of volatile components. In order to eliminate the first problem and to achieved high strength of pellets temperature in interval 1140-1180^{O}C is requested. We have tested with temperature 1120^{O}C and 1140^{O}C only few tests are carried out at 1160^{O}C. The temperature for this process must be at 1140^{O}C because at a temperature higher than this the fusion process is caused. The results of this test are given in table 6.

Table 6. The results of weight loss, adsorption and strength from the different temperature in sinterisation process.

Temperature ^{O}C	Weight loss %	Adsorption %	Compression Strength MPa
1120	22.90	40.27	9 35
1140	25.98	27.44	9.65
1160	27.89	20 13	9.95

Another problem in the sinterisation process is the volatile components which in the fast heating caused the destroying of pellets. We have risolved this problem with different cycles used in sinterisation and time of the sinterisation step. We think that the process with three steps and time of 30 minutes at temperature of sinterisation must be requested. The nature of these components for the reason of nonequipped laboratory is unknown.

4d. Determination of the optimum size of particles use in balling process,

As generally valid rule is that the finer the particles the higher ball strength and the particle fineness of the material must be at least below 0.2 mm to make it ballable to any extent. In our case when we have treated fly ashes this size is achieved form two product, for the third material a size reduction process is needed. In our tests we have begin the work at size -0.2 mm till to -0.074 mm. we have see that good results are achieved at -0.1mm and at this value the cohesion of particle and the strength after drying process will be the same till to -0.074mm. So we have decide that the size of particles in balling process must be -0.1mm.

4e. Determination of the optimum quantity of ultrafines particles.

Ballability is closely connected with the granulometric distribution of particles and the amount of particles smaller than 0.04 mm is at least 60 % by weight. Particles fine in size envelop and bind the bigger ones. The content of fines smaller than 0.04 mm is decisive for the ballability and strength of balls. For the materials that we have used for the production of balls these property is realised and for the dust of metallurgy it is achieved from grinding process. The quantity of fines under 0.04 mm used in our tests is varied at 58-65 % by weight.

5.• MACHINERIES AND EQUIPMENTS

The selection of technological equipment for material preparation is governed by the number of valuables types of feedstock and their physico-chemical condition. The materials may be shipped in for screening and grinding in order that all constituents at a time will be homogenize perfectly, provided in material with a lower specific gravity is separated. Milling will be in dry way as we have experimented. The target state is flowability of the material enabling transport and uniform metering into the balling device. Essentially to obtain balls with a satisfactory strength the fineness of the materials must be ensured as required. The amount of components and strengthening methods are factors decisive for the selection of the blending device. Different types of equipments for reclaiming fines from storage bins will be used such as screw feeder, rotary feeder or vibratory for this last exist a great experience in our local condition. The technological flowsheet of ball preparation depend by type, amounts and physico-chemical properties of the input materials as well as from the method of ball hardening. Ball preparation will be achieve by disc pelletizer. the characteristics of equipment will be selected in base of the production of pellets designed. In the heat-hardened two lines to make the ball are required, in this way the arrangement will give maximal utilization of equipment and/or individual cycle can be interconnected. The main advantage is that the balls can be delivered uniformly into the firing unit. Uniform heating of all pellets is technologically important. The pellets can be heat-hardened on travelling grates or rotary kiln, this last gives a higher uniformity of pellet firing, thanks to the motion imparted to the pellet charge. Travelling grate firing is also an operationally safe method.

6. APPLICATION OF ASHREC TECHNOLOGIES IN LOCAL CONDITION.

In local condition the flowsheet which will be used is shown in figure 5and 6.

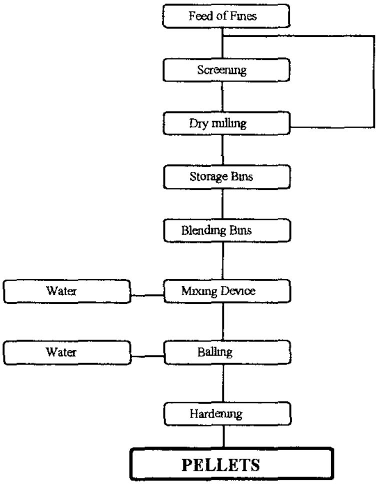


Figure 5 The technological flowsheet of pellets preparation

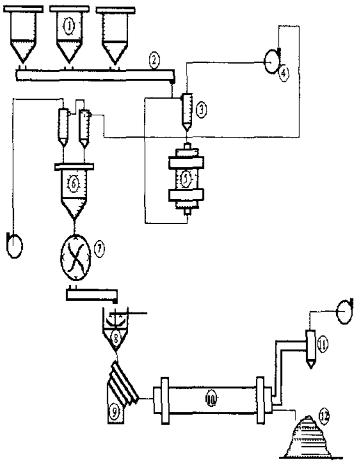


Figure 6. The flowsheet of equipments used in the pelletization process

1 Storage Bin
2 Screw transports
3 Cyclone
4 Ventilator
5 Dry mill
6 Storage bin
7 Blending bin
8 Mixer
9 Disc pelletizer
10 Hardening
11 Cooler
12 Pellets storage

DATA SHEET

Title of project	**"ASHREC" - ASH RECYCLING TECHNOLOGIES**
Project number	**ERB EV5V CT92-0196**
Starting date	**01.04.1994**
Duration	**31.07.1995**
List of adresses	**Prof.dr. PURI Annemarie** **Prof.dr. GEORGESCU Maria** **Prof.dr. BALTA Petru** **University "POLITEHNICA" Bucharest RUMANIA** **Faculty of Industrial Chemistry** **Dep. Science and Engineering of Oxide Materials** **P.O.Box 12134** **Tel. 40 1 3129647 ; 40 1 6503289/285;** **Fax. 40 1 3129647**

Main objectives

A. Study of the inertization capacity and the binding properties of blended cements containing municipal solid waste (MSW) incineration ashes (Prof.dr. A.PURI and Prof. dr. M. GEOR-GESCU)

B. Introduction of MSW incineration ashes in the composition of glasses, in order to obtain glass fibers (prof.dr. P.BALTA).

Main results

A. The tests were carried out on blended cements on the basis of ordinary Portland cement as well as iron rich ferroportland cement, containing four different MSW ashes. The Portland cements were partially replaced by granulated blast furnace slag or thermal station fly ash. The MSW ashes proceed from Germany and France. Their content in the blended cements varied from 0 to 30 %.
We can state the followings:

The immobilization capacity

The **sulfate content** in the investigated MSW incineration ashes occurs mainly as $CaSO_4$ but also as alkaline sulfates, especial K_2SO_4. The alkaline sulfates react with the $Ca(OH)_2$ formed at the hydration-hydrolyses reactions of the Portland cements, to form $CaSO_4.2H_2O$. Both, $CaSO_4$ and $CaSO_4.2H_2O$ react with the anhydreous and hydrated aluminate and ferritaluminate compounds and form important amounts of Ettringit. This compound is rather stable in water, therefore the immobilization capacity of the sulfate ion in the blended cements hydrated 28 days is very high, in most of the investigated samples more than 90 %.

The **chloride content** in the MSW ashes occurs mainly as alkaline chlorides and only in very small amounts as calcium chloride. At the hydration of the blended cements, the alkaline chlorides react with $Ca(OH)_2$ and the resulted calcium chloride participates at the formation of hydrocalciumchloride aluminate. The stability in water of these compounds is rather low and therefore, the immobilization capacity of the chloride ion in the 28 days hardened blended cements is in most of the investigated samples less than 50 %. It is to expect that the high chloride content in the pore fluid of the hardened cement stone will corrode the steel reinforcement embedded in the concrete.

Both, the formation of Ettringit and of hydrochloride aluminate are improved if the Portland cements are partially replaced (10 to 20 %) by slag or thermal station fly ash, but there doesn't occur sensible alterations in the immobilization capacity of the blended cements.
The immobilization capacity concerning the Zn^{2+} ion exceeds in most of the investigated samples 75 % and that of the Pb^{2+} ion we found to be total.

Mechanical properties of the hardened blended cements

We tested the compressive strength of mortar specimens, hardened till 1 year.
After 28 days hardening, the mechanical strengths of blended cements containing **no more than 20 %** MSW ash are comparable but more often than not even higher in comparison with those of the corresponding unitary Portland cements. These improvements are dependent both of the composition of the MSW ashes as well as of the composition of the Portland cement. This behaviour may be due to the well known accelerating effect of chlorides on the hydration and hardening of Portland cement. The partial replacement of Portland cements by thermal station fly ash or slag usually doesn't affect and sometimes even improves the mechanical strength of the hardened mortar samples.
At some, but rather few blended cements, we observed little decreases of the mechanical strength at later hardening terms (90 days). These may be induced by a belated Ettringit formation which can strain the hardening structure and therefore diminish the mechanical strength or may be due to the negative influence of the high alkali salt content on the long term hardening properties of Portland cement. By a suitable matching of the constituent materials, the mechanical strength values of the blended cements hardened 1 year are comparable, but usual higher in comparison with those of the corresponding unitary Portland cements.
The **increase of the MSW ash content up to 30 %** deteriorates the mechanical strength of the blended cements, unaffected of the composition of the cement or the MSW ash.

B. The MSW incineration ashes can be included in glasses prepared in different ways, using the industrial row materials or, more advantageous, some natural rocks.
Two different MSW ashes were included in the raw material batches composed of usual raw materials as well as a mixture of 37 %, respectively 50 % MSW ash and the rest basalt rock. Carbon black was added to avoid the occurrence of immiscible sulfate melts. The batches were melted at about 1400°C.
In principle the glass composition may be varied in certain limits, to match the glass basicity value to the basicity of the reaction medium.
Fibers drawing was possible from the melted glasses. The increase of the glass basicity determines an increased tendency towards crystallization that complicates the drawing process.
A new testing method for the chemical stability of small glass samples in alkaline media was elaborated. The method is based on the measurement of the light reflectivity of grinded glass surfaces, which changed after their exposure to chemical attack.
The tested glasses show a clear dependence of the intensity of the chemical interaction upon the difference between the basicity of the glass and those of the reaction medium. It seems that it is necessary to match as exactly as possible the basicity (composition) of the glasses to the basicity of the medium in which those fibers are going to be used.

PROJECT ERB EV5V CT92-0196 "ASHREC" ASH RECYCLING TECHNOLOGIES

1. OBJECTIVES

The immobilization of some hazardeous substances contained in the Municipal Solid Waste (MSW) incineration ashes, in blended cements on the basis of Portland cement.

The influence of MSW ashes on the hydration processes and the properties of the hardened blended cements.

The fixation of the different hazardeous substances in cement based materials can be attributed to several processes, as there are:

- the reduction of the solubility and the precipitation of heavy metals at the high pH-values existing in the hardened cement stone;
- the addition of heavy metals into existing hydrocompounds in the form of solid solutions;
- the formation of new hydrocompounds like hydrosulfate aluminates and hydrochloride aluminates;
- the adsorption of the toxic substances on the high surface area of the hydrated cement paste.

We tested the influence of the following parameters on the environmental stability and hardening capacity of the blended cements:

- the composition and the amount of the MSW ash added
- the composition of the Portland cement
- the partial replacement of Portland cement by granulated blast furnace slag or thermal station fly ash.

2. EXPERIMENTAL CONDITIONS

Table 1 shows the characteristics of the starting materials. Three of the MSW ashes proceed from Germany (Bonn I, Bonn II and Essen) and one from France. Their content in the blended cements was varied from 0% to 30%. At the same MSW ash content, the Portland cements (one ordinary Portland cement "P"and one ferroportland cement "F") were partially replaced by slag or thermal station fly ash.

Table 1 - Characteristics of the starting materials

Characte-ristics	Cement "P"	Cement "F"	Slag	Thermal sta-tion fly ash	MSW ash Bonn I	MSW ash Bonn II	MSW ash Essen	MSW ash France
L i (%)	0 39	0.43	0 28	4.60	6.58	40.4	20.34	2.14
SiO2(%)	20.51	21 48	37 69	54.6	38.91	8 29	39.04	17 07
Al2O3(%)	6.59	4 05	9.64	23.73	9.23	2.78	14 18	12 55
Fe2O3(%)	3.59	5 74	0.26	7.72	3.20	0.65	3.27	1.59
CaO(%)	64 52	64.03	43.67	3.90	17.94	31.94	18.35	20.60
MgO(%)	1.59	1.80	5.62	0.99	1 95	1.22	2 08	2 71
K2O(%)	1 03	0 80	0 71	2.37	5 67	5 77	3 13	8.25
Na2O(%)	0 50	0 24	0.44	0.50	5 93	8.42	3.87	6.50
TiO2(%)	0.22	0 29	0.71	1.04	1.35	0 58	1 72	1.53
PbO(%)	n.i.	n.i	n.i.	n.i.	0 29	0.75	0.17	0.0
ZnO(%)	n.i	n i	n i	n.i.	1 70	2.68	3.79	3.97
P2O5(%)	n.i	n.i.	n.i.	n.i	1.31	0.36	1 57	n i
SO3(%)	1 13	1.32	0.12	n i.	14 31	11.31	2.94	10 31
Cl^- (%)	n i.	n.i.	n i	n i.	1.62	28.49	5.64	12.48
Cao free(%)	1.01	1 0	n.i.	n.i.	n.i	<0 5	1 27	n.i.
Carbon (%)	0.0	0 0	n i.	n.i.	0.48	1 94	3.48	n.i.
Solub H2O(%)	-	-	n i.	n.i.	16 1	63.4	n.i.	n.i.
Specif surface area (cm^2/g)	3230	3170	3404	2930	2447	6383	6650	4872

The hardening capacity of the blended cements was appreciated on the basis of compressive strength tests carried out on little specimens (15x15x60 mm) made from plastic mortars (cement/sand=1/3; water/cement=0.5) and densified by vibration. In order to avoid uncontrollable leaching processes, the preservation of the specimens was made in humidity saturated air at 20°C, and not in water as usual. Leaching tests were carried out on 28 days hardened mortar specimens, in respect of DIN 38414-S4. The electric conductivity, the pH-values and the Cl^-, SO_4^{2-}, Pb and Zn contents in the leachates were determined.

3. RESULTS AND DISCUSSION

3.1. LEACHING AND SOLUBILITY TESTS

Within the first five minutes after introducing the crushed mortar in the distilled water, the pH-values increase to a level of about 10.5 and attained to 11.5 after 30 minutes, for all the investigated compositions. This value doesn't change any more till the end of the stirring period, and doesn't depend on the chloride or sulfate content of the leachate.

The immobilization capacity of the blended cements is different for the four investigated substances:

* Pb^{2+} is practic entirely immobilized in the 28 days hardened mortar specimens; anyway the Pb^{2+} content of the investigated MSW ashes is rather small.

* Zn^{2+} is better immobilized by the blended cements on the basis of ferroportland cement in comparison with those containing ordinary Portland cement. In most of the investigated samples, the Zn^{2+} immobilization capacity exceeds 75%.

* SO_4^{2-} is almost entirely linked as stable Ettringit ($3CaO.Al_2O_3.3CaSO_4.31H_2O$), identified by X-ray diffraction analyses in all the investigated samples. The immobilization degree exceeds in most of the specimens 90%.

* Cl^- is linked in hydrochloride aluminate ($3CaO.Al_2O_3.CaCl_2.12H_2O$) identified by X-ray diffraction analyses in the hydrated samples containing chloride rich MSW ashes. This compound is somewhat soluble in water and therefor the immobilization capacity of the chloride ion is usually less than 50%.

It seems that the electric conductivity of the leachates depends mainly of their chloride content but is also influenced by the composition of the Portland cement and its partial replacement by slag or thermal station fly ash.

3.2. HYDRATION PROCESSES

DTA and X-ray diffraction analyses on hydrated cement pastes showed that the presence of the MSW ashes in the blended cements determines certain alteration in the composition of the hydrated cements, as well as in the nature of the hydrocompounds.

The addition of sulfate rich MSW ashes favours the formation of important amounts of Ettringit. The partial replacement of the Portland cements by alumina rich thermal station fly ash improves the Ettringit formation.

The addition of chloride rich MSW ashes favours the formation of important amounts of hydrochloride aluminate and the partial replacement of cement by alumina rich thermal station fly ash improves the formation of this compound, too.

At the hydration of the blended cements containing MSW ashes, the $Ca(OH)_2$ amount is smaller, especially in the case of chloride rich MSW ashes. This fact may be due to the interaction between $Ca(OH)_2$ and the alkaline chlorides, in order to form $CaCl_2$ and afterwards hydrochloride aluminate.

3.3. MECHANICAL PROPERTIES

The results of the compressive strength tests on mortar specimens hardened till one year are listed in table 2 and 3. These values show that the mechanical properties of the blended cements are influenced by the composition and the amount of the MSW ash added, as well as by the composition of the Portland cement and its partial replacement by slag or thermal station fly ash.

Table 5 Compressive strength of the blended cements on the basis of ordinary Portland cement

Symbol	Composition of the blended cements (%)							Compressive strength (MPa) after			
	cement	slag	fly ash	MSW Bonn I	MSW Bonn II	MSW Essen	MSW France	7 days	28 days	90 days	1 year
P0	100	-	-	-	-	-	-	14.9	15.5	20.8	28.2
P1	70	30	-	-	-	-	-	12.5	21.1	27.0	34.4
P2	70	-	30	-	-	-	-	14.9	23.3	25.4	25.6
P3	70	-	-	30	-	-	-	7.4	17.3	17.8	22.3
P4	80	-	-	20	-	-	-	14.9	16.7	18.6	22.0
P5	90	-	-	10	-	-	-	15.6	16	22.9	22.7
P6	70	20	-	10	-	-	-	15.0	15.0	21.1	24.3
P7	70	10	-	20	-	-	-	12.9	13.6	17.9	20.4
P8	60	20	-	20	-	-	-	14.4	16.3	19.7	26.1
P9	70	-	20	10	-	-	-	15.8	16.8	23.5	25.9
P10	70	-	10	20				15.8	15.8	19.2	26.5
P11	70	-	-	-	30	-	-	7.8	12.0	16.7	21.2
P12	80	-	-	-	20	-	-	13.2	17.7	29.7	26.8
P13	90	-	-	-	10	-	-	14.2	19.4	30.1	29.2
P14	70	10	-	-	20	-	-	11.9	15.7	18.3	37.1
P15	70	20	-	-	10	-	-	15.7	16.2	31.3	28.3
P16	60	20	-	-	20	-	-	11.1	16.1	20.3	33.3
P17	70	-	20	-	10	-	-	16.9	22.6	24.5	34.0
P18	70	-	10	-	20	-	-	13.1	17.9	18.3	34.6
PE3	70	-	-	-	-	30	-	14.0	19.5	16.9	22.3
PE4	80	-	-	-	-	20	-	15.3	24.8	21.7	25.2
PE5	90	-	-	-	-	10	-	15.3	21.6	21.7	22.3
PE6	70	20	-	-	-	10	-	13.6	20.6	19.1	22.8
PE7	70	10	-	-	-	20	-	14.6	25.5	24.4	22.3
PE8	60	20	-	-	-	20	-	15.1	20.5	19.5	19.5
PE9	70	-	20	-	-	10	-	15.5	30.1	27.3	31.5
PE10	70	-	10	-	-	20	-	18.5	19.4	23.9	24.7
PE11	60	-	20	-	-	20	-	16.0	25.4	24.5	25.7
PF3	70	-	-	-	-	-	30	0.2	18.6	n.i.	25.1
PF4	80	-	-	-	-	-	20	15.1	24.2	21.6	38.9
PF5	90	-	-	-	-	-	10	15.8	24.1	21.3	37.7
PF6	70	20	-	-	-	-	10	15.6	25.9	25.9	37.1
PF7	70	10	-	-	-	-	20	15.0	33.6	29.4	38.0
PF8	60	20	-	-	-	-	20	14.0	27.9	n.i.	37.2
PF9	70	-	20	-	-	-	10	17.9	37.4	39.1	43.6
PF10	70	-	10	-	-	-	20	15.2	35.5	30.7	41.6
PF11	60	-	20	-	-	-	20	7.6	26.8	23.2	37.2

Table 3 Compressive strength of the blended cements on the basis of ferroportland cement

Symbol	Composition of the blended cements (%)							Compressive strength (MPa) after:			
	cement	slag	fly ash	MSW Bonn I	MSW Bonn II	MSW Essen	MSW France	7 days	28 days	90 days	1 year
F0	100	-	-	-	-	-	-	14.5	15.3	26.6	36.2
F1	70	30	-	-	-	-	-	11.6	13.9	23.8	33.5
F2	70	-	30	-	-	-	-	15.6	25.2	32.3	35.9
F3	70	-	-	30	-	-	-	11.3	17.3	18.0	31.3
F4	80	-	-	20	-	-	-	15.1	24.8	23.1	29.9
F5	90	-	-	10	-	-	-	16.0	24.0	23.6	35.3
F6	70	20	-	10	-	-	-	15.1	24.5	21.8	31.4
F7	70	10	-	20	-	-	-	12.5	24.0	23.1	31.3
F8	60	20	-	20	-	-	-	11.7	18.8	23.3	34.8
F7	70	-	20	10	-	-	-	15.1	21.9	22.9	35.5
F8	70	-	10	20				14.8	28.9	25.4	36.2
F9	70	-	-	-	30	-	-	5.7	9.5	15.5	27.9
F10	80	-	-	-	20	-	-	14.9	27.8	26.1	41.3
F11	90	-	-	-	10	-	-	16.0	30.4	29.8	34.7
F12	70	20	-	-	10	-	-	15.6	25.7	25.1	n.i
F13	70	10	-	-	20	-	-	9.1	14.7	26.3	n.i
F14	60	20	-	-	20	-	-	9.3	22.3	22.9	n.i.
F15	70	-	20	-	10	-	-	15.5	25.7	38.0	38.6
F16	70	-	10	-	20	-	-	13.4	25.5	31.1	41.9
EF3	70	-	-	-	-	30	-	10.0	14.3	16.9	28.3
EF4	80	-	-	-	-	20	-	8.5	17.1	18.2	26.7
EF5	90	-	-	-	-	10	-	9.4	18.0	21.4	32.1
EF6	70	20	-	-	-	10	-	11.7	16.3	19.1	29.2
EF7	70	10	-	-	-	20	-	9.6	15.0	21.5	27.6
EF5	60	20	-	-	-	20	-	8.9	20.9	18.5	26.2
EF6	70	-	20	-	-	10	-	14.3	24.5	27.4	35.9
EF7	70	-	10	-	-	20	-	7.9	22.9	26.8	25.7
EF8	60	-	20	-	-	20	-	14.7	19.2	24.0	28.2
FF3	70	-	-	-	-	-	30	3.7	17.7	18.7	28.2
FF4	80	-	-	-	-	-	20	12.1	20.3	28.5	29.9
FF5	90	-	-	-	-	-	10	15.3	23.6	28.5	31.9
FF6	70	20	-	-	-	-	10	15.1	22.8	22.4	32.5
FF7	70	10	-	-	-	-	20	15.5	19.5	22.3	29.1
FF8	60	20	-	-	-	-	20	10.2	17.2	23.7	24.2
FF9	70	-	20	-	-	-	10	15.2	19.9	32.2	32.2
F10	70	-	10	-	-	-	20	10.7	21.4	22.8	22.7
F11	60	-	20	-	-	-	20	14.2	21.6	24.4	27.2

At the most of the investigated blended cements, additions till 20% MSW ash do not affect or decrease only a little the mechanical strength after 7 days hardening and may determine improvements after 28 days hardening, in comparison with the unitary Portland cements. This behaviour may be due to the well-known accelerating effect of chlorides on the hydration and hardening of Portland cement. The replacement of 10% or 20% Portland cement by slag or thermal station fly ash sometimes even improves the mechanical strength.

The mechanical strength values are better by association of ordinary Portland cement with the MSW ash type France, and respectively the ferroportland cement with the MSW ashes type Bonn I and Bonn II.
It occurs in a few cases that at later terms (90 days and sometimes even after one year) the mechanical strengths are somewhat lower than those after 28 days. This behaviour may be due to several reasons which at the present moment are only hypotheses and need to be verified:
* a belated Ettringit formation can strain the hardened structure and therefore diminish the mechanical strength;
* The high alkali salts content in the MSW ashes - it is known that the presence of alkali salts at the hydration of Portland cements diminish the mechanical strength values after long terms of hardening.

The increase of the MSW ash amount till 30% deteriorates the mechanical strength of the blended cements, unaffected by the composition of the cement or the MSW ash.

4. CONCLUSION

The obtained information suggest that 10 to 20% MSW ashes can be added in blended cements on the basis of ordinary Portland cement or better, iron rich ferroportland cement, containing also 10 to 20% slag or thermal station fly ash.

The sulfate and chloride content of the MSW ashes are linked in hydrocompounds like Ettringit and hydrochloride aluminate.

The immobilization capacity of Pb^{2+} and SO_4^{2-} exceeds 90%, of Zn^{2+} - 75%, but that of Cl^- is less than 50%. One can expect that the low stability of the hydrochloride aluminate will determine an intense corrosion of the steel reinforcement embedded in the concrete made from this type of blended cements.
We consider that the conditions in which the leaching test in respect of DIN 38414-S4 is carried out don't reflect the actual conditions at the exploitation of building materials. We consider that bulk tests carried out at different hydration ages and maintaining the bulk specimens different periods in the stirred water, may be more edifying.

The mechanical strength of the blended cements are influenced by the composition of the constituent materials. A correct matching of the constituent materials results in blended cements with comparable or even better mechanical strength than those of the corresponding unitary Portland cements.

Taking into account the high alkali salt content of the MSW ashes, we suggest as necessary to test the occurrence of alkali-aggregates interactions, which can also deteriorate the mechanical properties after long terms of hardening.

Treatment of fly ash for sound material utilization

ENV4-CT95-0085

Coordinator: A. Buekens

Vrije Universteit Brussel
Dept. of Chemical Engineering
B - 1050 Brussels
Tel: +32-2.629.32.44
Fax: +32-2.629.33.33

DATA SHEET

TITLE	Treatment of fly ash for sound material utilization		
Project number	ENV4-CT95-0085		
Starting Date	January 1996	**Duration**	36 months

PROF. DR. IR. A. BUEKENS		
Vrije Universiteit Brussel		
Department of Chemical Engineering (CHIS)	Tel	+32 2 629 32 44
Pleinlaan 2	Fax	+32 2 629 33 33
B-1050 Brussel	E-Mail	abuekens@vnet3.vub.ac.be
DR. P.B. KRÖHL		
Sulzer Chemtech GmbH (CTRV)	Tel	+49 751 83 29 92
Escher-Wyss-Strasse 25	Fax	+49 751 83 30 33
D-88212 Ravensburg	E-Mail	
DR. B. DETTWILER		
Sulzer Chemtech AG		
Waste Management and Flue Gas Systems	Tel	+41 52 262 43 61
Postfach 65 (ER0662) - (CTW)	Fax	+41 52 262 01 79
CH-8404 Winterthur	E-Mail	bernhard.dettwiler@sulzer.ch
MR. H.M.S. TEMMINK		
TNO Institute of Environmental Sciences		
Energy Research and Process Innovation (TNO-MEP)	Tel	+31 55 493 508
	Fax	+31 55 493 287
P.O. Box 342	E-Mail	hmg.temmink@mep.tno.nl
NL-7300 AH Apeldoorn		
DR. A. DITZE		
Technische Universität Clausthal		
Institut für Metallhüttenwesen und	Tel	+49 5323 72 22 77
Elektrometallurgie (MHW-TUC)	Fax	+49 5323 72 23 24
Robert-Koch-Strasse 42	E-Mail	andre.ditze@tu-clausthal.de
D-38678 Clausthal-Zellerfeld		

MAIN OBJECTIVE :

The objectives of this project are to develop a treatment process for waste incineration residues, especially fly ash. In a thermal process the residues shall be treated in such a way that the heavy metals are separated from the fly ash almost *completely*. The residual phase will mainly consist of mineral material with virtually no hazardous potential. The determination of its physical properties and the opportunities for its utilization (e.g. as a cement additive or civil construction material) is included in the objectives of this project. The heavy metal fraction shall be refined to a grade at which the material is easily accepted as raw material resources in existing metal refining processes. The project therefore aims on closing material cycle steams and it must be considered as a real *upcycling* of the end of pipe material formed in waste incineration.

MAIN RESULTS :

The basic idea to separate the heavy metals from the inert material is to evaporate them as chloride salts at temperatures below sintering and melting of the fly ash. In fly ash many heavy metals are present as chlorine salts, others may have to transformed into metal chlorines first.

Filter ashes from several municipal and special waste incineration plants (Germany, the Netherlands) are collected and investigated. Initial characterization of all the samples to be investigated is performed like thermal analysis, particle size analysis, bulk density and fluidization properties.
Thermogravimetrical analysis of fly ash shows that the temperatures at which a sizeable loss in weight occurs are quite specific, giving an indication of the composition of the fly ash.

Preliminary thermodynamic equilibrium computations on the chloridization of heavy metals were carried out in circumstances, which are typical for a real municipal solid waste incinerator. The influence of the presence of chlorine, bromine and fluorine on each other was tested. Also the influence on the mutual presence of zink, copper and lead was investigated.

Equilibium experiments on the chloridization of heavy metal using real and synthetic ashes are carried out. Kinetic investigations with single particles in a gas stream are performed, with regard to the processing of the fly ash in a fluidized bed reactor with chlorine containing gases. Also the thermal treatment of fly ash in a water/HCl environment (pyrohydrolysis) is investigated. However, since the project has started just recently, the experimental setup is still under construction.

A preliminary pilot plant design for heavy metel recovery from fly ashes was made.

ENV4-CT95-0085

TREATMENT OF FLY ASH FOR SOUND MATERIAL UTILIZATION (UPCYCLE)

A. Buekens, P.B. Kröhl, B. Dettwiler, H.M.S. Temmink, A. Ditze

Filter ashes from waste incineration contain large amounts of heavy metals and are therefore disposed as special wastes. The present project aims at the separation of heavy metals from the inert (mineral) material, making possible the total utilization of the fly ash. The basic idea is to evaporate the heavy metal in a fluidized bed system. Most of the heavy metals are vaporizable as chloride salts at a temperature at about 800°C. Some metals volatilize as pure metals (e.g. Hg, Cd, partly Zn). In fly ash many heavy metals are present as chlorine salts, others may have to transformed into metal chlorines first. In this work some process techniques from primary metallurgy which have been developed considerable time ago will be investigated for the treatment of fly ash.

Filter ashes from several municipal and special waste incineration plants (Germany, the Netherlands) are collected and investigated. The samples are homogenized and analyzed, devided into representative samples, and distributed to the partners. Initial characterization of all the samples to be investigated is performed like thermal analysis (TG, DSC, loss on weight at different temperatures), particle size analysis (sieve, laser diffractometry, BET surface), bulk density and fluidization properties.

Thermogravimetrical analysis of fly ash shows that the temperatures at which a sizeable loss in weight occurs are quite specific, giving an indication of the composition of the fly ash. Some losses in weight can be attributed to the drying of the sample or to the evaporation of single compounds out of the sample, like hydrate water and CO_2 from the decomposition of carbonates. However, most losses in weight are yet unexplained, so further investigation is needed.

Thermodynamic equilibrium computations on the chloridization of pure substances is known to a large extent. But in the fly ashes the substances exist as composite compounds. The contents are small and change with the feed and kind of incineration plants. Since no investigation was done in that area, determination of the parameters of the volatilization of the heavy metals is carried out. Various experimental conditions are tested in the program. On the basis of CHEMSAGE and OUTOKOMPU computer models conditions can be established under which various elements (Hg, Pb, Zn, Cu, Cd, As, Sb, Fe, Mn, Ni, Ca, Mg, Ba, Na, K, ..) will volatilize when exposed to incineration or gasification conditions and to reaction products such as HCl, HBr, HF, SO_2, etc.

Preliminary calculations were carried out in circumstances, which are typical for a real municipal solid waste incinerator. It was tested in what extent bromine and fluorine are influencing the chloridization of lead. Chlorine and bromine exhibit both a comparable behaviour, which is not influenced by the presence of each other. When fluor was added no fluorines were formed . Also the chloridization of lead in presence of zink and copper was tested. It was seen that the behaviour of the metals was not influenced by one another as long as chlorine is present in an large enough extent. When adding iron to zink, stable ferrites are formed

Different thermal separation techniques for heavy metals at temperatures below sintering and melting of the fly ash are compared. The experiments will give inputs for the conceptual design and for the fluidized bed experiments. In complementation to the process related studies, some more scientifically oriented investigations on synthetic fly ash are performed. Also some kinetic studies are made.

Equilibium experiments on the chloridization of heavy metal using real and synthetic ashes are carried out. In a silica tube fly ash is heated up to the desired temperature (750 to 1000°C) by a tube furnace. A measured gas volume flows over the fly ash and takes the evaporated chlorides to a diffusion cooler, where the chlorides are condensed. By using different gas mixtures (oxidizing or reducing) and changing the chlorine content it is possible to control the degree of metal extraction. The experiments are carried out with a synthetic fly ash as a reference material and with real fly ashes from different European incineration plants. In that way, the parameters time, temperature, gas velocity and gas composition for the processing of fly ashes with different composition and origin will be determined. However, since the project has started just recently, the experimental setup is still under construction.

Kinetic investigations with single particles in a gas stream are performed, with regard to the processing of the fly ash in a fluidized bed reactor with chlorine containing gases. Particles of fly ash are fixed at a platinum wire and are then investigated by thermal analysis. The registratioon of the mass - time - dependence gives references to the required residence and reaction time in a moving bed process.
The objective of this part is to deliver the basic data for pilot scale experiments and process development.

The thermal treatment of fly ash in a water/HCl environment (pyrohydrolysis) is investigated. First experiments on laboratory scale are carried out . Samples of approximately 2g are brought into the reaction zone of a horizontal tube furnace. By changing the temperature, the (absolute) HCl concentration and the water/HCl ratio an optimization of the process conditionsis performed. Because of a poor contact between the chlorine gas and the sample, the laboratory facility is modified into a small fluidised bed.

These experiments are to be repeated in a semi-continuous fluidised bed reactor on mini-pilot scale. The influence of the fluidization velocity in relation to the residence time, the temperature and the gas atmosphere will be investigated.

The segragation technique is known in primary metallurgy and is now tested on fly ash. The process parameters like atmosphere, temperature, reagents and residence time will be investigated.

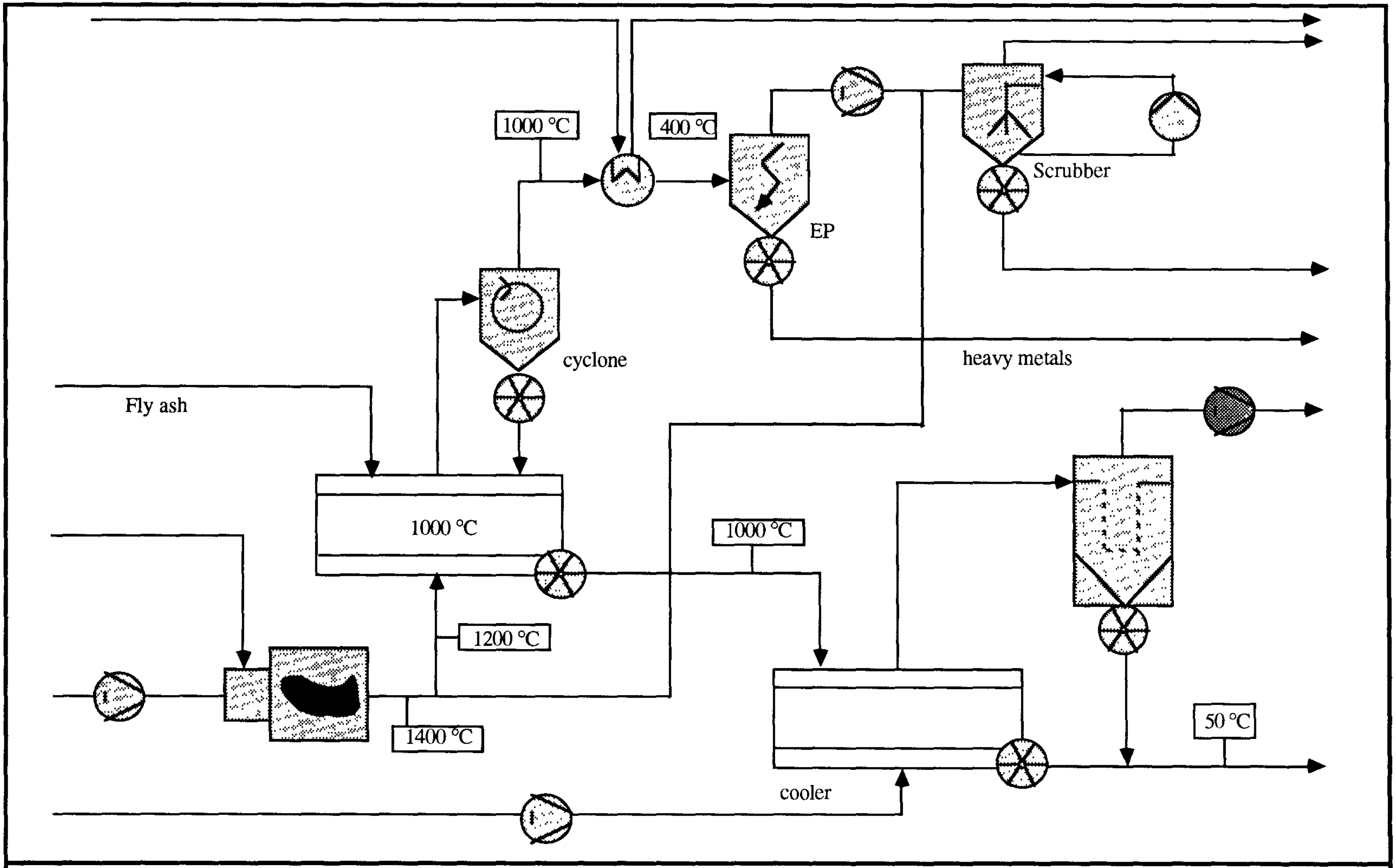
Special attention is paid to the ash pretreatment ant to the metal recovery from the calcined product. The results from the lab-scale test work will be verified on a small pilot scale.

It will be investigated if - for specific fly ashes and under suitable conditions - the heavy metals may be evaporated without addition of gaseous chlorination reagents. For heavy metals which are possibly not sufficiently removed a subsequent hydrometallurgical step has to be studied.

The literature survey and the preliminary laboratory experiments will give input for the deriving of alternative process designs - their advantages, disadvantages and bottle necks. This study work shall show critical steps for a bigger, technical realization at a very early stage and help to focus the pilot plant investigations on the solution of respective problems.
A second part will be established after finishing test work on pilot scale. It will take into account those results and process know how. The best process design will be evaluated for further detailing.

A preliminary pilot plant design for heavy metel recovery from fly ashes was made (fig 1). Main aspect is the volatilization and subsequent condensation in a closed gas circuit using a fluidized bed as volatilizer. Evaporation of heavy metal chlorides occurs at a temperature level of approximately 1000 °C, making refractory materials necessary.
The dust entrained from the bed will be separated in a cyclone and recirculated. Cooling to 400 °C will condensate the chlorides. The heat carried off can be used for other demands. An electrostatic filter will separate these fines from the circulating gas. The excess gas is blown of to a scrubber for chlorine recovery.
The main circuit fan is operating at a reasonable temperature (400 °C). The heat demand is supplied by flue gases fed into the gas circuit. The fly ashes are brought into the fluidized bed, heated up at approximately 1000 °C for an adequate retention time before leaving to the cooler, where they are cooled from 100 °C to 50 - 80 °C.

In a later stage of the research project the heavy metal condensation will be investigated, both to understand the mechanisms which result in vaporization of metal contaminants on fly ash and to investigate the sequential condensation of volatile chlorine salts. The processing and utilization of metal condensate is to be studied. At the same time investigation will be done on the assessment and utilizaton of mineral product.



Preliminary Pilot Plant Design UPCYCLE
Heavy metal recovery from fly ashes

Development of a combined methodology to evaluate recycling processes bases on the life cycle assessment (LCA) and economic valuation analysis (EVA)

ENV4-CT95-0091

Coordinator: D. Cockburn

Pira International
UK - KT22 2RU Surrey
Tel: +44-1372.802000
Fax: +44-1372.802238

Title of project: Development of a combined methodology to evaluate recycling processes based on life cycle assessment (LCA) and economic valuation analysis (EVA)

Project no: ENV4-CT95-0091

Starting date: February 1996

Duration: 24 months

Addresses, telephone and fax numbers for group leaders:

Co-ordinator:
Philippa Nichols
Pira International
Randalls Road
Leatherhead
Surrey
KT22 2RU
GB
Tel: + 44 1372 802000 (Switchboard)
+ 44 1372 802189 (Direct line)
Fax:+ 44 1372 802238
E-mail: nichols@pira.co.uk

Contractors:
Mr Frans Oosterhuis
Institute for Environmental Studies (IVM)
De Boelelaan 1115
1081 HV Amsterdam
NL
Tel: +31 20 4449511
Fax:+31 20 4449553
E-mail: oosterhuis@ivm.vu.nl

Mr Michael Heyde
Fraunhofer - Institut München
Betriebsstätte Sending
Steinerstraße 15
D 81549 München
DE
Tel: +49 89 72485126
Fax:+49 89 72485111

Main objectives of the project

- To develop a practical, transparent methodology for evaluating the environmental and economic life cycle costs and benefits of recycling processes
- To exemplify and illustrate the methodology through two case studies
- To evaluate the implications of the methodology and case study results for existing environmental policies, particularly the European Council directive 94/62/EC on Packaging and Packaging waste
- To produce 'guidelines' describing the application of the methodology

Main results

None to date

List of publications

None to date

Development of a combined methodology to evaluate recycling processes based on life cycle assesssment (LCA) and economic evaluation analysis (EVA)

Project No. ENV4-CT95-0091

Partners involved:

Co-ordinator: *Pira International, UK*

Pira International is the leading independant centre for research, consultancy, training and publications in the paper and board, packaging, printing and publishing industry sectors. In the field of LCA, Pira is actively involved in standardisation efforts at both national and international levels. Pira's LCA team has conducted LCA studies for many multi national organisations, mainly in the paper and board and packaging sectors. Its client base also includes a number of organisations from the petrochemical, electrical and electronic, pharmaceutical and automotive sectors.

Contractor: *Institute for Environmental Studies, IVM, The Netherlands*

IVM is the oldest and largest professional academic institute for basic and applied environmental research in the Netherlands. Its primary objective is to carry out multi and interdisciplinary research on environmental issues. It employs around 60 researchers from a wide variety of disciplinary backgrounds including economics, econometrics, chemistry, ecology, earth sciences, law and social sciences.

In terms of expertise in EVA, IVM has considerable experience valuing the environment in terms of cost benefit analysis (CBA), looking at costs and economic effects of environmental policy measures, evaluating life cycles and substance flows and also in evaluating economic, environmental and social effects of recycling in various regions.

Contractor*: Fraunhofer-Institut, FhG-ILV, Germany*

Fh-ILV is Germany's leading institute in the fields of consumer packaging, their functional profile and their environmental impacts. In the field of LCA, Fh-ILV carried out pioneering work on LCA with two other institutes, in a joint project commissioned by the German Federal Environmental Office.

In addition, Fh-ILV have performed many different LCA studies for industrial clients both on a national and European level.

Introduction

The project specifically addresses the evaluation of process technologies and in particular recycling processes in view of net benefits in environmental and economic terms.

The general aim of the study is to develop a combined methodology to enable process technologies to be evaluated, with the main emphasis being on recycling processes.

Objectives

- To develop a practical transparent methodology for evaluating the environmental and economic life cycle costs and benefits of recycling processes
- To exemplify and illustrate the methodology through two case studies
- To evaluate the implications of the methodology and case study results for existing environmental policies
- To produce guidelines describing the application of the methodology

Project methodology

The development of a combined methodology for the evaluation of the environmental and economic costs and benefits of recycling comprises of the following main research tasks:

- description and enhancement of LCA methodology
- description and enhancement of EVA methodology
- development of a combined LCA-EVA methodology
- evaluation of the methodology relative to environmental policies
- application of the methodology to two case studies
- refinement of the methodology
- generation of a set of guidelines/recommendations on the use of the methodology

Project start date

The official start date for this project was 1 February 1996. A meeting of the partners was held in March 1996 and work has commenced on the initial phase of the project which involves outlining the methodologies of both EVA and LCA to create a common understanding of methodologies and terminology.

Work programme

At the first meeting of the partners, the work programme for the first three months was formulated. The case studies to be used in the project were defined and it was decided that these should be used throughout the project to provide a framework for the description of the methodology. The case studies were chosen in order to represent different decision environments.

Description of case studies

The two case studies chosen for this study are described below.

1. Product life cycle. This case study will look at a plastic bag packaging system and a cardboard packaging system. For each scenario, two different recycling strategies will be considered. All of the scenarios will be looked at from the perspective of the producer.

2. Waste management. This case study will be looked at from the perspective of, for example, a local council and will specifically consider HDPE and aluminium at different recycling rates. The material recycling scenario will be compared with other types of waste disposal for example, incineration and landfill.

Initial work programme

1. Within one month, the principal environmental impacts associated with the life cycle of each of the two scenarios will be identified and the area at which they will be emitted indicated.

2. Within three months, a detailed description of the relevant methodologies should have been prepared with particular regard to recycling issues. Work should also have begun on the identification of the principal methodological differences between life cycle assessment and economic valuation analysis.

Outline of the methodologies involved in the project

Life cycle assessment

Life cycle assessment has been defined by the Society of Environmental and Chemistry (SETAC) as 'a process to evaluate the environmental burdens associated with a product, process or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify and evaluate opportunities to affect environmental improvements'.

LCA's are generally composed of several inter-related components: goal and scope definition, inventory analysis, impact assessment and improvement assessment.

Goal and scope definition involves defining the goal of the study and the scenarios to be studied along with the system boundaries, the functional unit and data quality considerations. The inventory analysis component of an LCA quantifies the environmental burdens associated with a product, process or activity. The impact assessment component seeks to relate the environmental burdens quantified in the inventory analysis to measures of environmental concerns.

In defining the LCA component, the technical focus will be given specifically to the scope of the parameters included in the inventory as well as the environmental impact categories included at the impact assessment stage. In addition, the rules used to define the 'system' will be made clear as well as the calculation procedures adopted to take account of 'avoided burdens' resulting from the process of recycling itself (for example, by displacement of virgin materials).

Economic valuation of recycling processes

In order to become a suitable tool for decision making, LCA has to be supplemented by an appropriate method for the valuation of the various environmental impacts. These impacts are usually expressed in physical terms, such as tonnes of SO_2 or BOD. Comparing and ranking alternatives implies that the different dimensions of these parameters are brought to a common denominator, either explicitly or implicitly.

There are various approaches for the valuation stage of an LCA. These include, among others, methods in which the weight of a parameter is determined by the environmental policy objectives which have been expressed ("distance to target" methods) or by the costs of controlling that particular emission. Other techniques use the scores attributed to the different environmental impacts by experts, interested parties or public opinion as weighting factors. In the present project, the valuation will be based on an economic (cost-benefit) approach, in which the importance of environmental quality (like that of any other scarce good) is determined by individual preferences. These preferences are expresssed in monetary terms, reflecting the individual's willingness to pay for environmental improvements (or willingness to accept compensation for environmental deterioration).

Several methods have been developed in the past to estimate the monetary value of unpriced environmental goods. In some cases, such as damage from air and water pollution to crops, building materials, drinking water etc., the approach is straightforward because these goods have market values. If the physical damage is known, the monetary damage can easily be calculated. In other cases, market prices can also be used, but this time as proxies for the immaterial damage. Examples are the decrease in the value of a house (reflecting the value of, say, nuisance caused by a nearby landfill site), and the differences in wages paid to workers exposed to different levels of risk (which can be used as a basis for calculating the value of risk reduction from environmental causes as well). Finally, there are several environmental effects which cannot be valued with the help of market prices. In these instances, individuals have to be asked directly for their willingness to pay for the prevention of these effects (or their willingness to accept compensation). This approach is known as the "contingent valuation method" (CVM). It is being applied mainly to scenic landscapes, unique natural areas etc..

LCA and valuation have to be linked by transformation procedures which translate emissions and other environmental loads into (physical) impacts: decreases in fish catches due to water pollution, increases in lung cancer incidence due to exposure to carcinogenic substances, etc.. Obviously, this transformation step is a crucial one and it may turn out that it is the main bottleneck in the combined LCA/valuation methodology. Reliable dispersion models (translating emissions into immissions or ambient concentrations) and dose-response relationships (translating concentrations into physical effects) are only available for a limited number of pollutants.

Moreover, the spatial and temporal distribution pattern of the sources of pollution, often neglected by LCA, is usually an extremely important factor determining the size of the environmental damage. In the case studies which will be carried out in the present project, this complication will be dealt with by making assumptions regarding the location of the different links in the production and recycling chains. This, of course, reduces the generalizability of the outcomes. A similar issue arises with respect to the valuation step. To what extent are the values revealed in one country transferable to another one? Is the value of, for example, one hour of breath problems due to smog the same for a citizen in London and one in Athens? The present study does not pretend to give final answers to such questions, but at least aims at contributing to a more systematic way of addressing these problems.

A full cost-benefit analysis of recycling processes obviously not only requires the valuation of the external (environmental) costs and benefits (based on LCA), but also information on the internal costs and benefits of the recycling business. This information will not always be easy to obtain, because of confidentiality reasons. Therefore, assumptions will often have to be made in order to estimate the internal costs as well.

Conclusions

In summary, it is hoped that this project will yield a transparant methodology which can be used to evaluate both the environmental and economic costs and benefits of recycling processes. It is anticipated that the methodology will be capable of adaption by the incorporation of alternative data values thereby rendering it widely applicable for evaluating other recycling processes or more general applications.

The Noell conversion process for the environmentally friendly treatment of residual waste

Y. Leipnitz

Noell-KRC Energie- und Umwelttechnik GmbH
D - 97064 Würzburg
Tel: +49-931.903.4142
Fax: +49-931.903.4001

Introduction

Entrained-flow gasification offers a proven alternative to the thermal treatment of residual wastes by incineration. The synthesis gas produced (CO, H_2) can be used as a chemical product or to convert into energy like electrical power, district heating or process heating.

In addition, the inorganic components in the residual wastes are encapsulated in a non-leaching coarse granulate which is approved for use in the construction industry.

The development of the process for entrained-flow gasification, known as the GSP process, had already begun in the mid 1970`s. The entrained-flow gasification process was developed and industrially applied to produce combustible gas such as city gas from solid combustible materials. A 3 MW trial plant based on the first results was established in Freiberg in 1975, which was in accordance with the design of the 130 MW commercial sized plant at the „Schwarze Pumpe“ (Lausitz, East Germany).

Feed stocks such as lignites, coals, wood and straw, tars, oils, slurries, fly ashes, municipal sludges and domestic wastes have been tested successfully.

The application of the Noell Conversion Process allowed a conversion each kind of waste residuals like domestic waste, municipal sewage sludge, industrial sludges and coals or lignites in a IGCC. Figure 1 is a schematic overview of the possible process combinations for the thermal conversion of residual waste and combustible materials. The conversion of solid heterogenous mixed residual wastes is realized by pretreatment the input material in form of either a liquid or solid suspension. Grinding residual waste, even cold grinding, expends too much energy; therefore, a pyrolysis oven is installed as a thermal pretreatment system upstream of entrained-flow gasification.

The NOELL CONVERSION PROCESS

Figure 2 is a schematic overview of the complete process.

The delivered residual and waste materials are reduced in size by means of shear shredders and then fed into the pyrolysis reactor.

The pretreated waste is returned to the feeding system of the pyrolysis unit under inert conditions, in order to prevent the influx of oxygen. The pyrolysis system serves to homogenize the input material by means of a chemical-thermal pretreatment process. The waste is decomposed in the cylindrical kiln at temperatures of approximately 550 °C at retention times of one hour. This produces a coke-like pyrolysis fraction and a pyrolysis gas containing condensable oil.

Upon exiting the reactor, the pyrolysis coke is cooled and sorted mechanically. During this procedure ferrous and non-ferrous metals are collected separately for further conversion.

Subsequently, the pyrolysis coke is ground into a pulverized fuel and then transported to the entrained-flow gasification reactor via special dense phase conveyer.

The hot pyrolysis gas is cooled, dedusted and fed into a gas holding tank. The gas is taken from this tank, compressed and then fed to the entrained-flow gasification system.

The condensates which are discharged after gas cooling sytem are also fed to the gasifier separately via a condensate pump.

This ensures that all pyrolysis products are treated under the best possible thermal conditions in the entrained-flow gasification system.

The feed materials and the oxygen are fed to the gasifier burner which is located at the top of the reactor.

The actual gasifying process, i.e. the partial oxidation with technically pure oxygen in a flame reaction, occurs within a cylindric reaction space, the contours of which are formed by a water cooled tube wall. Organic substances are decomposed in a flame reaction, producing a gas rich in CO and H_2 and free of high-order hydride carbons.

The molten mineral compounds of the feed stock and the crude synthesis gas jointly leave the reaction chamber and through a central opening located at the base. In the quench zone, located beneath the reaction chamber, the gas and the slag are cooled directly by quench water injected via nozzles. After then the gas is cooled further and freed of sulphur compounds in a gas purifier.
After gasification and the gas cleaning, the product gas can be used as a form of energy.

The volatile, toxic heavy metals occuring in the prevailing reaction condition, such as mercury, cadmium, lead or zinc, reoccur in the sulfide-rich sludges in the process water where they are filtered out. The water is fed partially into the circuit and introduced again in the quenching stage, and the remaining portion evaporated with low-temperature heat (waste water-free operation).

Conclusions

A process that meets modern residual and waste material processing requirements, as an alternitive to combustion, is entrained-flow gasification. The entrained-flow gasification procedure offers a series of advantages for thermal conversion of residual and waste materials, namely:

- the production of a clean gas which can be used as synthesis or combustible gas.
- the production of granular slag with a crystalline structure by melting the mineral feed compounds and then flash quenching.

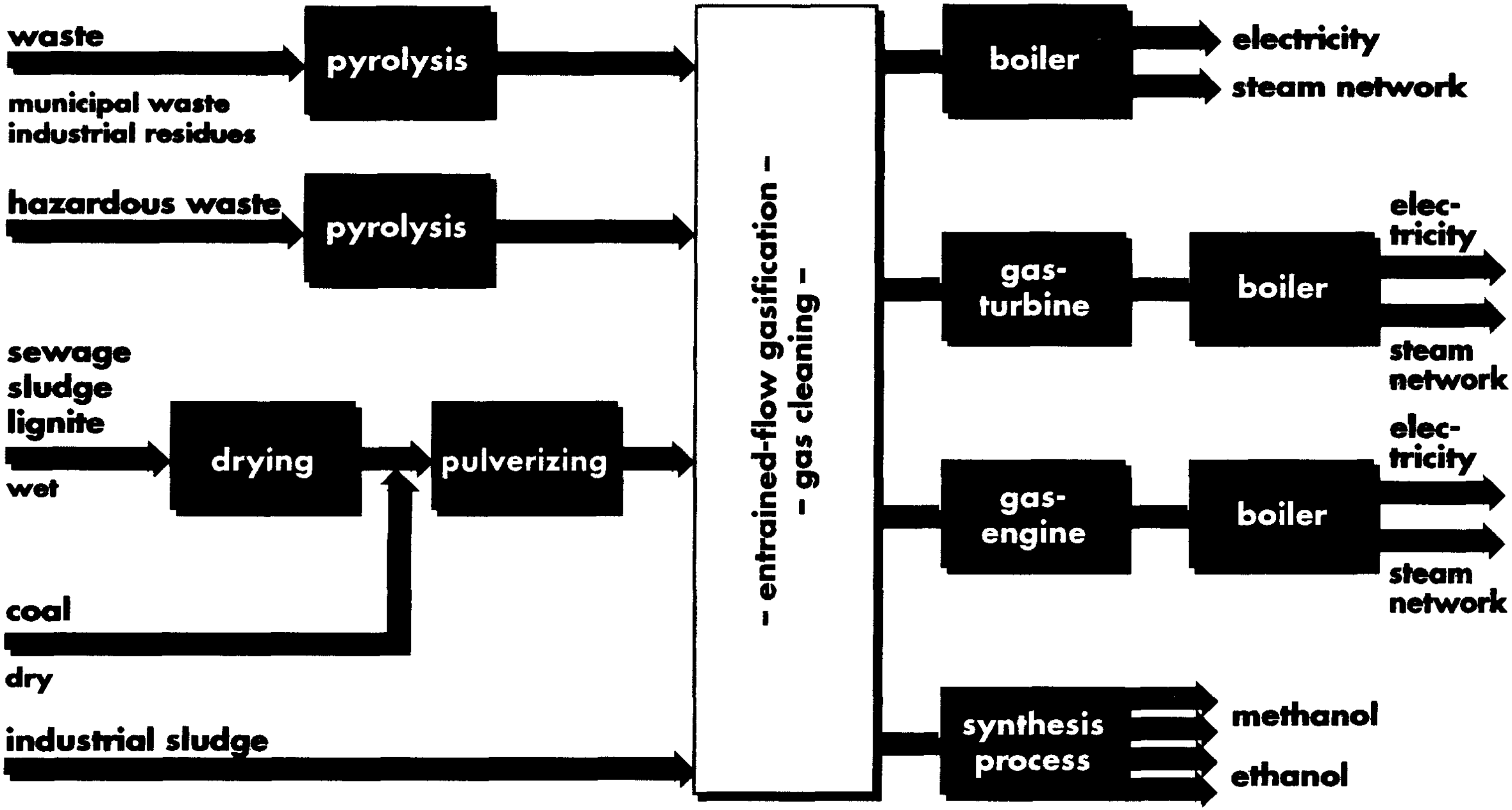
- the destruction of high order hydride carbons, especially chloro-organic compounds by high reaction temperatures.
- the prevention of the reformation of dioxins and furans due to the reduced atmosphere.
- transportation of heavy metals as insoluble heavy metal sulphides which can be separated easily from the gasification products.
- low gas volumes and, as a result, high efficiency in crude gas cleaning.

Project Development

The NOELL CONVERSION PROCESS will go into operation for the first time in Germany in Northeim, Lower Saxony. The planned annual capacity of the plant is 100,000 tons of municipal waste and 16,000 tons of dewatered sewage sludge. A combined cycle process (gas turbine, steam boiler, steam turbine) has been chosen to convert the energy released.

Preussag Noell is presently developing plants for the gasification of industrial sludges and oils and therefore plants for IGCC worldwide.

Possible Variations of the Noell Conversion Process

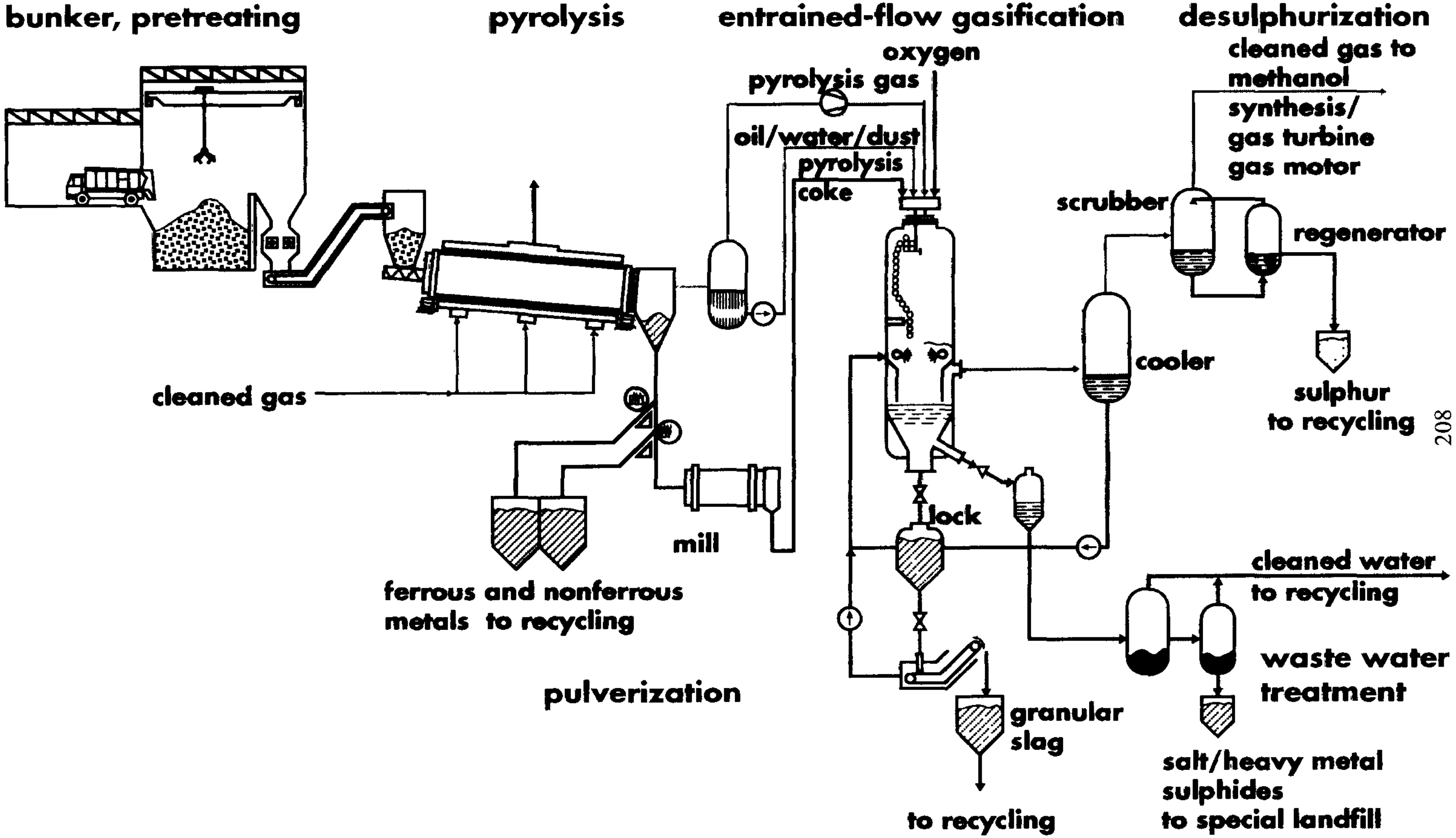


PREUSSAG
NOELL

Noell-KRC Energie-
und Umwelttechnik GmbH

Figure 1

THE NOELL CONVERSION PROCESS



**NOELL ABFALL- UND
ENERGIETECHNIK GMBH**

A member
of Preussag

Figure 2

Emission of methane isotopomers due to production and oxidation in landfills "EMITPOL"

EV5V-CT94-0522

Coordinator: H. Fischer

Max-Planck-Institute for Chemistry
D - 55020 Mainz
Tel: +49-6131.305451
Fax: +49-6131.305436

Title of project:
Emission of Methane IsoTopomers due to Production and Oxidation in Landfills (EMITPOL)

Project number:
EV5V-CT94-0522

Starting date:
1.6.1994

Duration:
1.6.1994 - 31.12.1996

Participants

Name: Dr. H. Fischer / Dr. P. Bergamaschi
Adress: Max-Planck Institut für Chemie
D-55020 Mainz, Germany

Tel.: +49-6131-305451 / +49-6131-305449
Fax: +49-6131-305436

Name: Dr. A.C. Veltkamp
Adress: Netherlands Energy Research Foundation
1755 ZG Petten, The Netherlands

Tel.: +31-2246-4251
Fax: +31-2246-3488

Main objectives:

Characterization of the isotopic composition ($^{13}CH_4/^{12}CH_4$; $^{12}CH_3D/^{12}CH_4$) of CH_4 from landfill sites, which is important (1) for isotope budgets on various scales (regional, European, global) and (2) for our knowledge of the interplay between production, oxidation and transport CH_4 into the atmosphere. Different kinds of landfill gas samples were taken:

- surface emission samples taken by static chambers (box samples)
- depth profile samples taken from the landfill covers (soil air samples)
- samples from the landfill gas collection system (if available)
- atmospheric samples (upwind, downwind)

On these samples the following mesurements were carried out:
- CH_4, CO_2, 0_2, N_2 concentration (GC-FID, GC-TCD)
- ^{222}Rn activity (slow pulse ionisisation chamber)
- $\delta^{13}C$ (CH_4), δD (CH_4) (mass spectrometry (IRMS), tunable diode laser absorption spectroscopy (TDLAS))
- $\delta^{13}C$ (CO_2) (MS)

Main results:

- $\delta^{13}C$ and δD values of samples from the gas collection system (different branches) ($\delta^{13}C$ = -59.3 ± 2.6 $^0/_{00}$ V-PDB (1 σ ; n = 69); δD = -305 ± 11 $^0/_{00}$ V-SMOW (n = 51)) are within the range typical for biogenic CH_4 sources dominated by acetate fermentation. Noticeable is the very small $\delta^{13}C$ and δD variability of the various samples

- in contrast to the samples from the gas collection system, soil gas samples from the landfill covers (profiles) exhibit a considerable variability of their $\delta^{13}C$ and δD values ($\delta^{13}C$ = -72 ... -16 $^0/_{00}$ V-PDB (n = 88); δD = -348 .. -207 $^0/_{00}$ V-SMOW (n = 61)). The main reason for this behaviour is the strong influence of CH_4 oxidation by methanotropic bacteria within the landfill cover, which distinctly shifts the original $\delta^{13}C$ (determined by methane production) towards more enriched, i.e. more positive values.

- The box samples (representing the small-scale fluxes into the atmosphere) also exhibit a very large $\delta^{13}C$ and δD variability ($\delta^{13}C$ = -64 ... -33 $^0/_{00}$ V-PDB (n = 57) and δD = -334 ... -175 $^0/_{00}$ V-SMOW (n = 33)), mainly due to the (spatially highly variable) influence of CH_4 oxidation.

- The $\delta^{13}C$ values derived from the upwind-downwind measurements (representing the spatially averaged $\delta^{13}C$ of the CH_4 emissions) exhibit a very small temporal and site to site variability $\delta^{13}C$ = -54.9 ± 1.7 $^0/_{00}$ V-PDB (n = 11)]. The mean emission is significantly enriched in ^{13}C compared to the samples from the gas collection systems. This isotopic shift of 4.4 $^0/_{00}$ corresponds to an average fraction of 39 % (31 % - 52 %) CH_4 being oxidized during the transport through the landfill cover (assuming fractionation factors of 1.006 - 1.012 for bacterial oxidation; first order approximation assuming a single Rayleigh process).

A more comprehensive interpretation of depth profiles has meanwhile been begun at MPI-C. First results indicate:

1. Plotting measured $\delta^{13}C$(or δD) values against calculated CH_4 fluxes ($\ln(j/j_0)$ yields the fractionation factors α for bacterial oxidation. Results for $\alpha(^{13}C)$ are in the range 1.006...1012, which is lower than the range 1.013...1.025 determined by Coleman et al., 1981 on cultures of methanotrophic bacteria, but consistent with α determinations (α = 1.008 ± 0.003) in CH_4 from single landfill gas collection system branches, where admixture of atmospheric air lead to bacterial oxidation [Bergamaschi and Harris, 1995].

2. A key parameter, which controls the degree of CH_4 oxidation during the passage through the landfill cover, has been found to be the residence time of the landfill gas in the aerobic part of the landfill cover. Long residence time causes high degrees of CH_4 oxidation and vice versa.

Publications:

P. Bergamaschi, G.W. Harris, "Measurement of stable isotope ratios ($^{13}CH_4/^{12}CH_4$; $^{12}CH_3D/^{12}CH_4$) in landfill methane using a tunable diode laser absorption spectrometer " Global Biogeochemical Cycles, Vol. 9, NO. 4, Pages 439-447, December 1995.

EXTENDED ABSTRACT

presented at EC workshop
"RECYCLING TECHNOLOGIES,
TREATMENT OF WASTE and CONTAMINATED SITES"
Hannover, 20/24 May 1996

EMITPOL

Emission of Methane IsoTopomers due to Production and Oxidation in Landfills

(1) Dr. Horst Fischer
Dr. Peter Bergamaschi
Max-Planck Institute for Chemistry (MPI-C)
Air Chemistry Department
P.O. Box 3060
D-55020 Mainz
Germany
(Coordinator)

(2) Dr. A.C. Veltkamp
Netherlands Energy Research Foundation (ECN)
1755 ZG Petten
The Netherlands

Emission of Methane IsoTopomers due to Production and Oxidation in Landfills (EMITPOL)

1. OBJECTIVES

The main scientific objectives of EMITPOL are:

- Determination of the isotopic composition ($^{13}CH_4/^{12}CH_4$; $^{12}CH_3D/^{12}CH_4$) of CH_4-emissions from landfills into the atmosphere, which is important for regional, European, and global isotope budgets (model inputs)

- Investigation of CH_4-production related factors affecting the stable isotopic signatures of the produced CH_4 (e.g. CH_4-production pathways [acetate-fermentation vs. CO_2-reduction], isotopic enrichment in the course of degradation [substrate depletion])

- Investigation of CH_4-transport related factors affecting the isotopic signature (diffusive vs. advective transport)

- Investigation of bacterial methane oxidation within the landfill covers with particular emphasis on correlations with temperature, soil humidity, oxygen availability and transport mechanisms

The overall goal is to find key parameters, which determine the CH_4-flux into the atmosphere and its isotopic composition, thus allowing predictions for CH_4-budgets on various scales and providing model inputs.

A) Process studies are carried out at the landfills. For this purpose, three kinds of landfill gas samples are taken:

1. surface emission samples taken by static chambers
2. depth profile samples taken from the landfill covers (soil air samples)
3. samples taken from the landfill gas collection systems (if available)

Additional parameters are temperature and relative humidity of the soil.

B) Atmospheric samples around the landfills were taken in order to determine the mean isotopic composition of the CH_4-emission (upwind - downwind). $\delta^{13}C$ - and δD - measurements of samples with different CH_4-concentration around the landfill sites will yield the averaged isotopic signature of this source.

The measurement campaigns were carried out at German and Dutch landfill sites. They took place on October 1994, March 1995, August 1995 and February 1996.

2. MAIN RESULTS

An overview on $\delta^{13}C$ and δD data for the different types of samples is given in Fig. 1 and 2. (Also included are data from preceding studies (Budenheim -1992 and Sprendlingen -1992) [Bergamaschi, 1993]). The main features are:

- $\delta^{13}C$ and δD values of samples from the gas collection system (different branches) ($\delta^{13}C$ = -59.3 ± 2.6 $^{0}/_{00}$ V-PDB (1 σ ; n = 69); δD = -305 ± 11 $^{0}/_{00}$ V-SMOW (n = 51)) are within the range typical for biogenic CH_4 sources dominated by acetate fermentation. Noticeable is the very small $\delta^{13}C$ and δD variability of the various samples. The main reasons for the low variability are (1) the single branches of the gas collection system pump the landfill gas from a horizontal radius of > 50 m and vertical layers of > 10 m, resulting in an averaging of small scale spatial variabilities in the composition of the organic matter and the conditions for methanogenesis and (2) the temperature inside landfills are known to be nearly independent from ambient temperatures (the optimum for mesophilic digestion is around 35 ^{0}C). Therefore, a possible temperature dependence of fractionation factors associated with methanogenesis would be irrelevant. (3) The isotopic signature of the CH_4 from the gas collection system is mainly determined by the CH_4-production processes, while secondary effects, which could modify these signatures (in particular bacterial oxidation), are of minor importance within the landfill [Bergamaschi and Harris, 1995].

- in contrast to the samples from the gas collection system, soil gas samples from the landfill covers (profiles) exhibit a considerable variability of their $\delta^{13}C$ and δD values ($\delta^{13}C$ = -72 ... -16 $^{0}/_{00}$ V-PDB (n = 88); δD = -348 .. -207 $^{0}/_{00}$ V-SMOW (n = 61)). The main reason for this behaviour is the strong influence of CH_4 oxidation by methanotropic bacteria within the landfill cover, which distinctly shifts the original $\delta^{13}C$ (determined by methane production) towards more enriched, i.e. more positive values.

- The box samples (representing the small-scale fluxes into the atmosphere) also exhibit a very large $\delta^{13}C$ and δD variability ($\delta^{13}C$ = -64 ... -33 $^{0}/_{00}$ V-PDB (n = 57) and δD = -334 ... -175 $^{0}/_{00}$ V-SMOW (n = 33)), mainly due to the (spatially highly variable) influence of CH_4 oxidation.

- Despite the large $\delta^{13}C$ (and δD) variability of the single box samples, the $\delta^{13}C$ values derived from the upwind-downwind measurements (representing the spatially averaged $\delta^{13}C$ of the CH_4 emissions) exhibit a very small temporal and site to site variability $\delta^{13}C$ = -54.9 ± 1.7 $^{0}/_{00}$ V-PDB (n = 11)]. The mean emission is significantly enriched in ^{13}C compared to the samples from the gas collection systems [$\delta^{13}C$ = -59.3 ± 2.6 $^{0}/_{00}$ V-PDB (n = 69)]. This isotopic shift of 4.4 $^{0}/_{00}$ corresponds to an average fraction of 39 % (31 % - 52 %) CH_4 being oxidized during the transport through the landfill cover (assuming fractionation factors of 1.006 - 1.012 for bacterial oxidation; first order approximation assuming a single Rayleigh process).

A more comprehensive interpretation of depth profiles has meanwhile been begun at MPI-C. First results indicate:

1. Plotting measured $\delta^{13}C$(or δD) values against calculated CH_4 fluxes (ln(j/j_0) yields the fractionation factors α for bacterial oxidation. Results for $\alpha(^{13}C)$ are in the range 1.006...1012, which is lower than the range 1.013...1.025 determined by Coleman et al, 1981 on cultures of methanotrophic bacteria, but consistent with α determinations (α = 1.008 ± 0.003) in CH_4 from single landfill gas collection system branches, where admixture of atmospheric air lead to bacterial oxidation [Bergamaschi and Harris, 1995].
2. A key parameter, which controls the degree of CH_4 oxidation during the passage through the landfill cover, has been found to be the residence time of the landfill gas in the aerobic part of the landfill cover. Long residence time causes high degrees of CH_4 oxidation and vice versa.

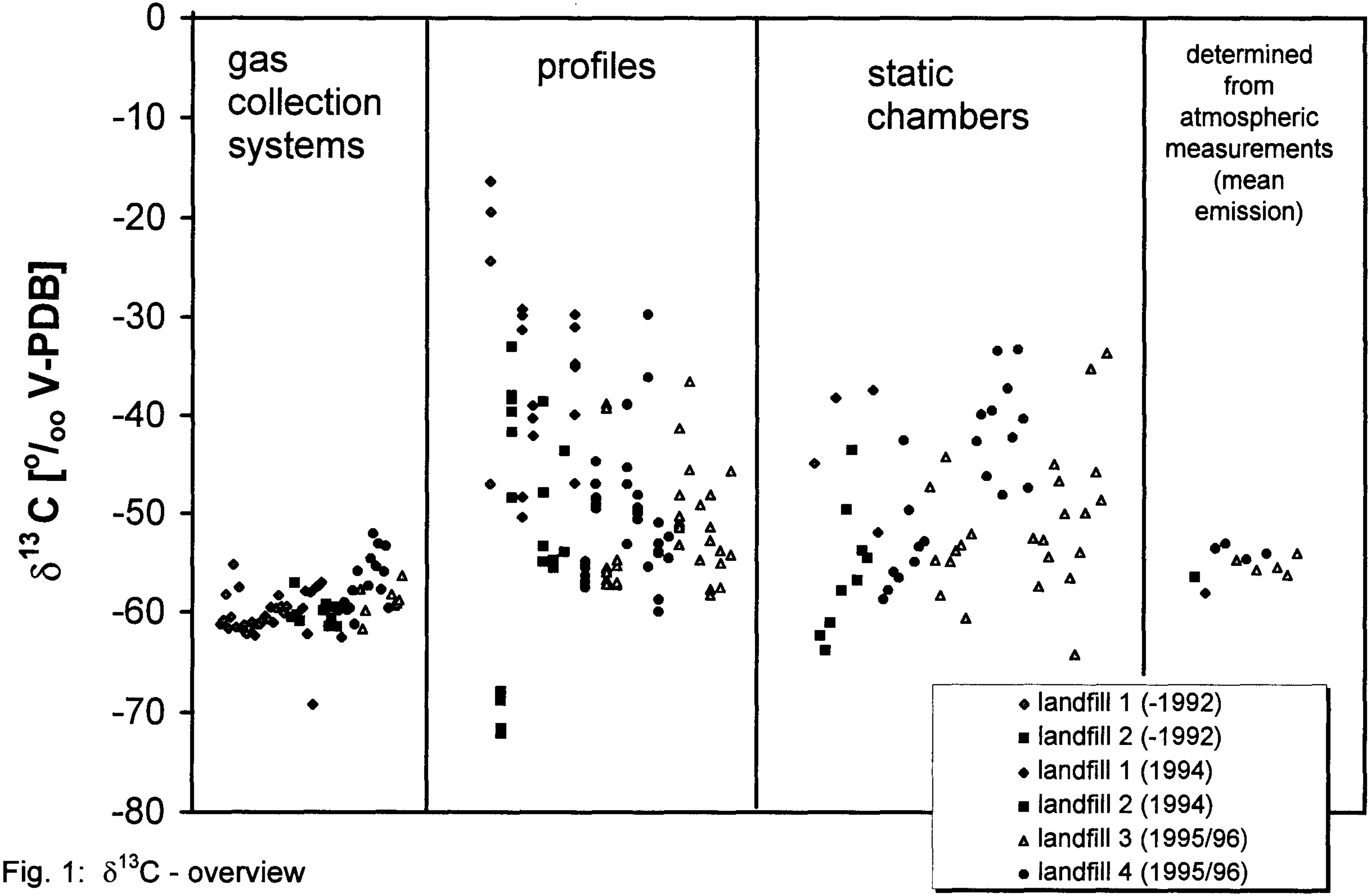


Fig. 1: $\delta^{13}C$ - overview

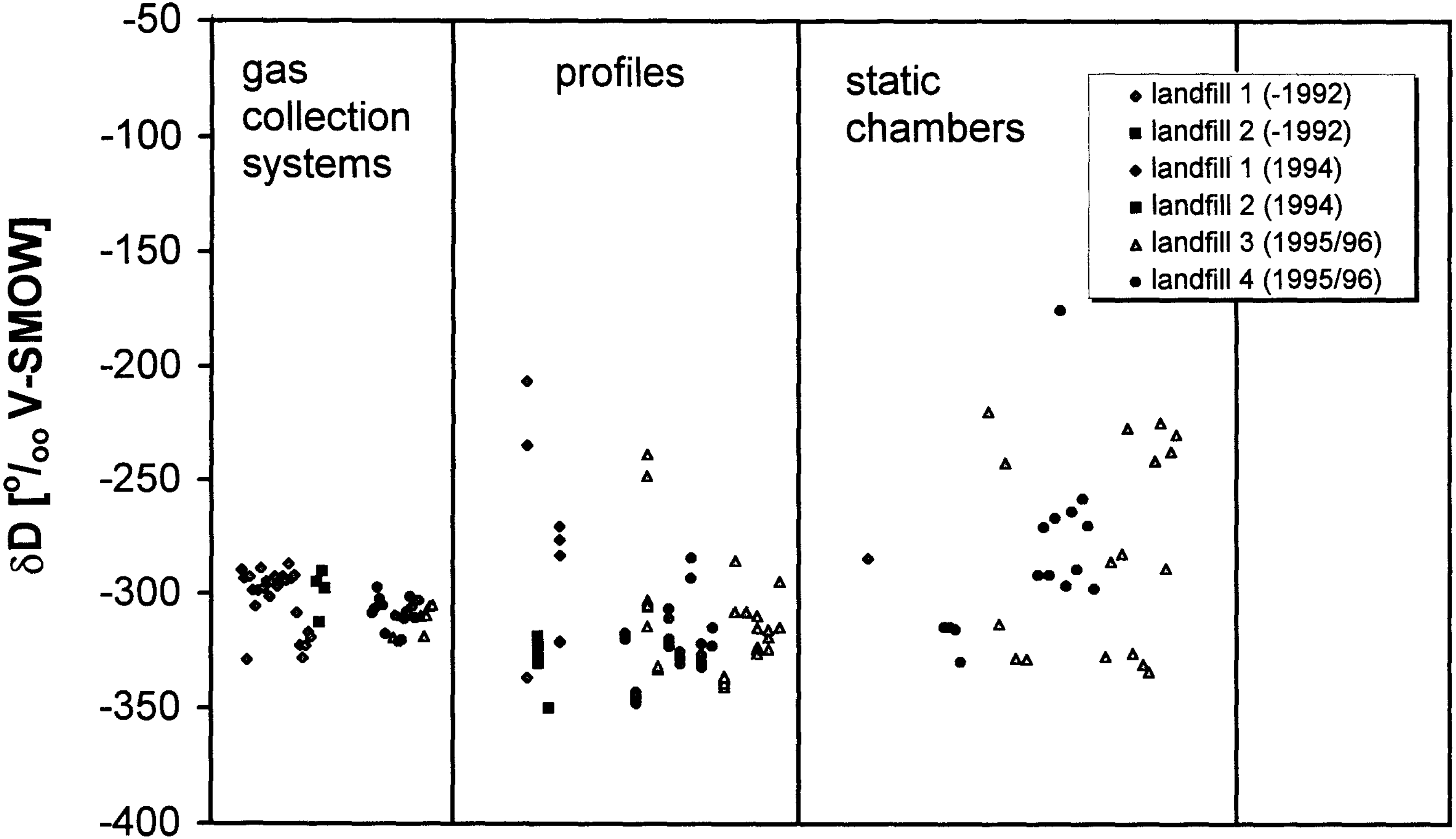


Fig. 2: δ D - overview

How to improve chemical and physical stability of Waelz slag to withstand long term exposure to weathering or leaching conditions

EV5V-CT94-0549

Coordinator: C. Desnoyers

Métaleurop Recherche
F - 78193 Trappes
Tel: +33-130.66.28.68
Fax: +33-130.66.27.28

Contribution not yet received

PROJECT Nr EV5V-CT94-0549

"HOW TO IMPROVE CHEMICAL AND PHYSICAL STABILITY OF WAELZ SLAG TO WITHSTAND LONG TERM EXPOSURE TO WEATHERING AND LEACHING CONDITIONS"

STARTING DATE . . : 1st of September 1994

DURATION . . . . : 36 months

MAIN OBJECTIVES

To develop the recycling of Electric Arc Furnace dusts from Steel Industry, the European Waelz Industry wants to get slags which could safety substitute for quarry materials.

This will be possible if release of potential contaminants meet existing and forthcoming standards and if properties reach specifications of fields of use.

To achieve this purpose, a scientific research programme is implemented on diverse types of Waelz slags :

* Chemical and mineralogical characterization
* Study of leaching behaviour
* Modification of compatible operating parameters
* Combination of Waelz slag with other matters.

The valorization of Waelz slag is not expected to be a direct achievement of the programme ; valorization needs to consider local regulations, local market and local economic conditions. This study has to be considered as an essential step of feasibility assessment for further valorization, and should provide recommendations for slag quality improvement.

RESULTS (near programme mid-term)

Five Waelz plants have been selected to cover the two types of slags : silica rich (acid) .

* A preliminary study carried out on the size fractions of one acid slag and one acid slag has shown :
  - no major chemical difference between size fractions ;
  - size fractions display the same mineralogical structure ;
  - very low release of contaminants, high pH sensitivity but not evident relation with size fractions.
* Comparative investigations have been developed on large samples (200 kg) of the five slags.
  - the basicity of two slags corresponds to low silica contents with very high lime content for one of them, and these two slags are richer in iron than the three acid slags ; the lowest Zn and Pb contents occur in the acid slags ;
  - quantitative mineralogical compositions have been determined : the acid slags are characterized by a glassy matrix which copiously coats other phases ; the highest basic slag is mainly constituted of oxides partially cemented by a tenuous Ca rich glassy silicate.

* Several leaching tests have been applied on the five slags.

  - the contaminants release in water is low, but higher for basic slags and appears both related to elements contents and mineralogical structure ;

  - a similar pH sensitivity is observed for the two types of slags ; leaching behaviour as function of pH is largely solubility controlled ;

  - the slags display the same trend of long term leachability, but higher release is observed for basic slags.

<u>CONTRACTANTS</u> . . : **METALEUROP RECHERCHE (MER) - Coordinator**
1, Avenue Albert Einstein - BP 120
78193 TRAPPES Cedex (France)

Scientist . . : Mr Christian DESNOYERS
Tel : (33) 1 30 66 28 68
Fax : (33) 1 30 66 27 28

INSAVALOR SA - Division POLDEN - CEI
27, Bd du 11 Novembre 1918 - BP 2132
69603 VILLEURBANNE Cedex (France)

Scientist . . : Mr Jacques MEHU
Tel : (33) 78 89 51 65
Fax : (33) 72 44 07 32

ENERGIENONDERZOEK CENTRUM NEDERLAND (ECN)
Westerduinweg 3, P.O. Box 1
1755 ZG PETTEN (The Netherlands)

Scientist . . : Dr Hans A. Van Der SLOOT
Tel : (31) 224 564 249
Fax : (31) 224 563 163

BUS METALL GmbH
Am Burgacker 30-42
47051 DUISBURG (Germany)

Scientist . . : Dr Ernst WALLIS
Tel : (49) 203 8093 113
Fax : (49) 203 8093 192

PROJECT Nr EV5V-CT94-0549

"HOW TO IMPROVE CHEMICAL AND PHYSICAL STABILITY OF WAELZ SLAG TO WITHSTAND LONG TERM EXPOSURE TO WEATHERING AND LEACHING CONDITIONS"

1. CONTEXT AND OBJECTIVE

Waelz process is the operative industrial way for recycling Electric Arc Furnace (EAF) dusts, zinc bearing waste coming from the steel industry. The Waelz furnaces (rotary kiln) produce impure zinc oxides (Waelz oxides) which are recycled in the zinc primary industry, and iron reduced slags locally used as banking. Today, the annual capacity of European Waelz plants allows to treat only half of the EC EAF dusts. For environmental benefit, the treatment of all these EAF dusts can be developed if the economical burden of Waelz slag dumping can be avoid.

In this context, The European Waelz industry wants to get slags which could safely substitute for quarry materials. This will be possible if release of potential contaminants meet existing and forthcoming standards and if properties reach specifications of fields of use.

To achieve this aim, two companies operating most of European Waelz plants (BUS METAL GmbH, Germany - METALEUROP, France) and two research centres specialist in leaching behaviour of materials (ECN, The Netherlands - POLDEN-INSAVALOR, France) combine their competence to implement a work programme regarding the following fields :

- * Chemical and mineralogical characterization of slags
- * External factors influencing the release of contaminants
- * Physical properties
- * Metallurgical modification of slag formation to increase stability.

To cover the chemical range of slags, five Waelz plants have been selected :

SLAG TYPE	WAELZ PLANT : Town, country	OWNERSHIPS
Acid	Duisburg - Germany	BUS Metall
	Fouquières-lez-Lens - France	RECYTECH (BUS 50 % - Metaleurop 50 %)
	Oker - Germany	HARTZ Metall GmbH (Metaleurop 100 %)
Basic	Freiberg - Germany	BUS ZINKRECYCLING GmbH (BUS 100 %)
	Pontenossa - Italy	SAMIM (BUS partly)

2. PRELIMINARY STUDY

Slags from Duisburg, Fouquières-lez-Lens and Freiberg plants being produced in several size fractions, the first mineralogical investigations and leaching tests were carried out on the three size fractions of Duisburg slag (0-5, 5-20, 20-40 mm) and on the two fractions of Freiberg slag (0-5, 5-20 mm) to identify eventual differences among size fractions of each type of slag.

For each slag, no major chemical difference was observed between the size fraction, except the metallic iron and carbon contents for Duisburg (effect of recovery of carbon rich small fragments by magnetic separation).

The two slags have a very low release of contaminants and high pH sensitivity but no evident relation with size fractions.

The results led to develop comparative investigations on large samples of the five raw slags.

3. CHARACTERIZATION OF THE FIVE WAELZ SLAGS

A) CHEMICAL COMPOSITIONS

The **Table 1** displays the results of analytical determinations performed on powder representative of 200 kg sample of each slag.

These results confirm the basic nature of the two slags from Freiberg (1FG) and Pontenossa (3FG). They display a high basicity index, respectively 1,7 and 3,5, which correspond to low silica contents and the highest lime content for 3FG.

These two basic slags are also characterized by total iron contents (1FG : 32 % - 3FG : 37 %), higher than those of the three acid slags (21 - 27 % Fe), but 3FG is the only slag containing a very low amount of metallic iron, that indicates a particular mineralogical nature.

The zinc and lead contents are low. The slag from Fouquières-lez-Lens (1FQ) displays the lowest contents (Zn : 0,24 % - Pb : 0,36 %), the highest contents belong to the basic slags, 4,6 % Zn for 1FG and 4,2 % Pb for 3FG.

B) MINERALOGICAL COMPOSITIONS

The mineralogical characteristics of the five slags (structure and nature of constituting phases) have been determined by X-Ray Diffraction on powder, reflected light microscopy and in situ Electron Microprobe Analysis (qualitative and quantitative) on polished sections. Approximate proportions of principal phases have been obtained by iterative calculation of phases-elements balance (**Table 2**).

* ***ACID SLAGS*** (Duisburg, Fouquières-lez-Lens, Oker)

About 60 % of these three slags correspond to a silica rich - Ca poor glassy matrix (~ 25 to 50 %) containing crystals close to $CaMgSi_2O_6$ (~ 35 to 10 %).

The other phases are completely embedded in the matrix :

- metallic iron globules more and less aggregated (17 to 19 %) ;
- small and dispersed oxide crystals close to $(Fe,Mg)(Cr,As)_2O_4$, (5 to 10 %) ;
- scarce Fe, Mn, Zn, Cu sulphides (1 to 3 %) often associated to iron globules ;
- very low amount of lead (< 1 %) trapped inside iron aggregates ;
- residual coke particles (2 to 12 %) and residual rounded SiO_2 sand grains (1 to 7 %)

* ***BASIC SLAGS*** (Freiberg 1FG - Pontenossa 3FG)

In these two cases, the silicates part corresponds only to 20 - 30 % of slag, but for 3FG (high basicity index 3,5), the glassy component is scarce (5 %) and corresponds to a Ca very rich iron silicate sulphate ; it occurs as a tenuous cement which partially solders Ca_2SiO_4 and $CaMgSiO_4$ crystals (21 %) and/or large amount (58 %) of various oxide grains (Fe rich-Ca -Pb, Fe rich-Mn-Mg, Mg rich-Mn, Ca-Al) to form small granular aggregates up to 10 mm in which are trapped iron globules (6 %), low amount of sulphides (2 %) and lead as metal (1 %) and chloride.

Slag 1FG(basicity index 1.7) displays a texture similar to that of the three acid slags, since 25 % correspond to a glassy matrix (Ca rich aluminous silicate) containing silicate crystals $Ca(Mg,Fe)SiO_4$ (6 %). This matrix coats abundant grains of Fe rich-Mg-Mn aluminous oxides (15 %) and iron globules (19 %) which the aggregates can contain sulfides (3 %) and some lead metal.

The mineralogical structure of the slag 1FG appears intermediate between that of the three acid slags and that of the highly basic slag 3 FG.

4. LEACHING BEHAVIOUR OF SLAGS

Several laboratory leaching tests were achieved to compare the behaviour of the five slags.

* *French regulatory tests for landfill acceptance of fragmented waste NF X 31-210* (slag crushed to 4 mm, 3 times 16 hours, with demineralized water).

Except for the basic slag 3FG, the Waelz slags display a very low release. Globally, the release is higher for the basic slags and appears both related to the level of element contents and the mineralogical structure ; it is particularly the case of the slag 3FG which present a high lead release.

* *Sensitivity to pH controlled and chemical medium* (slag crushed to 4 mm - pH 5, HNO_3 - pH 12,5, NaOH - pH 12,5, $Ca(OH)_2$).

The two types of slags (acid or basic) present a similar sensitivity to pH : higher Zn release at pH 5, higher Pb release at pH 12,5. The chemical nature of the leaching medium appears important in the case of Pb for an acid slag since its release is much higher with $Ca(OH)_2$ than with Na(OH) at the same pH.

The general trend of leaching behaviour of the different Waelz slags as a fonction of pH is largely solubility controlled in the range pH 4 to 12 ; the minimum Pb and Zn release is reached around pH 8-9.

* *Leaching behaviour on the long term by combination of Column test NEN 7343 and of Serial batch test NEN 7349 covering liquid to solid range ratio 0,1-10 and 20-100* (slag crushed to 4 mm - demineralized water acidified at pH 4 with HNO_3).

Pb and Zn releases are low and all the slags display the same trend of long term leachability, but the levels of Zn and Pb release from basic slags are higher than form acid slags.

* *Availability for leaching - Test NEN 7341* (slag ground to < 125 µm - pH 7 for 3 hours + pH 4 for 3 hours - HNO_3).

This test is presently used to simulate the potential element amount which could be leached from a material under extreme conditions, e.g. in very long time after complete disintegration and fully oxidized (geological time).

Since the fine grinding corresponds to liberation of all the phases embedded in silicate matrix, the availability of element such as Zn and Pb are related to proportions and elemental content of phases which are preferentially leached by HNO_3 acid, and not the total element content of the slag.

The difference observed between the availability classification and long term behaviour classification is related to the mineralogical structure of the slags since the tests which simulate long term leaching are performed on slags crushed to 4 mm where the fragments partly keep the mineralogical structure of slag.

TABLE 1 : CHEMICAL COMPOSITION OF THE FIVE WAELZ SLAGS

ELEMENTS (Weight %)	1DU	1FQ	1OK	1FG	3FG
Al_2O_3	5,52	3,82	7,07	4,31	2,66
CaO	6,41	15,3	7,58	10,5	23,5
Fe^t	20,7	27,6	22,3	32,4	37,1
K_2O	0,06	0,11	0,29	0,21	0,23
MgO	2,26	2,52	4,55	2,70	3,85
MnO	2,30	3,0	2,46	2,22	4,94
Na_2O	0,21	0,39	0,41	< 0,1	0,92
SiO_2	36,70	37,03	31,40	7,90	7,77
Ag	0,01	0,01	0,01	0,01	n.d.
As	0,02	< 0,02	< 0,02	0,02	< 0,05
Bi	< 0,02	< 0,02	< 0,02	< 0,02	n.d
Cd	< 0,01	< 0,01	< 0,01	< 0,01	< 0,05
Cu	0,24	0,32	0,49	0,34	0,32
Cr	0,28	0,08	0,16	0,04	0,36
Ni	0,05	0,04	0,20	0,04	0,03
Pb	1,15	0,36	1,07	1,80	4,22
Sb	0,02	< 0,02	0,04	< 0,02	n.d.
Sn	0,02	0,02	0,27	0,02	0,08
Zn	0,39	0,24	2,38	4,61	0,35
PO_4	0,38	0,53	0,60	0,65	n d.
Cl	< 0,05	< 0,05	< 0,05	< 0,05	n d.
F	0,08	n.d.	n.d.	n d.	n d.
S	0,60	0,75	2,03	0,97	1,12
C	13,4	2,12	5,33	20,7	5,85
Fe°	16,9	24,9	17,2	18,9	6,21
IB	0,24	0,48	0,39	1,67	3,52

Index Basicity = IB = (CaO + MgO) / SiO_2

TABLE 2
WAELZ SLAG SAMPLES - APPROXIMATE CALCULATED PROPORTIONS OF PRINCIPAL PHASES (WEIGTH %)

PHASES SAMPLE Ref.	GLASSY MATRIX	SILICATE CRYSTALS	IRON METAL	CARBON	OXIDE CRYSTALS	SULFIDES	FREE SILICA	LEAD METAL
1DU	48	8	17	12	5	2	7	1
1FQ	25	39	25	2	6	1	1	0,3
1OK	40	17	17	5	10	2,5	3	1
1FG	24	~ 6	19	21	15	3	-	1,5
3FG	5	21	6	6	58	2	-	1

Extraction and degradation of wastes contaminated by halogenated organics in an environmentally friendly way by supercriticals fluids

EV5V-CT94-0545

Coordinator: N. Eisenreich

Fraunhofer-institut für Chemische Technologie
D - 76327 Pfinztal
Tel: +49-721.4640138
Fax: +49-721.4640111

CONTRACT NO.: EV5V-CT94-0545

TITLE: **Extraction and Degradation of Wastes Contaminated by Halogentated Organics in an Environmentally Friendly Way by Supercritical Fluids**

STARTING DATE: June 1st 1994 DURATION: 24 months

PARTICIPANTS:

Fraunhofer-Institut für Chemische Technologie (ICT)
Scientist in charge: Dr. Norbert Eisenreich (Coordinator),
D-76327 Pfinztal, Germany
Tel.: +49 721 4640138, Fax: +49 721 4640111

Centre de Recherche et de Services (CELABOR)
Scientist in charge: Jean Brach,
B-4650 Chaineux, Belgique
Tel.: +32 87 322454, Fax: +32 87 341387

Solvay S.A. , Direction Centrale Recherches
Scientist in charge: Christian Biver
B-1120 Bruxelles, Belgique
Tel.: +32 2 2642793, Fax: +32 2 2643475

Contributions from project teams: FhG-ICT - CELABOR- SOLVAY

OBJECTIVES:

The objective is to provide a waste disposal technology which does not burden air and water with harmful effluents. The quality of this technology is that the wastes are completely mineralized to CO_2, water and salts. The products like CO, SO_2, NO_x, dioxines, arsine, mercury, etc., typical for incineration, are avoided. The technology is based on the properties of supercritical fluids which are the high extraction efficiency of supercritical CO_2 (SCE) and the degradation chemistry which occurs in supercritical water (SCWO). This chemistry is different from the chemistry occurring in high temperature oxidations and, consequently, results in different and more desired, harmless end-products.
On long term, a process is expected to be realized where large masses of moderate contamination are treated at the moderate conditions of the SCE and only smaller amounts must be degraded by the SCWO. In addition, the emission of CO_2 should also be prevented.

MAIN TASKS:

- Investigation of the physics and chemistry of the extraction of halogenated organics from chemical wastes by supercritical carbon dioxide and producing extracts for SCWO-process
- Investigation of chemistry and reaction mechanisms of the SCWO of model substances and extracts from the extraction step

- Modelling of the SCE and SCWO based on the reaction mechanisms depending on temperature and pressure resulting in a conceptual model for the SCE-SCWO facility.
- Preparation and characterisation of model waste samples
- Design of the combined bench scale (SCE-SCWO)-process with special attention to the interface and the mass flow over the interface

SUPERCRITICAL FLUIDS:

The technology to be applied is based on the properties of fluids at high pressures and temperatures especially at the critical point. Fluids passing the critical point change drastically their physical properties. This is similar to a phase transition where e.g. the density is strongly decreasing during evaporation. Two fluids, where these properties are used to establish an environmentally friendly disposal method, are carbon dioxide and water.

Supercritical CO_2 can substitute many of the conventional organic solvents without their the disadvantages. Properties are:

- Completely inoffensive, cheap, non-toxic, non-flammable, easily to removed from extracts
- A critical point at 31 °C and 7.3 MPa, which permits extraction at moderate pressure and temperature conditions
- Covering a wide range of pressure and temperature conditions different extracts can be obtained from the same starting material
- Modifiers can strongly improve the extraction efficiency

Supercritical water exhibits interesting effects above the critical point at 374 °C and 22,1 MPa:

- The dielectric constant decreases drastically from 80.
- Water behaves like a perfect organic solvent. Organic substances form a homogeneous mixture, inorganic substances precipitate.
- Gases like O_2, N_2, CO_2 and H_2 are completely dissolved.
- Water degrades organic materials.
- A mixture of water, oxidizer and some organic materials should produce pure carbon dioxide and water. Inorganics precipitate.

WASTE SAMPLES:

The feasibility of the disposal concept is investigated by using model wastes and industrial waste samples based on chlorinated compounds hexachlorocyclohexane (HCH) and hexachlorobenzene (HClBz). The model samples were sand contaminated with HCH and HClBz of a low and a high nconcentrations each. The industrial wastes to be investigated are a sludge contaminated with chlorinated organics and a lime contaminated with chlorinated organics.

RESULTS:

Table 1 gives an overview on the chlorinated compounds and wastes which were treated. The results demonstrate the high efficiency of the supercritical extraction by CO_2 and the degradation or oxidation power of the SCWO when applied to wastes. Of special interests are

halogenated, in this case, chlorinated compounds and wastes. Temperatures and pressures are parameters to adopt the conditions for the waste to be disposed within a broad range.
In the case of extraction, the use of modifiers can strongly enhence the effects. In the cases of the model wastes the residual contaminations are below the detection limits. Also industrial wastes show substantial weight loss and nearly complete removement of organics. In cases the extraction yield of one run is not sufficient the process can be cycled. The modifier for the selected application was methanol which can also used a fuel to the SCWO if the caloric value of the contaminants is not sufficient for self sustained reaction.

As oxidizers for SCWO H_2O_2, Na_2O_2 and O_2 were used. H_2O_2 and Na_2O_2 degrade HClBz with similar efficiency. Oxygen reacts instantaneously leading to high conversion rates. The corrosion is small with Na_2O_2 as an oxidizer. The extracts of the industrial wastes are on investigation. Preliminary results show high conversions similar to pure substances.
The conversion of HCH is already substantial at subdritical conditions. In contrast, for HClBz the conversion is very small below the critical point. It increases strongly to 99.5 % near 400 °C at pressures of supercritical conditions.

Table 1: Treatment of wastes by extraction and degradation

Waste type	Composition	Extraction/Conditions supercitical CO_2	Degradation of extracts/pure materials by supercritical water
model waste	sand + 500 and 2000 ppm HCH	15 MPa, 60°C 8.33 Solv.ratio yield >90%	500 °C, >22MPa conversion > 99%, no organic residues
model waste	sand + 2000 ppm HClBz	20 MPa, 70 °C residue < detection limits	>400 °C, >22MPa conversion > 99% no organic residues
industrial waste	sludge with chlorinated organics	20 MPa, 70 °C 11 - 14.5 % of the material extracted	on investigation (seems to be similar to pure materials)
industrial waste	lime with chlorinated organics	20 MPa, 70 °C partially extracted	on investigation(seems to be similar to pure materials)

The modelling of especially the SCWO which is up to now not used in large scale industrial applications is important for the design of pilot plants and, later, plants. A PVT-data-code was generated to calculate phase equilibria, critical curves and thermodynamic excess quantities of quaternary systems. This program uses the Christoforakis-Franck-equation of state

$$p = RT\frac{V_m^3 + V_m^2\beta_x + V_m\beta_x^2 - \beta_x^3}{V_m(V_m - \beta_x)^3} + RT\frac{B_x}{\left(V_m^2 - V_m\frac{C_x}{B_x}\right)}$$

This equation is based on the Carnahan-Starling-One-Fluid Model for the repulsion term and the Square-Well-Pade-Approximant for the attraction term.
The following substances which are in relation to the process were chosen as the needed basic data (e.g. Tetrachlorobenzene instead of Hexachlorbenzene) were available: water/carbondioxide, water/methanol, water/benzene, water/hexane water/tetrachlorobenzene, methanol/tetrachlorobenzene (input waste stream from extraction).

A two-dimensional FEM computer code solving the Navier-Stokes-equations was used for a numeric calculation of fluid dynamics and reaction phenomena. The programme to be applied to model the flow in a continuous reactor is called CAST for Computer Aided Simulation of Turbulent Flows. CAST allows the two dimensional calculation of laminar or turbulent flows with heat transfer at low Mach numbers.
For laminar flows, CAST solves the Navier-Stokes equitations. For turbulent flows, the Reynolds-averaged Navier-Stokes equitations are solved in connection with the k-ε two-equitation turbulence model of Launder and Spalding.

To use the code to model a continuos flow reactor at supercritical conditions several changes had to be done:

- the buoyancy in the transport equations had to be taken into consideration. In the transport equation for the x-component of the velocity u the force of the buoyancy
$$F_A = -(\rho(x,y) - \rho_{ref}) \cdot g \cdot V$$
is added to the source term.
- two additional transport equations had to be solved
- a combustion model for gaseous fuels based on the mixing graduation was implemented
- supercritical water implementation for variable material constants (ρ, Sc, c_p) was included
- more than one obstacle are possible now
- modified pressure correcture algorythm and changed calculation of the velocities on the boundaries

The model system characterized in table 2 which simulates a possible streamflow from the extractor was calculated including temperature profiles and flow fields.

Table 2: Input conditions of the continuous flow reactor

	Waste / Methanol + HCH	Oxidizer / water + H_2O_2
Diameter	5 mm	20 - 5 mm
velocity	20 mm/s	15 mm/s
Volume flow	1.5 l/h	16 l/h
Mass flow	360 g/h	4 kg/h

The main task of the project was to consider the combination of both methods. The results from extraction and reaction mechanisms and the conversion rates using calculations of mass and volume flows should lead to the definition of an interface. This interface has to feed the output of the extraction (the contaminant) , if needed with the modifier as fuel, to the SCWO which operates at temperature more than 300 °C than the SCE. The SCWO produces CO_2 as a result of the oxidation. The SCWO gives the chance to keep the CO_2 pressurized or within a closed loop.

The CO_2 can be partially used to be fed to the extraction to substitute leakage. The SCWO provides an oxidation process with the CO_2 being recovered and not being released to the environment like the incineration.

In an industrial plant, large installations have more than one extractor, i.e. 4 extractors, which work parallelly. With this technique, variations decrease, but it could be necessary to have a buffer-tank at the end of the SCE process to regulate the composition and the flow of extracts. This buffer-tank could be under pressure or not, according to the interface process.
Three types of interfaces to connect SCE and SCWO are considered:

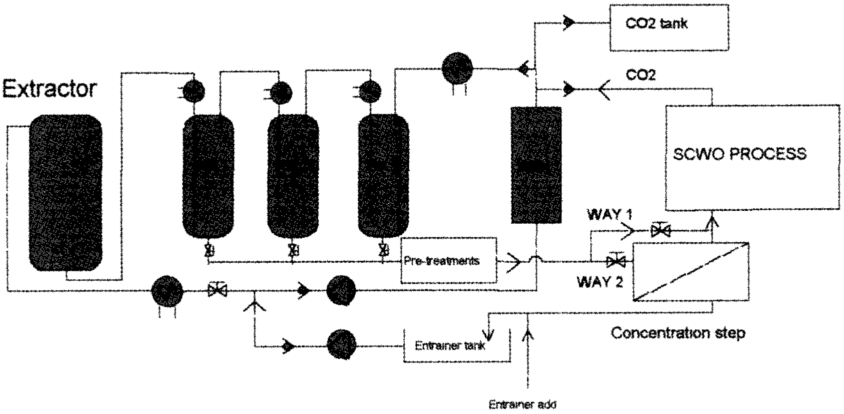
- Case 1: Without injection of an entrainer during the extraction.

- Case 2: With injection of an entrainer during the extraction.
- Case 3: With injection of a "washing" solvent after the extractor pressure vessel.

The cases have to be examined which is best suited for a target process. It is expected to use the different cases for different applications.

Fig. 1: Scheme of the reactor concept based on the interface case 2

Case 2 : Entrainer injection during the extraction



CONCLUSIONS:

The results confirm the effective extraction of contaminants by supercritical CO_2 and the degradation power of supercritical water oxidation. A combination of both methods leads to an economic total degradation system of high interest for waste disposal in chemical or pharmaceutical industry: Large masses are treated at moderate temperature and pressure conditions and harmful compounds are concentrated only smaller amounts are subjected to the higher temperatures and pressures.

The engineering of supercritical processes can be based on calculations by the adapted numerical code.

The SCWO provides an oxidation process with the CO_2 being recovered. When developed straight forward it can act as a disposal process competitive to incineration without releasing the oxidation products to the environment.

The work is part of two on-going doctoral thesis on degradation chemistry of SCWO and on modelling of SCWO reactors.

Toxicity Reduction of Organic Effluents by Electrochemical Treatment

EV5V-CT92-0237

Coordinator: D. Gilroy

EA Technology
UK - CH1 6ES Capenhurst
Tel: +44-151.347.2220
Fax: +44-151.347.2138

TOXICITY REDUCTION OF ORGANIC EFFLUENTS BY ELECTROCHEMICAL TREATMENT

CONTRACT No : EV5V-CT92-0237

STARTING DATE : 1/01/93 DURATION : 36 MONTHS

GROUP LEADERS :

Dr. D.Gilroy Phone: +44-151-347-2220
EA Technology Fax: +44-151-347-2138
Capenhurst, Chester, CH1 6ES, UK.

Dr. R.Solozabal Phone: +34-43-218022
INASMET Fax: +34-43-217560
Camino de Portuetxe, 12, 20009 San Sebastian, Spain.

Dr. J.Parkes Phone: +353-503-42795
Inter Euro Technology / Faraday Centre Fax: +353-503-41392
Green Road, Carlow, Ireland.

Dr. A.Anselmo Phone: +351-1-716-5141
INETI Fax: +351-1-716-0901
Azinhaga dos Lameiros à Estrada do Paço do Lumiar, 1600 Lisboa Codex, Portugal.

Dr. N.Theophilopoulos Phone: +301-9241-800
Impetus Consultants Fax: +301-9234-059
9 Syngrou Avenue, GR-11743, Athens, Greece.

Prof. M.Hitchman Phone: +44-141-553-4189
University of Strathclyde Fax: +44-141-552-5664
Pure & Applied Chemistry, 295 Cathedral Street, Glasgow, G1 1XL, Scotland, UK.

MAIN OBJECTIVES

- Modification or destruction of toxic groups by fundamental studies of the electrochemical reactions of compounds containing these groups.
- Application of practical electrochemical treatments to reduce the toxicity of the compounds studied.
- Development and assessment of techniques and apparatus to achieve these objectives.
- Identification of organic pollutants in aqueous effluent streams in certain industrial sectors.
- Classification of organic groups which are toxic to biological treatment systems.
- Survey of applications.

TOXICITY REDUCTION OF ORGANIC EFFLUENTS BY ELECTROCHEMICAL TREATMENT

Abstract

The treatment of effluents containing organic compounds is preferentially achieved by biological methods, but this approach may not always be possible when toxic materials are present. This project sought to develop electrochemical pre-treatment or treatment methods to overcome such problems.

An initial survey of certain industrial sectors of interest highlighted the classes of compound to be expected, and enabled the particular groups, which apparently were responsible for the major part of the toxic effect, to be identified. Two approaches are then possible, either a modification of the toxic groups, or a more complete destruction of the whole molecule. Both routes have been investigated in this project.

The first experimental task was to study the fundamental electrochemistry of the identified groups. The work included the reactions of phenols, aromatic hydrocarbons, aromatic nitro-compounds, cyanides, and amines. These substances were generally treated anodically, although the reduction of nitro groups was a possibility. It soon became apparent that the results obtained depended to a great extent on the anions present in the electrolyte. Chloride ions tended to ensure that complete oxidation occurred, presumably through the action of hypochlorite intermediate. In the absence of chloride, on the other hand, the nature of the anode assumed greater significance. In general, materials with a high oxygen overvoltage, such as the oxides of tin and lead, were more likely to bring about the required reactions, and less toxic partially oxidised intermediates could be detected. Precious metal electrodes were often ineffective.

In the early stages of the project, attempts were made to reduce aromatic carbon-chlorine bonds by cathodic reaction. If successful this would greatly reduce the toxicity of the starting chemicals for the expenditure of relatively small amounts of electricity. Pentachlorophenol (PCP) was used as the target molecule, and it proved to be possible to remove one of the chlorine atoms. Unfortunately the other bonds remained resistant.

After the initial studies, laboratory scale electrochemical cells were constructed by two members of the consortium, and delivered to the other partners. The electrode areas were of the order of 100 cm^2 in both cases. One cell was a flow design based on plate and frame construction, which enabled high mass transport rates to be achieved. The other was a tank cell. Both could be operated with or without a membrane.

The cells were used initially to study synthetic effluents, ie solutions containing only one toxic organic compound. Treatments of phenols, cyanides, nitro compounds, formate, PGMEA (propylene glycol methyl ether acetate), and aniline are reported. All of these compounds have been destroyed, often in the absence of chloride, which means that the method can be generally applicable. However, the importance of electrode material was again emphasised.

In view of this, the properties of several electrode types have been examined throughout the project. Commercially available precious metal anodes are normally suitable for operation in chloride containing media, but do not possess sufficient catalytic activity to enable intransigent molecules, such as phenols, to be destroyed in the absence of chloride. Alternatives were therefore examined in some detail. Tin dioxide shows good catalytic activity, but lifetimes are poor. Lead dioxide may also be suitable, except that lead ions may pass into the electrolyte. Nickel ferrite gave good results. Other materials, of high surface area, were also investigated.

An alternative approach, which may enable the electrode stability problems to be overcome, is that of photoelectrochemistry. The electrodes here are based on titanium oxides, which are inherently quite stable and non-toxic. Preliminary work on cell design and construction is reported, together with techniques for constructing the electrodes. Oxidations of MPA (methyl phosphonic acid) and PCP were studied on illuminated powders, and photocurrents were measured at the prepared electrodes.

Throughout the project the results of electrolyses have been assessed in many cases by performing toxicity measurements on the resulting liquors, to ensure that the products are less noxious than the starting materials. A study of two methods, Microtox and Thamnotox, is reported, the objective being to decide which test is the most appropriate in particular circumstances. Factors such as availability, cost, and convenience are discussed. Other methods of assay, notably COD, were also used.

In the final part of the project real effluents obtained from industrial organisations were investigated. The problems associated with olive oil wastewaters received much attention. These solutions contain complex mixtures of phenols and other compounds. Some success was achieved by electrolysis in the presence of chloride, and nickel ferrite electrodes gave good results. However, prolonged trials are still necessary. Effluents containing cyanides, phenols, nitro compounds, and furan derivatives, respectively, were all treated successfully. The cells and electrodes performed well.

PAPERS PUBLISHED

The following papers have been submitted :

"An investigation of the electrochemical reduction of pentachlorophenol with analysis by hplc.", N.C.Ross et al., J. Appl. Electrochem.

"A feasibility study of the destruction of chemical weapons by photocatalytic oxidation." M.L.Hitchman et al., Science & Global Security.

"A survey of disposal methods for chlorinated aromatic waste.", M.L.Hitchman et al., Chem. Soc. Revs.

The project was included in the European Workshop on Technologies for Environmental Protection, Bilbao, Jan-Feb 1995. (The proceedings are published by the European Commission as Report 7, EUR 16200 EN.)

A paper entitled "Oxidation of Toluene and Ethylbenzene at Lead and Tin Dioxide Electrodes." by D.Gilroy & D.A.Campbell (EA Technology), & A.Anselmo (INETI), was presented at "Electrochem 94", Edinburgh, Sept 1994.

Urmal, M.L., Anselmo, A.M., Rangel, C.M. (1995). Electrochemical treatment of olive oil waste waters for toxicity reduction. Second European East West Workshop on Chemistry and Energy. Sintra, Portugal.

Urmal, M.L., Anselmo, A.M., Rangel, C.M. (1995). Redução da toxicidade das águas ruças por processos electroquímicos. 1º Congresso Ibérico sobre contaminação e Toxicologia Ambiental. Coimbra, Portugal.

Paixão, S.M., Mendonça, E., Picado, A., Anselmo, A.M. (1995). Avaliação da toxicidade aguda de águas ruças. 1º Congresso Ibérico sobre contaminação e Toxicologia Ambiental. Coimbra, Portugal.

Paixão, S.M., Anselmo, A.M. Inhibitory effect of olive oil wastewaters on the oxygen consumption of activated sludge microorganisms. Submitted to Sixth SETAC - Europe Annual Meeting to be held in Sicilia, Italy, May 1996.

Paixão, S.M., Mendonça, E., Picado, A., Anselmo, A.M. (in preparation). Study on the acute toxicity of olive oil mill wastewaters. (to be submitted as a paper to an international publication).

The destruction of environmentally offensive waste halocarbons using sodium metal

EV5V-CT92-0238

Coordinator: M.R. Hillis

EA Technology
UK - CH1 6ES Capenhurst
Tel: +44-151.347.2320
Fax: +44-151.347.2138

THE DESTRUCTION OF ENVIRONMENTALLY OFFENSIVE WASTE HALOCARBONS USING SODIUM METAL

EV5V-CT92-0238

Starting Date : **1 January 1993**

Duration : **36 months**

Participants:

Dr M R Hillis (Co-ordinator)
EA Technology
Capenhurst
Chester
England
CH1 6ES
United Kingdom

Tel No : 44 151 347 2320
Fax No : 44 151 347 2138

Professor Emeritus R E Banks
Chemistry Department
UMIST
P O Box 88
Manchester
M60 1QD
United Kingdom

Tel No : 44 161 236 3311
Fax No : 44 161 200 4505

P B Jones, now at
Wormald (Ansul) UK Ltd
Grimshaw Lane
Newton Heath
Manchester
M40 2WL
United Kingdom

Tel No : 44 161 455 4418
Fax No : 44 161 455 4448

Dr S Boghosian
Foundation for Research & Technology - Hellas
Institute of Chemical Engineering and
High Temperature Chemical Processes
P O Box 1414
GR 265 00 Patras
Greece

Tel No : 30 61 997 582
Fax No : 30 61 993 255

Objectives

The main objective of the project was to investigate the potential of the reaction with metallic sodium as a means of destroying waste halocarbons, such as CFCs and halons.

A number of different forms of molten sodium were to be studied both theoretically and experimentally for the reaction with halocarbons : a bath of molten sodium; molten sodium dispersed into suitable liquids; molten sodium supported on particulate solids. In addition, sodium in the form of sodium naphthalenide was studied for comparison.

Reaction systems showing promise on the smaller laboratory scale were to be investigated further on a larger scale (200g-400g of sodium per reaction).

The final objective of these studies was to produce an outline design for a commercial scale plant.

Results

Theoretical models of the three different metallic sodium systems were prepared including energy and mass balances.

It was found experimentally that sodium dispersed in liquids, and sodium naphthalenide, both had disadvantages as reagent systems for the destruction of halocarbons. The dispersion system was found to produce variable results dependent on the liquid used and the halocarbon being destroyed. Toluene was found to give the best results but even in this case utilisations of sodium were relatively poor (~75%). With sodium napthalenide the reaction was "unclean". Unwanted tarry mixtures were produced and over 20% of the napthalene was lost by incorporation into the carbonaceous residue.

Using a stirred bath of liquid sodium or liquid sodium supported on particular solids, complete destruction of halocarbons was achieved with very high (>99%) utilisations of sodium. The sodium method was shown to completely destroy a wide variety of halocarbons with high utilisations of sodium. In all 25 different halocarbons were destroyed showing the wide applicability of the method.

Based on the small scale laboratory experiments, steel reactors were constructed and the sodium bath process tested using up to 200g of sodium per batch. The supported sodium was tested up to 400g of sodium per batch. The laboratory results were confirmed and controlled and easy destruction of halocarbons achieved.

Finally, a design for a plant destroying 250kg of halocarbon per single shift day was produced. This was a modular design based on a ribbon-impeller reactor utilising sodium dispersed on particulate solid support material.

Publications

Patent Application GB9506067.9 "Process for the destruction of halocarbons", EA Technology Application, M R Hillis, D A Gardner and D J Ambrose (and corresponding PCT international application).

Patent Application GB9525894.3 "Destruction of Halocarbons", UMIST Application, R E Banks and Z O El-Koussa.

EV5V-CT92-0238

THE DESTRUCTION OF ENVIRONMENTALLY OFFENSIVE WASTE HALOCARBONS USING SODIUM METAL

Introduction

The first objective of the project was to investigate the potential of metallic sodium as a reagent for destroying waste halocarbons by means of small scale laboratory experiments. Building on these studies the next objective was to develop and test a process whereby these potentially violent reactions could be carried out in an efficient and safe manner. Finally, an outline plant design was prepared and indicative costings of the process assessed.

Background to the Problem

Certain volatile man-made halocarbons, containing chlorine and bromine, when released into the atmosphere can be transported to the ozone layer where they react with and destroy ozone. This permits greater quantities of UV-B to reach the ground and there is increasing concern that this will lead to increases in skin cancer and cause other problems such as depression of our immune system, damage to crops and the killing of plankton, fish larvae and other important links in the sea's food chain.

The most important of the halocarbons that are depleting the ozone layer are chlorofluorocarbons (CFCs), which are used in refrigeration, air conditioning, foam blowing and as solvents, and halons, which are used in fire-fighting equipment. Most of these compounds also have significant global warming potentials and they, therefore, contribute to another global environmental problem - the greenhouse effect.

The international response to these problems has been the Montreal Protocol, which came into force in 1989. This put restrictions on the production of CFCs and halons. The Protocol has subsequently been amended to include more rapid phase-out of these halocarbons and to include further types of halocarbons. The EU has enacted even more restrictive legislation relating to the production of halocarbons and certain European countries have banned the use of halons or legislated against new halon installations.

This legislation has lead to stocks of halocarbons that are at present "banked" either in use or in strategic reserves. If these stocks should be released into the atmosphere it could delay for decades the recovery of the earth's ozone layer. There is thus keen interest in environmentally acceptable methods of destroying such halocarbons and the Halon Technical Options Committee (which advises on the Montreal Protocol) is currently considering eventual destruction strategies.

Halocarbon Destruction by Sodium

A process based on this reaction would be environmentally benign, since it would convert volatile halocarbons with high ozone depletion and global warming potentials into solid, inert products that cannot harm the ozone layer nor contribute to the greenhouse effect. For example the reaction for the refrigerant CFC-12 is:

$$CF_2Cl_2 + 4Na \rightarrow 2NaF + 2NaCl + C$$

One tonne of CFC-12 (CF_2Cl_2) would be destroyed by 760 kg of sodium and produce only solid products: 694 kg of sodium fluoride, 967 kg of sodium chloride and 99 kg of carbon.

Reaction systems

During the course of the project four different reaction systems were studied on the laboratory scale. Three of these involved the reaction of halocarbons with metallic sodium in different forms, while the fourth, for comparison, studied the use of sodium naphthalenide. The three reaction systems involving metallic sodium were also studied theoretically and mathematical models for the simulation of the destruction process were prepared. These three systems were: halocarbons reacting with a bath of molten sodium, with sodium that had been dispersed into hot liquids above its melting point and with molten sodium coated onto particles of a solid support medium.

Theoretical studies and mathematical models

In these studies mathematical models were developed for the three different reaction systems for the use of metallic sodium to destroy halocarbons. For each system the differential equations resulting from mass and energy balances across the reactor were constructed and the appropriate initial and boundary conditions set-up. The models were then solved using numerical methods.

Experimental studies

1 Sodium naphthalenide

This reactant had, compared with metallic sodium, the potential advantages of operation at lower temperatures and, as the exothermicity is in two stages, possibly being easier to control. It was found, however, that the reaction was "unclean", with the production of unwanted tarry mixtures and the loss of over 20% of the naphthalene due to its incorporation into the carbonaceous residue. This loss would be uneconomic and would also create an undesirable waste product.

2 Sodium dispersed into liquids

The dispersed sodium reaction system was found to give variable results in our experiments with halocarbons dependent on the liquid used and the halocarbon being destroyed. The liquids investigated included naphthenic oils, xylene, triethylbenzene, decane and toluene. The liquids were first heated to above the melting point of sodium and the sodium was then dispersed into them by vigorous stirring. Halocarbon was then bubbled into the reactor. The efficiency of the reaction was judged by the percentage of sodium utilised in the reaction. Dispersions in toluene gave the best results and carbon product could readily be observed. However, even in toluene utilisations of sodium were only about 75% and reaction times were long.

It was found that this was due to reaction products forming an impervious layer on the surface of the sodium particles and limiting access of the halocarbon to unreacted sodium. For this reason studies on sodium dispersed in liquids were not progressed further.

3 Bath of molten sodium

In this reaction system the gaseous or vaporised halocarbon was fed into the head space of the stirred reactor, which contained a bath of molten sodium. It was found that the design of stirrer was most important in achieving good utilisations of sodium and a novel spiral-spoke design was developed that constantly stirred the reaction mixture, cleaned the wall of the reaction vessel and effected a grinding action on the solid products that were formed. This allowed utilisations of sodium >99% to be achieved. Control of the very exothermic reaction between molten sodium and halocarbons was achieved by operating at sub-atmospheric pressures.

Based on the small scale laboratory experiments a stainless steel 1 litre sub-atmospheric pressure stirred reactor was constructed and used with up to 200 g of molten sodium to destroy halon 1301.

4 Sodium coated onto particulate solid supports

The use of particulate solid supports, onto which sodium was coated as a thin adherent layer, was also found to be an effective method of achieving high sodium utilisations and allowing control of the exothermicity of the reaction. Laboratory experiments were conducted using different support materials, different percentage loading of sodium on the support and different stirring regimes of the particulate bed. The effect of pressure and temperature on the destruction of halocarbons by supported sodium was also studied.

Based on the small scale experiments a 5.5 litre mild steel reaction vessel was construuted. This capable of operating up to 5 bar and 300°C and was fitted with a ribbon type impeller. This reactor was used for experiments with up to 400 g of sodium per batch. The effect of recirculating and re-using the support material for successive destruction reactions was studied. In one series of experiment the support was re-used twenty times with no drop in efficiency. Therefore, the limit on the re-use of support material will be much higher than this

Halocarbons studied

A wide variety of halocarbons were subjected to the sodium destruction method during the course of the project. Mineralisation was achieved with excellent utilisation of sodium in every case. As well as CFCs 11, 12, 113, 114 and 115 and halons 1202, 1211, 1301 and 2402, a variety of HCFCs, cyclic halocarbons, and perchlorocarbons were studied. The relative rates of reaction were determined and mechanistic information obtained.

Product separation

The separation of carbon from the sodium halide products was studied by various methods. The recovery of sodium fluoride and sodium bromide of good purity from mixed halide reaction products was also undertaken. The carbon product was characterised by various chemical and physical methods.

Outline Plant Design

An outline plant design was prepared based on the ribbon-impeller reactor utilising sodium dispersed on a particulate solid support material, the scale-up of this type of system being well understood. The design is for a unit that can destroy 250 kg of halocarbon per day in single shift operation. Sodium storage, support storage, mixing vessel, reactor, product treatment, and control and monitoring were all considered. Particular attention was given to removal of the heat of reaction and the effect that this will have on reactor size and shape. It is suggested that the reactors should be supplied in modular form.

The plant would be constructed from fairly standard components and manufacturers' quotes have been obtained to permit a plant costing to be arrived at

Process Costing and Sensitivity Analysis

A running cost estimate for the conceptual process has been made to include fixed charges (including capital cost depreciation), raw materials costs, labour costs, utilities, maintenance and repairs, and contingencies etc. This was first done for a 250 kg/day destruction capacity operating at five destruction cycles per day over one eight hour shift.

A series of perturbations of the process parameters was considered in order to assess the sensitivity of the resulting running cost.

Parameters altered included size of destruction plant, number of shifts per day, number of destruction cycles per day, percentage of sodium on the support material, percentage utilisation of the sodium, price of sodium. This analysis allowed optimisation of the more important variable parameters to be performed.

Finally the process profitability was assessed in terms of payback period and profitability index.

A costing was also prepared on the sub-atmospheric reactor containing a bath of molten sodium. It was assumed that halocarbon destruction capacities from 160 kg/day to 300 kg/day would be possible with a reaction time of approximately eight hours. Taking an assumed reactor cost and single ten hour worker shift running, cost estimates indicated that this design could be favoured at lower destruction capacities. Further experiments at larger scale and manufacturers' quotations are needed to confirm this.

Market Analysis and Alternative Technologies

As part of the project first hand information on the potential market for the destruction of halocarbons was obtained and assessed. Competing destruction processes were also assessed.

One partner in the consortium has in-depth knowledge of the fire protection industry and therefore is well aware of the situation regarding halon inventories and possible destruction technologies. To supplement this direct information the services of a market research agency were used to obtain similar information for CFCs by means of direct interviews with relevant companies.

From this data halocarbon inventories have been drawn up for different countries and the tonnages available for destruction and the destruction schedules have been estimated.

Finally, the cost of halocarbon destruction by incineration was established. Incineration is the only commercial scale destruction technology that can currently destroy both CFCs and halons. Newer technologies currently at the research or development stage, were also assessed in order to establish the viability of the sodium destruction method. It was concluded that the sodium process is likely to be cheaper and more environmentally acceptable than incineration as no toxic by-products are produced, nor gaseous or liquid emissions.

Conclusions

- The destruction of gaseous halocarbons by metallic sodium is an environmentally benign process that produces only solid products.
- The conditions under which these potentially violent reactions can be carried out have been studied and it has been shown that it is possible to evolve reactor designs and working regimes whereby the destruction of halocarbons by sodium can be carried out safely and efficiently.
- An outline plant design has been prepared and a process costing and sensitivity analysis have been carried out. This has allowed optimisation of the more important variable parameters.
- A market analysis has established the size of the potential market for halocarbon destruction and has also examined the position of competitive destruction technologies.
- It is concluded that the sodium destruction process could be operated at lower charges than those currently made for incineration of halocarbons. It is also likely to be cheaper than other newer technologies currently being investigated.
- The consortium partners are currently considering how best to exploit the successful results obtained in this project.

Mercury removal from waste sources

ENV4-CT95-0097

Coordinator: G. Sunderland

EA Technology
UK - CH1 6ES Capenhurst
Tel: +44-151.347.2411
Fax: +44-151.347.2138

MERCURY REMOVAL FROM WASTE SOURCES (MERWAS)

PROJECT N^{O} ENV4-CT95-0097

PROJECT
COORINATOR :

Dr GARRY SUNDERLAND
EA TECHNOLOGY
CAPENHURST
CHESTER CH1 6ES, **UNITED KINGDOM**
TEL. 00-44 (0)151-347-2411
FAX. 00-44 (0)151-347-2138

PARTNERS :

Mr. PATRICIO AGUIRRE
INASMET - ASOCIACION DE INVESTIGACION
METALURGICA DEL PAIS VASCO
P.O. BOX 1689
CAMINO DE PORTUETXE, 12
20009 SAN SEBASTIAN
PAIS VASCO, **SPAIN**
TEL. 00-34-43-218-022
FAX. 00-34-43-217-560

Mr. ANTONIO UBARRECHENA
EHER - ELECTROQUIMICA DE HERNANI, S.A.
AVENIDA DE MADRID n-13
20011 SAN SEBASTIAN
PAIS VASCO, **SPAIN**
TEL. 00-34-43-451-140
FAX. 00-34-43-453-965

PROF. MARGARIDO FERNADA
IST - INSTITUTO SUPERIOR TECNICO UNIVERSITY
AVENIDA ROVISCO PAIS, Nº 1
1096 LISBOA, **PORTUGAL**
TEL. 00-351-184-181-07
FAX. 00-351-184-992-42

PROF. MARIA ONDINA FIGUEIREDO
IICT - INSTITUTO DE INVESTIGAÇÃ CIENTIFICA TROPICAL
RUA DA JUNQUEIRA, Nº 30
1300 LISBOA, **PORTUGAL**
TEL. 00-351-184-765-96
FAX. 00-351-136-314-60

DIPL.- ING. DIOGO SANTO
UNITECA - UNIÃO INDUSTRIAL TEXTIL E QUIMICA, S.A.
P O. BOX 4482
199, RUA JOSE FALCÃO
4050 PORTO, **PORTUGAL**
TEL. 00-351-34-411-74
FAX. 00-351-34-417-40

START DATE 01/03/96 **DURATION 36 MONTHS**

MERCURY REMOVAL FROM WASTE SOURCES (MERWAS)

1 OBJECTIVES

1.1 Mercury Toxicity

Heavy metals are toxic and their disposal represents a serious hazard to the environment. Discarding to landfill results in a permanent loss of non-renewable resources and imposes on future generations the responsibility for monitoring such sites to prevent contamination of ground waters. Mercury has been classified as the most dangerous of all of the heavy metals due to its toxicity; persistence in the environment; and capacity for bio-accumulation. Only small quantities of mercury are required to contaminate large areas and thus its use is governed by several community directives.

Most compounds of mercury are also toxic. Methyl mercury may be formed by both inorganic and organic mercury compounds and this form of mercury is readily absorbed by bio-organisms. Thus the potential to enter the food chain is high.

In man, mercury and its compounds cause serious damage to the brain, genetic damage, particularly to the developing foetus, and disruption of body chemistry causing injury to internal organs.

Clearly the use of mercury in the future needs to be reviewed and where possible safer efficient alternatives need to be developed.

1.2 Current Techniques for Mercury Removal

A number of processes exist for removing mercury from discharge lamps. These involve removing the ends from the tubes, stripping the powder filling from the tubes by aeration and crushing the remaining glass. The majority of the mercury is contained in the phosphor powder and after separation of the materials into glass, metal and powder fractions, the powder is heated in a vacuum chamber. Most of the mercury vapour generated in the heating process is condensed in cooling traps, the remainder is adsorbed by an activated charcoal system. The charcoal adsorbent must be treated at some point to recover the mercury, if combusted micro particle emissions must be prevented. This is not a simple operation.

Incineration is often used to remove mercury from certain components. Of the mercury generated in incinerators from the combustion of fossil fuels or incineration of mercury containing wastes, (dental amalgams, electrical components etc.), 95% is filtered out from the stack emissions. The remainder is electrostatically attached to micro particles on cooling and this constitutes a health problem. The majority of the 95% is retained in the fly ash and a common disposal route for this is via landfill.

However, the mercury is not chemically bound into a stable compound and so is readily leached by rain water. Incineration of mercury and its compounds is thus not a recommended disposal route. In fact, mercury contained in landfilled waste which has not been incinerated has a better chance of forming stable compounds within the landfill although this will still not prevent ultimate leaching.

Mercury cell chlorine plants have been the largest contributors to mercury pollution in the chemical industry. The process consists of the electrolysis of a concentrated brine solution in a cell where the cathode is a flowing stream of mercury. The mercury leaves the cell as a mercury amalgam and passes to a decomposer where upon reaction with water hydrogen gas and 50% sodium hydroxide are the products formed. The mercury is then recycled to the electrolysis cell. The depleted brine is re-concentrated with fresh salt and treated to remove impurities by precipitation techniques.

The precipitates can entrain a quantity of mercury containing brine or even co-precipitate mercuric ions, flocculate suspended mercury droplets or particles of mercury sulphide. If these sludges are rejected as brine sludges without significant processing for mercury recovery then significant mercury losses can occur. This situation at present exists in Spain and Portugal. Austria still has the problem of mercury brine ponds and to some extent the U.K. has the problem of sludges remaining in river estuaries following the closure of the mercury cells a decade ago.

A system of hypochlorite leaching of brine sludges to remove mercury has been developed, oxidative leaching with sulphuric acid and potassium permanganate has also been used to remove mercury from solids. These mercury contaminated liquors can then be passed over a bed of activated carbon impregnated with silver. Alternatively the solutions can be contacted with a strong anion exchange resin. An alternative approach is to precipitate mercury from alkaline liquors as the sulphide by reaction with sodium sulphide, potassium sulphide or calcium polysulphide.

1.3 Proposed Objectives in the Treatment of Mercury Wastes

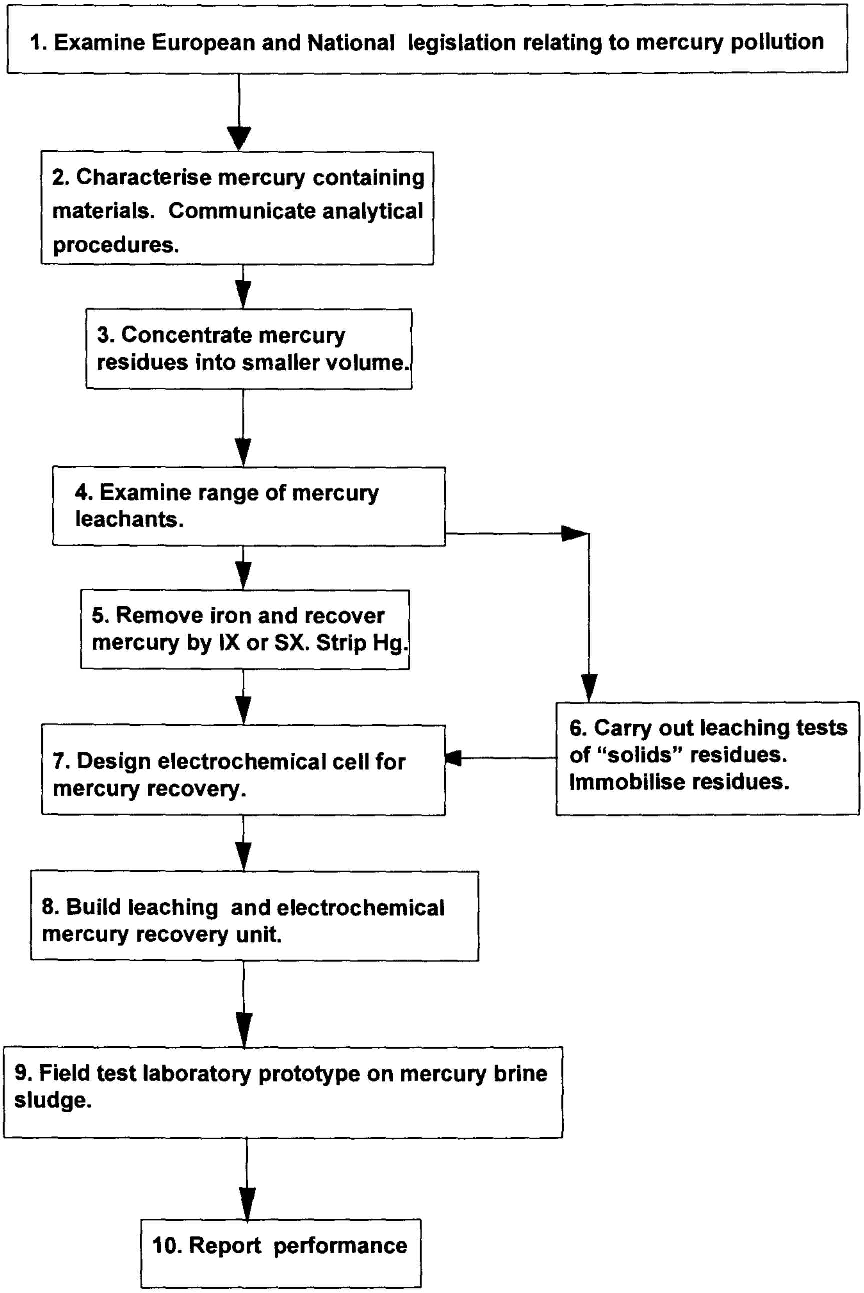
Most of the techniques described for the treatment of mercury bearing waste result in the generation of another material for disposal, or generate a smaller mercury waste in the reclamation of a portion of the mercury for reuse. The toxicity of mercury is such that it is vital to recycle the mercury contained in existing wastes thereby reducing the amount extracted as a raw material and limiting the total amount in circulation.

The only technique in which metals can be **reclaimed directly in the elemental form is electrodeposition**.

- ☐ Hydrometallurgical techniques designed to selectively leach or concentrate mercury compounds into a form suitable for electrolysis will be developed.
- ☐ An electrochemical cell will be developed whereby mercury can be recovered continuously and efficiently in a form suitable for re-use.
- ☐ It is the objective of this proposal to develop an integrated process for the recovery of mercury from a variety of sources.

2.1 Project Flow Diagram

PROJECT FLOW DIAGRAM



3.1 The Partners Skill Base

The above tasks require a wide range of skills to successfully reduce the amount of mercury leaching from mercury rich brine sludges and solid residues remaining following the breaking up of the fluorescent tubes.
The individual partners have the following expertise:

EA Technology

Fundamental and applied electrochemistry, including cell design and construction extensive analytical facilities. Expertise in the management of EC projects and commercialisation of industrial processes.

INASMET

Fundamental and applied electrochemistry. Wide range of industrial contacts and extensive analytical facilities. Experts in hydrometallurgy.

ELECTROQUIMICA

A Spanish chemical company producing chlorine and caustic soda from rock salt brine. Electroquimica will be involved in the supply of mercury containing sludges and will provide the necessary background to the brine sludge. They will be involved in the testing of the small laboratory test plant.

INSTITUTO SUPERIOR TÉCNICO

IST is a part of the University of Lisbon and has the necessary skills for preparing materials for characterising their physico-chemical properties. Experts in metallurgical pre-treatments.

INSTITUTO de INVESTIGACÃO CIENTIFICA TROPICAL

IICT are experts in the minerology and the adsorptive properties of clays and oxide/hydroxide minerals, an essential requirement of the work required in this project. Experts in the field of X-ray diffraction and fluorescence spectrometry.

UNIÃO INDUSTRIAL TÊXTIL E QUIMICA

UNITECA is a Portuguese chemical company producing chlorine and caustic soda from rock salt brine. They will supply mercury brine sludge and the necessary background knowledge on the behaviour of brine sludges. They will be involved in the testing of the small laboratory test plant.

Clean: innovative technology in automatic control of waste incineration processes

EV5V-CT94-0566

Coordinator: J. Jager

Technische Hochschule Darmstadt
WAR
D - 64287 Darmstadt
Tel: +49-6151.16.2748
Fax: +49-6151.16.3758

CONTRACT NO.: EV5V-CT94-0566
TITLE: INNOVATIVE TECHNOLOGY IN AUTOMATIC CONTROL OF WASTE INCINERATION PROCESSES

OBJECTIVES:

The CLEAN Project deals with the automatic control of urban waste incineration processes.

Objectives of the Project CLEAN are the following:

I. optimisation of the combustion and process behaviour
II. reduction of the emissions into the atmosphere (reduction of the „de novo syntheses" of the chemical substances (better burn-out of the gas) like PCDD, PCDF, CO or NO_x and thereby reduction of their emitted masses);
III. minimisation of the problems of landfill sites (better burn-out);
IV. reduction of costs related to the installation of extra cleaning systems;
V. improvement in energy efficiency.

PARTICIPANTS:

P1 **Project Leader**
THD (Technische Hochschule Darmstadt)
WAR (Institut für Wasser, Abfall und Raumplanung)
Petersenstraße 13
64287 Darmstadt
GERMANY
Tel. +49/6151/16-2748
Fax +49/6151/16-3739
Scientific Official: Johannes JAGER

P2
Forschungszentrum Karlsruhe (former KfK)
Technik und Umwelt
Institut für Angewandte Informatik - IAI
Abt. Umweltinformatik, Postfach 3640
D-76021 Karlsruhe
GERMANY
Tel. +49/7247/82-5756
Fax +49/7247/82-5730
Scientific Official: Hubert B. KELLER

P3
RISO (Riso National Laboratory)
Optics and Fluid Dynamics Dept.
P.O. Box 49
DK-4000 Roskilde
DENMARK
Tel. +45/4677-4677
Fax +45/4675-4064
Scientific Official: Carsten ROGAARD

METHODOLOGY / APPROACH:

The objectives listed in the previous page will be achieved by applying „Neural Networks“ to the incineration process control.
Neural Networks (advanced information technology approach) have been already successfully applied in the field of control systems (e.g. industrial automation and aero-spatial control).

During the CLEAN Project a higher order control system for waste incinerators is being developed consisting of:

* an incoming waste classifier (software module based on Neural Networks);
* an incineration controller (software module based on Neural Networks).

Furthermore, a simulator of the incineration process (software module based on Neural Networks) is being developed, too.
The final software product will be validated by using real data acquired from an incineration plant located in Germany.

RESULTS:

Deadline / Expected Results

1. End of month No.6 from Project Start
   Internal review point on:
   - preliminary results related to the analysis on the characterisation of waste;
   - investigation on suitable Neural Network models.
2. End of month No.12 from Project Start
   Internal review point on:
   - preliminary version of the incineration plant simulator;
   - first part of the investigation about selection / extraction of waste meaningful variables (features).
3. End of month No.24 from Project Start
   Internal review point on:
   - test results of the „vision“ system as an additional sensor system.
4. End of month No.24 from Project Start
   Internal review point on:
   - model for controller tuning and estimation of controller input variables;
5. End of month No.27 from Project Start
   Internal review point on:
   - waste classification model;
6. End of month No.27 from Project Start
   Internal review point on:
   - incineration plant simulator;
7. End of month No.27 from Project Start
   Internal review point on:
   - control system model;
   - prospects for future developments.

GENERAL ABSTRACT:

In the field of environmental protection, special attention is directed towards „cleaner technologies" which reduce the generation and emission of toxic substances.

In the near future waste incineration is expected to remain the dominant method for disposal of waste. As a consequence, the regulatory requirements for waste disposal are becoming more and more stringent. Such requirements greatly increase the costs for building waste incinerators (up to 50 % of the total costs).

Waste incinerators cause production of CO, NO_x and toxic organic substances such as PCDDs („dioxins"), PCDFs („furans") and PAHs. Such substances are known for their damaging effects on human health. Furthermore, the toxic organic substances are known for their bio-accumulation.
It is thus of increasingly importance to reduce the emissions and residues from waste incinerators.

An intelligent incineration control provides an efficient and cost beneficial strategy for achieving the required emission levels. The costs for cleaning equipments are reduced if an advanced control system is applied. This makes it possible for old plants to fulfil legal requirements and reduces construction costs for new plants.

Waste incinerators, like other complex plants, require a high level of know-how for a complete process monitoring and control. In the 90's fuzzy logic control systems applied to waste incineration plants proved to be far beyond the capabilities of conventional control systems.
However, the main problem in building fuzzy logic systems concerns the „bottleneck" of acquiring knowledge from human operators and the difficulties in porting a fuzzy system from one plant to another.

Neural Network technologies provide the advantages of fuzzy logic systems and, furthermore, have the unique capability of extracting information from process data without human intervention and the possibility of on-line self-adjustments based on changes in plant behaviour during time.

PUBLICATIONS:

- „Innovative technology in automatic control of waste incineration processes",
  Third European Workshop on Waste Treatment, Darmstadt, March 1995
- „Innovative technology in automatic control of waste incineration processes",
  European Workshop Recycling Technologies, Treatment of waste and contaminated sites,
  Hannover, May 1996
- Poster: „Innovative combustion process control for incineration plants",
  European Workshop Recycling Technologies, Treatment of waste and contaminated sites,
  Hannover, May 1996
- „Neural Networks for Combustion Process Modelling"
  B. Müller and Dr. H. Keller to appear at EANN 96 (engineering applications in neural networks),
  London, 18.-20.6.1996

Starting date: 01/11/1994	**Duration:** till 30/01/1997

THD

TH Darmstadt chose, in agreement with the other partners, the incineration plant in Darmstadt as the main reference plant for measurements during the CLEAN project. Up to now several visits and measurement sessions took place at the incineration plant.

Waste classifier

THD investigated the question whether it is possible to detect the composition of waste concerning the major components like paper, plastics, organic, metals, etc. In several sorting campaigns for domestic waste, company waste and bulky waste the THD could achieve experience in defining the composition of the waste and in detecting different materials.

Incineration classifier

The actual problem of the control of the incineration process is the question, if it is possible to automatically adjust a bigger number of set parameters, for example the air supply or the grid velocity, by a lower number of control parameters, for example, the combustion temperature or the steam mass flow.

Another question is whether the visual information of the process is necessary to run the control process automatically. There are several characteristics of the combustion processes on the grid and in the secondary combustion chamber, which are relevant to the drying and combustion process and which might also be detected by visual sensor techniques. Beside the conventional recorded process parameters especially the information coming from video- or infrared-cameras contain fundamental details about the incineration process.

From the video- and IR-pictures one can extract information like the co-ordinates of the fire front, the length of the fire front, process influencing holes in the waste layer on the grid and the waste bed thickness. Special IR-features are the temperature level on the grid and by using wavelength absorbing filters combustion processes behind heavy flame activities.

Concerning the handling of the process a set of rules can be stated like for example:
- the oxygen level characterises the short term process behaviour
- the steam flow level characterises the long term process behaviour

Data recording

The data recording of thirty different parameters at the Müllheizkraftwerk Darmstadt was continuously throughout the complete time period (06/06/1995 - 14/06/1995). The cameras (three VHS cameras and one IR camera) were used on 07/06/1995.

The data recorded were: the date, the time, the total air mass flow, the temperature of the crude gas after the boiler, the carbon monoxide concentration of the crude gas after the boiler, the oxygen concentration of the crude gas after the boiler, the correction value of the heating value, the steam mass flow, the steam nominal value, the primary air mass flow, the temperature of the primary air flow after the air pre-heater, the positioning of the four zone air flaps, the crude gas mass flow, the temperature of the crude gas after the washer, the temperature of the crude gas at the exit, the temperature of the crude gas at the neck, the temperature of the crude gas at the interface, the grid drive, the grid temperature, the secondary air mass flow, the ram drive, the total gas mass flow of the gas burner, the positioning of the main air flap, the pressure in the combustion chamber, the pressure of the crude gas after the boiler.

There are two other plants which have recently been contacted. The first one is the MVB Müllverwertung Borsigstraße GmbH situated in Hamburg, Germany. The other plant is the incineration plant in Düsseldorf, Germany.

In Figure 1 the Müllheizkraftwerk Darmstadt (waste incineration plant in Darmstadt) can be seen.

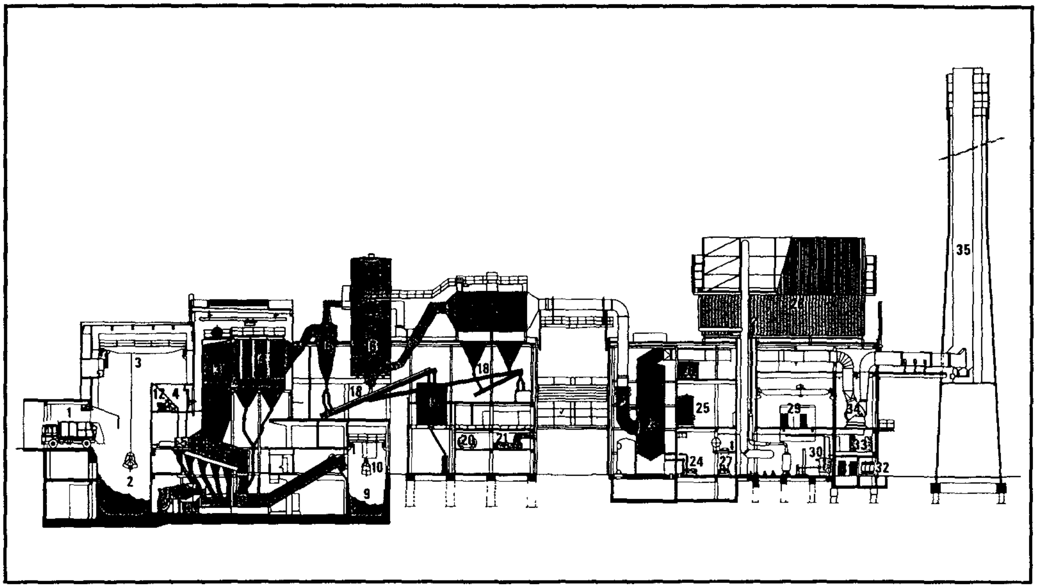


Figure 1

FZK

The contents comprise the current activities in the topics data analysis, data compression, neural model of the incineration process, process simulation and process control.

Data analysis

The large data sets obtained from THD are analysed in order to find meaningful parameters and reduce the range of parameters to a processable amount. A Principle Component Analysis (PCA) is used for finding redundancies between process parameters and to reduce data by producing a transformation into a lower dimensional space. The PCA algorithm contains several steps: centralising and standardising the data, building the correlation matrix, computing it's Eigenvalues and building the transformation matrix.
Estimation of the process dynamics describing the process state showed that parameters with a delay of 10 minutes have to be considered, but only a real subset of the data is needed.

Data Compression

Data compression can be yielded by mapping the data sets into their principal components by a linear transformation matrix. In this section the feasibility of non-linear compression is investigated and compression results between linear and non-linear methods are compared.

In the following tests non-linear compression is performed with a two layer feedforward network. The compression rate is determined by the number of output neurons of the net.

The neural compressor is received by splitting a neural encoder into two pieces. The encoder consists of three layers. Input and output layer have the same size and they correspond to the data set to be encoded. The hidden layer consists of less neurons than input/output layer in order to present a bottleneck in data flow. During training of the encoder data sets are applied to the input of the net, and the desired output is the data set itself.

After the encoder is trained, it is divided into two parts: the compressor and the decompressor.

The compression rate vs. the reproduction quality of the encoded data depends on the redundancy of the data itself. As with PCA coding it is possible to eliminate linear dependencies (correlation) neural networks can eliminate non-linear dependencies. In the actual application a data set consists of the 28 input parameters.

Compression techniques are applied when data processing is performed with high effort. But compressed data is less accurate than the original data. This can be compensated with the gain of better training results (convergence) as training of high dimensional data sets implies a higher risk of suboptimal training. The benefit of better convergence against the loss of accuracy has to be investigated further.

It must be emphasised, that unlike linear encoding, non-linear encoding cannot be adapted on-line (in the case of taking new data sets into account). For neural encoding a full retraining cycle has to be applied to the network.

Neural model of the incineration process

A neural model can be implemented that simulates the input/output behaviour of the process. The results are measured by validation with a validation data set. This is performed by the mean square error between process data and neural output. The quality of prediction is measured by the number of iterations. As the network has to simulate a function with no internal states, the use of standard models like Backpropagation and Self Organizing Feature Maps SOFM can be considered.

Process simulation

Data sets describing the process parameters are applied to networks in different representations during training phase. The process state is approximated by 10 to 20 previous data sets.

In all further neural applications the learning algorithm used is Rprop. (Resilent backpropagation). One advantage of this algorithm is it's lack of adjustable parameters. So no heuristics like parameter tuning of the network have to be applied. Other advantages are that it's all over convergence on the net and it's usually good convergence among gradient methods.

Simulations are performed on one process parameter as well as on all.

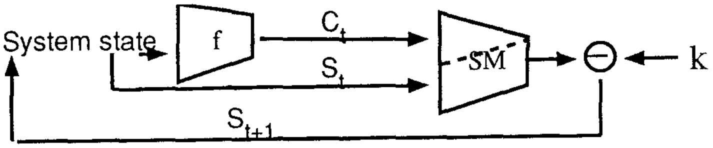
Networks trained with larger data sets seem to have a better generalisation ability according to the error between training data and validation data.

Closed loop process simulation for a single parameter works well but simulation of all parameters is not yet feasible for long term predictions because of the absence of the heating value parameter. Full autonomous process simulation can be improved by:

- using bigger networks with higher storage capability
- direct training of longer terms
- using single networks for each parameter
- introducing the heating value of the waste as a new parameter.

Process control

The process control is currently under implementation (Figure 2). The control is tested with a toy example. The here used toy example is an iterative mapping of the *sin* function. This function acts as the system model. Its argument is the product of the previous output multiplied with a control value. The system has to be controlled to produce a constant value.
The neural controller *f* gets the output of the system model *SM* as the system's state and produces the control value to lead to the constant system's state *k*.
Figure 3 shows the output of the toy process with and without control applied. This application is called a toy example because the system model consists of one parameter and disturbing parameters do not occur.



The neural control model

Figure 2

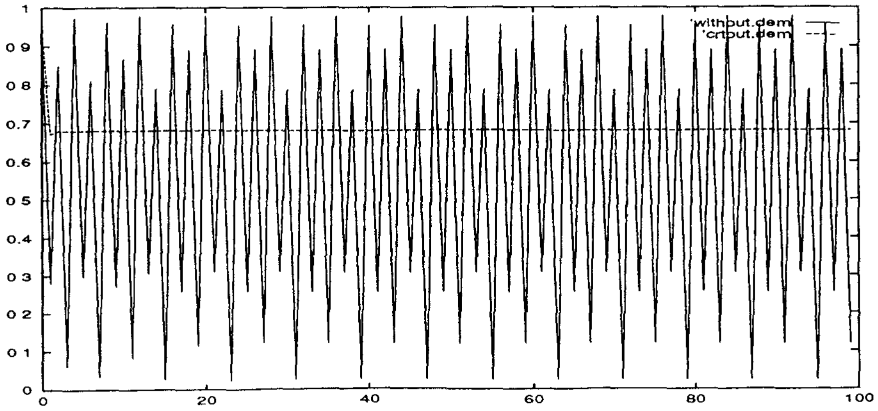


Figure 3

RISO

Identification of meaningful parameters with respect to a neural network approach

It will be investigated to which extent parameters only indirectly related to the quantities characterising the wastes but easier to be measured and/or controlled, could be useful instead of parameters impossible to be determined or regulated.
Data related to these parameters will be used as an input to the Neural Network models.
The specific objective is to identify visual features from the video data material supplied by THD.

The following image features in the video have been focused on:

1) Flares (jet streams of bright burning gases): a flare usually indicates holes in the bed of burning waste and these are undesirable. See point 7.
2) Start of the burning zone: this parameter is important for the control of the incineration chamber, because movements in it give an idea about the water contents and heating value of the incoming waste. Probably very important.
3) End of the burning zone: this parameter is important for the control of the incineration process in the kiln chamber. Here the operators look to find the size of the burning zone and where it is positioned in the chamber.
4) Movement of burning gases: from a visible inspection some information about the flow condition in the kiln chamber can be deduced and this information could be useful for the control. But how is not understood at the moment.
5) Movement of waste on the grid: movements give an indicator to when the waste might be turned over, which can bring new material in direct contact with the air flow.
6) Height of waste on the grid: after talking to the operator at the plant in Darmstadt we got the impression that this is probably the most important parameter to know. An indication of this parameter might be possible to get from the video set used now but a stereo set would be desirable.
7) Holes in waste bed: these are undesirable and therefore important to monitor: holes give an uneven and insufficient burning that makes it hard to control the plant.
8) Form and colour of flames: in the burnout zone it was noted that some contaminants could give abnormal colour to the flames and a detection of these will be interesting to hold track of in relation to toxins emission control. In the ignition (end of the pyrolysis zone) zone the way the flames ignite might reveal information about combustion gases commission.
9) Smoke: smoke gives a quality parameter of the burning process. The generation of visible smoke could be an indicator of the amount of solid particles in the gas. These particles surface are often involved catalytically in the digression of toxic contaminant.
10) Flying pieces of waste: these easy to see in the chamber but we were told that they are of no primary importance for the control.

So on this basis it has been agreed
Firstly) to look on simple ways to find the beginning and ending of the burning zone.
Secondly) to look for movements of the gases and to use this together with the intensity of the burning gases to find flares.
Thirdly) to work on a neural classifier to automatic classification of the burning materials into three classes flames, smoke and waste bed.

Study of the possibility of introducing a vision system as an advanced sensor to be integrated in a Neural Network Approach

The human operator of incineration plants heavily depends on video monitoring of the grids and the surface of the burning waste in the kiln, if such a monitoring exists.
A Neural Network image classifier can classify the video pictures into a range of categories, which then can free the neural waste classifier and neural controller module.
In order to cope with the massive data stream from the infra-red CCD-camera, it is necessary to introduce an image pre-processor. The main purpose of the pre-processor is to extract the important image features and to throw away superfluous information. The extracted image features constitute a reduced data space that act as input data for the Neural Network advanced sensor.
On the basis of the experience matured in the field of image classifying (some of them under the BRITE program), a study for the possibility of introducing a „vision" system into the Neural Network controller as an advanced sensor, will be afforded as a promising challenge.
In this period the attempt was made to design a neural classifier to perform the flame classifications.
A small sequence of 10 frames has been digitised one by one manually in full 24bit colour resolution and in an uncompressed format.
A cluster algorithm will be used to describe the input data and then the clusters will be used as a first guess for the neural classifier. A first cluster algorithm has been developed and makes sure that the data manifold will be fully covered by spheres. In a second pass an algorithm finds the closest quanta point to a data point. This gives an input picture for further processing.
The first step towards making the data reduction pyramid has been taken: a simple vector quantization algorithm implemented and tested in two versions. This algorithm provides a tool to probe the data manifold which has been done and shows that the dimensionality is only slowly growing as a function of the kernel size.
In Figure 4 an input picture for further processing is shown.

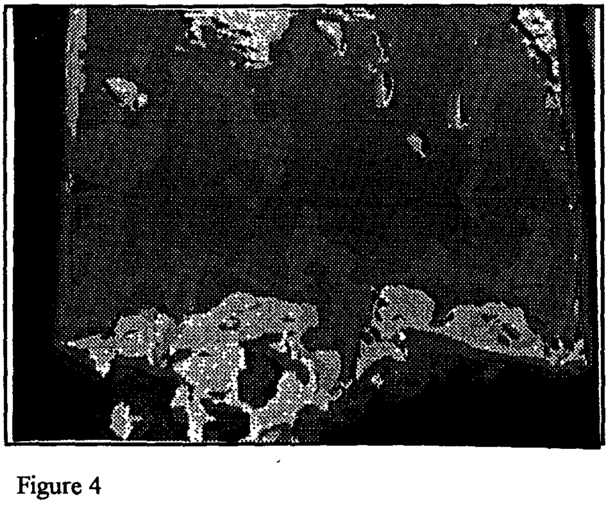


Figure 4

Development of a neural network based simulator

The collected experimental data is used to develop a neural network based simulator of the waste incineration, a higher order non-linear process. The method used is the Levenberg-Marquardt method for training the neural networks (second order optimisation method). The activation functions used include mostly sigmoids.

System identification of a higher order process

System identification can be performed by using feed-forward neural networks. This was done using a simulated fifth order linear dynamic system. Since the change in the state variables x can be more sensitive than the actual values of the state variables, it was chosen over a time δt as the output. The process input u is assumed to be known for any time.
The training data set is constructed from nine simulations of the system with different process inputs and the test set is formed from one simulation.

Feed-forward neural networks and their training

The feed-forward neural networks used are referred to as Adeline networks. The software applied is ANNAT.

Identification of the dynamic system

On training a few networks, starting with 8 delayed values of the measurable state variable x, it was found that the best configuration is a linear network. Networks with hidden layers had lower errors on the training set because of larger numbers of parameters, but they did not generalise as well on a test set.

Identification with fewer delayed measurements

When only three or four delayed measurements were used the errors increased by about an order of magnitude, but the results were still sufficiently good. Using two delays, the error got comparatively large, but the predicted output is still more or less the same as the simulated output.

Complete catalytic combustion of halogenated (waste) materials

EV5V-CT94-0530

Coordinator: R. Louw

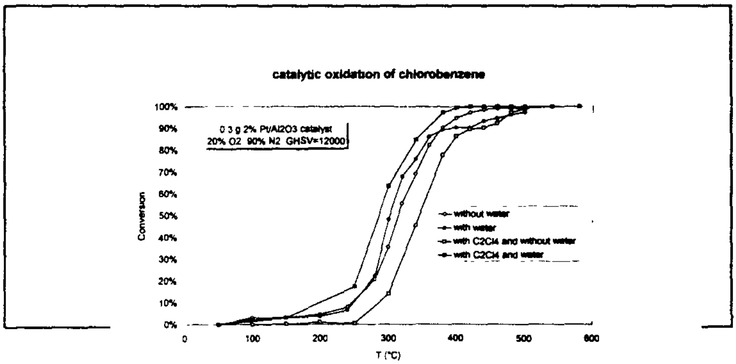
Rijksuniversiteit Leiden
NL - 2300 RA Leiden
Tel: +31-71.527.42.89
Fax: +31-71.527.44.88

CONTRACT NO.: EV5V-CT94-0530.

TITLE : COMPLETE CATALYTIC COMBUSTION OF HALOGENATED (WASTE) MATERIALS

OBJECTIVES :

To design, develop and test the best possible heterogeneous catalyst(s) for the title process; to arrive at a broadly applicable catalyst system, durable and effective under well-defined process conditions.



PARTICIPANTS :

Name : Prof. Robert LOUW/ Dr P. Mulder Address : CCE, LIC, Leiden University POB 9502, 2300 RA Leiden, Neth. Tel : (31) 71 527 42 89 Fax : 71 527 44 88	Name : Dr B.E. Nieuwenhuys Address : Catalysis Dept. LIC POB 9502, 2300 RA Leiden Tel : (31) 71 527 45 45 Fax : 71 527 45 37
Name : Prof. J.P. Hindermann and Address : Prof. A. Kiennemann, LERCSI, EHICS, 67008 Strasbourg, France Tel : (33) 88 41 68 61 Fax : 88 41 68 63	
Name : Prof. J. Corella Address : Fac. de Ciencias Quimicas, UCM, Ciudad Un., 28040 Madrid, Spain Tel : (34) 1 394 41 64 Fax : 1 394 41 64	

METHODOLOGY / APPROACH :

CATALYSTS (to be) studied

- existing/commercial materials (selection)
- (mixed) metal oxides
- (promoted) supported noble metals
- (mixed) perowskites

HOW ?

1 MODEL GASES with V-OHC's:
  - 1,1,1-trichloroethane
  - methylene chloride
  - (di)chlorobenzene

in O2/N2, O2/He; plus H2O vapor

\# check & compare Activity, Life,
Selectivity

\# study Rates, Products
characterize Cat. Surface
before and after

\# SELECT most promising ones;
try broader mix of (V-)OHC,
understand Function & Mechanism,
design & prepare IMPROVED Cat's

2. REAL GASES, from technical combustor
  - employ slip-streams
  - achieve COMPLETE after-burn
  - spike with V-OHC
  - VERIFY lab results
  - define PROPER TECHNOLOGY

RESULTS :

In Leiden, a number of supported noble metal catalysts (Pt/alumina; ibid with oxide promoters, of Co, Fe, Mn, La, Ce) and others have been prepared, and are tested in the cat. comb. of dichloromethane, trichloroethane, and chlorobenzene. Comparison is made with several commercial catalysts. In Strasbourg, perovskites ABO_3 (A = La, etc.; B = Co, Mn, Cr, Fe) have been made and compared in the catalytic combustion of mostly dichloromethane. Catalysts differ in reactivity, but most of them entail complete destruction at below 500 °C. Some (e.g. Co-based) materials form higher-chlorinated organics 'under way'. Free Cl_2, next to HCl, is often an end product. At present, $LaMnO_3$ is the best catalyst, probably resistive enough to metal chloride formation up to 500 °C.
In Madrid a new labscale combustion facility has become operative in which both granular and configurated catalyst materials can be used. Feeds may be synthetic or can come from a nearby pilot incinerator for real wastes; chlorine compounds can be added to those real combustion gases before the catalytic reactor. Effectivities of six commercial cat's have been compared in the destruction of chloroethane.

PUBLICATIONS :

Several conference papers; publications in preparation.

Starting date : 1/VI/94

Duration : till 30/11/97

COMPLETE CATALYTIC COMBUSTION OF HALOGENATED (WASTE) MATERIALS

Project EV5V-CT94-0530.

Aim: To design, develop and test the best possible heterogeneous catalyst(s) for the title process; to arrive at a broadly applicable catalyst system, durable and effective under well-defined process conditions.

The project is conducted by the following groups (with names of the scientific responsible persons given):
Leiden Institute of Chemistry, Leiden University, Netherlands:
  * Center for Chemistry and the Environment (Prof. R. Louw)
  * Department of Heterogeneous Catalysis (Dr. B.E. Nieuwenhuys)
Université Louis Pasteur-E.H.I.C.S., Strasbourg, France:
  * Laboratoire d'Etudes de la Réactivité Catalitique des Surfaces et Interfaces (LERCSI) (Prof. J.P. Hindermann, Prof. A. Kiennemann)
Universidad Complutense de Madrid, Spain:
  * Departamento de Ingeniera Quimica, Faculdad de Ciencias Quimicas (Prof. J. Corella).

GENERAL.

In Leiden, noble metal, promoted noble metal, and (mixed) metal oxide catalysts are made, characterised and tested, in their activity, selectivity/scope and durability. To this end, catalytic oxidation experiments are conducted mostly in (two) automated reaction/GC facilities. In a comparable fashion, the Strasbourg group designs, prepares, and tests (mixed) perovskite catalysts.
Gaseous model compounds - e.g. CH_2Cl_2, dichloromethane; 1,1,1-trichloroethane; chlorobenzene - are passed through the (granular, powdered) catalyst bed of choice (about 0.5 g), typically at a level of 2000 ppm chlorine, in nitrogen or helium with 3 - 20 % oxygen. This carrier gas can be dry or wet. Reactions may involve a single starting compound, or mixtures - also with chlorine-free hydrocarbons. A general procedure is to determine a temperature-conversion curve (usually sigmoid in shape), with T50 - the temperature at which 50 % of the starting compound is converted - as a key parameter (likewise, T90, or T99 are instructive).
The ultimate goal is of course a steady 100 % conversion, but it is of great importance to know if intermediate or side products arise, which may be more resistant to catalytic combustion - or more toxic - than the starting material. The ideal catalyst must be able to convert any (poly)chlorinated compound regardless its structure.
Experiments at incomplete conversion are of course instrumental in determining the kinetics and mechanisms involved; one can quantify the effect of changes in conditions such as concentrations, water content, and see if catalytic activity changes with time. To detect if and how the (surface) structure, composition, of a catalyst changes, a number of spectroscopic and other techniques are available, which will help in understanding the cause if a catalyst would deactivate (too rapidly).

Apart from 'home made' catalysts a number of commercially available catalytic materials will be tested as well. Although it is a drawback that (details of) their composition (and methods of preparation) are mostly kept secret, it is instructive to compare their performances under our well defined conditions. The 'same' catalyst when home made may differ in especially activity, but this is not really important: We are investigating the underlying catalytic-chemical principles so as to develop (novel) chemical compositions with better catalytic properties, and if succesful, these principles should be applicable to restyle, upgrade, existing commercial catalysts.
The Madrid group has several facilities for investigation of - pilot scale - real combustion. One has been newly built during the first year of the project; it has different reactors to allow working with both granular/spherical and configurated catalysts (monoliths). Gaseous feeds may be synthetic mixtures, or a real combustion gas coming from a waste incinerator close by in the pilot plant area of the DIC-UCM. Thus far, Madrid has worked solely with commercial catalysts; promising, selected catalysts coming from the Leiden and Strasbourg research will expectedly be available soon.

RESULTS; overview, examples.

In Madrid, in first instance, half a dozen commercial catalysts have been tested as to their capacity to bring down CO levels in real combustion gases to below 50 ppm. Thereafter, runs have been performed in the new facility with a number of commercial catalysts, under various conditions, with chloroethane (1000 ppm) as the halocarbon, and a SV of 10 000 h^{-1}. Monoliths gave better results as to total conversion than granular, pelleted catalysts. T50's ranged from 200 - 325 °C. The best catalyst gave > 90 % conversion at 250 °C, was not particularly sensitive to conditions - change of SV, chlorocarbon concentration, and no deactivation was noticed in 60 hours.

In Leiden, a series of catalysts have been prepared and tested for the most part, including: 1.7 w% Pt/alumina; ibid + 0.6 w% Co; 20 w% Co/alumina, by wet impregnation. Likewise, Pt, and Pt/Co on zirconia, more acidic than alumina. Also, Pt/alumina has been prepared by homogeneous deposition precipitation (urea decomposition). Thereafter a variety of metal oxides have been added by wet impregnation: Co_3O_4, Fe_2O_3, MnO_2, La_2O_3, CeO_2, to give 2 w% Pt, 2 w% metal oxide on the carrier.
Dichloromethane, over the Pt/alumina cat., SV = 3000/h, had a T50 of ca 300 °C and reached completion at T →500 °C. At partial reaction mono-chloromethane was seen as an intermediate product. Using the Pt+Co catalyst, however, chloroform and tetrachloromethane were observed instead. For comparison, a commercial noble metal cat., Pt(0.15%)/Pd(0.15%)/alumina, also had T50 = 300 °C and showed chloromethane as intermediate. Both chlorinated methanes were completely converted at 420 °C.
The Pt catalysts promoted by Fe_2O_3 and by Cr_2O_3 showed a higher activity than that with Pt alone, T99 being down from 500 to 425 and 375 °C, respectively. 2 w% of Fe_2O_3 on alumina was much less active, with T99 = 550 °C.

With the commercial Pt,Pd/alumina catalyst -see above - 1,1,1-trichloroethane was used next. Now T50 is only 160 and conversion is complete at 250 °C, but this substrate clearly demonstrates that 'disappearance' is not the only point of interest: At moderate T, most of the trichloroethane has lost HCl to become dichloroethene. This vinylic chloride requires at least 420 °C for its total destruction, which presumably holds for other vinylic chlorides also (see further on). Analogously, chlorobenzene as such is completely converted at 300 °C.

Interestingly, ethane itself, in separate runs, reacts slower than dichloromethane (T50 ca 350, vs 300 oC). When fed together, ethane conversion becomes sizeable only if that of dichloromethane nears completion, and its T50 is increased to ca 420 °C.

The combustion of chlorobenzene has also been studied on a home made Pt/alumina catalyst - less active than the commercial Pt,Pd catalyst mentioned earlier. A closer analysis shows that a range of Cl_2- Cl_6 benzenes (PCBz's) are intermediately formed at low level, requiring higher T's for complete destruction. The composition of the PCBz's suggest the operation of a gas-phase, radical chlorination of chlorobenzene, etc. Substantiated by independent analysis, free chlorine is formed; this most likely is due to catalytic oxidation of HCl (the 'Deacon' reaction, thermodynamically more favoured at T < 500 °C than in thermal combustion).

A key question is if the C,H,Cl-compounds hitherto discussed start to react by C-H, and/or C-Cl bond activation - and, how this will depend on the type of catalyst. Perchloro-derivatives (H absent) may be a separate category. Anyway, in runs with chlorobenzene over Pt/alumina with added tetrachloroethene, C_2Cl_4, the levels of - intermediate - PCBz's and of Cl_2 are considerably higher. Probably, the tetrachloroethene generates quite some chlorine, at least under the present conditions.

In a separate off-line setup a number of commercial catalysts are now being compared in their capacity to combust dichloromethane (TEMPUS programme, visiting student from Poland).

The Strasbourg group works with perovskites, ABO_3, wherein A,B, stand for a variety of bi- tri- tetra- or even highervalent metal cations. Examples of discrete structures are $LaBO_3$, B = Co, Mn, Cr, Fe. Also, $ACoO_3$, with A = e.g. Sm, Gd, next to La. More than two metals can be accomodated, as in $La_{0.6}$ $Sr_{0.4}O_3$. Furthermore, doping with e.g. noble metals is possible. This expectedly leads to a range of properties, due to differences in (surface) structure and electronic character. When prepared via the sol-gel method, BET surface areas are between 5-20 m^2/g. This is less than for a typical commercial chromium oxide/alumina hydrocarbon oxidation cat., which has 170 m^2/g. So, for promising new catalysts it will be worth while to improve the surface area.

In cat. combustion of dichloromethane, T50 for $LaBO_3$ were found to be: Cr, 500; Fe, 380; Mn, 360; Co, 320; the commercial Cr-oxide cat. had T50 = 230 °C. This cat., however, formed red, volatile CrO_2Cl_2; remarkably, the - rather inactive - $LaCrO_3$ perovskite did not show this adverse behaviour.

Obviously, a general point is to avoid deactivation by formation of metal chlorides.

The relatively active Co-containing catalysts give chloroform and some CCl_4 as side products in the reaction of dichloromethane; this is consonant with results in [illegible] Co-oxide catalysts.

Rates - also that to give CCl_4 - inceased with increasing $[O_2]$. Polychloromethanes were not seen with the Mn, Fe, or Cr-based perovskites. However, $LaFeO_3$ gradually formed $FeCl_2/FeCl_3$, and XRD analysis supports the gradual destruction of this material.

At low concentrations (e.g. 140 ppm of dichloromethane) $LaCoO_3$ and $LaMnO_3$ seem to be resistant to chlorinated compounds whereas at higher concentrations (1000 ppm dichloromethane, or 500 ppm CCl_4) $LaCoO_3$ is quite rapidly decomposed at 500 °C to form LaOCl and Co_3O_4. Under these conditions, LaMnO3 remains stable and active.

As CCl_4 is one of the side products, separate attention is given to this compound as a feed, again with the two last-named perovskites as a cat. Lacking H in this feed, the added water vapour is the only H containing compound used. Variation of the oxygen concentration has shown that with CCl_4 the reaction could be conducted without oxygen. An increase in $[O_2]$ displaces the Deacon equilibrium to the side of Cl_2, but does not increase the conversion of CCl_4. Therefore, conceptually, 'combustion' of carbon tetrachloride is hydrolysis: $CCl_4 + 2\ H_2O \rightarrow CO_2 + 4\ HCl$.

Results substantiate that $LaMnO_3$ is both stable and active. Note that Mn is very 'flexible' in its oxidation state, which may lead to greater tolerances for e.g. (surface) oxygen concentrations, thence stability.

EPILOGUE.

Obviously, many variables can influence rates - and mechanisms - of catalytic oxidation, even of a single starting compound containing one chlorine atom. Next to temperature, space velocity, type and constitution of the catalyst, the presence of

* other organic compounds (Cl free or not); * concentration of oxygen, and * concentration of water (which can exert its influence in different ways) will determine the overall result.

Although the contours of what determines a 'good catalyst' are becoming visible, several bottlenecks need further consideration:

* formation of free chlorine; * catalyst deactivation; * formation (and survival?) of nasty organochlorine derivatives.

Leiden, March 1996

Prof. Robert Louw, project Coordinator
E mail: Louw_r@chem.leidenuniv.nl

Extended Abstract for the European Workshop on Recycling Technologies, Treatment of Waste and Contaminated Sites 1996, Hannover, Germany, 20 - 24 May 1996.

Detoxification of toxic industrial waste: microbial degradation of polychlorinated biphenyls (PCBs) by sequential anaerobic-aerobic processes

EV5V-CT92-0192

Coordinator: W. Reineke

Bergische Universität - GH Wuppertal
D - 42097 Wuppertal
Tel: +49-202.439.2456
Fax: +49-202.439.2698

CONTRACT NO.: EV5V-CT92-0192

TITLE:

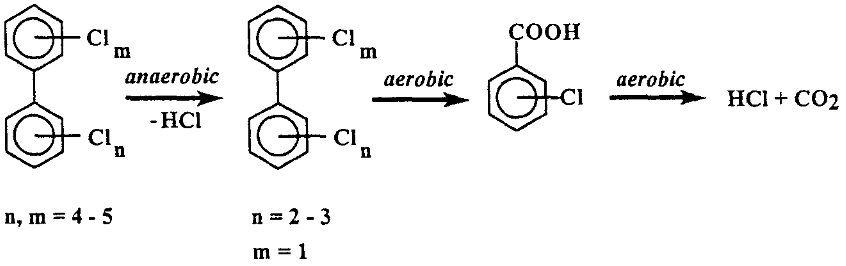
Detoxification of toxic industrial waste: Microbial degradation of polychlorinated biphenyls (PCBs) by sequential anaerobic-aerobic processes

OBJECTIVES:

The goal of the project is to obtain information on:

1. the feasibility of a process to mineralize highly chlorinated biphenyls (formation of inorganic compounds like CO_2, HCl) by a suitable sequential anaerobic-aerobic process and
2. its application (especially the factors which are determining the kinetics of the degradation process in a bioreactor).

CHARACTERISTIC DIAGRAMME:



PARTICIPANTS:

Prof. Walter Reineke
Bergische Universität - GH Wuppertal
Fachbereich 9, Chemische Mikrobiologie
Gaußstr. 20, D-42097 Wuppertal, Germany
Tel.: +49-202-439-2456
Fax: +49-202-439-2698

Dr. Dirk Springael
Vlaamse Instelling voor Technologisch Onderzoek
Boeretang 200
B-2400 Mol, Belgium
Tel.: +32-14-335511
Fax: +32-14-320372

Dr. Gosse Schraa
Wageningen Agricultural University
Department of Microbiology
Hesselink van Suchtelenweg 4
6703 CT Wageningen, The Netherlands
Tel.: +31-8370-83620
Fax: +31-8370-83829

Prof. Christopher J. Knowles
University of Kent at Canterbury
Biological Laboratory
Canterbury, Kent CT2 7NJ, UK
Tel.: +44-227-764000 (ext 3696)
Fax: +44-227-763912

APPROACH:

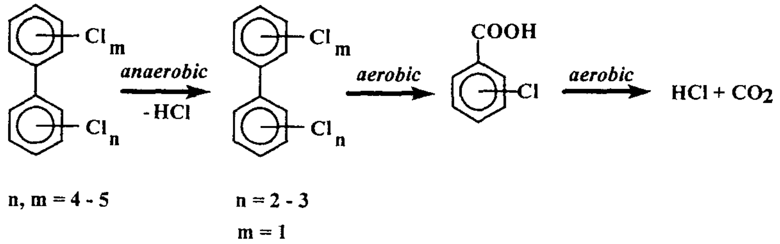
Prior to the 1970s, PCBs were widely used for a variety of industrial purposes, including fluid-filled capacitors and transformers, hydraulic fluids, heat transfer fluids, plasticizers, and carbonless copy paper. The commercially used PCBs were complex mixtures of many congeners. 300,000 tonnes have entered the environment in widely disseminated form, 450,000 tonnes are either still in service or in landfills. Since storage in landfills has been used for PCB contaminated wastes in the past, the persistence of the compounds led to the contamination of water, soil, air and even biological tissues.

The project consists of four parts:

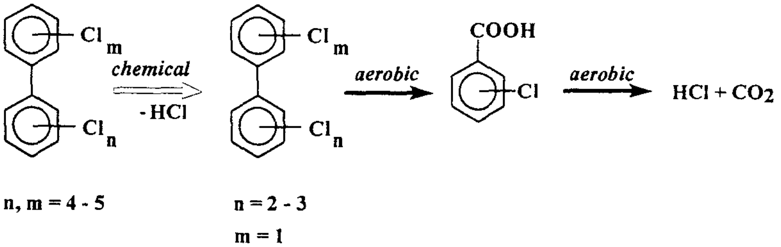
1. Establishment of anaerobic microbial populations from polluted soils/sediments, capable of reductive dechlorination of highly chlorinated biphenyls to lower chlorinated biphenyls. Research is focused on the occurrence of this process in polluted soils and sediments, the kinetics of the process and the influence of various (environmental) factors, and the bacteria involved.
2. Establishment of aerobic bacterial cultures, capable of mineralizing low chlorinated biphenyls, by isolation from polluted soils/sediments or by *in vivo*-construction. Research is focused on the biochemistry and the kinetics of degradation.
3. Genetic analysis of the isolated and *in vivo*-constructed PCB-degrading organisms and genetic engineering of these strains, which includes the introduction of heavy metal resistance genes and marker genes. Research is focused on the molecular biology of PCB degradation pathways and genes of heavy metal resistance.
4. Investigations on the biotechnology of the anaerobic-aerobic process. Research is focused on the procedure to clean contaminated soils and wastes in bioreactors.

Alternative approaches for the sequential processes in the degradation of chlorinated biphenyls

a) Proposed sequential anaerobic-aerobic processes



b) Alternative sequential chemical-microbial aerobic processes



PROFILE OF THE INSTITUTIONS:

Chemische Mikrobiologie, Bergische Universität - GH Wuppertal

Academic institute with an international reputation for research on the field of the microbial degradation of haloaromatic compounds and a long-standing experience in: aerobic degradation of chloroaromatics; biochemical research on degradation pathways; construction of hybrid degradation pathways via conjugative DNA-transfer; and application of specialized chloroaromatics-degrading bacterial strains for the clean-up of contaminated soils.

Department of Microbiology, Wageningen Agricultural University

Academic centre with an international reputation for research on biochemistry, physiology and ecology of anaerobic bacteria and with experience in: aerobic and anaerobic degradation of chlorinated aromatics and aliphatics, anaerobic degradation of polycyclic aromatic hydrocarbons; role of surface areas in the degradation of xenobiotic compounds like dibenzodioxines and dibenzofurans; and degradation of xenobiotic compounds at low concentrations.

Laboratory of Genetics and Biotechnology, Vlaamse Instelling voor Technologisch Onderzoek, Mol

Research centre with an international reputation for research on the field of environmental microbiology and biotechnology and with experience in: aerobic degradation of xenobiotics; genetic analysis of xenobiotic-degrading strains including transfer of catabolic genes between different bacteria and gene cloning; microbiology of heavy metal resistant bacteria including identification and cloning of heavy metal resistance genes; gene fusions and application of bacteria for environmental biotechnology; strain tagging and risk assessment of genetically engineered microorganisms.

Biological Laboratory, University of Kent at Canterbury

University department with an international reputation in microbial biotechnology, especially in biotransformations, environmental microbiology and fermentation technology. Considerable experience in technology transfer and development of commercially applicable systems. Work on microbial mixed cultures for treatment of a wide range of end-of-pipe pollutants has been scaled-up and used industrially. Within the department there is much experience in pesticide degradation in soils, metal remediation and binding, and degradation of a range of highly toxic materials.

Detoxification of toxic industrial waste: Microbial degradation of polychlorinated biphenyls (PCBs) by sequential anaerobic-aerobic processes (EC contract EV5V-CT92-0192).

Chemische Mikrobiologie, BUGH, Wuppertal, Germany (J. Havel, H. Mokross & W. Reineke); Dep. of Microbiology, Wageningen Agricultural University, Wageningen, The Netherlands (P. Middeldorp, J. de Wolf & G. Schraa); Environmental Technology, VITO, Mol, Belgium (D. Springael, P. Dengis, A. Ryngaert, D. van der Lelie, M. Mergeay & L. Diels); Research School of Sciences, Univ. of Kent, Canterbury, UK (G. Robinsin, J. Stratford, M. Wright, S. Jackman & C. Knowles).

For more than 20 years polychlorinated biphenyls (PCBs) have been one of the most researched classes of chemical compounds which have entered the environment due to anthropogenic activities. They are considered as prevalent, toxic and persistent environmental pollutants. The most efficient method to destroy PCB contaminated material is incineration at high temperature. However, the process is expensive, the capacity is low and high public concern has raisen about the incineration of hazardous wastes due to the risk of dioxin production. Currently, PCB contaminated equipment is deposited and is waiting for terminal destruction.

An EC consortium comprising laboratories from Germany, Holland, Belgium and the UK has been involved in an EC project to treat PCB contaminated waste and to destroy PCBs completely by a combined anaerobic/aerobic microbiological process. The chemical structure, low solubility in water and the fact that commercial PCB-products contain more than 60 to 80 different congeners make PCBs as a particulary difficult challenge for microbiological degradation. Highly chlorinated PCBs (with more than three substitutions) can be converted by anaerobic microorganisms into lower chlorinated biphenyls with less than three substitutions by a reductive dechlorination process. Lower chlorinated biphenyls can be attacked by aerobic microorganisms and converted into chlorinated benzoates. Other microorganisms are able to mineralize the chlorinated benzoates. A combination of the reductive dechlorination process under anaerobic conditions and a mineralization under aerobic conditions can in principle lead to the formation of harmless endproducts (H_2O, CO_2, Cl^- and biomass) (Fig. 1). The goal of the project was to obtain information about the anaerobic and aerobic degradation of PCBs by microorganisms isolated from polluted soils and sediments or obtained by *in vivo* genetic engineering and to establish a microbial process in which highly chlorinated biphenyls are mineralized by a sequential anaerobic-aerobic process. The partnership involved in this program included the Agricultural University of Wageningen, Netherlands (anaerobic PCB degradation), the Bergische Universität of Wuppertal, Germany (aerobic PCB degradation), VITO, Mol, Belgium (aerobic PCB degradation) and the University of Kent, Canterbury, UK (combination anaerobic/aerobic process).

In Wageningen, microbial consortia were enriched from anaerobic PCB contaminated sediments and were shown able to reductively dechlorinate technical PCB mixtures as Aroclor 1260 and Aroclor 1242 under methanogenic conditions. Aroclor 1260 was converted to mainly tetra- and tri- chlorinated biphenyls. Aroclor 1242 was converted into tri-, di- and mono- chlorinated biphenyls. The incubation time for complete conversion ranged from 30 to 90 days. As the anaerobic degradation of PCBs was a slow process, a cost competitive chemical reductive dechlorination process was developed at the University of Kent (UK). This method was based on the method of Liu & Schwarz. In this process, PCBs are converted using an inert atmosphere at elevated temperature using titanocene dichloride as a catalyst in the presence of sodium borohydride and a catalytic amine. It was observed that Aroclor 1242 was mainly converted into mono-chlorinated biphenyls which should be easily mineralized by aerobic PCB dgrading bacteria. Dechlorination was completed after 24 hours in liquid cultures.

In Wuppertal, a selection of new aerobic PCB degrading bacteria were isolated able to grow on biphenyl and monochlorinated biphenyls with accumulation of chlorinated benzoates (upper pathway isolates). Other new strains were isolated able to use chlorinated benzoates as sole carbon source (lower pathway isolates). Mixtures of bacterial strains able to convert chlorinated biphenyls into chlorobenzoates and strains able to mineralize chlorinated benzoates were tested in soil microcoms for complete mineralization of the chlorobiphenyls or Aroclor 1221, a commercial PCB mixture existing primarly of di- and monochlorinated biphenyls. The congeners present in Aroclor 1221 are considered as the expected final products of the reductive dechorination step of higher chlorinated PCBs. Due to the endogenous transformation by the natural microbial flora of intermediates produced by the introduced bacteria, toxic products accumulated which inhibit complete degradation.

On the other hand, the combination of both upper and lower pathways in one and the same strain lead to complete mineralization of the chlorinated biphenyls. These so-called bacterial hybrid strains were constructed in Wuppertal using the natural genetic engineering capacities of the bacteria. Plasmids and mobile elements carrying these degradation pathways were isolated and characterized by Mol and were used in the construction of the hybrid strains by exchange of the catabolic genetic material. The chlorobiphenyl catabolic diversity of the constructed hybrid strains was further expanded by selective pressure using none-utilizable chlorobiphenyl compounds as sole carbon source. The new strains were able to completely mineralize several mono- and dichlorinated biphenyls and most of the congeners present in Aroclor 1221 in liquid batch cultures, in continuous liquid bioreactors and in non-sterile soil. Mol also introduced metal resistance genes into the strains to degrade PCBs in mixed waste. Some of the strains were labeled with the *lux* reporter gene producing a light emitting phenotype to follow their behaviour in the soil.

In the last stage of the project, the compatibility of the different processes for integration in a combined process will be tested, either anaerobic biodegradation followed by aerobic degradation, either chemical dechlorination followed by aerobic biodegradation.

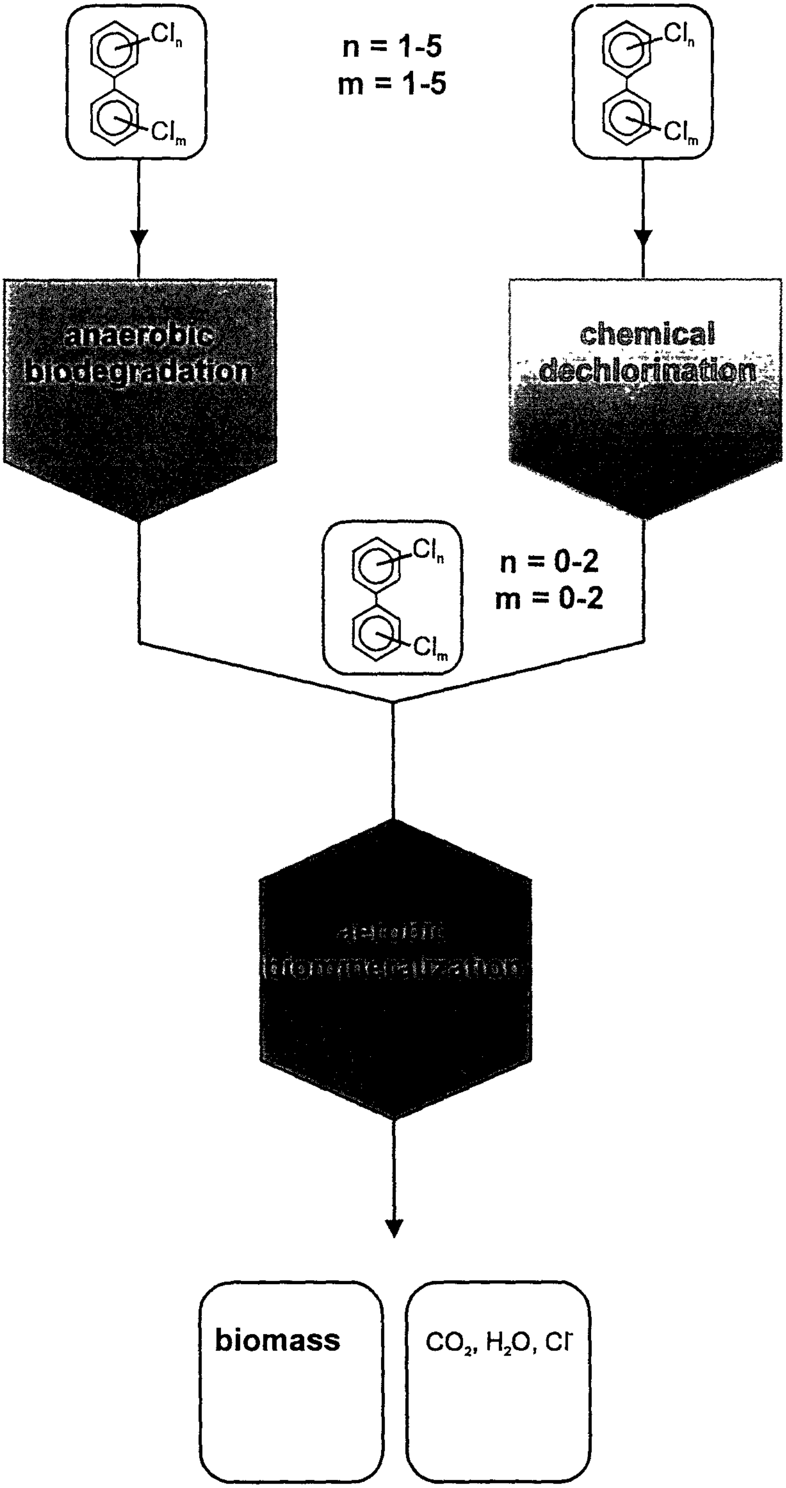


Fig. 1 : Sequential anaerobic/chemical - aerobic process for complete mineralization of PCBs.

Dechlorination of highly chlorinated PCBs: Microbial and chemical solutions (EC contract EV5V-CT92-0192).

Wageningen Agricultural University, Wageningen, The Netherlands : P. Middeldorp, J. de Wolf and G. Schraa.
Research School of Biosciences, Univ. of Kent, Canterbury, UK : G. Robinson, J. Stratford, M. Wright, S. Jackman & C. Knowles.

Sequential anaerobic-aerobic biodegradation of polychlorinated biphenyls (PCBs) is considered as an attractive process to clean-up PCB contaminated material. Complex mixtures of highly chlorinated biphenyls can be reductively dechlorinated by anaerobic microorganisms or by means of chemical dechlorination into lower chlorinated biphenyls (CBPs). The resulting mixture is primarly consisting of dichlorinated and monochlorinated CBPs and can be treated by aerobic biphenyl (BP) catabolic bacteria.

In Wageningen, microbial consortia were enriched from anaerobic PCB contaminated sediments. The microbial consortia showed the ability to reductively dechlorinate technical PCB mixtures as Aroclor 1260 and Aroclor 1242 under methanogenic conditions. Aroclor 1260 was converted to mainly tetra- and tri- chlorinated biphenyls. Aroclor 1242 was converted into tri-, di- and mono- chlorinated biphenyls. The incubation time for complete conversion ranged from 30 to 90 days. As the anaerobic degradation of PCBs was a slow process, a cost competitive chemical reductive dechlorination process was developed at the University of Kent. This method was based on the method of Liu & Schwarz[1]. In this process, PCBs are converted using an inert atmosphere at elevated temperature using titanocene dichloride as a catalyst in the presence of sodium borohydride and a catalytic amine. It was observed that Aroclor 1242 was mainly converted into mono-chlorinated biphenyls which should be easily mineralized by aerobic PCB dgrading bacteria. Dechlorination was completed after 24 hours.

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[1] Liu & Schwartz (1994) J. Org. Chem. 59: 940-942.

Mineralization of lower chlorinated biphenyls by aerobic microorganisms (EC Contract EV5V-CT92-0192).

Chemische Mikrobiologie, BUGH Wuppertal, Germany : J. Havel, H. Mokross, K. Englebert and W. Reineke.
Environmental Technology, VITO, Mol, Belgium : D. Springael, P. Dengis, A. Ryngaert, D. van der Lelie, M. Mergeay and L. Diels.

Sequential anaerobic-aerobic biodegradation of polychlorinated biphenyls (PCBs) is considered as an attractive process to clean-up PCB contaminated material. Complex mixtures of highly chlorinated biphenyls can be reductively dechlorinated by anaerobic microorganisms or by means of chemical dechlorination into lower chlorinated biphenyls (CBPs). The resulting mixture is primarly consisting of dichlorinated and monochlorinated CBPs and can be treated by aerobic biphenyl (BP) catabolic bacteria. However, most BP metabolizing strains are only able to convert CBP into their corresponding chlorobenzoates (CBAs) which are accumulated and finally inhibit biodegradation. The use of mixtures of different bacteria able to cope with as well CBPs as CBAs or bacteria which display a combination of both degradation capabilities is necessary for final complete mineralization of PCBs.

A selection of new aerobic PCB degrading bacteria were isolated at Wuppertal (Germany) able to grow on BP and CBPs with accumulation of chlorinated benzoates (upper pathway isolates). The transformation potential of CBPs and of possible intermediates by the new strains was examined. Other new strains were isolated able to use CBAs as sole carbon sources (lower pathway isolates). Mixtures of bacterial strains able to convert CBPs into CBAs and strains able to mineralize CBAs were tested in soil microcosms for complete mineralization of the CBPs or Aroclor 1221, a commercial PCB mixture existing primarly of di- and mono-CBPs. The congeners present in Aroclor 1221 are considered as the expected final products if the reductive dechlorination step of higher chlorinated PCBs. Due to the endogenous transformation by the natural microbial flora of intermediates produced by the introduced bacteria, toxic products accumulated which inhibit complete degradation.

On the other hand, the combination of both upper and lower pathways in one and the same strain lead to complete mineralization of the chlorinated biphenyls. These so-called bacterial hybrid strains were constructed in BUGH, Wuppertal using the natural genetic engineering capacities of the bacteria. Plasmids and mobile elements carrying these degradation pathways were isolated and characterized in VITO, Mol and were used in the construction of the hybrid strains by exchange of the catabolic genetic material. The chlorobiphenyl catabolic diversity of the constructed hybrid strains was further expanded by selective pressure using none-utilizable chlorobiphenyl compounds as sole carbon source. The new strains were able to completely mineralize several mono- and dichlorinated biphenyls and most of the congeners present in Aroclor 1221 in liquid batch cultures, in continuous liquid bioreactors and in non-sterile soil. VITO, Mol also introduced metal resistance genes into the strains to degrade PCBs in mixed waste. Some of the strains were labeled with the *lux* reporter gene producing a light emitting phenotype to follow their behaviour in the soil.

Dry Solid Reactors to Evaluate Biodegradation of Organic Pollutants in Soil

Van Houtven D , Carpels M ,Kinnaer, L., Elslander H., Hooyberghs L., Diels L.

Environmental Technology, Vlaamse Instelling voor Technologisch Onderzoek (VITO), Boeretang 200, B 2400 - MOL, Belgium

Microbial degradation of organic pollutants in soil is very oftenly tested in slurry test systems. The translation of these results into a working industrial process is still a matter of trial and error Especially these tests are done in liquid or slurry systems which is not always a real soil situation Therefore a new bench-scale test system was developed. This system meets the need for a larger scale and is a completely closed and fully controlled instrument that can be used to design full-scale bioreactor installations This Dry Solid Reactor (DSR) can be used to simulate all kinds of soil bioremediation systems like landfarming, bioventing, soil reactors, and slurry reactor systems

Three identical stainless steel, closed, batch reactors were built each with a total volume of 200 L. Soil volume can be up to 100 L or about 50 kg providing enough material to ensure noninteracting sampling A computer equipped with the LABVIEW program controls a number of functions and fulfills data acquisition. the reactor was first evaluated for the biodegradation of soil contaminated with mineral oil

The internal temperature of the reactor is PID (proportional-integral-differential) controlled through a duouble-wall circuit The inlet gasflow rate (oxygen, nitrogen, air) can be set or controlled with the carbon dioxide, oxygen or hydrocarbons concentration. The outlet of the gas can be automatically sampled and analyzed for hydrocarbons (via gas chromatography), oxygen, and carbon dioxide content. The solid phase can be sampled by an hydraulic system so that the reactor is openend only for a few seconds to ensure minimal interaction with the outside Nutrients, liquids, extra inocula etc can be automatically injected without perturbation of the system. The soil is mixed using special abrasion-free paddles, permitting also tests with dry sandy materials.

Tests were done to measure the optimal temperature, oxygen consumption, nutrient addition, pH, mixing frequency, air flow rate and percentage of dry matter. Also evaluations were done with bacterial inoculations in different situations (historically contaminated soils or soils contaminated by an accident) and different soil compositions. Also different bacterial cocktails could be tested and evaluated as well as the influence of the autochtonous population.

The use of the reactor is now extended to the testing of the biodegradation of PAHs, PCBs and other contaminats as well as to the biological treatment of dredging sludge especially for the removal of PAHs More results will be presented.

The development of composting systems for xenobiotic waste treatment and for the bioremediation of contaminated land

EV5V-CT92-0240

Coordinator: A.J. McCarthy

University of Liverpool
Department of Genetics and Microbiology
UK - L69 3BX Liverpool
Tel: +44-151.794.4413
Fax: +44-151.794.4401

The Development of Composting Systems for Xenobiotic Waste Treatment and for the Bioremediation of Contaminated Land

Contract No. EV5V-CT92-0240

Start date: 1st January 1993 Duration: 36 months

Participants

Dr Alan J McCarthy, Department of Genetics and Microbiology, University of Liverpool, Life Sciences Building, Liverpool, L69 3BX,
Telephone: 44 151 794 4413, Fax: 44 151 794 4401
Dr Terry Fermor, Horticulture Research International, Wellesbourne, Warwick, CV35 9EF, UK, Telephone: 44 789 470382, Fax: 44 789 470552
Dr Kirsten S Jørgensen, Finnish Environment Agency, PO Box 140, FIN-00251 Helsinki, Finland, Telephone: 358 0 40300851, Fax: 358 0 40300890
Dr Michel Penninckx, ULB, Institut Pasteur, 642 rue Engeland, 1180 Brussels, Belgium, Telephone: 32 2 373 3303, Fax: 32 2 373 3174
Professor Dr Ing T Schmitt, Fachgebiet Siedlungswasserwirtschaft, Gebaude 14, 67663 Kaiserslautern, Germany, Telephone: 49 631 205 2946, Fax: 49 631 205 3905
Dr Ognian Kostov, N Poushkarov Institute of Soil Science and Agro-ecology, Shossee Banya 7, 1080 Sofia, Bulgaria, Telephone: 359 2 247643, Fax: 359 2 248937

Main Objectives

To explore the use of composting processes for the biodegradation of chlorinated xenobiotics arising from the use of chlorophenols as biocides. To determine the nature of the halogenated material that results from sludges out of paper processing and evaluate its potential contribution to groundwater contamination. To characterise the microbial communities that mediate chlorophenol removal during composting and determine the fate of chlorophenols and their degradation products. To evaluate at laboratory, intermediate bioreactor and field-scale the use of compost matrices for both waste treatment and bioremediation.

Main Results

Chlorinated components of printing inks were identified as an important source of AOX in paper sludges and our analyses lead to the conclusion that alternatives to yellow inks in particular must be actively sought. Otherwise, we found that chlorinated cellulosic material was also an important source of AOX. Lysimeter experiments and model calculations showed that harmful AOX loads from paper sludges into groundwater can be excluded. Nevertheless, the potential for mobilisation of these xenobiotics by microbiological transformations exists. This supports the drive to develop chlorine-free bleaching in the paper industry.

Waste mushroom compost and animal manures are widely available as matrices for xenobiotic waste treatment and soil decontamination. Chlorophenols, and particularly pentachlorophenol (PCP), have been widely used as biocides and their recalcitrance has resulted in the persistence of contaminated sites where appreciable quantities of contaminated wood materials and soils exist. A wide range of experimental strategies was adopted to investigate chlorophenol removal by composting, with a number of analytical techniques applied to properly monitor the disappearance and fate of chlorophenols. In laboratory experiments, chlorophenol removal could readily be achieved by composting with various matrices under different conditions and across a wide range of chlorophenol concentrations. Mushroom compost could be conditioned to be reactive to added PCP, as determined by tests on $^{14}CO_2$ evolution from ^{14}C-PCP. In scaled-up experiments in 30 kg composting units under controlled conditions however, PCP mineralising activity was greatest with waste compost, for which no pre-conditioning requirement was found necessary. Animal manure composts in 0.5 m^3 units rapidly removed PCP from contaminated soil with good evidence for sequential reductive dechlorination.

At field-scale, PCP removal from contaminated woodchips was achieved within 20 days, with no PCP detected in leachates. At a Finnish sawmill site, $52m^3$ and $520m^3$ composting trials on chlorophenol contaminated soil and woodchips were conducted, and a number of variables applied. Again, chlorophenol removal was always efficient irrespective of the incorporation of mushroom compost in addition to bark chips as a bulking agent. Composts were reactive in converting ^{14}C-PCP to $^{14}CO_2$ indicating that mineralisation was the most significant contribution to chlorophenol disappearance. In all of the experiments, chloroanisole formation was minimal and always transitory. Furthermore, there was no evidence of chlorophenol polymerisation during composting of contaminated soil at the field site.

Analyses of the populations of microorganisms that developed during composting, revealed the expected diverse community structure. Despite the PCP mineralising activity of the compost microflora, none of the isolates were found to be capable of PCP conversion to CO_2 in pure culture. Various reactions were identified in pure culture including resistance to high concentrations of PCP in the absence of any transformation, PCP binding to microbial biomass, and conversion to water soluble but unidentified products.

It is concluded from this detailed and collaborative evaluation of composting technology that chlorophenols can be efficiently removed, that the nature of the compost matrix and process control parameters are not critical, and that mineralisation is significant without appreciable formation of recalcitrant transformation products.

Publications

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ABSTRACT

Background

In composts, the degradation of organic material is mediated by the activity of a diverse community of microorganisms. The degradative process is accelerated by careful adjustment of nutrient composition and particularly by ensuring the maintenance of an aerobic environment. Composts are used as soil conditioners and under controlled conditions, for the cultivation of edible fungi, but they also have potential as bioreactors for the removal of pollutants and xenobiotic residues from soils. This collaborative project aimed to evaluate composting as a strategy for the remediation of contaminated sites, targetting the chlorophenols as an important group of environmental contaminants. The hypothesis was that degradation of xenobiotics would be best achieved through the activities of such a microbial consortium and that composting is a cost effective, low technology process that can be applied universally. Rigorous analytical procedures were applied to define xenobiotics, monitor their fate and determine the parameters that influenced the degradative performance of the compost microflora. Of particular significance is the development of experiments from the laboratory to intermediate chambers and finally to field scale on-site, using different compost matrices and sources of contaminants. The requirement, if any, for manipulation of compost populations by pre-enrichment or inoculation to achieve significant decontamination was also addressed.

Analysis of xenobiotic contamination and mobilisation

Pentachlorophenol (PCP) has been listed as the 31st most hazardous substance in the U.S. Federal Register (1991) but was used extensively as a biocide in the 1970s. Over 80% of PCP manufactured was utilized in wood preservation, and it has also been applied as a preservative in the textile industry. Its recalcitrant nature has resulted in the contamination of soils and groundwater throughout the developed world and contamination levels as high as 1900 mg PCP per kg dry weight of soil have been recorded. We studied its degradation and fate in composting experiments where the chemical was added directly, or in the form of contaminated woodchips or soils obtained from a number of sites. In some cases, other chlorophenols were also present and their fate was similarly monitored. A range of pentachlorophenol concentrations were used in the experiments, with emphasis on those concentrations and parameters that are relevant to the real environmental situation. Gas chromatography was used as the primary analytical method for determination of chlorophenol disappearance and transformation, with monitoring by high performance liquid chromatography and scanning spectrophotometry in certain cases. In most experimental series, confirmation of pentachlorophenol mineralisation was provided by radiorespirometry with ^{14}C-labelled PCP as substrate. In addition to mineralisation, chlorophenols can be methylated, polymerised, incorporated into humic fractions, adsorbed or transformed abiotically and experiments were designed to take these reactions into account. The aim was to provide an evaluation of chlorophenol decontamination by composting that was as rigorous and therefore as unambiguous as possible.

Another major source of environmental contamination with chlorinated xenobiotics are residues from the paper industry, particularly sludges that originate from waste paper processing. These chlorinated organic compounds (measured as AOX) are of ill-defined structure and our emphasis here was to ascertain their chemical identity, specific sources and potential for groundwater contamination. Chlorinated components of printing inks were identified as an important source of AOX in paper sludges and a

comparative analysis revealed that of the four basic colours in general use, yellow inks account for the great majority of AOX. In view of the encouragement provided by governmental authorities to waste paper insertion, our calculations of the contribution of de-inking sludges provide a firm conclusion that alternatives to high AOX-containing yellow inks must be actively sought. The chlorine bleaching process is the other main contributor to paper sludge AOX, and chlorolignins are usually implicated as the primary pollutants. By applying differential solvent extraction and size exclusion chromatography, we have obtained good evidence that chlorinated cellulosic material is also an important source of AOX here. Since polymeric AOX compounds identified in all of the paper sludges analysed were found to be poorly soluble in water and a number of organic solvents, their penetration into groundwater and environmental impact is likely to be insignificant. We were able to confirm this with artificial lysimeters to which paper sludges were added at high AOX concentrations. Sand columns and high artificial rainwater application were used to maximise the potential mobility of pollutants. The levels of AOX detected in leachate over a 6-month period were such that when soil organic content and physico-chemical sorption effects are incorporated into the calculation, harmful AOX loads from paper sludges into groundwater can be excluded. However, there is the potential for microbiological transformation, and therefore mobilisation, of polymeric chlorinated organic carbon in composts and soils, and the ongoing emphasis on the development of chlorine-free bleaching in the paper industry should be maintained.

Chlorophenol removal by composting

The mushroom cultivation industry generates waste compost in substantial quantities, for example 760,000 tonnes per annum are produced in the Netherlands. In the U.K., 500,000 tonnes per annum are disposed of mainly to landfill, and waste mushroom compost can therefore be regarded as a widely available matrix for application to land remediation. For xenobiotic degradation, it has the potential to provide a community of degradative organisms, a nutrient enhancement for indigenous degraders and an improvement in soil fertility for plant colonisation of sites.

Experiments initially aimed to demonstrate that chlorophenol removal could be achieved with mushroom compost. The scale varied from flasks containing a few grams of compost, to apparatus in which up to 1 kg. of compost was incubated under conditions of controlled temperature, humidity and aeration. In these laboratory scale experiments, disappearance of added chlorophenols was observed, typically in the range 500-9000 mg PCP per kg. compost and within a timescale of ca. 5 weeks. We were encouraged to discover that chlorophenol disappearance was promoted at mesophilic (30-37^{o}C) rather than thermophilic (50^{o}C) temperatures, and that compost from the later stages of the production cycle was more efficacious. In later laboratory experiments with PCP contaminated soil from a U.K. site, we were also able to demonstrate PCP disappearance by incubation with mushroom composts at 15^{o}C, albeit at a reduced rate. Determination of the fate of pentachlorophenol during composting and sequential scale-up of the process were identified as our priorities.

Composting units.

Early experiments in which ^{14}C-labelled PCP was added to mushroom compost demonstrated little or no indigenous mineralisation activity. However, when mushroom compost was incubated in a column and percolated with PCP for three months, a compost that was highly reactive to added ^{14}C PCP (56% conversion to $^{14}CO_2$ in 25 days) could be produced. The requirement for preconditioning or enrichment of compost for chlorophenol degradation was investigated in composting units containing 30 kg compost with incubation temperature controlled at 30°C and constant sparging with humidified air to maintain biological activity. Waste compost (before and after pasteurisation) and compost from Phase 2 of the production cycle were spiked with sodium pentachlorophenate (500 mg kg^{-1}) and incubated for 12 weeks with sampling at intervals. Although, pentachlorophenol recovery efficiency was low, PCP and contaminating tetrachlorophenol concentrations as determined by gas chromatography, decreased dramatically, especially during the first two weeks. Small amounts of anisoles, indicating methylation of the PCP, were detected in the early stages of composting (1-3 weeks) but had disappeared after 12 weeks. No other degradation or transformation intermediates were detected. Of greater significance however, were the data on PCP mineralisation capacity of the composts as determined ny measurement of $^{14}CO_2$ evolution in ^{14}C-PCP challenge tests. The data are summarised in Table1 and show a clear enrichment effect for pasteurised waste and Phase 2 compost, but not for unpasteurised waste compost. We were also encouraged by the superior PCP mineralisation performance of the waste composts over Phase 2 composts. Incubation of sterilised composts with Na-PCP did not induce any mineralisation activity.

Table 1 PCP-mineralising capacity of different mushroom compost preparations

Compost preparation	Pre-incubation with PCP	Conversion of ^{14}C-PCP to $^{14}CO_2$ (%)
Phase II compost	+ -	16 1
Waste Compost	+ -	56 50
Waste Compost (pasteurised)	+ -	52 0

Composts were pre-incubated with or without 500 mg kg^{-1} sodium PCP for 12 weeks at 30-40°C. Compost samples (10g) were spiked with uniformly labelled ^{14}C-PCP (total PCP concentration 50 mg kg^{-1}), incubated for 1 week at 30°C with evolved CO_2 trapped in 5 M KOH and analysed by scintillation counting. The results are means of duplicates. Controls comprised sterilised composts spiked with ^{14}C-PCP and composts incubated in the absence of ^{14}C-PCP.

In certain regions, animal manures are available in large quantities for potential applications in composting. We used a 0.5 m^3 horticultural compost bioreactor loaded with a mixture of cattle manure compost and contaminated soil (212 mg PCP per kg dry weight) from a Finnish saw mill site. Gas chromatographic analysis revealed 95% disappearance of PCP within 3 days, and good evidence for extensive degradative activity was provided by the sequential appearance and disappearance of tetra-, tri- and di-chlorophenols over a 6-day composting period. This demonstrates that cattle manure compost can be used to remove PCP from contaminated soil by reductive dechlorination.

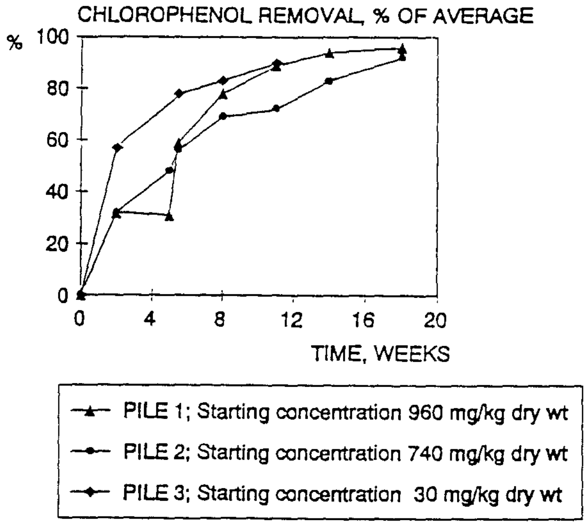
Large-scale composting trials.
These were directed towards the treatment of contaminated woodchips using animal manure compost in Belgium, and pilot and full-scale composting of contaminated soil and woodchips at a Finnish saw mill site where ca. 25 tons of a chlorophenol-containing wood preservative (Ky-5) had been used from 1955-1977 to impregnate wood..

The compost bioreactor used above to decontaminate soil was also applied to the composting of milled wood impregnated with PCP/cresote. After 15 days, PCP was undetectable (<5ppm) from an initial concentration of 103 mg per kg. compost. This was scaled up to $3m^3$ with two tonnes of manure compost (20% horse, 80% cattle) intimately mixed with 8.5 kg milled wood impregnated with PCP/cresote. The compost was turned at approximately 10 day intervals and temperature, nutrient staus and pH monitored. In two independent experiments conducted in this way, PCP concentrations decreased in an approximately linear manner from 100 to zero ppm in 20 days. PCP was not detected in the leachates.

At the Finnish sawmill site, four 13 m^3 compost piles were constructed with chlorophenol contaminated soil , pine bark chips as bulking agent and N-P-K fertiliser. A range of parameters were monitored including indicators of biological activity (respiration rates) and temperature. Within two months, 80% of the chlorophenols were removed to detectable levels of < 10mg kg dry weight^{-1}. Chloroanisole levels were low (0.1 - 2.4 mg kg dry weight^{-1}) and decreased to< 0.1 mg kg dry weight^{-1} after 5 months. The addition of PCP contaminated wood chips to one of the piles only served to introduce a lag to the chlorophenol removal rate, and the composts were responsive to further additions of contaminated soil. Parallel experiments at 1 kg bench-scale with ^{14}C-PCP indicated that a major proportion of the chlorophenols were being mineralized. Analysis of the molecular weight distribution of the organochlorine fraction of the compost also demonstrated that chlorophenol polymerisation was not occurring. However, the most striking observation was that the rate of removal of chlorophenols was not enhanced by the addition of mushroom compost nor of previously composted contaminated soil. Therefore, it is concluded that in this case chlorophenol removal is mediated by the indigenous microbial population of contaminated soil, whose activity is stimulated by the composting procedure.

It proved possible to further scale-up the composting of contaminated soil by constructing three windrows of total size 520 m^3. The pH was adjusted to neutral, nutrients were added and the piles aerated by mixing at three-week intervals. The highest average temperature in the piles was ca. 30°C. The results are presented in Fig.1, where the removal of chlorophenols in less than 5 months, over a range of starting concentrations is demonstrated. In fact, the degradation rate was higher than in the pilot study discussed above. Again, mushroom compost (piles 2 and 3) was comparable to bark chips (pile 1) as a bulking agent, but otherwise had no stimulatory effect on the rate of chlorophenol removal.

Fig. 1 **Mean chlorophenol removal from field scale composting of contaminated soil.**



Chlorophenol-degrading microorganisms

In the experiments described above, microbial consortia present in contaminated soils and composts were shown to be capable of degrading chlorophenols during composting processes. These consortia would be expected to contain species that can mineralise chlorophenols, species that can mediate transformation reactions and species that are merely resistant to high chlorophenol concentrations. Analyses of populations that developed across the range of composting experiments provided examples of all of these. Efficient chlorophenol-degrading bacteria have been described previously, and although their recovery, identification and characterisation was not a prioirity here, a number of isolates were obtained. Significant mineralisation of ^{14}C-PCP to $^{14}CO_2$ was not observed in any pure cultures of these isolates. Thus, although PCP mineralising activity was readily demonstrable in compost, this could not be equated with the activity of any key species identified by screening isolates in the laboratory. This is an emerging theme in environmental microbiology i.e. the degradative activity of isolates is a poor reflection of *in situ* activity mediated by microbial communities.

Studies on the diversity of microbial populations in composts to which PCP had been added, and subsequent study of their activity produced data that emphasised the need to determine the fate of xenobiotics. Large populations of fluorescent pseudomonads often developed in mushroom compost, and not only was there no ensuing evidence that they could degrade PCP, but they were able to bind PCP and therefore potentially affect its bioavailability. Screening studies on compost actinomycetes consistently identified *Saccharomonospora viridis* as an organism that could remove PCP from liquid cultures and from inoculated sterilised composts. Strains of this species could not attack any other chlorophenols, nor mineralise PCP, nor produce identifiable intermediates or transformation products such as chloroanisoles. *Saccharomonospra viridis* does however convert ^{14}C-PCP to a compound that is water-soluble and non-extractable in solvents, which if not further metabolised by other species, could represent xeniobiotic mobilisation.

Conclusions

- chlorophenols can be efficiently removed from contaminated soils and materials by composting

- chlorophenol removal can be achieved at laboratory and field scale, and in compost bioreactors

- chlorophenol removal is not significantly affected by the nature of the compost matrix and is a relatively robust process

- composts that have been exposed to pentachlorophenol exhibit reductive dechlorination and PCP mineralising activity

- formation of chloroanisoles is transitory and there is no evidence of polymerisation of chlorophenols during composting of contaminated soil

- the microbial communities responsible for chlorophenol removal are diverse and comprise species that mediate a range of physical and chemical transformations in pure culture

- efficient PCP mineralising activity demonstrable in different compost matrices was not observed in any of the pure cultures of microorganisms isolated

- yellow printing inks are an important source of chlorinated material in paper sludges

- the chlorinated constituents of paper sludges are largely polymeric and not significantly leached into groundwater

Bioremediation of chlorophenol-contaminated soil by composting in full-scale

M. Minna Laine and Kirsten S. Jørgensen
Finnish Environment Agency, Laboratory, Hakuninmaantie 4-6, Helsinki, FINLAND

The main objective for this study was to apply results from previous laboratory and pilot scale studies for a full scale bioremediation (520 m^3) of chlorophenol-contaminated soil. The aim was to test the applicability of using mushroom compost as an inoculum in comparison to addition of bark chips and nutrients to the contaminated soil. Several physico-chemical and microbiological parameters were followed during the composting.

The composting was performed in three windrows and the ratio of the materials was two parts of contaminated soil and one part of inoculum and/or bark by volume. The highest average temperature in compost piles was around 30°C. The temperature in the piles kept at least 6°C above the ambient day temperature during the composting even when the outdoor temperature was below 3°C.

The composting of chlorophenol-contaminated soil resulted in 92 to 96% removal of chlorophenols in 126 days with a starting chlorophenol concentrations of 740 and 960 mg (kg dry weight)$^{-1}$ in piles 2 and 1, respectively. A third pile was later constructed and 90% of the chlorophenols were removed in 87 days with a starting concentration of 29 mg (kg dry weight)$^{-1}$. According to the results of our laboratory experiments (*1*) and of the field test in pilot scale (4 x 13 m^3) (*2*), the mechanism of chlorophenol removal was complete mineralization without harmful side reactions as (bio)methylation or polymerization. The removal rates calculated as concentration of chlorophenols depleted per time were 7.3 and 5.4 mg (kg dry wt)$^{-1}$ d^{-1} in full scale piles 1 and 2, respectively. Thus, the pile inoculated with mushroom compost (pile 2) showed lower degradation rate that the pile where only bark chips had been added (pile 1).

As a conclusion, during the full scale composting of chlorophenol-contaminated soil, more than 90% chlorophenols were removed in less than five months. The chlorophenol degradation was fast regardless the high starting concentration of chlorophenols up to 960 mg (kg dry wt)$^{-1}$. The use of mushroom compost as inoculum did not enhance the chlorophenol degradation rate in comparison to addition of bark chips to the contaminated soil. Frequent mixing and control of the nutrient level enhanced the chlorophenol degradation activity of the indigenous microbes in the contaminated soil. The use of mushroom compost as inoculum may, however, be useful when composting soil without a chlorophenol degradation potential.

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Bioremediation of olive-mill wastes for use as fertilizer

EVWA-CT92-0006

Coordinator: N.J. Russel

University of Wales Cadiff
GB-CF1 3US Cadiff Wales
Tel: +44.1222.874120
Fax: +44.1222.874116

BIOREMEDIATION OF OLIVE-MILL WASTES FOR USE AS FERTILIZER

BALIS C., CHATJIPAVLIDIS J., FLOURI F. AND DIMOU D.

Laboratory of Microbiology, General and Agricultural, Agricultural University of Athens, Iera Odos 75, 118 55 Athens, Greece

ABSTRACT

Method for the biological processing of olive mills liquid wastes (OMWW) for the prepartion of a product suitable for agricultural use.

The method exploits the OMWW as microbial substrate for the cultivation of dinitrogen fixing microorganisms (*Azotobacter vinelandii*) capable to transforming the material into an organic liquid of high fertilizing and soil conditioning value.

The results which obtained from the application of bio-fertilizer on cultures (olive trees, vines and potatoes) was very optimist.

INTRODUCTION

Messinia (Fig. 1) is one of the major olive oil centers of Greece. It produces about 30,000 tone olive oil per year that amounts to about 14% of the total production in the country. The cultivars of olive trees that are dominant in the Messinia are: Kalamon, Koroneiki, Mastoedis and Mavrelia. The "Kalamon" one is exclusively cultivated for table olives, all the others for oil production. The olive oil extraction process in Messinia starts in around the end of October and is completed by the end of January or middle of February.

Fig. 2 shows the olive oil production in four districts of Messinia along with the number of the olive oil mills and the volumes of OMWW that are generated during their operation.

The 68% of total volume of OMWW is discharged indirectly into the Messinian Gulf all the rest in the Ionion Sea.

The bio-fertilization pilot plant was installed at Romanos, near Pylos, in Messinia.

The bio-fertilization pilot plant was installed at Romanos, near Pylos, in Messinia.

METHODOLOGY

Research studies on the microbiological and biochemical features of the olive oil mills waste water (OMWW) in our laboratory during the last ten years, lead us to the development of an alternative methodology for their valorization.

Due to their characteristic composition, OMWW constitute a rich and highly selective nutrient medium favoring the proliferation of free living N_2-fixing bacteria of the genus *Azotobacter*.

Operational characteristic of the system.

During processing the OMWW goes through the following two stages: (Fig. 3)

- Pre-treatment with hydrogen peroxide under alkaline conditions and,
- Bioconversion by a nitrogen-fixing microbial consortium under well aerated conditions.

In phase I the material is treated at first with calcium hydroxide to increase the pH to up 11-12 (<1% CaO) and then with a hydrogen peroxide solution at a rate of 0.5-1% (depending on the organic load). The mixing process is carried out in a tank equipped with a suitable mechanical stirring system.

In the second phase, the mixture after 6-12 h in the stirring tank (during which the pH is stabilized by itself at about 8.0) is transferred into the bio-reactor where an enriched diazotrophic microbial consortium is already established (*Azotobacter vinelandii*, strain A and others) (Chatjipavlidis *et al.*, 1994).

The bio-reactor consists of a tank equipped with an air-conducting system.

The process can be a repeated fed batch cultures with residence time that can be adjusted from 3 to 7 days according to the expected use of the final product.

During this phase:

- a strong nitrogen fixing activity is manifested
- the OMWW phytotoxic constituents are bio-degraded
- microbial exopolysaccharides are produced in large amounts
- the microorganisms produce growth promoting factors (auxins, etc.)
- the microbial populations and their metabolites enhance soil suppressiveness against soil born fungal root pathogens such as *Pythium* and *Phytophthora* spp.

Product and uses.

The product is a thick, yellow in color, non phytotoxic liquid, with a pH about 7.5 - 8.0 (Table 1). It is characterized as "**organic soil-conditioner bio-fertilizer in liquid form**" with the following characteristics:

-The **exopolysaccharides** that are present favor the formation of stable soil aggregates and thus contributes to the improvement of soil thilth and structure (Flouri *et al.*, 1990).

- It contains almost all the **major and trace plant nutrients** that were contained originally in the olive fruits and passed into the water fraction of the wastes.

- It is **biologically enriched with organic forms of nitrogen** through the mechanism of N_2-fixation at the expenses of the carbon sources of the wastes (sugars, organic acids, phenolic compounds, etc.), and with plant growth promoting factors (auxins, cytokinins) (Rubenchik 1963).

- It constitutes a **soil microbial inoculant** that allows the establishment of favorable to plants rhizospheric microorganisms, and enhances **soil suppressiveness** (Meshram 1984, Flouri *et al.*, 1990).

The product can be used as an organic fertilizer by mixing it at any proportion with the irrigation water, and at high doses as a soil conditioner.

The pilot plant unit.

The unit of bio-fertilization which was constructed to our specifications by "D. Callis and Son S.A." was installed at Romanos (Messinia).

Pre-treatment tank: 3.2 m^3 equipped with a stirring mechanism.

Bio-reactor: working volume of about 5.5 m^3. The air conductor is divided in five triangular boxes filled with hollow lengths (5 cm) of plastic tubing (Φ=5cm) offering an active surface area of 205 m^2 . The air conductor revolves a rate of 7 RPM.

For the inoculation and the establishment of the desirable microbial population, *Azotobacter vinelandii* (strain A) was used. The system of repeated fed batch culture with a rate of 1.7 m^3/3 days was adopted. During operation, after each new addition of fresh raw material, the nitrogen fixation (Hardy *et al.*, 1973) and phytotoxicity (Zucconi *et al.*, 1981) were monitored.

The course of N_2-fixation is shown in Fig. 4.

Phytotoxicity was particular high in the fresh raw material (germination index=0) but it diminished appreciably within a short period (about 3 days) of processing in the bio-reactor (germination index=104%).

Biofertilization trials

The biofertilization efficiency of the product was examined in field trials with olives, vines and potato (Table 2).

Olive grove

The experimental plan included 4 random group of 4 trees. That is: 4 replication x 4 trees x 3 treatments (bio-fertilizer, chemical fertilizer and control) = 48 olive trees.

Variety : Mavrelia

Bio-fertilizer : 100 kg/trees

Chem. fertilizer : 11-15-15, 4 kg/tree and ammonium sulfate 1.2 kg/tree.

No phytoxicity symptoms were detected in any of the trees (Table 3). Moreover yields of the bio-fertilizer and the chemical fertilizer series were comparable.

Vineyard

The experimental plan for the vineyard was similar to the olive grove: 4 replications x 4 vines x 3 treatments (bio-fertilizer, chemical fertilizer and control) = 48 vines.

Variety : Currant

Bio-fertilizer : 7.5 kg/vine

Chemical fertilizer : 11-15-15, 400 g/vine

The results (Table 4) show that in vineyard higher yields were obtained in the bio-fertilizer series than the control and chemical fertilizer ones.

No differences were noticed in sugar content and pH of the grapes juice (Table 5).

Potato field

The field trial was carried out in four replicate plots (2m x 5m).

The various treatments that were administered are presented in Table 6 along with the results

Each experimental plot had 48 potato plants.

Variety: Spunda.

In all cases the addition of the bio-fertilizer had no adverse effects. On the contrary all plots treated with bio-fertilizer at a rate of about 2 L/ plot gave higher yields (Table 6).

DISCUSSION

The pilot plant for bio-fertilization of OMWW which was installed in Messinia had as major target to produce an adequate amount of bio-fertilizer sufficient to cover the needs of field trials.

During the process was found that the air-conductor performed quite well in supplying air to the microbial population and in homogenizating the substrate. This enabled us to diminish the residence time from seven days to three.

Although the results are limited to one cultivating period, three cultivations and one type of soil, are altogether encouraging and considering its fertilization value and its remediated organic load the product is rendered particularly useful for the exhausted Mediterranean soils and offers perhaps a valuable tool in developing a "**sustainable**" agriculture system.

Further work is on the way in order to determine the optimal dose for various plants and soil types.

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Table 1. Characteristics of the fresh raw material and the end product (bio-fertilizer).

Characteristics	Raw material	Bio-fertilizer
Total Organic Carbon (mg/L)	40,250	37,600
Total Nitrogen (mg/L)	1,360	1,642
Total Solids (%)	8.9	9.6
pH	5.4	7.9
Conductivity (μs/cm)	10,000	18,000
PO_4^{-3} (mg/L)	423	550
K^+ (mg/L)	6,100	6,350
Germination index (dilution 25%)	0	104

Table 2. Soil characteristics of experimental field.

Soil characteristics	Olive grove	Vineyard	Potato field
Type of soil	sandy - clay	sandy - clay	sandy - clay
pH	4.60	5.80	5.500
$CaCO_3$	0.06	0.06	0.008
Total carbon (%)	2.10	2.00	0.700
Total nitrogen (%)	0.16	0.18	0.060
PO_4^{-3} (ppm)	1.30	0.74	2.300
K^+ (ppm)	12.20	11.40	12.100
Na^+ (ppm)	12.60	16.10	18.400

Table 3. Effect of bio-fertilization on Olive fruit production.

Replications	Average yield (kg/tree)		
	Bio-fertilizer	Chem. fertilizer	Control
A	81.7	108.0	___
B	86.3	77.5	83.3
C	92.1	89.0	95.3
D	78.0	72.7	64.3
Aver. value	**84.5**	**86.8**	**81.0**
Stand. deviation	± 6.1	± 15.7	± 15.6

Table 4. Effect of bio-fertilization on vines production.

Treatments	Bio-fertilizer		Chem. fertilizer		Control	
Replications	Num. of grapes / vine	Yield kg / vine	Num. of grapes / vine	Yield kg / vine	Num. of grapes / vine	Yield kg / vine
A	47.50	8.81	49.30	7.80	43.30	6.00
B	49.75	8.25	39.80	5.90	42.00	6.30
C	41.00	7.00	42.00	6.25	33.67	5.33
D	39.50	5.38	33.00	5.00	42.00	6.13
Aver. value	**44.44**	**7.36**	**41.03**	**6.24**	**40.24**	**5.94**
Stand.dev.	± 4.96	± 1.52	± 6.72	± 1.17	± 4.42	± 0.42

Table 5. Effect of bio-fertilization on sugars content and acidity of grapes juice.

Treatments	Bio-fertilizer		Chem. fertilizer		Control	
Replications	BRIX	pH	BRIX	pH	BRIX	pH
A	25.53	3.45	27.00	3.20	24.70	3.20
B	25.23	3.30	25.70	3.20	26.30	3.50
C	27.50	3.23	25.88	3.23	26.57	3.23
D	26.03	3.20	26.87	3.20	26.80	3.28
Aver. value	**26.07**	**3.30**	**26.36**	**3.21**	**26.09**	**3.30**
Stand.dev.	± 1.01	± 0.11	± 0.67	± 0.01	± 0.95	± 0.14

Table 6. Field trial of remediated OMWW on potatoes.
(Experimental plots = 2m x 5m).

TREATMENTS	**YIELD Kg /PLOT**
A= Surface fertilization at rate 0,165 kg/plot ammonium nitrate x 3 times	**33.75** ± 4.25
B= As in A+1 L Bioremediated OMWW x 3 times.	**31.38** ± 5.19
C= As in A+2 L Bioremediated OMWW x 3 times.	**37.38** ± 3.94
D= As in A+3 L Bioremediated OMWW x 3 times.	**32.50** ± 5.63
S= Basic fertilization with phosphate and potassium at rate 0.5kg/plot for each element respectively. Three surface application with 0.165kg/plot ammonium nitrate.	**33.20** ± 5.78
H= As in S+1 L Bioremediated x 3 times.	**37.25** ± 4.63
M= Control (No treatments)	**30.75** ± 3.94

Fig. 1. Map of Greece

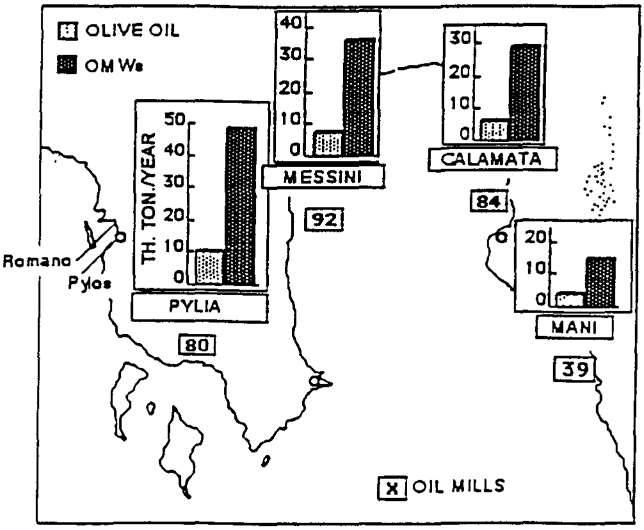

Fig. 2. Olive oil production, distribution of oil mills and volumes of effluents in four districts of Messinia.

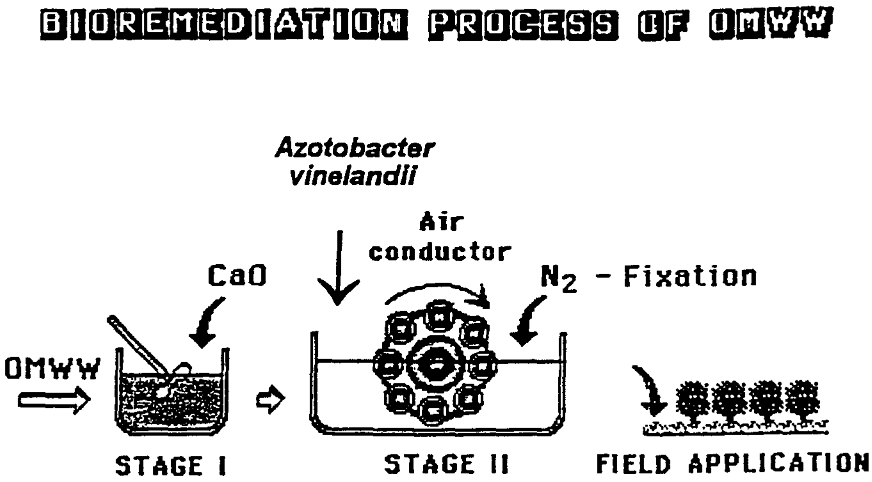

Fig. 3. Schematic diagram of diazotrophic bioremediation process of OMWW.

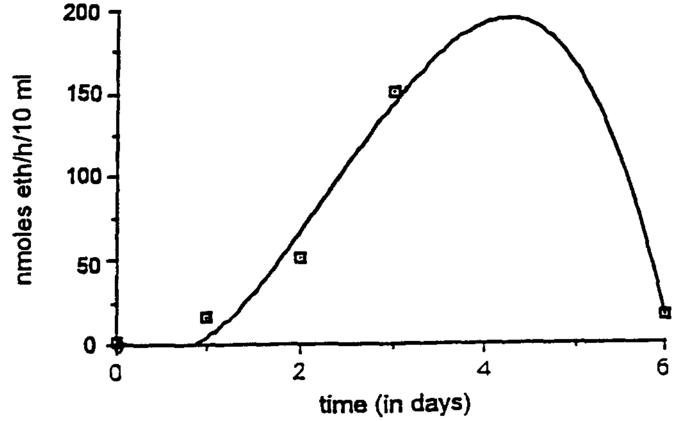

Fig. 4. Time course of N_2-fixation.

A network for industrially contaminated land in Europe (NICOLE)

ENV4-CT95-0082

Coordinator: D.A. Laidler

ICI Research & Technology Centre
UK - WA7 4QD Cheshire
Tel: +44-1928.511521
Fax: +44-1928.581864

NICOLE

A Network for Industrially Contaminated Land in Europe

(co-funded by the CEC)

Contract N°: ENV4 - CT95 - 0082

Start Date: 1 February 1996

Duration: 36 months

NETWORK COORDINATOR

Dr Dale A Laidler
ICI Research & Technology Centre
PO Box 8
The Heath
Runcorn
Cheshire WA7 4QD
UK

Tel: +44 1928 511521
Fax: +44 1928 581864

NETWORK SECRETARIAT

Mr H Johan van Veen
TNO Institute of Environmental Sciences, Energy Research & Process Innovation
PO Box 342
7300 AH Apeldoorn
Netherlands

Tel. +31 55 5493 927
Fax: +31 55 5493 410

NETWORK PARTNERS

Name	Affiliation	~~Name~~
ENEL SpA	Eng Giuseppe Frego	Italy
Institut Recherche de Hydrologique	Dr Michel Jauzein	France
Nottingham Trent University	Dr Paul Bardos	UK
Port of Rotterdam	Ir Cees Buijs	Netherlands
Repsol Petroleo SA	Dr Manuel Bravo	Spain
Solvay SA	Mrs Patricia de Bruycker	Belgium
TNO-MEP	Dr Henk Leenaers	Netherlands
Universite de Technologie de Compiegne	Professor Jean-Michel Lebeault	France
University of Reading	Professor Brian Alloway	UK
Usinor-Sacolor SA	Dr Francis Klein	France

NICOLE

A Network for Industrially Contaminated Land in Europe

(co-funded by the CEC)

Introduction

European manufacturing industry in particular and European society in general, has the prospect of responding to problems arising from the contamination of soil and groundwater due to diverse and largely historical industrial activity. The problem exists throughout all industrial regions of Europe and is an expensive problem that is expected to extend well into the next millenium. It is characterised by its highly multidisciplinary nature and the need for European industry to become better informed of methods for identifying, assessing and managing its solution. In general, these capabilities lie within the academic and related research communities.

The need to create a forum for the interaction of the problem holders and those well placed to help them has been recognised. NICOLE is such a forum.

Aims of NICOLE

- To provide a European network for the dissemination and exchange of scientific and technological knowledge and ideas relating to all aspects of contaminated land (soil and groundwater) arising from industrial activities
- To promote coordinated, multi-disciplinary collaborative research that will enable European manufacturing and processing industry to efficiently and cost-effectively identify, assess and manage contaminated sites
- To inform planners of National and European research programmes of priorities for future research and to improve the synergy and coordination of research being carried out in EU programmes and other initiatives at European and National levels

Benefits of NICOLE

◆ *For European Industry*	an improved understanding of the underpinning scientific and technological principles that will guide its response to this important environmental issue
◆ *For European Acadamy*	improved contacts between academics and industry and opportunities for initiating new collaborative research aimed at solving real problems
◆ *For Research Programme Planners*	a consultative forum to advise on future research priorities
◆ *For European Society*	a more rapid and better response to a potentially serious environmental problem.

Nicole Coordination:
Dr Dale A. Laidler
ICI Research & Technology Centre
P.O. Box 8, The Heath, Runcorn,
Cheshire, WA7 4QD, UK
Tel : +44-1928-511521, Fax: +44-1928-581864

Nicole Secretariat:
H J.van Veen and M. Euser
TNO-MEP
P.O Box 342, 7300 AH Apeldoorn, NL
Tel +31-55-5493 927, Fax: +31-55-5493 410
E-mail: m euser@mep.tno nl

Membership of NICOLE

NICOLE is a forum for problem holders, research performers, technology developers end research planners. Membership of NICOLE is open to individuals and organisations which fulfill the following criteria:

- Industrial manufacturing companies which have potential contaminated land problems and the need to become better informed of the scientific and technological issues
- Academic and independent research organisations with demonstrable relevant programmes of research that can be discussed in the open forum of the network
- Representatives of National and EU research programmes who have responsibilities for planning and funding contaminated land research
- Technology developers or service providers who undertake demonstrable research or development activities that they are willing to discuss in the open forum of the network
- National and European Industrial Trade Associations whose members (particularly their SME members) need to be made aware of contaminated land issues

NICOLE has the target of involving at least 50 companies representing a range of diverse industrial sectors and of involving representatives of all relevant current EU-funded research projects.

NICOLE is <u>strictly</u> intended as a forum for the discussion and exchange of research results and ideas, Network members <u>may not</u> participate for commercial benefit.

Funding

NICOLE is dual funded through the EU Environment & Climate RTD Programme and participant subscriptions.

Problem owning companies, technology developers, service providers and trade associations will pay a fee of 10,000 ECU for a 3 year membership. Companies from East European countries may pay only 5,000 ECU.

Academic researchers and research funding bodies may participate without a subscription cost.

The network cannot fund the participation of any organisation.

Concerted action on risk assessment for contaminated land (CARACAS)

ENV4-CT95-0095

Coordinator: V. Franzius

Umweltbundesamt
D - 14191 Berlin
Tel: +49-30.8903.2496
Fax: +49-30.8903.2285

Title of project. **Concerted Action on risk assessment for contaminated land - CARACAS**

Project number: **ENV4-CT95-0095**

Starting date: **1.2.1996** Duration: **30 months**

Topic Group Leaders (= Scientific Core Group):

Prof. Colin FERGUSON, The Nottingham Trent University-CRBE
Burton Street, GB-NG1 4BU Nottingham, UNITED KINGDOM
Tel : +44-1159-486 888, Fax· +44-1159-486 510, e-mail: cbe3nathacp@ntu.ac.uk
[Leader of Topic Group 1 "HUMAN TOXICOLOGY" and Chairman of the Core Group]

Prof. Dr. Dag BROMAN, University of Stockholm
Department of Zoology, S-10691 Stockholm, SWEDEN
Tel.· +46-8-164 018, Fax: +46-8-67 47 199, e-mail: Dag.Broman@zoologi.su.se
[Leader of Topic Group 2 "ECOLOGICAL RISK ASSESSMENT"]

Dr. Bjorn Kaare JENSEN, VKI-Water Quality Institute
Agern Alle 11, DK-2970 Horsholm, DENMARK
Tel.: +45-42-86 52 11, Fax: +45-42-86 72 73, e-mail: bkj@vki.dk
[Leader of Topic Group 3 "FATE AND TRANSPORT OF CONTAMINANTS"]

Dr. Dominique DARMENDRAIL, BRGM
Fort de Lezennes, F-59260 Lezennes, FRANCE
Tel.: +33-20-19 15 40, Fax: +33-20-67 05 56, e-mail: p.charbonnier@brgm.fr
[Leader of Topic Group 4 "SITE INVESTIGATION AND ANALYSIS"]

Dr. Karin FREIER, Umweltbundesamt
Postfach 33 00 22, D-14191 Berlin, GERMANY
Tel.: +49-30-8903-20 08, Fax: +49-30-8903-22 85
[Leader of Topic Group 5 "MODELS"]

Dr. Arantzazu URZELAI, IHOBE, S.A.
Viceconsejeria de Medio Ambiente; Ibanez de Bilbao, 28 - 8, E-48009 Bilbao, SPAIN
Tel.: +34-4-423 0743, Fax: +34-4-423 5900, e-mail: SL 000001@sarenet.es
[Leader of Topic Group 6 "SCREENING AND GUIDELINE VALUES"]

Dr. Joop J. VEGTER, The Technical Committee on Soil Protection
P O. Box 30947; Willen Witsenplein 6, NL-2500 GX Den Haag, NETHERLANDS
Tel.: +31-70-339 3034, Fax: +31-70-339 1342
[Leader of Topic Group 7 "METHODS FOR RISK ASSESSMENT"]

CARACAS - Coordinator: Dipl Ing. H. **KASAMAS**, CARACAS-Office, A-1120 Vienna
Tel· +43.1.804 93 192, Fax: +43.1.804 93 194
e-mail: 101355.1520@compuserve com

MAIN OBJECTIVES:

The primary objectives of the Concerted Action on Risk Assessment for Contaminated Sites - CARACAS are:

- to identify, compile, assess and review all relevant RTD projects and scientific approaches for risk assessment developed in the Member States of the European Union;
- to propose scientific priorities for future programmes and projects of the European Commission and the EU-Member States;
- to elaborate guidelines and recommendations for assessing risk of contaminated sites.

The Partnership:

The Concerted Action CARACAS will be carried out by participants from 14 Member States of the European Union: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, the Netherlands, Portugal, Spain, Sweden, the United Kingdom. Each of these Member States is represented by the national Environment Ministry and one or two scientific institutions.

Additionally, countries like Norway, Switzerland, the United States, and Australia will contribute with their experience and knowledge to the scientific programme of CARACAS.

RESULTS:

- **First meeting of the CARACAS-Coordination Group:** The inaugural meeting of the CARACAS-Coordination Group (40 participants) took place in Brussels on 28th and 29th of March, 1996. At this meeting the CARACAS-participants specified the scientific programme and formed seven scientific topic groups regarding

  - human toxicology
  - ecological risk assessment
  - fate and transport of contaminants
  - site investigation and analysis
  - models
  - screening/guideline values
  - methods for risk assessment

- **Working Plan/Key Issue Papers of Topic Groups:** Every Topic Group described the scope of its work in a one page "Key Issue Paper".

PUBLICATIONS:

Hans-Joachim Stietzel, Harald Kasamas (1996) *"New Initiatives for Co-operation in the European Union regarding Contaminated Land"*, NATO/CCMS-Pilot Study on *"Evaluation of Demonstrated and Emerging Technologies for the Treatment and Cleanup of Contaminated Land and Groundwater (Phase II)"*, Meeting Proceedings, Adelaide February 11-16, 1996

CARACAS

CONCERTED ACTION ON RISK ASSESSMENT FOR CONTAMINATED LAND IN THE EUROPEAN UNION

1./ INTRODUCTION

The Concerted Action CARACAS will be carried out by participants from 14 Member States of the European Union: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, the Netherlands, Portugal, Spain, Sweden, the United Kingdom Each of these Member States is represented by the national Environment Ministry and one or two scientific institutions Additionally, countries like Norway, Switzerland, the United States, and Australia will contribute with their experience to the scientific programme of CARACAS.

2./ METHODOLOGICAL ASPECTS

The primary objective of the Concerted Action CARACAS is the elaboration of recommendations and guidelines for assessing risk of contaminated land. In order to achieve this goal an international working group (*"Concerted Action Coordination Group"*) will identify, compile, assess, and review all relevant RTD projects and all scientific approaches developed in the Member States Based on this synopsis, scientific priorities for future programmes and projects of DG XII and the EU-Member States will be proposed and a trans-national collaboration of ongoing and planned RTD projects will be stimulated.

Furthermore, CARACAS will exchange information with other international initiatives in the field of contaminated land, like the Concerted Action NICOLE, the relevant ISO/CEN-Working Groups, the EEA-Topic Center Soil, the Ad Hoc Working Group on Contaminated Land, and the relevant NATO/CCMS-Pilot Studies (see Appendix). In order to inform all interested parties on the progress of the Concerted Action, a CARACAS-Newsletter will be issued.

3./ STATE OF THE PROJECT

The Concerted Action CARACAS has started on **1st of February, 1996**. The first Meeting of the CARACAS-Coordination Group was held in Brussels on **28th and 29th of March, 1996** At this inaugural meeting, the **scientific programme** of CARACAS has been defined, and **seven Topic Groups** have been developed for key issues concerning risk assessment:

- **Topic Group 1 "Human Toxicology"** (Review the key issues in using toxicity data for assessing risks to human health, and identify key principles)
- **Topic Group 2 "Ecological Risk Assessment"** (Recommend ecotoxicological evaluation systems for characterisation of ecological risk)
- **Topic Group 3 "Fate and Transport of Contaminants"** (Select processes affecting fate and transport of contaminants and evaluate their role in risk assessment)
- **Topic Group 4 "Site Investigation and Analysis"** (Recommend site investigation strategies to obtain the quality of data necessary to estimate risks with confidence, taking into account data variability and cost-effectiveness)
- **Topic Group 5 "Models"** (Explore and advise on the central issues relating to the use of models for risk assessment)
- **Topic Group 6 "Screening/Guideline Values"** (Evaluate scientific basis of screeing/guideline values and their role in decision making)
- **Topic Group 7 "Methods for Risk Assessment"** (Provide a general framework for risk assessment, a set of practical tools for investigation & assessment and options for priority settting)

Following, the working programme of each Topic Group will be described in detail.

Topic Group 1: HUMAN TOXICOLOGY

Assessing the impact of soil contaminants on human health requires reliable data on human exposure and the resulting possible adverse effects. Contaminated soils typically contain mixtures of chemicals, some of which are more hazardous to humans than others **It is important to identify the most toxic compounds or groups of compounds according to their likely occurence on contaminated sites and their relevance to the major exposure pathways of ingestion, inhalation and skin contact.**

Most of the toxicology data used in contaminated land risk assessment (CLaRA) were derived from animal experiments performed for different purposes, such as the establishment of "acceptable" daily intakes of additives and environmental contaminants in food. Usually, the chemicals to be tested were administered orally in the feed or via gavage in a pure and soluble form. **Thus, the chemical form, mode of delivery and exposure conditions are not necessarily appropriate for CLaRA; nor are the conventional safety factors used by WHO/FAO and similar agencies.** In addition to this question of the applicability of toxicological data, another key issue relates to **the general interpretation of toxicological data, including extrapolation from high dose to low dose, from animal to man, species and strain differences in toxic potency, mechanistic differences between genotoxic and nongenotoxic carcinogens and the use of alternative methods for establishing threshold doses (NOAEL, LOAEL, Benchmark).**

The **exposure to mixtures of chemicals** is a general problem in environmental risk assessment. Multiple chemicals exposure can give independent, additive synergistic or antagonistic effects **Structure-activity relationships and theoretical work, such as physiologically-based pharmacokinetic (PBPK) modelling to assess uptake, distribution and disposition of compounds in humans, may help in resolving this issue.** PBPK modelling also offers improved prospects for selecting the most appropriate animal studies for use in CLaRA and for adjusting for physiological differences between animals and humans.

Some of the most fundamental problems for CLaRA relate to **bioavailability of contaminants** relative to the study or studies on which the toxicity criteria were based. Factors that may influence the bioavailability of soil contaminants are differences in chemical speciation, immobilisation by mineral lattices and adsorption by soil particles. Soil may act as a competitive sink for ingested contaminants although the soil matrix may also result in a longer residence time in the gut.

The **fractional distribution in a soil matrix** is also important Many contaminants are preferentially associated with the finer grained fractions of soil This consideration is important in the assessment of exposure via inhalation, skin contact or ingestion of leafy vegetables.

In principle **epidemiological studies** allow complex issues of bioavailability and combined exposure to be taken into account. In practice, however, general population or occupational cohorts are usually too small to enable studies with sufficient statistical power. In addition it is difficult to get properly matched control groups and reliable data on duration and magnitude of exposure.**Exposure assessment by biological monitoring using either chemicals (e.g. contaminant concentration in blood) or biological endpoints (e.g. adduct levels) are important in this context. Improved toxicological information on sensitive subgroups in the exposed population is needed also.**

Topic Group 2: ECOLOGICAL RISK ASSESSMENT

In most European countries work is carried out to identify, investigate and classify contaminated sites However, there are limited criteria for comparative ecotoxicological risk characterization of contaminated sites as well as site related contaminants. The work of Topic Group 2 in the CARACAS-Project is to "**Recommend ecotoxicological evaluation systems for characterization of ecotoxicological risk**" in association with contaminated sites. The work will be based on available scientific literature or papers and communications from national and international environmental authorities and research organizations **Therefore, Topic Group 2 will review available information and data on research results, methods, strategies and principles on the area of ecotoxicological risk assessment in close cooperation with the various national participants in CARACAS-Project.**

The group will evaluate and consider national differences, address research needs and recommend further actions towards research and guidelines with the final aim to develop recommendations of ecotoxicological risk assessment necessary to include in the overall risk assessment of contaminated sites.

Work will be carried out in following steps: **/i/ defining goals and objectives in relation to the characterization of ecotoxicological risk; /ii/ in relation to the goals and objectives define a structure for dealing with ecotoxicological risk; /iii/ based on this structure identify the most important issues; /iv/ make an inventory of the state of the art of these issues; /v/ implement the state of the art and identify most important lacks of knowledge.**

Examples of important issues to be dealt with in the above mentioned work are as following:

Exposure assessments:

- characterization of fate and transport of contaminants in the site media (also dealt with in topic group 3)
- characterization of exposure to the biological systems and organisms.
    - exposure ways in the contaminated site ecosystem (also dealt with in topic group 3)
    - exposure of terrestrial and aquatic organisms
        - bioconcentration, bioaccumulation and biomagnification (also dealt with in topic group 3 and 5)
        - toxicokinetics (also dealt with in topic group 5)

Effect assessments:

- experimental versus field evaluations
- single species tests, multispecies tests, micro- and mesocosm test systems
- site and substance relevant test organisms and test systems
- unknown compounds or degradation products, hydrophobic and hydrophilic
- compounds
- combination of known and/or unknown compounds

Evaluation strategies:

- interpretations, predictions and extrapolations of result
    - dose-effect relationships, LOEC, NOEC etc.
    - exposure length, acute or chronic toxicity
    - combination of contaminants, tolerance and adaptation
    - effects on biochemical-, physiological-, organisms-, population- or community levels,
    - harmonize terminology
    - protocol standardization and quality control

Topic Group 3: FATE AND TRANSPORT OF CONTAMINANTS

The group will review the state of knowledge of those biological, chemical and physical processes which effect the fate and transport of organic and inorganic priority contaminants in contaminated soils and groundwater and thereby the exposure and bioavailability of such contaminants. In particular, the relative importance attached to these processes in contemporary risk assessment practice will be reviewed and critiqued. **The group will recommend how the subject of fate and transport of contaminants should be integrated into risk assessment practice in the future. It will also highlight gaps in knowledge and recommend research priorities to fill those gaps.**

The topic will be reviewed within the context of typical hydrogeological and geological conditions found in European soils and aquifers and will include fate and transport in fractured layers.

Removal, attenuation and phase transfer processes together with processes defining the bioavailability of compounds will be reviewed and evaluated with respect to their relevance to risk assessment and modelling. These processes include:

- **Biodegradation**, including formation of metabolites and substrate interaction, i.e. cometabolism, competitive inhibition, compound and product inhibition, concentration thresholds and adaptation,
- **Photooxidation**;
- **Bioaccumulation**;
- **Plant uptake**;
- **Sorption/desorption**;
- **Dispersion**;
- **Immobilisation/incorporation** of parent compounds and metabolites;
- **Extraction/dissolution** from free phases including films, pools and ganglia;
- **Evaporation**;
- **Dust/particle spreading**,
- **Diffusion**;
- **Complexation**;
- **Speciation**,
- **Precipitation**
- **Binding** of free phase product to the soil matrix.

Other factors which influence fate and transport will also be reviewed and evaluated, incl.:

Facilitated transport mediated by colloids, macrophores and fractures;
Redox processes such as oxygen depletion following iron reduction.

Topic Group 3 will pay particular attention to **effects and influences of complex mixtures** on the fate and transport of specific contaminants and groups of contaminants and how these effects and influences impact on risk assessment. This area needs particular attention because many contaminated sites in Europe are contaminated by complex mixtures of primary contaminants and secondary metabolites. Furthermore, much of the available information on the fate and transport of specific contaminants is derived from studies on either single contaminants or relatively simple mixtures of contaminants which may not adequately describe the behaviour of contaminants when part of a complex mixture.

TOPIC GROUP 4: SITE INVESTIGATION/ANALYSES

Based on the available scientific information collected by the national environmental authorities, Topic Group 4 will **elaborate state of the art knowledge on site investigation strategies (including sampling and analyses, and in particular those recommended by the International Standard Organisation - ISO/TC 190), and make recommendations on the factors which lead to good scientific practice.**

In particular, work of Topic Group 4 will include

- review the national approaches to sampling and analytical strategies,
- recommendations on the factors which affect, or lead to, good scientific practice (not the development of standard practices),
- review and recommendations on achieving a satisfactory balance between the information needed for risk assessment and what can realistically be obtained, e.g.
  - which parameters are most crucial to assessing risks?
  - which parameters are most sensitive?
  - what level of confidence or accuracy can we realistically expect to achieve (or should look for) for key parameters and other less crucial parameters?
- review and recommendations on the use of statistical approaches or tools in sampling strategies, - which circumstances are they suited to and for which circumstances are they less effective?
- liaison with topic groups 3 and 5, to input their views/comments on data needs to our deliberations on site investigation and analyses.

Topic Group 4 will evaluate existing methodologies and strategies in the light of data requirement for risk assessment for contaminated land. In particular, methodologies and strategies will be evaluated against requirements that the data generated is statistically valid, cost effective, quality assured and most suiteable for use in a risk assessment context.

On the basis of this evaluation, Topic Group 4 will make recommendations on the factors which lead to good scientific practice for site investigation methodologies and strategies.

To fulfill these objectives, the topic group will address various questions including

- What information is important in a risk context? What information do we need for the use of guidelines/screening values/transport and exposure models? (in collaboration with the other topic groups)
- What kind of information can be provided from site investigation (preliminary, main, in situ or in laboratory)?
- What level of confidence is needed for each kind of investigation and what is possible? (uncertainties of methods, scale of investigations, representativeness of samples)
- How can the variability of data be taken into account and be minimised for risk context use? (quality assurance)
- How can suiteable background samples be obtained for all the relevant media?

TOPIC GROUP 5: MODELS

Objective:

Topic Group 5 will elaborate the state of the art and the knowledge on models used for risk assessment of contaminated sites It will be focused on formalized priority setting models, e.g. ranking systems as well as exposure assessment models for site by site risk analysis. The aim of Topic Group 5 is to give a summarized overview on the most common models in different EU Member States (plus USA and Canada) and to evaluate, explore and advice suiteable methods, and concepts that can be subjects of risk assessment models in the European Community.

Work Programme:

☐ **Phase I - Inventory (1996)**

- collect available models as well as other formalized systems for risk assessment and give an overview on the most common tools in the different EU Member States (and US and Canada?)
- classify the models in different types concerning to their
    - purpose of application (industrial or waste contaminated sites, preliminary or detail investigation phase, ranking for priority setting, quantitative exposure assessment to determine the kind and extent of human exposure with contaminates by different pathways)
    - targets of concern (human health, ecosystem, soil, groundwater)
    - scientific basis (risk classes, risk index, dose-effect relation, in-/tolerable toxicological data)
    - status of development and practical use:
      a) under R&D,
      b) in practical test (=validation)
      c) in successful use
- identify the scientifically R&D requirements latest to 11/95 because of the new R&D programme of EU-DG XII.
- identify such risk assessment models (like CSOIL, CLEA or UMS) of which scientific basis were also used for deriving guideline values.

☐ **Phase II - Evaluation (1997)**

A - Models for ranking contaminated sites
B - Models for site-by-site risk analysis

- evaluate the scientific concepts of the models as well as their applicability, "user-friendliness" and validation, sensitivity/uncertainty analysis
- compare the availability of needed input data and the consideration of toxicity of substances, the distribution in the environmental medium and the transfer to the different targets
- elaborate the advantages and disadvantages of ranking systems and exposure assessment models
- specify their role in the comprehensive decision making process of contaminated site management
- analyse common feature and lacks of the different methods and concepts
- identify the scientifically R&D requirements

☐ **Phase III - Applicability (1997/98)**

- summarise the most important concepts for risk assessment and give first recommendations for special models in practical manner
- initiate further R&D projects improving applicability and validation including bi- and multilateral practical tests
- specify the future role of risk assessment models

Additional Remark:

It is useful to make a link with Topic Group 6 (see last point in Phase I) and also with Topic Group 7 used our results concerning risk and exposure assessment models for the whole framework.

TOPIC GROUP 6: SCREENING/GUIDELINE VALUES

Strategic aim: Evaluate scientific basis of screening/guidance values and their role in decision making

Context: The starting point of this topic group is the generalized "a priori" assumption that *"screening/guidance values are a useful tool for contaminated soil management"*. Consequently, most countries draw up specific values for the media soil, groundwater, surface-water and air within their soil policy framework but with different particular aims. It is the objective of Topic Group 6 to compare these differences, as well as the basic scientific differences supporting these values in order to answer, among others, the following question: *Do the derived values fulfill the objectives they were defined for?* Technical aspects such as high uncertainty or gaps between actual and general situations, as well as social-economic ones should be taken into account.

Working protocol/phases:

- Collection of information from different countries: inquiry about regulatory approaches and relevant R&D projects.
- Evaluation within the group: identification of crucial and labile points.
- Discussion of these points together with the rest of the specific topic groups.
- Final evaluation and recommendations.

Topics of interest:

1. Definition of screening/guidance values in different countries according to:

- Soil policy approach.
    - focused on prevention/remediation/risk management
    - functionality vs. multifunctionality
    - protection objectives/media adressed: human health, ecosystem, surface and groundwater, etc.
- Role within soil management framework:
    - to differentiate between natural and anthropogenic levels
    - to assist in risk management
    - to set-up remediation goals
- Country particularities:
    - soil pollution nature and extent: list of pollutants and media of concern
    - degree of development of soil and general environmental protection policies: connection with screening values for other media
    - temporal aspects and development of guidelines

2. Protocol for the derivation of these values:

- Basic assumptions:
    - definition of acceptable risk, acceptable clean-up level, etc.
    - assessment approach: worst-case vs. realistic
    - exposure/use scenario definition
    - spatial scale (area and depth) of guidelines
- Methodological aspects:
    - used database: toxicological, ecotoxicological, others
    - account for background values (specially for metals)
    - used models: exposure, effects, contaminant fate and transport in soil (in particular bioavailability)
    - assessment approach. deterministic vs. stochastic
    - evaluation of uncertainties
    - ways of interaction with guidelines in other sectors

TOPIC GROUP 7: METHODS FOR RISK ASSESSMENT

Introduction: The main task of the topic group is to review and make recommendations on methods to integrate basic elements of risk assessment such as soil, sediment and groundwater sampling, exposure pathway modelling, exposure measurement, effect assessment and evaluation. Risk assessment is an umbrella term covering widely different methods. The choice of a method will depend, amongst other things, on scientific ambitions. for instance site specific modelling and measurement of exposure versus simple comparison with predetermined generic soil screening levels or guidelines.Appropriate methods will also depend on the purpose of the assessment: Estimation of risks in the classic toxicological sense or setting of priorities involving value judgements and preception of risks by politicans or the general public. Some general methodological framework will be needed to classify and compare different approaches in risk assessment.The framework must include vari- ous aspects of general environmental risk like human health risk, ecological risk, risks related to the protection of groundwater and surfacewater and has to address the use of a statistical background for decision making. After all, the scientific definition of risk as *"a combination of the consequence of a negative effect and the probability of that effect to occur"*, and the large uncertainties in risk estimation both encourage the use of a statistical approach.

The work of the topic group will consist of **three phases**:

1./ Reviewing and evaluating existing R&D work relevant to Risk Assessment methods

The review of research projects and existing general integrative risk assessment protocols might result in a number of suggestions to other topic groups of the CARACAS project on the relation between the various "topics" discussed. Risk assessment is an integration of a number of widely different subjects. As most groups will collect and evaluate different building blocks of risk assessment, compatibility of the different elements must be addressed. A general analysis of the level and nature of "compatibility" which is needed for a general framework for risk assessment might be useful at relatively early stages of the work by other topic groups.

2./ Development of a general conceptual framework

The availability of a general framework for risk assessment based on sound scientific principles will provide a valuable means of integrating the recommendations of other topic groups. Topic group 7 will address the crucial components of a general framework and the factors which affect the effectiveness of the overall process of risk assessment.

Risk assessment can be performed at various levels of sophistication, from an assessment based on simple generic criteria or screening levels to an assessment based on measurements of adverse effects in real situations. Criteria for the choice of appropriate methods might be proposed from a (natural) scientific basis but other aspects must be considered as well. Although a characterisation of risk from the point of view of natural sciences (soil sciences, toxicology, etc) is important, the perception of the risk by decision makers and the general public is also governed by ethical and economical values, political considerations and NIMBY (not in my back yard) effects. Decisions about clean up objectives and priority setting (is housing more important than nature?) and even about the acceptability of assessment methods can be significantly affected by other aspects than "risk" in the natural scientific sense.

3./ Integration of results from other topic groups

At the end of the CARACAS project topic group 7 must evaluate whether the methodological framework can accommodate the results of all other working groups, or whether adjustments in the framework are needed. Also "gaps" in knowledge and R&D work should be identified by topic group 7, since it has an overview role.

Non invasive method for locating the HC-contaminants by combination of resistivity and ground penetrating radar

ENV4-CT95-0079

Coordinator: C. Bocard

Institut français du pétrole
F - 92506 Rueil-Malmaison
Tel: +33-1.47.52.64.03
Fax: +33-1.47.52.70.00

Detecting and Locating Non-Aqueaous Phase Contaminants in Soils by Three Geophysical Methods

Contract: CT95-0079

Starting date:	1 Apr 1996
Duration:	24 months

Coordinator:

Institut Français du Pétrole
Geophysics and Instruments
Department
Avenue de Bois-Préau 1&4
FR - 92506 Rueil-Malmaison

C. BOCARD
Tel: +33-1 47526403
Fax: +33-1 47527001

Partners:

Universität Köln
Institut für Geophysik und Meteorologie
DE - 50923 Köln
A. HOERDT

Deutsche Montan Technologie-Gesellschaft
für Forschung und Prüfung mbH
Institut für Lägerstätte, Vermessung und
Angewandte Geophysik
DE - 44787 Bochum
E. RAKERS

Imaging Arts Co
GR - 54624 Thessaloniki
V. CHOUVARDAS

Detecting and Locating Non-Aqueous Phase Contaminants in Soils by Three Geophysical Methods

Objectives:

The developed methodology aims at locating and possibly determining the volume of Non-Aqueous Phase Liquid pollutants (NAPL) in the non saturated zone of soils up to the water-table in the depth-range 0-20 m. The methodology will especially apply to liquid hydrocarbons such as gasoline, diesel fuel and heavy fuel, to HAP-containing tars and to chlorinated hydrocarbons such as solvents and PCB's, for the investigation of industrially and accidentally contaminated sites with the interest of avoiding many boreholes.

It consists in combining three existing geophysical tools (Ground Penetrating Radar, Radiomagnetotellurics and Electrical Direct Current or Electromagnetic Tomography) to take advantage of their complementarity and in enhancing their respective resolution by using improved processing methods. The operational methodology will be completed by a dedicated graphic software for interactive 3D data visualisation.

Brief Description of the Research Project:

The general approach of the project is to test the geophysical methods on already investigated contaminated sites on which complementary analytical measurements by core sampling will be carried out to better characterize the spatial distribution of contaminants.
Two sites will be investigated:

- a former coke plant (HAP main contamination)
- a closed petroleum products depot (gasoline - fuel contamination).

The physical parameters (electric permittivity and electrical resistivity) which are involved in the selected geophysical methods (GPR, RMT, ET) are sensitive to both NAPL-and water-content. Hence, geophysical measurements will be carried out on both sites in different hydric states of soil (winter and summer campaigns).

The interest of combining the three geophysical method is :

- decreasing the uncertainty in the pollution recognition
- separating the structural effects from the pollution effects using the different sensitivities of each method related to the kinds of soils
- compensating the methods weaknesses by their complementarity
- reaching a robust cross-interpretation allowing to give a better spatial distribution of the contaminated volume.

The end-product methodology will be defined as the combination of geophysical methods and data processing methods which will give the best field-correlated results.2

The role of colloids in the transport of pollutants in shallow groundwater: development of monitoring and assessment procedures

EV5V-CT92-0228

Coordinator: M. Ivanovich

RMC-Environmental
UK - OX14 1RA Oxon
Tel: +44-1235.555755
Fax: +44-1235.434917

CONTRACT NO: EV5V-CT92-0228
TITLE: The role of colloids in the transport of pollutants in shallow groundwaters: development of monitoring and assessment procedures (COLTRAMP)

OBJECTIVES: To assess the role of colloids in transport of metals in shallow groundwaters

AIMS:
(1) To develop a cost-effective sampling and analytical protocol for characterisation of polluted sites
(2) To apply modelling techniques capable of describing transport and predicting contaminant movement based on laboratory and field work
(3) To develop effective guidelines for recognising the significance of colloids in the transport of contaminants
(4) To assess the implications of colloid transport for remediation strategies/ methods

CHARACTERISTIC DIAGRAMME:

Task 1
Collation of existing data into effective data base

Task 2
Field monitoring and sampling

Task 3
Sample analyses and physicochemical characterisation of groundwater colloids

Task 4
Laboratory studies of metal-associated colloid transport through relevant solid matrix materials in column and batch experiments

Task 5
Modelling of contaminant transport in the presence of colloids

Task 6
Project co-ordination, reporting and recommendations

PARTICIPANTS:

Name:	Dr M Ivanovich (1)*	Name:	Prof Dr R Nießner, Dr T Baumann (2)
Address:	AEA Technology	Address:	Institut für Wasserchemie
	Analytical Services Group		und Chemische Balneologie
	551 Harwell		der Technischen Universitat München
	Oxon OX11 ORA		Marchioninistr: 17 (Grosshadern)
Tel:	+44 235 434063		D-81377 Munich
Fax:	+44 235 434917		Germany
		Tel:	+49 89 7095 7980/7981/7993
		Fax:	+49 89 7095 7999
Name:	Dr J H Tellam, Prof J W Lloyd (3)	Name:	Dr David Read (4)*
Address:	School of Earth Sciences	Address:	WS Atkins Environment
	The University of Birmingham		Woodcote Grove
	Edgbaston		Ashley Road, Epsom
	Birmingham B15 2TT		Surrey KT18 5BW
Tel:	+44 21 4146138	Tel:	+44 3727 26140
Fax:	+44 21 4143971	Fax:	+44 3727 40055

* Present address: RMC-Environmental, Suite 7, Hitching Court, Abingdon, Oxon. OX14 1RA Tel: 01235 555755

METHODOLOGY/APPROACH: Many of the 50-100,000 waste disposal sites in the UK (with similar numbers in Germany and a substantial, if incomplete, inventory of sites in central and eastern Europe) may represent a potential source of aquifer contamination. Assessing the risk of such an event occurring would benefit from the development of a flexible European-wide risk assessment procedure whereby limited data could be used to assign risk categories to a given site. The reliability of such risk estimates, however, is dependent on factors such as the availability of site history information and the quality/completeness of site geological and hydrogeological data. Additional uncertainties may be introduced if potentially important processes such as colloid transport are not considered when carrying out contaminant release risk estimates or devising remediation strategies.

Colloidal particles (<1 µm diameter) represent a mobile surface to which heavy metals (and organics) may adsorb, thereby both increasing the effective solubility of the metal and providing an additional transport mechanism. As a result, chemical, biological, or even electrochemical methods of remediation may be affected if colloids are significant. For example, a remedial procedure based on pumping may use a retardation factor based on laboratory-determined sorption isotherms relating to the adsorption of aqueous species to the matrix; the economics of a remediation procedure can be rather sensitve to retardation factors. On the other hand, enhanced metal recovery might be possible using introduced colloids. Hence, investigation of the role of colloids in the transport of heavy metals is essential.

The following project deliverables have been defined: (1) Collation of existing data into skeleton site-specific data bases, (2) Characterisation of liquid, solid and colloidal samples, (3) Results of laboratory column experiments, (4) Testing of predictive models, (5) Sampling and analytical protocols, (6) Guidelines for recognising the importance of colloids in the transport of toxic metals, and (7) Assessment of the implications of colloidal transport for potential remediation strategies.

RESULTS: Three sites with diverse industrial histories have been chosen for this study: (1) an urban sandstone aquifer (Birmingham, UK), (2) Kanena /Hufeinsee mixed waste disposal site (Leipzig, Germany), and (3) the Budelco Zn smelter (The Netherlands).

Task 1 has been completed and the historic data bases for each site have been set up. Task 2 has also been completed at all three sites and sampling of groundwater, solid matrix materials and colloids has been carried out. Colloids were sampled either in-situ using several ultrafiltration techniques or off-line on unfiltered water samples but always under a controlled (inert) atmosphere to avoid artifacts. The results of the physico-chemical characterisation of groundwater colloids at all three sites have been reported through regular Progress Reports and Task 3 has been completed. In each case colloid populations are of the order of 10^{10} particles/litre with negative effective charges. With the exception of organic colloids (most likely humic substances) the inorganic colloids (mostly silica) did not appear to carry large proportions of total dissolved trace metals. However, metals found associated with colloids at all three sites could be related to historic or present industrial use of the site. Laboratory studies (Task 4) using latex particles (Birmingham University) with the natural aquifer materials have yielded evidence for colloid particle transport through sandstone columns. Experimentation with 80 nm diameter silica colloids in the presence of Zn and Cr and the corresponding batch experiments are also complete. Parallel experiments involving the Kanena site materials have been carried out by TUM. These experiments involve Cd and Co and are complete. Task 5 involves: experimental design, collation of thermodynamic data and modelling of metal transport in the presence of colloids. Review of thermodynamic data for additional metals Co, Cd, Zn and Cr has been completed and some development of the coupled processes code CHEMTARD has been carried out to describe metal transport in the presence of colloids. BU and TUM batch experiments have been successfully modelled and a suite of surface complexation parameters for the behaviour of each of the metals in the presence of silica colloids and rock matrix have been derived. Modelling of the column experiments is almost complete. Participants 2 (BU) and 3 (TUM) have submitted draft reports and work on the final report by Participant 1 (AEA) will be completed once the final report from Participant 4 (WSA) has been received.

PUBLICATIONS: M. Ivanovich (1994) Enhanced heavy metal transport in the presence of groundwater colloids. In Colloids and Bacteria Transport in the Geosphere of Proc. Western Pacific Geophysics Meeting July 1994, Hong Kong.

Kleinert, U. O., Godbold, P., Tellam, J. H., Lloyd, J. W., Ivanovich, M. and Gardiner, M. P. (1995). The preliminary characterisation of groundwater colloids in a polluted urban aquifer. European Geophysical Society, General Assembly, Hamburg.

Kleinert, U. O. The role of heavy metals in urban pollution. PhD thesis, University of Birmingham (in preparation).

Starting date: 1 March 1993	Duration: 1/3/92-31/08/95 (2½ yrs)

THE ROLE OF COLLOIDS IN THE TRANSPORT OF POLLUTANTS IN SHALLOW GROUNDWATERS: DEVELOPMENT OF MONITORING AND ASSESSMENT PROCEDURES

CEC CONTRACT EV5V-CT92-0228

M. Ivanovich[01*], R. Nießner[02], T. Baumann[02], J.-I. Kim[02], J. H. Tellam[03], J. W. Lloyd[03], D. Read[04*], D. Ross[04], D. Wilcox[*].

Participant 01: AEA Technology, Analytical Services Group, 551 Harwell, Oxon. OX11 0RA, UK

Participant 02: Institut fur Wasserchemie und Chemische Balneologie der Technischen Universitat Munchen, Marchioninistr: 17 (Grosshadern), D-81377 Munich, Germany

Participant 03: School of Earth Sciences, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Participant 04: WS Atkins Environment, Woodcote Grove, Ashley Road, Epsom, Surrey KT18 5BW, UK

*Present address: RMC-Environmental, Suite 7, Hitching Court, Abingdon Buisiness Park, Abingdon, Oxon. OX14 1RA, UK.

1 Introduction

Many of the 50-100,000 waste disposal sites in the UK (with similar numbers in Germany and a substantial, if incomplete, inventory of sites in central and eastern Europe) may represent a potential source of aquifer contamination. Assessing the risk of such an event occurring would benefit from the development of a flexible European-wide risk assessment procedure whereby limited data could be used to assign risk categories to a given site. The reliability of such risk estimates, however, is dependent on factors such as the availability of site history information and the quality/completeness of site geological and hydrogeological data. Additional uncertainties may be introduced if potentially important processes such as colloid transport are not considered when carrying out contaminant release risk estimates or devising remediation strategies.

Colloidal particles (<1 µm diameter) represent a mobile surface to which heavy metals (and organics) may adsorb, thereby both increasing the effective solubility of the metal and providing an additional transport mechanism. As a result, chemical, biological, or even electrochemical methods of remediation may be affected if colloids are significant. For example, a remedial procedure based on pumping may use a retardation factor based on laboratory-determined sorption isotherms relating to the adsorption of aqueous species to the matrix; the economics of a remediation procedure can be rather sensitve to retardation factors. On the other hand, enhanced metal recovery might be possible using introduced colloids. Hence, investigation of the role of colloids in the transport of heavy metals is essential.

2 Objectives and scope

The main objective of this joint research programme carried out under CEC Contract EV5V-CT92-0228 is to address the question of whether colloids have an important role in the transport of metals in shallow groundwaters. The aims are: (1) to develop a cost effective sampling and analytical protocol for characterisation of polluted sites; (2) to apply modelling techniques capable of describing transport and predicting contaminant movement based on laboratory and field work; (3) to develop effective guidelines for recognising the significance of colloids in the transport of contaminants; and (4) to assess the implications of colloidal transport for the purpose of devising remediation strategies.

The following project deliverables have been defined: (1) Collation of existing data into skeleton site-specific data bases, (2) Characterisation of liquid, solid and colloidal samples, (3) Results of laboratory column experiments, (4) Testing of predictive models, (5) Sampling and analytical protocols, (6) Guidelines for recognising the importance of colloids in the transport of toxic metals, and (7) Assessment of the implications of colloidal transport for potential remediation strategies.

3 Work programme

Task 1: Collection and processing of existing data (TUM, BU, WSA)

Task 2: Sampling of waters, colloids and solids (AEA, TUM, BU)

Task 3: Analysis of waters and solids/physico-chemical colloid characterisation (AEA, TUM, BU)

Task 4: Laboratory study of colloid associated metal transport through relevant matrices (TUM, BU, AEA#, WSA# (#limited to design stage))

Task 5: Modelling of contaminant transport in the presence of mobile colloids (WSA)

Task 6: Project co-ordination, reporting and liaison with other projects (AEA)

4 Results

Three sites with diverse industrial histories have been chosen for this study: (1) an urban sandstone aquifer (Birmingham, UK), (2) Kanena /Hufeinsee mixed waste disposal site (Leipzig, Germany), and (3) the Budelco Zn smelter (The Netherlands).

Task 1 has been completed and the historic data bases for each site have been established. The data available include information on geology, topography, well distribution, well water chemistry and well design.

Task 2 has also been completed at all three sites and sampling of groundwater, solid matrix materials and colloids has been carried out. At Birmingham nine sites have been sampled, representing a range of chemistries and land-use. At each site, a methodology for colloid sampling has been applied by both the AEA Technology and Birmingham University teams. The methodology used was based on a prefilter/tangential ultrafiltration system allowing sample collection under nitrogen (inert) atmosphere preventing formation of artifacts due to contact with the atmosphere. Field centrifuging allowed preparation of samples for TEM examination. Further size fractionation was achieved using a laboratory-based flat bed filter system. Similar techniques have been applied at the Kanena site. However, at the Budelco site unfiltered samples of groundwaters collected under controlled atmospheric conditions were processed for colloid extraction off-line in the laboratory. Some hydrochemical data were recorded in the field (pH, Eh, DO, temperature and electrical conductivity). Remediation activities have recently commenced at the Kanena site and a field campaign to determine the effects of the earthen liner installed to prevent rain water infiltrating the waste deposit is underway.

The results of the physico-chemical characterisation of groundwater colloids at all three sites have been reported through regular Progress Reports and Task 3 is now complete. In each case, colloid populations are of the order of 10^{10}-10^{11} particles/ litre with negative effective charges. In the case of the Birmingham aquifers, colloids are predominantly inorganic, mainly silica. Their morphology varies from euhedral to anhedral. The most commonly identified elements in the colloids were Ca, S, Fe, N and Al suggesting clay is an additional ingredient in the colloidal phase. Trace metals Ni, Cr, Ti, As, Co, Mn, Zn, Sn and Zr have all been identified as part of the colloid-borne inventory suggesting a link with the metal workings known to have operated or still being operated at these sites. With the exception of organic colloids (the most likely humic substances) found at Kanena site, the inorganic colloids (mostly silica) do not appear to carry large proportions of total trace metal load in sampled groundwaters.

Task 4 has been completed at both Birmingham University and TUM. Initial experiments at Birmingham University were carried out on 100 nm latex beads since their ease of detection using fluorescence allowed more time to concentrate on developing the experimental methods. During these experiments, the latex beads were shown to coagulate at very low ionic strengths and to interact with the sandstone. Great care had to be taken in running these experiments. It was shown that the colloids were retarded during flow through sandstone columns, and that the final breakthrough concentrations reached only 80-90% of input concentrations over hundreds of pore volumes. This work, and work on the solid phases is complete. Later laboratory work concentrated on 80 nm silica colloids produced by AEA Technology. Both batch and column experiments are also complete. The experimental set up at TUM was established in glove boxes (to allow controlled atmosphere conditions). Batch experiments using 'artificial' groundwaters to determine the distribution of Zn, Cd, Cu and Co between silica colloids and solution under different boundary conditions were performed. The TUM experimental programme has been completed.

Task 5 involves experimental design, collection and evaluation of thermodynamic data, and modelling metal transport in the presence of colloids. The experimental design for both Birmingham University and TUM has been completed. A review of thermodynamic data for the additional metals Cd, Co, Zn and Cr has been completed resulting in an internally consistent and traceable database of thermodynamic formation constants. Batch experiments have beeen successfully modelled using the PHREEQE code and Participant 4 has produced equilibrium constants which define metal partitioning between the aqueous phase and rock matrix/silica colloids. Figures 1 and 2 give examples of the fit of modelled Cr and Co adsorption to experimental data from BU and TUM respectively. Table 1 gives the surface complexation parameters derived from this modelling. Similarly satisfactory modelling results have been obtained for Cd and Zn.

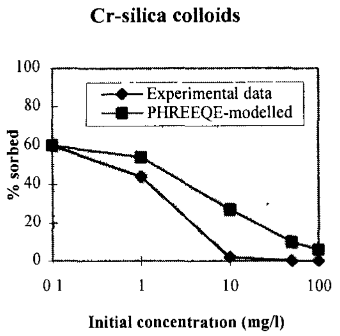

Figure 1: Adsorption of chromium to synthetic silica colloids.

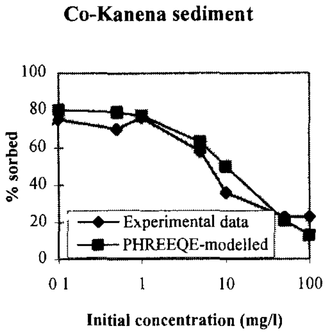

Figure 2: Adsorption of cobalt to Kanena sediment.

Table 1: Summary of findings from modelling batch experiments.

Surface complexation parameters	Silica colloids	B'ham sediment	Kanena sediment
Specific surface area (m^2/g)	400	10	6.8
Site density (eq/m^2)	7.6E-6	1.5E-5	1.5E-5
Inner layer capacitance ($\mu F/cm^2$)	120	120	120
Outer layer capacitance ($\mu F/cm^2$)	20	20	20
log K [SOH_2^+]	-2.8	-2.8	-2.8
log K [SO^-]	-6.8	-6.8	-6.8
log K [SOZnOH]	0.1	-7.0	
log K [$SOCo^+$]	-6.3		-6.3
log K [$SOCd^+$]	-6.0		-5.9
log K [$SOCr(OH)_3^-$]	-8.5	-5.0	

The colloid transport model in the coupled chemical transport model, CHEMTARD, has been developed to include explicit representation of colloid retention/filtration and coagulation. The model accounts for ionic strength and electrical double layer effects in the simulation of these processes. The additional numerical constraints imposed on the CHEMTARD solver by this phase of model development, however, has required slight relaxation of the convergence criteria for calculations involving colloidal particles. Modelling of the BU and TUM column experimental data is almost complete.

Under Task 6, regular Progress Reports have been produced at six-montly intervals. The Fourth Progress Report was published in March 1995. Task 4 was delivered late which has delayed Task 5 and ultimately Task 6, the writing of the final progress report. So far deliverables (1), (2), (3) and (4) have been completed and draft reports from Participants 2 and 3 have been received. Work on the final report from Participant 1 has begun and will be completed once the final report from Participant 4 has been completed.

Deliverables (1) to (5) are complete. Deliverables (6) and (7) are being formulated in the course of preparation of the final project report.

5 Further research needs

Further research should be extended to a variety of organic contaminants. The present laboratory experiments are being carried out on a small scale with 'artificial' groundwaters and small matrix columns. Thus, the scaling up of experiments is essential to demonstrate the appropriateness of extrapolations from laboratory experiments (on a scale of centimetres) to real matrices (on a scale of metres). An artificial aquifer (10 m length) operated by TUM can provide the means for upscaling experiments under well defined and controlled conditions and the

University of Birmingham has access to sandstone aquifers which could be used for upscaled in situ tracer experiments. Transport of colloids within the unsaturated zone remains an open issue which should be addressed urgently. Furthermore, development and testing of colloid tracers is required to better understand the long-distance effects of colloidal/metal transport, generation of colloids and to develop further their potential for remediation of contaminated shallow aquifers.

Multicomponent multiphase pollutant transport in contaminated soils: chemical and spatial heterogeneity

EV5V-CT94-0536

Coordinator: I. Kögel-Knabner

Arbeitsgruppe Bodenkunde & Bodenökologie
Universität Bochum
D - 44780 Bochum
Tel: +49-234.7003661
Fax: +49-234.7094180

Multicomponent Multiphase Pollutant Transport in Contaminated Soils: Chemical and Spatial Heterogeneity

Contract N° **EV5V-CT94-0536**

TOPICS

TRANSPORT OF POLLUTANTS
IN CONTAMINATED SOILS

Starting date: **July 1st, 1994** duration **24 months**

Participants

Prof. Dr. I. Kögel-Knabner (coordinator)
Soil Science Group (RUB)
University of Bochum
NA 6/131
D-44780 Bochum, Germany
Tel +49-234-7003661
Fax +49-234-7094180

Present address
Department of Soil Science
Technical University of Munich
D-85350 Freising-Weihenstephan, Germany
Tel +49-8161-713677
Fax +49-8161-714466
e-mail koegel@pollux.edv agrar
tu-muenchen de

Dr. M. Borkovec
Institut für Terrestrische Ökologie (ETHZ)
Fachbereich Bodenchemie Grabenstraße 3
CH-8952 Schlieren
Tel +41-1-6336003
Fax +41-1-6331118
e-mail borkovec@aeolus.vmsmail.ethz.ch

Prof. S. van der Zee
Wageningen Agricultural University (WAU)
Dreijenplein 10
6703 HB Wageningen, The Netherlands
Tel +31-317482339
Fax +31-317483766
e-mail sjoerd.vanderzee@bodhyg.benp wau.nl

Dr. M. Jauzein
Institut de Recherches Hydrologiques (IRH)
Genie de L'Environnement
11 bis rue de Gabriel Peri
54500 Vandoeuvre-les-Nancy, France
Tel +33-83503600
Fax +33-83503699
e-mail mjauzein@irh fr

Dr. M. Sardin
Laboratoire des Sciences du Genie chimique (LSGC)
CNRS-ENSIC
1 rue Grandville
BP 451
54001 Nancy Cedex, France
Tel +33-8317-5254, -8317
Fax +33-83322975
e-Mail· sardin@ensic.u-nancy fr

Objectives

The objective of the TOPICS project is to provide a basis for a mechanistic understanding of pollutant transport and mobility in contaminated soils It is not concerned with specific case studies, but rather with the development of general methodologies to tackle a wide range of contaminated site problems with special emphasis on the problem of soil heterogeneity Experimental data and mechanistic models are used in creating and optimizing numerical models leading to a predictive understanding of pollutant mobility that contributes to soil remediation and risk assessment

Methodology/Approach

In the TOPICS project experiments are performed with different pollutants such as heavy metals and hydrophobic organics focusing on sorption and desorption behaviour The problem is attacked with experiments problem for two main groups of hazardous compounds in contaminated soils (heavy metals Cd and Cu, PAH) at different experimental levels laboratory sorption and column transport experiments, upscaling with a pilot scale system, and assessment of site heterogeneity in the field

Results

Heavy metals

∇ A flow-through reactor technique was developed for the investigation of the sorption behaviour of strongly sorbing compounds by ETHZ A modeling scheme that predicts transport of inorganic pollutants, such as heavy metals, in soil columns has been developed by the ETHZ The applicability of the modeling approach to multi-component systems is investigated at present

∇ Chemical speciation models, linked with a flow and transport model (NICA, TSF-model), developed by WAU, describe the interactions of heavy metals and soil. Break through curves of heavy metals were modeled in initial calculations with qualitative acccuracy The multi-dimensional transport modeling has been tested for homogenous domains and will be tested for heterogenous domains

Polycyclic aromatic hydrocarbons (PAH)

∇ Sorption experiments (Germany) in a batch system suggest that soil organic matter composition has a decisive effect on the sorption behaviour of PAH, with respect to both kinetics and partition coefficients. This has major implications for the modelling of PAH sorption/desorption and leaching from contaminated materials Further experiments with soils of different soil organic matter composition and particle size fractions will establish the relationship in detail Heterogeneity of a tar contaminated site was simulated by contamination of a reference soil with tar material (coke-oven site) to provide information about the influence of soil organic matter composition and ageing on the sorption/desorption behaviour of PAH

∇ The contribution of major soil components to retention of phenanthrene is studied in soil columns (LSGC) The interaction between phenanthrene and sandy soil are weak and reversible In contrast it seems that retention is irreversible and is kinetically controled when clay or organic material is added. Interpretation of the breakthrough curves using the two sites model developed is an important tool for modelling phenanthrene retention in soils

∇ The soil system simulator of IRH has been set up for the final experiments to be performed in a multiphase mode to allow results on the effect of heterogeneities of physico-chemical and biological soil functions to be obtained

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Multicomponent Multiphase Pollutant Transport in Contaminated Soils: Chemical and Spatial Heterogeneity

TOPICS

(Transport of Pollutants in Contaminated Soils)

1 Introduction

The objective of the TOPICS project is to provide a basis for a mechanistic understanding of pollutant transport and mobility in contaminated soils. It is not concerned with specific case studies, but rather with the development of general methodologies to tackle a wide range of contaminated site problems with special emphasis on the problem of soil heterogeneity.

Risk assessment and soil remediation require detailed knowledge of the behaviour of pollutants in natural and contaminated soils and the capability to predict the fate of hazardous compounds. The interaction of sorption and transport is complex even in a non-contaminated natural soil. At contaminated sites the phenomena of sorption and transport become even more complex, due to

- the man-made spatial heterogeneity of the soil and
- the man-made heterogeneity of chemical structural properties of the sorbing components.

2 Approach

The project TOPICS attacks this problem for two main groups of hazardous compounds in contaminated soils:

- heavy metals, (Cd, Cu) and
- hydrophobic organic pollutants (PAH)

Experimental efforts at various scales provide the basis for optimizing the mechanistic description and subsequent numerical modeling. Such simulation tools will be used to estimate pollutant mobility in contaminated soils.

The problem is attacked with experiments at different levels of complexity:

- laboratory batch sorption experiments
- laboratory column transport experiments
- soil system simulator for pilot scale experiments
- assessment of site heterogeneity in the field

The experiments at laboratory scale are tailored to provide information about the influence of soil solution composition (ionic strength, pH, DOC) on sorption and transport of pollutants representative for contaminated sites. These results at the laboratory scale determine the design of the pilot system experiments to simulate pollutant behaviour at a larger scale, intermediate between the laboratory and the real site situation.

Numerical simulation based on an integrating mechanistic model help to extrapolate to the real site situation. The simulation of realistic scenarios leads to a predictive understanding of pollutant transport in contaminated soils that contributes to risk assessment and soil remediation.

3 Results

3.1 A flow-through reactor system for studying heavy metal sorption

The contribution of ETHZ was to investigate adsorption of various major and minor cations to soil minerals. On the experimental side, the group has developed an flow-through reactor technique for the investigation of strongly sorbing cations. This technique allows a sufficient preequilibration of the samples, which is necessary for proper measurements of adsorption isotherms. The applicability of this technique was verified by comparison with batch and column experiments. Column experiments we also carried out to investigate transport of major and minor cations in soils. On the modeling site, the group has devised an empirical modeling scheme for the description of experimental adsorption data. This modeling scheme applies even in the case of several components, and is very useful to carry out transport calculations. This was possible to demonstrate by various successful predictions of transport behaviour of cations in soil materials.

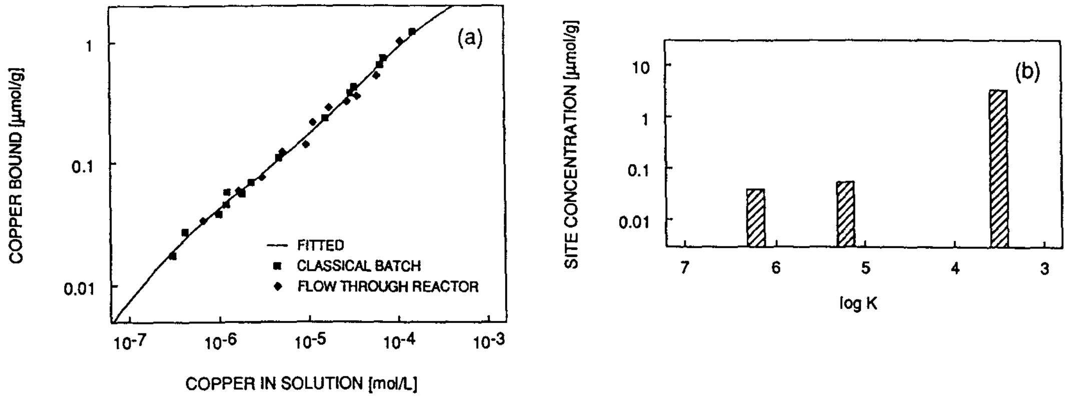


Fig. 1: Binding isotherm of copper (II) to a non-calcareous soil at constant pH 4.2 in 0.01 mol/L calcium nitrate. (a) Doubly logarithmic plot of the experimental data points based on two different experimental techniques. One technique is the classical batch experiment, while the other technique uses a flow-through reactor. Solid line is the fit based on the empirical binding model. (b) Affinity distribution of specific Langmuir binding sites which are used to model the isotherm

3.2 Sorptive heterogeneity of soil organic matter for PAH

First sorption experiments have been carried out with A-horizons from a Dystric Gleysol (the project's reference soil) and a Haplic Alisol. The soils investigated are similar in organic carbon content with 20g/kg for the Gleysol and 19 g/kg for the Alisol, respectively. However, they differ in SOM composition as determined by ^{13}C CPMAS NMR-spectroscopy. Whereas both soils show the same percentage of hydrophobic domains, the domains show differences in the amounts of alkyl C and aromatic C (Table 1): Hydrophobic regions of the Gleysol are composed of relatively higher aromatic regions in comparison to the Alisol. Hydrophobic compounds such as PAHs are supposed to interact predominantly with hydrophobic regions within SOM. Thus, differences in these domains may have an impact on the sorption and desorption behaviour of PAHs.

Table 1: Integrals of ^{13}C CPMAS NMR Spectra of bulk soil from the Ah-horizons of the Dystric Gleysol and the Haplic Alisol

	Carboxylic C	Aromatic C	O-Alkyl C	Alkyl C
	[%]	[%]	[%]	[%]
Dystric Gleysol, Ah	20	25	32	23
Haplic Alisol, Ah	18	17	34	31

Sorption isotherms show a two times higher sorption of pyrene to SOM in the Gleysol compared to the Alisol expressed in K_{OC} values of 19 x 10^4 and 9 x 10^4 l/kg, respectively. Since the organic carbon content in both soils is similar the differences in SOM composition are supposed to cause the differences in the sorption behaviour of pyrene. The hydrophobic regions within SOM of the Gleysol are more influenced by aromatic C compared to the Alisol. These results indicate that the sorption behaviour of PAHs is determined by the SOM composition in addition to the carbon content of the sorbent. They further suggest that aromatic structures within SOM may provide higher sorption capacity for PAHs than aliphatic structures. These results have major consequences for the modelling of contaminant mobility in tar contaminated sites, which are composed almost exclusively of aromatic carbon.

Perspectives: Further experiments with soils of different soil organic matter composition and particle size fractions will establish the relationship in detail. The simulation of a tar contamination (coke-oven site) will provide information about the influence of soil organic matter composition and ageing on the sorption behaviour of PAHs.

3.3 Column experiments with phenanthrene

Sorption of polynuclear aromatic hydrocarbons (PAH's) onto the different components of natural soils (mineral quartz, organic matter, clay minerals...), results in retarding their mobility. To study the contribution of each predominant soil component onto the retention of phenanthrene, as representative PAH, dynamic studies have been performed in laboratory soil columns by LSGC. The column experiments with phenanthrene are designed to allow a mechanistic understanding of the contribution of different sorbing components in soils. To study the contribution of the organic matter (heptamethylnonane) and the clay mineral (kaolinite), dynamic adsorption/desorption studies were performed thanks.

The breakthrough curves (BTC's) obtained at the same time from five column experiments seem to firstly confirm the previous results at the end of which we observe a reversible retention of the phenanthrene onto the mineral surfaces of the quartz sediment. Secondly, the clayey soils give BTC's quite similar with a lower retention effect than a sandy soil alone. Finally, the organic soils reconstituted from quartz sand mixed with the organic matter for the fourth column and from Entraigues mixed with kaolinite and organic matter, give BTC's indicating a great power of retention. If the presence of clay minerals seems to have no real effect on retention, it however reduces the transfer kinetics. In the last part of this study we simulate the behaviour of phenanthrene by the two site model in which we consider the organic soil as presenting two sites: mineral hydrophobic surfaces in which the phenanthrene can be adsorbed and an organic phase trapped by capillary forces into the grain pores which behave as a partitioning phase (Fig. 2)

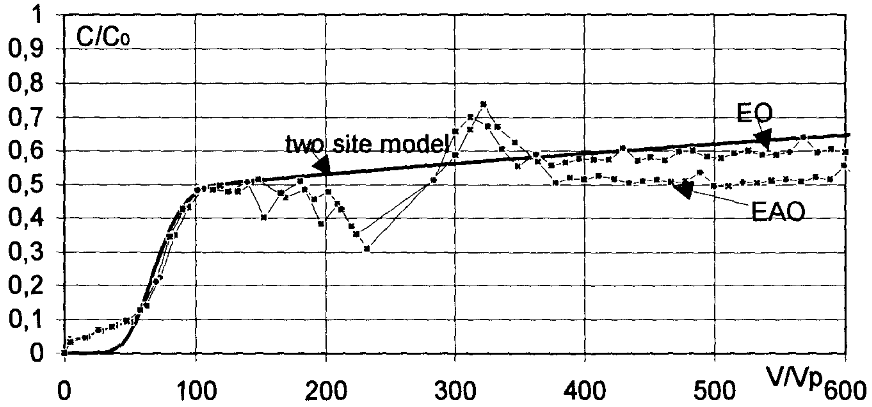


Fig. 2: Two site model simulation of phenanthrene transport onto the organic soil

Perspectives: The two site model seems to be a good way for the phenanthrene BTC's simulation, but new experimental studies must be done in order to confirm the application of this model like kinetic experiments.

3.4 Modelling of phenanthrene dissipation in soil

A model developed for the interactions of PAH with soil under the influence of dissolved organic matter (DOM) was applied to a sandy podzol profile by RUB. As can be seen from the column experiments done at LSGC, the composition of the soil has a decisive influence on phenanthrene mobility. In this example, the complex interaction between DOM, bulk organic matter content and sesquioxides controls the distribution of phenanthrene with depth. The depth distribution (Fig. 3) obtained from numerical simulation is in good agreement with the PAH depth profile as measured at the podzol site. This shows the potential of the model developed to simulate the dissipation of hydrophobic pollutants in soils.

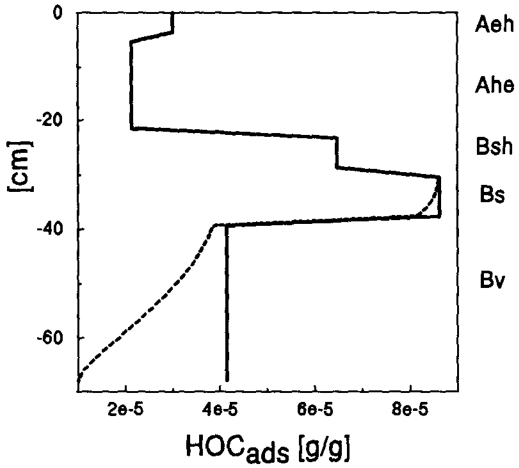


Fig. 3: Simulated phenanthrene distribution in a podzol with known PAH concentrations.
--- phenanthrene after 900 porevolumes, —phenanthrene after 1800 porevolumes

Perspectives: The model will be applied to other sites, especially contaminated sites with known compositional characteristics and PAH contents, in order to evaluate the potential of the simulation model for risk assessment purposes.

3.5 Preliminary test performed with the soil simulation

An experimental plan was developed designing a specific experimental soil system simulator and choosing monitoring techniques. In addition preliminary experiments using laboratory columns has been performed to detect limiting factor concerning monitoring techniques and experimental conditions (IRH).

These results obtained with the soil simulator gives a clear view of the importance of microbial transformation of phenanthrene at the time scale of more than one month. Consequently it will be necessary to take into account this transformation in transfer models. In addition the microflora responsible to phenanthrene transformation seems to modify the properties of heptamethylnonane oil after 25 days. This modification can be induced by tensioactive products of microbial activity which increase the mobility of the oil phase in the soil system. Another experiment without oil is now running to give more insight in the different processes involved in the phenanthrene release suppressing the interference with the artificial oil phase input.

Perspectives: Considering the results obtained during these first tests with the soil simulator a detailed experimental plan has been developed. Considering that these experiments are performed in a multiphase mode (unsaturated conditions and presence of a stationary organic phase) and in a multicomponent gradient mode (carbon source, mineral medium, microbial activity), the results obtained will give a clear view of the effect of heterogeneities of physico-chemical and biological soil functions on the mobility of pollutants.

3.6 Improvement of numerical simulation models for soil remediation

A model has been developed at WAU to describe the interaction between heavy metals (Cu, Cd) and acid sandy soil. This model, entitled the Three Species Freundlich (TSF) model, accounts for organic matter fraction, heavy metal concentration, pH, ionic strength, cation (Ca, Na) and anion (NO3, Cl) effects as well as the interaction between DOC and Cu This model appears to be in good agreement with the more complete NICA model, which is more versatile and complicated. The TSF-model is applied to understand heavy metal content-profiles in the heavily polluted Kempen region, to describe Cd and Cu break through curves in columns, and to define optimal conditions for soil remediation by flushing chemicals. In another research line, this model is used to assess the effect of changing land use on heavy metal mobility and bio-availability and the implications for setting 'sustainable' soil quality standards. The TSF-model is also successfully applied to understand Cu uptake and adverse effects on Collembola and earthworm species (D. venata, L. rubellus). Because unconsolidated aquifers are usually coarse-textured, also for these media the TSF-model may be applicable. Currently, we try to 'fine-tune' the TSF-model for sandy soil and DOC, by assessing parameter values for different types of organic matter and different fractions as associated with texture classes of the project's reference soil in co-operation with RUB.

The applicability of detailed process knowledge to optimization of in-situ remediation of soil and groundwater depends also on physical and contaminant properties. To assess the effects of such properties on remediation, 2 and 3D models were developed for describing flow and transport in heterogeneous porous media. As currently most data from actual remediation sites are generated for organic contaminants, the actual modeling has been addressed to these contaminants rather than heavy metals. For remediation strategy, the spreading (rate and pattern) of contaminants is very important. For organics floating on ground water, this multiphase spreading was described successfully. The removal by pumping of free organics could be described analytically with excellent agreement compared to numerical results of this multiphase problem. These results indicate the expected residual contamination which may be treated with proven technologies like air-sparging below phreatic water level. In sparging, air is injected into aquifers to enhance volatilization and aerobic biodegradation. Its success depends on the homogeneity of air flow and the possibility of oxygen to invade low-permeability zones. With the newly developed model BIODIG (BIOlogical Degradation In Groundwater), we screen conditions (heterogeneity, mean conductivity, contaminant, pumping rate, ...) to assess whether or not in-situ remediation is likely to be successful.

Perspectives: Results of this part of research have led to co-operation regarding actual remediation of soil and ground water with the Dutch consultancy sector. Primary aims are to calibrate the formulae developed and described above and improve chances for successful in-situ treatment.

4 Conclusions and perspectives

The influence of several soil characteristics on sorption and desorption processes of heavy metals and PAH have been investigated. Major progress has been made in the development of mechanistic models for these processes. Experimental data and mechanistic models were used in creating and optimizing numerical models leading to a predictive understanding of pollutant mobility.

FUNDAMENTALS OF *IN-SITU* REMEDIATION TECHNOLOGY

S.E.A.T.M. van der Zee, M.I.J. van Dijke, and H. Keijzer
Dept. Soil Science & Plant Nutrition, Wageningen Agricultural University, NL

The remediation of subsoil and contaminated aquifers often requires *in-situ* techniques. Unfortunately, few guidelines are available to assess the optimal dimensioning (intensity of injection and product wells, discharge) of these techniques or to predict whether or not the remediation will be frustrated by subsoil heterogeneity. Our aim is to develop such guidelines.

Organic liquids that leak into the subsoil, accumulate at the phreatic surface if they are lighter than water in the form of floating lenses. We numerically simulated this proces and developed formulae to predict their growth as a function of subsoil and fluid properties. These formulae proved to be accurate, compared with numerical data and enable our prediction of the extent of contaminated subsoil, taking capillary trapped organics into account. Also formulae developed for describing the situation when the lens is pumped away proved to be accurate. This enables us to optimally design e.g. the pump density, based on subsoil and liquid properties and the set out goals of remediation.

Part of accumulated organics liquids can not be removed by pumping, as it is trapped in the pores by capillary forces. Removal by air injection and extraction may be an alternative provided the contaminant is volatile, and injected oxygen may also enhance biodegradation. With sparging, air is injected below the phreatic level. For sparging, we developed a formula which indicates (i) the radius of influence and (ii) the air saturations within this radius of influence. Both are needed for making an optimal design of the sparging technique in practise. Currently, we are assessing with consultancy firms whether made assumptions are valid for the field, and to what degree subsoil heterogeneity affects the result and should be accounted for in the design. Additionally, the design of soil vapor extraction well fields is studied. It appears that mass transfer limitations in the subsoil need to be accounted for in choosing the optimal extraction rate.

A technique that can be used as an alternative to sparging, is the slow injection of water that contains oxygen or another electron acceptor. In our current modeling, we assess how the concentration of the electron acceptor and the specific discharge influence the cleaning up of contaminated ground water, taking the effects of heterogeneity into account. Our aim is to provide guidelines for dimensioning the technique and for advising its use or discouraging it for practical situations.

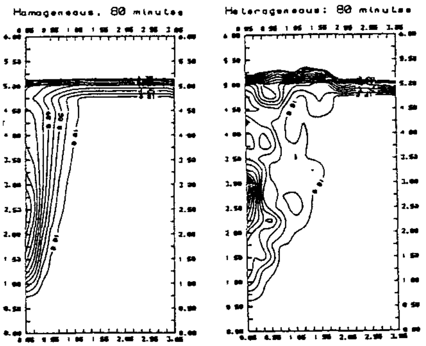


Figure: Air saturations for air sparging in a homogeneous (a) and randomly heterogeneous (b) subsoil

TRANSPORT OF POLLUTANTS
IN CONTAMINATED SOILS

Information: sjoerd.vanderzee@bodhyg.benp.wau.nl or fax +31.317483766

AVAILABILITY, MOBILITY AND SPATIAL VARIABILITY OF HEAVY METALS IN SOIL

S.E.A.T.M. van der Zee, E.J.M. Temminghoff and M.P.J.C. Marinussen.
Agricultural University Wageningen, Department Soil Science & Plant Nutrition, P.O. Box 8005, 6700 EC Wageningen, The Netherlands.Fax: +31.317.483766. E-mail: Sjoerd.vanderZee@bodhyg.benp.wau.nl

Risk assessment of heavy metal pollution of soils aims at predicting the fate of these compounds in the environment. Due to changes in environmental conditions (e.g. acidification) or changes in landuse, e.g. agricultural soils into forest soils, originally relative immobile heavy metals become available to organisms and are mobilized. Our aim is to quantify the relative importance of changes in environmental conditions in relation to availability and mobility of heavy metals in soil.

The availability and the mobility of heavy metals in soils is related with both the total heavy metal content in the soil and the concentration in solution. The latter depends among others on pH, competition and (in)organic complexation. We found that the **availability** (or heavy metal toxicity) for organisms (e.g. plants, earthworms) is (positively) correlated with the 'free' heavy metal concentration in the soil solution. Using simulation models, supported by data obtained by laboratory experiments, we found that heavy metal complexation (with e.g. humic and fulvic acids) strongly influences the heavy metal sorption in soils and consequently influences the **mobility** of heavy metals. (In)organic complexation, as well as pH and competition effects (with mono- and divalent cations) can be taken into account in a two Species Freundlich (TSF) or a three Species Freundlich model (3SF) model to predict the availability and mobility of Cu and Cd in laboratory as well as in the field.

Improvement of ecotoxicologically based risk assessment of polluted soil needs comparison of data obtained by experiments under laboratory conditions with data from field observations. Under field conditions, as a consequence of **soil spatial variability** the exposure of soil dwelling organisms to soil contamination varies with time. Application of data obtained from laboratory studies is erroneous when not taking this temporal variation in exposure into account. We are developing a simulation model to evaluate the role of soil spatial variability in exposure of organisms to contamination in heterogeneously contaminated sites. We performed laboratory experiments using soil from contaminated sites. These studies were followed by field studies at the contaminated sites to compare earthworm Cu accumulation under laboratory conditions with earthworm Cu accumulation under field conditions. Despite a large soil sampling density at the contaminated sites the observed tissue Cu accumulation under field conditions did not match exactly the expectations that were based on data obtained from laboratory experiments. The data obtained from the field studies show that also the vertical heterogeneity must be taken into account when estimating the exposure of earthworms to heavy metal contamination.

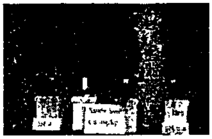
AVAILABILITY, MOBILITY AND SPATIAL VARIABILITY OF HEAVY METALS IN SOIL

Introduction

Risk assessment of soil heavy metal pollution aims at predicting the fate of these compounds in the environment Both heavy metal availability for plants and its mobility are correlated with its concentration in (soil) solution, which depends among others on pH, competition with other cations and (in)organic complexation mechanisms Also for earthworms only a fraction of the total heavy metal content is available Improvement of ecotoxicologically based risk assessment of polluted soil needs comparison of data obtained by experiments under laboratory conditions with data from field observations Under field conditions, the exposure of soil dwelling organisms to soil contamination varies with time as a consequence of soil spatial variability

AVAILABILITY

Plant



Heavy metal availability is related with both the total heavy metal content in soil and its in the soil solution. To estimate the latter, pH, competition and complexation mechanisms have to be taken into account.

photo. *Pot experiment with Ryegrass and a sandy soil at two Cu contents (20 and 100 mg/kg soil) and two pHs (4 5 and 6 8)*

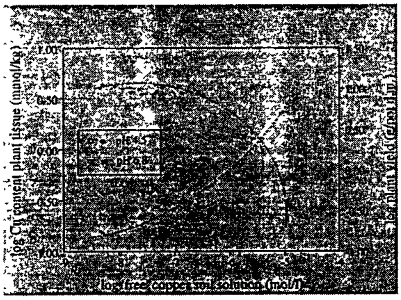


Figure 1 *Copper content and plant yield at two pHs as function of the 'free' Cu^{2+} concentration in soil solution.*

MOBILITY

Dominant factors affecting Cd mobility are pH, competition, ionic strength and complexation. With the 3SF model (three Species Freundlich) we can account for these factors. From Fig. 3 it is clear that the Cd mobility is strongly affected by the divalent cation Ca.

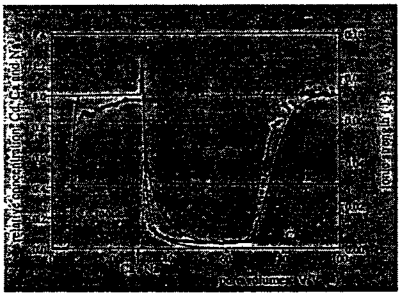
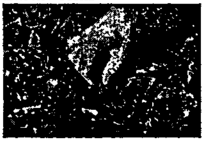


Figure 3· *Multicomponent transport of cadmium, calcium and sodium in sandy soil (data and model)*

Earthworms



Tissue Cu concentration in earthworms is better correlated with the total soil Cu content than with Cu in soil solution Mortality of earthworms, however, appeared to be affected by soil pH and soil Cu content.
Figure 2 shows tissue Cu accumulation determined under both laboratory and field conditions. Mortality was largest in soil from plot B

photo *Earthworm sampling at contaminated site.*

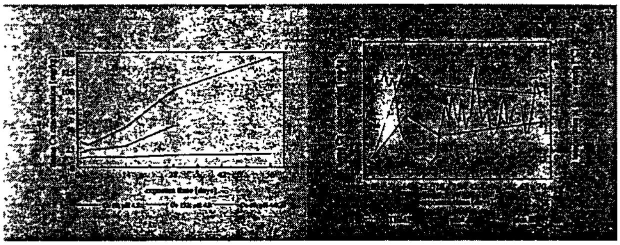


Figure 2. *On the left hand side, tissue Cu accumulation under laboratory conditions is shown. Earthworms are exposed to an uncontaminated reference soil (Cu=10 mg/kg) or contaminated soil from plot A (Cu=132 mg/kg), or contaminated soil from plot B (Cu=68 mg/kg). On the right hand side, tissue Cu accumulation under field conditions in earthworms introduced in Plot A or Plot B is shown.*

SOIL SPATIAL VARIABILITY

Soil spatial variability may play an important role in the accuracy of estimating the extend of a polluted area. Moreover, individuals of soil dwelling organisms meet a variation of contamination levels while foraging trough a polluted area. This phenomenon hampers extrapolation of laboratory toxicity data into field situations

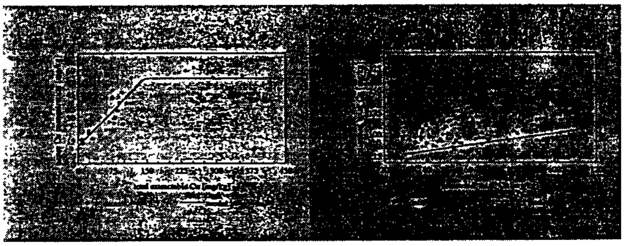


Figure 4: *The graph on the left hand side shows a correlation between total extractable Cu in soil and tissue Cu concentration as determined under laboratory conditions. This relationship is used to compose the graph on the right hand side; the measured total extractable soil Cu concentration is smaller than the bio-indicated soil Cu concentration,, therefore we conclude that earthworms are exposed to a larger extend than we expected from soil chemical analyses.*

Conclusions

- For ecotoxicological risk assesment, both total soil heavy metal content and the available/mobile fraction have to be taken into account.
- The available fraction can be different for different organisms
- We developed a model that accounts for the dominant effects of heavy metal availability/mobility in soil
- To extrapolate data obtained by laboratory experiments to field situations, soil spatial variability must be taken into account.

S E A T M VAN DER ZEE, E J M TEMMINGHOFF and M P J C MARINUSSEN
Wageningen Agricultural University, Dept. Soil Science and Plant Nutrition
P.O Box 8005, 6700 EC Wageningen, The Netherlands
Telefax. +31.317 483766, E-mail: sjoerd.vanderzee@bodhyg.benp.wau nl

TOPICS
TRANSPORT OF POLLUTANTS IN CONTAMINATED SOILS

EV5V-CT94-0536

Fate of polycyclic aromatic hydrocarbons (PAH) in soils: Effect of organic matter composition in bulk and aqueous phase

M. Schoone[1], B. Raber[1], M.W.I. Schmidt[2], I. Kögel-Knabner[2]

[1] Soil Science Group, University of Bochum, D-44780 Bochum, Germany

[2] Department of Soil Science, Technical University of Munich, D-85350 Freising-Weihenstephan, Germany

Soil organic matter (SOM) is the most important sorbent for hydrophobic organic chemicals (HOCs) e.g., PAH in soils A relationship between the content of soil organic carbon and the sorption behaviour of HOCs has been reported for sediments resulting in similar K_{OC} values for a specific hydrophobic organic compound. Recent investigations show different K_{OC} values for HOCs in soils and sediments suggesting that soil properties besides the organic carbon content influence the sorption behaviour of PAHs. The chemical structure of SOM could affect the sorption of PAHs to soil as they are supposed to interact predominantly with hydrophobic regions of SOM.

Dissolved organic matter (DOM) interacts with hydrophobic organic chemicals and thus can act as a carrier for these compounds in soils. The knowledge on interactions between DOM and hydrophobic organic chemicals is often restricted to data obtained from aquifers, natural waters, or humic acids which are not representative for soil systems. In the present study the influence of bulk organic matter composition and DOM on the behaviour in different soils is investigated.

The SOM in the A horizons of the soils investigated differs in chemical composition, i.e hydrophobic domains, as revealed by ^{13}C CPMAS NMR spectroscopy Concurrent differences are obtained for the partition coefficient of pyrene to these soils. These results suggest that the sorption capacity of soils for PAHs is controled not only by the SOM content but also by the chemical structural composition of SOM. The presence of DOM has a drastic effect on the sorption as well as desorption, and therefore on the mobility of PAH in contaminated soils This effect is more pronounced for hydrophobic PAH compounds

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TOPICS

TRANSPORT OF POLLUTANTS
IN CONTAMINATED SOILS

Multicomponent Multiphase Pollutant Transport in Contaminated Soils: Chemical and spatial heterogeneity

Transport of phenanthrene through soil columns

Sonia Dridi-Dhaouadi and Michel Sardin

Laboratoire des Sciences du Génie Chimique (LSGC), Nancy, France

Sorption of polynuclear aromatic hydrocarbons (PAH's) onto the different components of natural soils (mineral quartz, organic matter, clay minerals...), results in retarding their mobility. To study the contribution of each predominant soil component onto the retention of phenanthrene, as representative PAH, dynamic studies have been performed in laboratory soil columns. In order to minimize any adsorptive losses of phenanthrene, all tubing, connections and columns (0.8cm in diameter and 10cm in length) are made of stainless steel . A typical experiment consists of the injection of a step concentration of the contaminant (adsorption mode) followed by the injection of the flushing solution (desorption mode).

A quartz sediment from Entraigues, France, is, firstly used to evaluate the phenanthrene adsorption/desorption onto mineral surfaces. This sand consists of 98.7% SiO_2 and 1.3% of inorganic materials (Fe_2O_3, Al_2O_3,...). Experiments, done with different pore velocities don't allow us to display a kinetic effect. However, a non neglectible retention is observed on the breakthrough curves (BTC's) since the retention volumes are 10 times the porous volume. Nevertheless, the symetrical shapes of the adsorption/desorption BTC's indicate a reversible retention of the pollutant. The effect of the feed concentration on the transport of phenanthrene through Entraigues reveals a capillary condensation phenomenon since the retention volume is higher for a higher feed concentration.

In order to evaluate the impact of the clay minerals onto the phenanthrene behaviour, the same column experiments, as previously described, are done with, on one hand a natural clayey sand of Güe (2.3% of clay (76% of kaolinite)) and on the other hand the sand of Entraigues artificially mixed with a chosen clay mineral (5% of kaolinite). The BTC's so obtained, give results in contradiction with the literature *(D.R. Ghosh et al., 1994; R.E. Mace et al., 1992)*, since retention volumes of 16 and 10 porous volumes (for the sand of Güe and the sand of Entraigues mixed with kaolinite, respectively) are less important than that of the quartz matrix alone which is equal to 72 porous volumes. This neglectible retention compared to that of Entraigues alone may be due to the fact that the grain pore are henceforth occupied by clay minerals.

Organic clayey soils from the Netherlands (2% of organic carbon and 4% of clay mineral) and reconstituted from Entraigues mixed with a known organic matter (5% of heptamethylnonane) give breakthrough curves with significant tailing. We also note that the breakthrough point of the organic soil BTC's are influenced by the mineral site of the soil since the shape of this part of the curves are similar to that of the Entraigues curve. However, the elution part of the BTC's exhibit very long tailings which indicate that new mechanisms take place in the organic site of the soil. This tailing phenomenon, indicating a great consumption of phenanthrene, is more pronouced for higher flow rate. The retention on the organic soil is irreversible since no desorption, with the aqueous solvent, is observed.

Considering these results, we tried to simulate the phenanthrene behaviour toward organic soils by the two site model in which we considered the porous matrix as presenting two sites: mineral hydrophobic surfaces on which the phenanthrene can be reversibly adsorbed and an organic phase trapped by capillary forces into the grain pores which behave as a partitioning phase. This model seems to be a good way for modelizing the transport in a porous medium coupled with sorption phenomena.

Reference:

D. R. Ghosh and T. M. Keinath; Environmental Progress; Vol.13, N°1; 1994

R. E. Mace and J. L. Wilson; Transport and remediation of subsurface contaminants, edited by D. A. Sabatini and R. C. Knox; AC5 Syposium Series; 1992

Measurement and modelling of VOC mobility in soils and groundwaters for environmental risk assessment

EV5V-CT94-0546

Coordinator: M. Jauzein

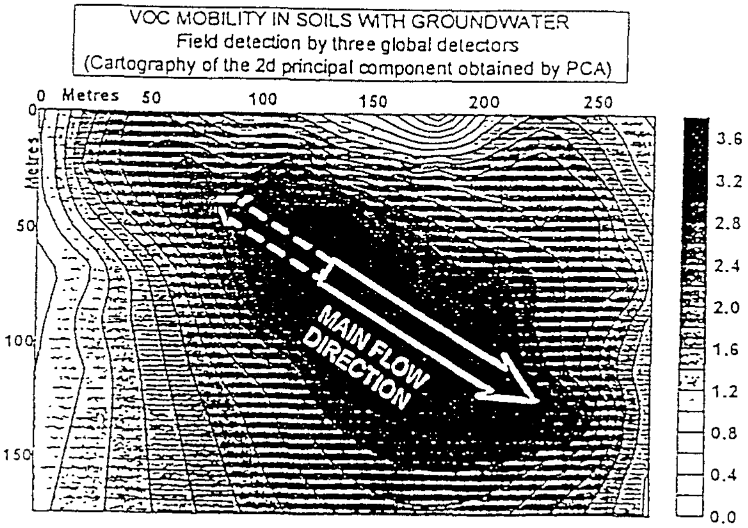
Institut de Recherches Hydrologiques
F - 54515 Vandoeuvre Les Nancy
Tel: +33-83.50.36.51
Fax: +33-83.50.36.99

OBJECTIVES :

The general objective of this project is to design, improve and validate conceptual and instrumental tools needed for the risk assessment related to the contamination of soil and subsoil by VOCs complex mixtures from wastes or accidents.

To solve this general problem three limited technical objectives characterize this project :

- the development of the performance and capacity of measurement systems.
- the development of a single model describing the transfer processes
- the definition of an operational procedure for the measuring system



VOC MOBILITY IN SOILS WITH GROUNDWATER
Field detection by three global detectors
(Cartography of the 2d principal component obtained by PCA)

PARTICIPANTS :

Name : IRH Environnement Adress : 11 bis rue Gabriel Péri, BP 286 F-54515 ANDOEUVRE-LES-NANCY CEDEX, FRANCE Tel : (33).83.50.36.51 - Fax : (33).83.50.36.99	**Name : Institut für Spektrochemie und Angewandte Spektroskopie** Adress : Bunsen-Kirchoff Str. 11 D-44139 DORTMUND, GERMANY Tel : (49).231.1392.238 - Fax : (49).231.1392.120
Name : Laboratoire des Sciences du Génie Chimique Adress :1 rue Grandville, BP 451 F-54001 NANCY CEDEX, FRANCE Tel : (33).83.17.52.54 - Fax : (33).83.32.29.75	**Name : Consejo Superior de Investigaciones** Cientificas, Centro de Technologias Fisicas Adress : C/Serrano 144 ES-28006 MADRID, SPAIN Tel : (34).1.561 8806 - Fax : (34).1.411.7651

Starting date : 1st July 1994 **Duration : 30 months**

METHODOLOGY/APPROACH :

Measurement systems for VOCs in soils :

A unique measuring technology developed by IRH Environnement allows the in situ measurement of VOCs transfer potential in different environmental media : soil, subsoil, unsaturated soil gas phases, groundwater systems. The basis of this method is the coupling of a permeation cell separating an internal gas phase from the external studied media, with continuous or sequential VOCs sensors. One technical objective is to develop multisensors or multidimensional signal systems on the basis of the present mono-sensor and mono-response concept. This measuring system will give vectorial or matricial response to be considered as a characteristic fingerprint of the contamination, extremely more informative than global numerical values.

VOCs transfer modelling :

To perform the quantification step, it will be necessary to develop a specific model applied to the measuring system. This specific model will integrate the transfer mechanisms from the external media to the internal gas phase within the permeation cell and will prevent the influence of transfer limitations on the measurement quality. The transfer limitations take place within and between the different environmental physical media and all along the transfer from the environment to the measuring system. This will allow a direct use of the field data obtained as inputs for this VOCs transfer model.

An operational procedure for contaminated land evaluation :

A specific procedure which allows an easier description and quantification of VOCs mobility in the field situation will be designed and validated. This procedure will include the designing of a specific sampling grid, the performing of continuous or sequential measurements, the multidimensional data treatment to describe spatial and temporal variability, and the quantification step based on the specific model applied to the measuring system.

RESULTS :

Measurement systems for VOCs in soils :

Three type of mutidimensional sensors are studied in this programme. Semi-conductor arrays are developed by the CSIC in Spain. Two generation or sensors has been designed and tested with single substances or mixtures to check the sensitivity and selectivity of the responses. Multi-Capillary-Columns pre-separation and Ion-Mobility Spectrometry (MCC-IMS) is developed by ISAS in Germany. Technical options has been tested and a comparison with classical fused-silica columns has been performed. Advantages and limits of the technique has been checked through measurements with linear and aromatic hydrocarbons as pure substances or in gasoline mixtures. IR absorption multifilters is tested in parallel by IRH in France as a complementary technique to flamme-ionization or photo-ionization detectors. All these techniques will be used in a multisensor approach of VOCs detection in contaminated soil systems.

VOCs transfer modelling :

A computer code has been developed and validated by IRH for the modeling of VOCs transfer from the external medium of the measuring system to the sensors through permeation cells and transfering tubes. This computer code describe the permeation of VOCs through the membranes used in the sampling probe, the dilution, residence time and dispersion in connecting tubes and the effect of the detection cell volume in the measurement dynamic. This model has been applied for the selection of adapted membranes and study of the whole measuring line. Another modeling tool is developed by LSGC for describing the transfer of VOCs in soil systems. This development is perform on the basis of laboratory column experiments giving breakthrough curve results (BTCs) which can be interpreted in terms of predominant physico-chemical interactions. The step by step modeling of single processes is thus possible and can be progressively validated.

An operational procedure for contaminated land evaluation :

Field tests of VOCs measuring systems has been used for the study of the general operational procedure. A set of detectors (FID, PID, IRD, ...) was used to collect multifactorial data on a spatial grid of about 80 points on a real site characterized by complex VOCs emissions. An optimized data treatment procedure coupling statistical principal component analysis with geostatistical interpolation techniques based on kriging has been applied. This procedure will be validated using the future enhanced system on pilot scale column experiments and then on real contaminated sites for demonstration.

MEASUREMENT AND MODELLING OF V.O.C. MOBILITY IN SOILS AND GROUNWATERS FOR ENVIRONMENTAL RISK ASSESSMENT

EV5V-CT94-0546
Coordinator : M. JAUZEIN

1 - INTRODUCTION

The general objective of this project is to design, improve and validate conceptual and instrumental tools needed for the risk assessment related to the contamination of soil and subsoil by VOCs complex mixtures from wastes or accidents.

To solve this general problem three limited technical objectives characterize this research project :

- the development of the performance and capacity of measurement systems.

A unique measuring technology developed by IRH Environnement in France allows the in situ measurement of VOCs transfer potential in different environmental media : soil, subsoil, unsaturated zone gas phases, groundwater systems. The basis of this method is the coupling of a permeation cell separating an internal gas phase from the external studied media, with continuous or sequential VOCs sensors. One technical objective is to develop a multisensors or multidimensional signal systems on the basis of the present mono-sensor and mono-response concept.

This measuring system will give a vectorial or matricial response to be considered as a characteristic fingerprint of the contamination, extremely more informative than global numerical values.

- the development of a single model describing the transfer processes

To perform the quantification step, it will be necessary to develop a specific model applied to the measuring system. This specific model will integrate the transfer mechanisms from the external media to the internal gas phase within the permeation cell and will prevent the influence of transfer limitations on the measurement quality. The transfer limitations take place within and between the different environmental physical media and all along the transfer from the environment to the measuring system. This will allow a direct use of the field data obtained as inputs for this VOCs transfer model.

- the definition of an operational procedure for the measuring system

A specific procedure which allows an easier description and quantification of VOCs mobility in the field situation will be designed and validated. This procedure will include the designing of a specific sampling grid, the performing of continuous or sequential measurements, the multidimensional data treatment to describe spatial and temporal variability, and the quantification step based on the specific model applied to the measuring system.

2 - STATE OF THE PROJECT

The results presented in this paper have been obtained mainly from the following tasks :

- Literature Survey about the theories of transport of VOCs in natural porous media (LSGC, France) : Specific survey of papers coupling experimental observations and transport model developments.

- Permeation cell diomensioning and using procedure optimization : final development of the numerical model to be used for predicting VOCs transfers from external media to detection cells through membranes and transfer tubes.

- Study of the performance of three specific VOC sensors :

  - Semi-conductor sensors arrays (CSIC, Spain) : development of a second generation of multisensors, design of a field measurement system, multisensor characterization for six single component gases, multisensor characterization for four components gas mixtures.

  - Ion mobility spectrometer (ISAS, Germany) : investigation of the main substances selected using beta-radiation and UV light sources, comparison of application of polycapillary-columns as pre-separation with UV-IMS driven as photoionization detector, selection of detection strategies and laboratory testing with gas mixtures for fingerprints analysis and pre-separated mixtures characterization, development of the data acquisition and treatment system for long term experiments and high speed data transfer rates.

  - Infra-Red spectrometer (IRH, France) : comparison of the Infra-Red absorption measurements with other sensors with specific insigh on multivariate analysis for about 30 VOCs.

- Setting up of pilot-scale column experiments for the testing of the whole methodology including the use of the sensors, the permeation cells and the data handling systems (IRH, France).

- Experiments on gas-water transfer through soil : Columns for the experimental study of the interactions between VOCs and soil components (LSGC, France) are run to obtain breakthrough curves (BTCs) in view to analyse their location and shape and to correlate them with physico-chemical interactions occuring in the natural porous medium.

3 - MAIN RESULTS OBTAINED

3 - 1. Specific literature survey of papers coupling experimental observations and transport model developments.

A list of latest important references in the field of VOCs transport and mass transfer kinetics in unsaturated media is has been studied. The analysis of this literature shows the scientific relevance of works developed in this research programme.

3 - 2. Development and validation of a computer code for multimedia transfer of VOCs from external media to detection systems.

The computer code INTERMIL allows to integrate multimedia mass transfer problems in the description of the measuring system. Advective or diffusive transfers can be described in a steady-state percolation system. The main interest of this code is to simulate and study the transfers involving continuous or porous media where permanent flow zones are separated by diffusion limitated barriers. Uniform temperature and pressure is assumed. This computer code can be applied for the study of VOCs sorption on polymeric sorbents, and their transfer through membranes which are homogeneous or porous. A specific application has been developped to simulate the VOCs transfers through the measuring system. A schematic view of the modelling concept is illustrated in the following figure n°1.

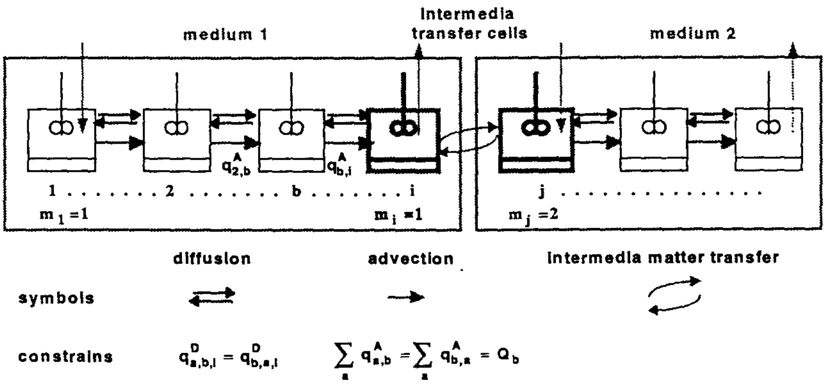


figure n°1 : Modelling concept for the measuring system

3 - 3. Development of measurement systems for VOCs in soils

3 - 3.1.Semi-conductor sensors arrays (CSIC).

The second generation of multisensor was fabricated. Four sensors elements are identical in order to reduce the dimentionality of the array to 10 sensors, having a characterization of measurement reproducibility.

The field measurement system is performed by a digital multimeter with a scanner card and via an RS232 port. Single component characterization has been performed for the concentration of the single gases was varied from 50 to 500 ppm per sample with 3 to 10 repetitions. A principal component analysis of results has been performed in order to obtain the classification of the six VOCs : the chloroform signal is more specific then for toluene, propanal and octane. The following figure n°2 is illustrating the discrimation between six compounds responses.

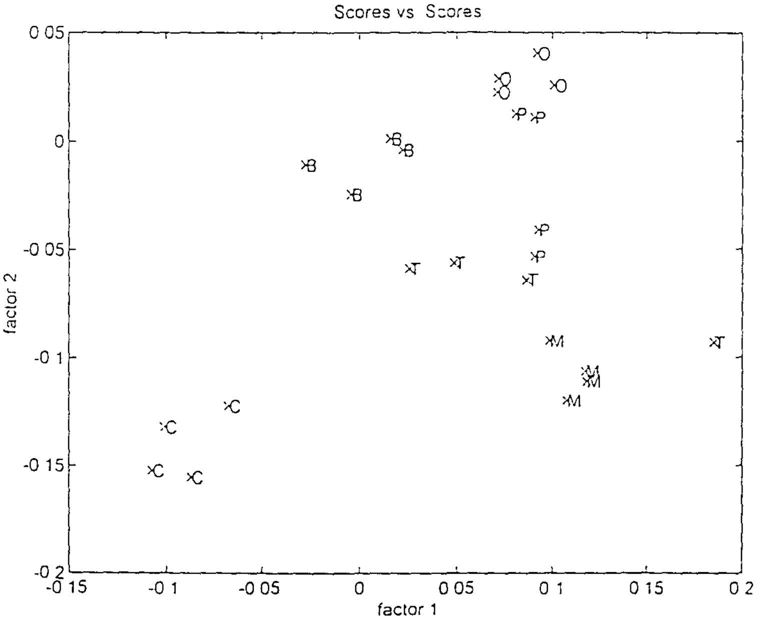


figure n°2 : Main factorial plan for principal components 1 and 2. B is benzene, C is chloroform, T is toluene, O is octane, P is propanal and M is methylethylketone.

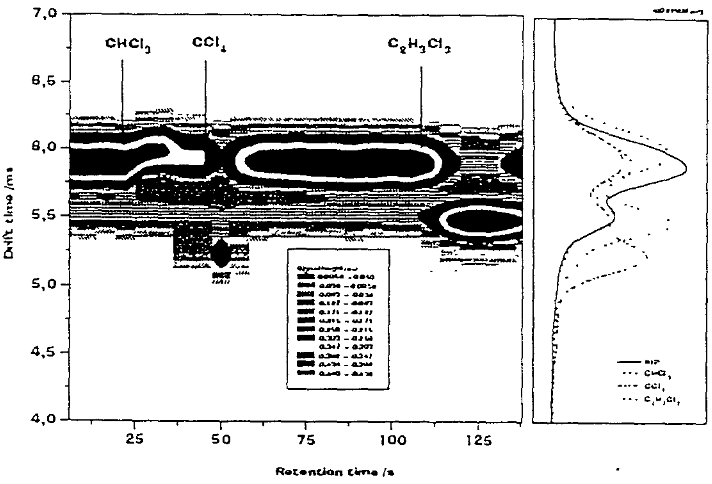
Using mixtures of four gases and 81 selected observations, a transformed least square regression has been used to obtain the parameters necessary to quantify components in unknown gas mixtures. The multiple regression shows r^2 values very close to one, indicating a good description of the calibration by the linear model. The validation of this approach for prediction gives better results for toluene and octane then for benzene and propanal.

3 - 3.2. Multi-Capillary-Columns and Ion Mobility Spectrometry (ISAS).

The main results obtained are from further laboratory investigations of the ion mobility spectrometer system and the test gas generation unit connected to an IMS driven as photoionization detector and an ion mobility Spectrometer with pre-separation using Multi-Capillary-Columns (MCC).

Mixtures of volatile alkanes, aromatic and chlorinated hydrocarbons was used to study a 160 mm long MCC at 27°. Comparison in the separation of volatiles in gasoline

Mixtures of volatile alkanes, aromatic and chlorinated hydrocarbons was used to study a 160 mm long MCC at 27°. Comparison in the separation of volatiles in gasoline showed comparable performance with the conventional fused silica capillary column. The major advantages of MCC seem to be for low sensibility in efficiency toward carrier gas flow routes and in sample loading to at least 100 mg. In addition, the mechanical advantages of a MCC were exploited in the simplicity of hardware and inattention to optimised connections. The following figure n°3 gives an example of two dimensional signal obtained from a mixture of chlorinated compounds.



<u>figure n°3</u> : Ion Moblity Spectra of Negative Ions formed in chloroform, carbon tetrachloride and 1,1,2-trichlorethane using Multi-Capillary Column coupled to an Ion Mobility Spectrometer.

3 - 3.3. IR absorption signals, FID and PID (IRH).

The use of a Brüel and Kjaer IR absorption detector and 3 other sensors (a flamme ionisation detector FID, a photo-ionization detector PID and a semi-conductor sensor SC doped with tin oxyde) with pure volatile chemicals (27 compounds) allowed to compared their sensitivity and complementarity. The IR absorption detection use six filters (1985, 2270, 2950, 2800, 1217 and 746 cm^{-1}). The first one is devoted to water detection, the second one to CO_2 detection, the third one is adapted to C-H links, the fourth one is more specific to aldehydes, the fifth one to esters, alcools and phenols and the six one to aromatic and chlorinated compounds.

A principal component analysis gives a good classification of the 27 compounds in physico-chemical families. Concerning IR absorption, chlorinated compounds are effectively correlated with 746 cm^{-1} filter response. Aromatics are linked to the 2950 cm^{-1} filter and FID signals, and they are correlated with the PID response. Alkanes are correlated to the 2950 cm^{-1} and 1034 cm^{-1} filters responses. Alcools are sensitively detected by the SC sensor and the 1217 cm^{-1} IR filter with other oxydized compounds.

Concerning mixtures, the presence of main compounds belonging to a specific family will allow its determination and characterization. If compounds from different families are present, discrimination and quantification will be more difficult.

3 - 4. Experimental study with laboratory columns and modelling (LSGC)

Column experiments are run with soil samples with different organic contents, to investigate the interactions between typical VOCs and soil organic matter. Two VOCs, among the initial list has been selected for those experiments in saturated condition : propanol and toluene. Residence time distribution, reversibility of sorption and specific behaviour of propanol and toluene have been studied. These experiments, performed in saturated columns packed with three different natural porous materials (sand, impregnated sand and sand-soil mixture) showed :

- no propanol retention,
- a low toluene retention by the sand,
- a higher toluene retention by the impregnated sand than by the sand-soil mixture even if the organic content of the latter is greater than the former.

The results obtained with toluene are illustrated in the following figure n°4. The comparison between the results obtained with the two media is not so obvious considering the different nature of the organic matter in the two cases. A few complementary experiments have to be run to check some points. These experiments constitute a basis in our global approach before the unsaturated runs.

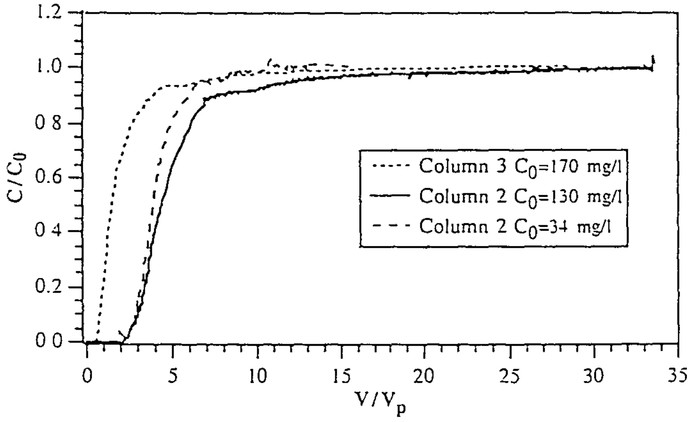


figure n°4 : Breakthrough curves obtained with impregnated sand (2), with toluene 34 and 130 mg/l and with a sand-soil mixture (3) with toluene 170 mg/l.

IV. RESEARCH PERSPECTIVES

The main perspectives for this on-going project are :

- the comparison of the three type of developed sensors on a laboratory scale test bench (IRH),

- the design of a common data handling and interpretation technique for multidimensional and multisensors data obtained (IRH, ISAS, CSIC),

- the test of the whole measurement methodology using pilot-scale experiments set up by IRH for the study of VOCs tranfers in soil systems (IRH, ISAS, LSGC),

- development of the theory of VOCs transport in soil, using modelling and column experiments in saturated and unsaturated conditions (LSGC).

In parallel to this main tasks, specific developments concerning the three types of sensors will be needed to perform all laboratory or pilot scale measurements and prepare in-situ demonstrations planned in the last period of the project (IRH, ISAS, CSIC).

ANALYSIS OF VOCs WITH A SEMICONDUCTOR SENSOR ARRAY

F.J. Gutiérrez, J. Getino, M.C. Horrillo, L. Arés, J.I. Robla, C. García,
J. Rodrigo, J. Rino, R. Sanjurjo

Laboratorio de Sensores, IFA-CSIC
Serrano 144, E-28006, Madrid, Spain

Abstract

Different non-selective semiconductor gas sensors arranged in array configuration can be used for multicomponent gas analysis. A sensor array of 15 tin oxide sensors has been fabricated and characterized for analysis of volatile organic compounds (VOC). High sensitivity values have been obtained for most sensors. The signals of the sensor array have been evaluated by pattern recognition methods in order to classify VOC families and determine quantitatively the components of VOC gas mixtures. Results from data analysis can be used as reference for future in situ experiments of these gases extracted from soils.

Keywords: semiconductor sensor arrays, volatile organic compounds, pattern recognition, gas analysis.

Introduction

The contamination of soil and subsoil by VOC can be continuously monitored in situ using field measurement systems based on semiconductor sensors. The extraction of VOC gases from soils and their transport to the field measuring system can be performed by a permeation cell based on specific membranes. The measured data can be evaluated by parametric pattern recognition methods. Most semiconductor gas sensors have nonlinear characteristics, so, some pre-processing techniques and previous linearization of the responses are needed [1]. The classification has been accomplished through the technique of principal component analysis (PCA) [1-3]. The multicomponent analysis has been performed using multivariate linear regression [3,4]. Four multivariate regression methods have been tested: classical least squares (CLS), inverse least squares (ILS), principal component regression (PCR) and partial least squares (PLS). The classification permitted to distinguish three families of VOCs: aliphatic & aromatic, chlorinated and oxygenated compounds. The best results of the multicomponent analysis were obtained for the ILS and PCR methods.

Experimental

The designed field measurement system consists in a stainless steel test chamber with gas inlet and outlet. A sensor array of 15 elements was placed inside the chamber and an electrical heater was used to achieve the operation temperature. The sensor signals were measured with a digital multimeter with a scanner card and the acquired data were sent to a portable PC via RS232 port. The semiconductor sensor array was formed by tin oxide thin film sensors deposited on an alumina substrate. The films (~ 180 nm.) were grown by r.f. sputtering. Some sensors were doped with Al, Pt and Pd, in intermediate discontinuous layer. See [5] for details on the fabrication process. The electrical characterization was carried out measuring the sensors resistances at 300 °C with a flow rate of 200 ml/min in dry air.

Results

The single component characterization has been performed to six VOCs: benzene, chloroform, toluene, octane, propanal and MEK. The concentration of the single gases was varied from 50 to 500 ppm per sample. The number of samples was comprised between three and ten per single gas. The responses were measured after 20 minutes of gas exposure. With the data from 94 observations we have performed the PCA (principal component analysis) in order to obtain the clasiffication of the six VOCs. The sensor signals, y_{ij}, for only one gas component j present in air can be approximated [4] by:

$$y_{ij} = (1 + B_j\ X_j\ )^{c_{ij}}$$

To eliminate the gas concentration the sensor signals are normalized by:

$$p_{ij} = \frac{c_{ij}}{\sum_{i=1}^{p} c_{ij}}$$

The normalized signals, p_{ij}, are mean-centered and variance-scaled and then used as the inputs for PCA. In Fig. 1, the loadings of the first two factors are shown, indicating the contribution of each sensor to PCA. Three groups of sensors can be shown: sensors 1-10, sensor 11 and sensors 12-15. The sensors in each group are redundant and indicate collinearity in the response matrix. So, only three individuals are susceptible to be well classified. The scores on PCA factor 1 vs. the scores on PCA factor 2 are shown in Fig. 2 for three VOC families: oxygenated, chlorinated and aromatic & aliphatic compounds. The chlorinated class can be separated from the other classes. Considering factor 3 vs. factor 1 (see Fig. 3), more efficient discrimination can be found.

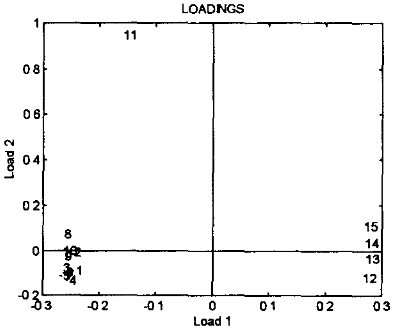


Fig. 1 PCA Loadings.

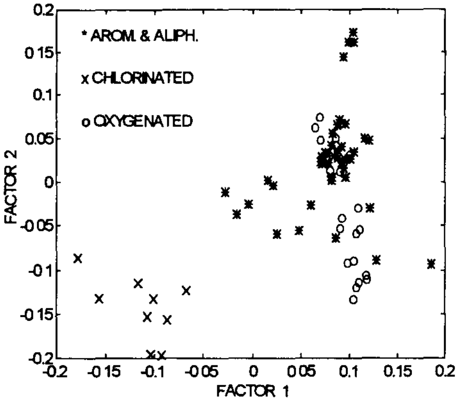


Fig. 2. PCA Scores for factors 1 & 2

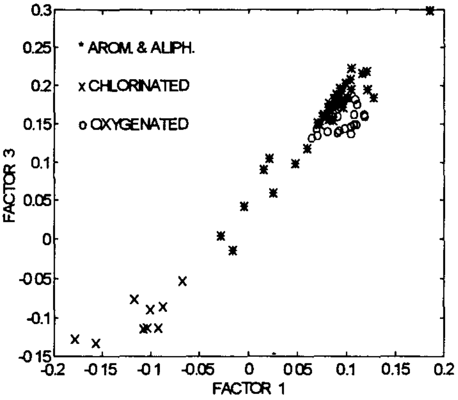


Fig. 3. PCA Scores for factors 1 & 3

The gas mixtures characterization has been performed to four VOCs: benzene, toluene, octane and propanal. The number of observations selected was 81, corresponding to the combinations of four gases and three concentrations per gas (0, 50, 100 ppm). The responses were measured after 10 minutes of gas mixture exposure. With these data we have performed the multicomponent analysis in order to obtain the quantitative determination of the components of an unknown VOCs gas mixture. The multicomponent analysis has been carried out in two steps: the linearization of the responses first, and second, the multivariate linear regression. The linearization consists in the transformation of the sensor responses and the concentrations into new sets of variables, so that the transformed response is a linear combination of the transformed gas concentrations. Assuming a dependence of the sensor signal, Y_i ,on the gas concentration, X_j, expressed [4] by:

$$Y_i = \left(1+\sum_{j=1}^{q}(A_{ij}X_j)^{m_j} \right)^{-\beta_i}$$

the transformed data are:

$$y_i = (Y_i)^{-1/\beta_i}$$
$$x_j = X_j^{m_j}$$

The model parameters have been estimated for each sensor using the Levenberg-Marquardt method applied to Y_i and X_j. The coefficients of multiple determination, r^2, are very close to one, indicating that the residual sums of squares decreases and hence that the model describes the calibration set well. With these transformed variables we have applied linear regresion methods, like MLR (multiple linear regression), ILS (inverse least squares), PCR (principal component regression) and PLS (partial least squares). A validation matrix of nine observations was used to test the different methods. The mean values of the relative prediction errors in percent and the mean values of the width of the 95% prediction intervals in ppm [4] were calculated for each method in order to estimate the quality of the applied methods. The concentrations of octane are predicted with the lowest error (20-28%) whereas the concentrations of benzene are predicted with the highest error (34-400%). In general, the lowest errors are obtained for PCR (25-34%) and ILS (20-60%) methods. The broadest intervals are obtained for benzene (120-800 ppm), and CLS method (50-800 ppm). The narrowest intervals are obtained for octane (20-60 ppm) and ILS method (20-150 ppm). In Fig. 4 are shown the predictions from PCR method for each VOC. In each plot are shown the real concentrations (circles), the predicted concentrations (x) and the 95% prediction intervals (bars) for the nine observations. All the circles lie inside the prediction intervals and the predicted concentrations lie near the true concentrations.

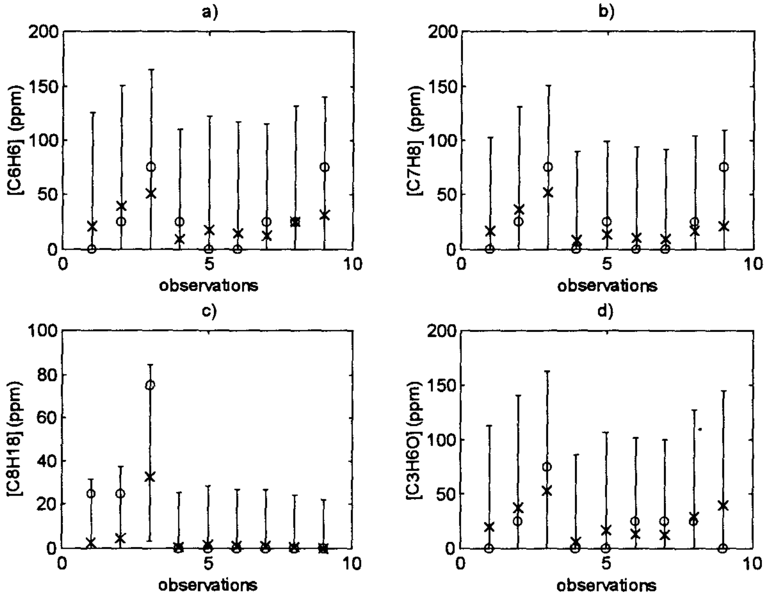


Fig. 4. PCR predictions. a) benzene, b) toluene, c) octane, d) propanal.

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MULTI-CAPILLARY COLUMN GC COUPLED TO ION MOBILITY SPECTROMETRY

J.I.Baumbach[1], S.Sielemann[1], O.Soppart[1], G.Walendzik[2], D. Klockow[1]

[1] Institut für Spektrochemie und Angewandte Spektroskopie,
Bunsen-Kirchhoff-Str 11, D-44139 Dortmund, Germany
[2] Institut für Entsorgung und Umwelttechnik, Kalkofen 6, D-58638 Iserlohn, Germany

ABSTRACT

The combination of a gas chromatograph with an ion mobility spectrometer (IMS) has been a key theme since the earlier publications dealing with IMS, the aim being to achieve further enhancement of the resolution. One major problem has been the difficulty in optimising ion mobility spectra collection at rates of 50 ms with retention times typical for conventional capillary columns and orders of magnitude higher. A main feature that GC columns exhibit for IMS is the delivery of vapours to the ionisation region of the IMS under conditions that are ideal. The gas flow rates in GC, however, differ considerably from those usual in IMS applications.

The idea to employ bundles of parallel capillaries (MCC) as a single chromatography column offers not only separation efficiencies determined by some 1000 theoretical plates/meter, but also unusually high carrier gas flow rates and consequently retention times in the range of some seconds are achievable as demonstrated by separations carried out with alkenes and other volatile organic compounds. The coupling of MCC with IMS leads to a significant increase of the scope of application of IMS. The influence of inter-molecular charge transfer reactions on the IMS signal can be reduced and the application of IMS to the analysis of more complex matrices be considered.

First results illustrate the potential of MCC-IMS for environmental real time pollution monitoring, one example being new strategies of chemical waste processing and risk assessment.

MEASUREMENT AND MODELLING OF VOC MOBILITY IN SOILS AND GROUNDWATERS FOR ENVIRONMENTAL RISKS ASSESSMENT

TRANSIENT TRANSPORT OF VOLATILE ORGANIC COMPOUNDS (VOC) IN NATURAL POROUS MEDIA : SATURATED COLUMN EXPERIMENTS

M.O. Nicolas-Simonnot, B. Harmand and M. Sardin
LSGC-CNRS-ENSIC, 1 rue Grandville, BP 451, 54001 Nancy Cedex France

Laboratory column experiments have been performed to investigate the transport of toluene (chosen as a representative VOC) in saturated conditions. Three types of porous media have been tested: a clayey sand (Güe sand, France), mixtures between a natural soil (la Bouzule, F) and a sand, and a "model" soil obtained with Güe sand impregnated with heptamethylnonane (C_{16}).The sand-soil mixture columns have organic content between 0.41 and 0.66% and the model soil between 0.05 and 0.42%.

The apparatus is composed of a reservoir, a double plug pump, a glass column, an on-line UV spectrophotometer (wavelength 261 nm) and a computer for data acquisition. A typical column run consists of injecting a step of feed solution (aqueous solution containing dissolved toluene) until the effluent concentration reaches the influent concentration (adsorption step), and then of eluting the contaminant by feeding the column with contaminant-free water (desorption step).

In all cases, the adsorption and desorption curves are symmetrical, which proves the reversibility of phenomena.

The runs performed on the sand column (20 and 130 ppm toluene, pore velocity 0.47 cm/min) show that toluene breakthrough is hardly not delayed. The runs made on the sand-soil columns (75-25 and 60-40 sand and soil weight percent) showed that toluene delay is proportional to the porous medium organic content as it is the case for the model soil. For each adsorbent type, the plot of the mass of adsorbed toluene at equilibrium (mg toluene/mg porous medium) against the toluene concentration in the aqueous phase gives an adsorption isotherm, which is almost linear, slightly convex. However the partition coefficients K_d are poorly predicted by the correlations found in the literature.

Moreover, it is experimentally observed that the model soil retains toluene more strongly than our natural soil: for a lower organic content (e.g. 0.11% against 0.40%), toluene breakthrough occurs later on a model soil column than on a sand-soil column, all parameters (toluene concentration, pore velocity etc.) being kept constant. This may be mainly due to the different nature of the organic matter of the two media: humic acids are present in the natural soil, as the model soil is impregnated by an alkane. The difference in polarity leads to a different partitioning of toluene between water and the soil organic phase: the retention is favored in the case of the model soil. Besides, the spatial repartition of the organic carbon is different: the impregnation chemical is located on the surface of the sand particles as the organic carbon can be hidden inside the soil particles, thus toluene could not interact with the totality of the organic carbon.

The influence of the pore velocity was investigated on a 0.5% impregnated model soil column (0.09 ; 1.84 and 3.68 cm/min). The breakthrough curve are sensitive to pore velocity, which shows a kinetic effect.

At present, we propose a representation of toluene transport in saturated columns by a linear transport model: mixing cells in series including transfer with a dead zone. We have to take into account kinetic effects.

Evaluation and improvement of the bioavailability of pollutants in soils and sediments for better remedial practices and risk assessment methods

EVWA-CT92-0004

Coordinator: M. Jauzein

Institut de Recherches Hydrologiques
F - 54515 Vandoeuvre Les Nancy
Tel: +33-83.50.36.51
Fax: +33-83.50.36.99

METHODOLOGY/APPROACH :

Bioavailability has been studied through bioevolution processes and ecotoxicity effects. Different type of techniques has been developed for this study : physico-chemical characterization of soil fractions exhibiting different levels of PAHs bioavailability, monitoring methods to study the potential bioevolution of PAHs and their byproducts, ecotoxicological testing applied to soil materials and associated leachates, monitoring techniques for microbial colonization processes. The design of soil system simulators has allowed to understand bioavailability processes upscaling in less controlled conditions, in one hand for the mobility of biological activity, and in the other hand for the availability of PAHs for degradation and ecotoxicity potential effects.

The results presented in this paper have been obtained from the following main tasks involving different specific objectives and applied methods :

- Physico-chemical characterization of PAHs availability in soil materials using fractionation methods to define non-available contaminants and application to the study of the availability of PAHs for biodegradation (DMT).
- Laboratory study of the potential bioevolution of PAHs in soil systems through the use of labelled compounds for a specific tar polluted soil (WQI) and the monitoring of phenanthrene evolution in five reference soil materials (IRH).
- Development and application of ecotoxicological testing for the monitoring of bioavailable PAHs in soil materials (DMT, WQI and IRH).
- Study of the potential behaviour of degradation byproducts (1-naphtol and catechol) through biological or physico-chemical processes (UCL and UTC).
- Study of selection processes and activity evolution of bacterial consortia in complex media including aqueous and organic phases containing toxic substances in laboratory pilot-scale experiments (UTC and UCL).
- Physico-chemical, biological and ecotoxicological monitoring of the evolution of PAHs contaminated soils in pilot-scale soil simulator experiments (IRH).

RESULTS :

The main conclusions of this research programme are the following :

- PAHs in soils are mainly retained by an organic carbon fraction naturally occuring in < 10 µm particles size fraction and anthropogenically occuring in > 1000 µm particles (coal, coke, wood, ...). The non available fraction is close to 2.5 g of PAHs per 100 g of Total Organic Carbon.
- PAHs in soils are mainly transformed through biological processes in compounds accumulating in the alkaline extractable humic and fulvic acids fractions or in the non extractable humin fraction. These compounds are analogs of humus polymers, their availability for acute ecotoxicological effects is less important then initial PAHs. The half-life observed for phenanthrene is between 23 and 65 days for five different soils but the related acute ecotoxicological hazard exhibit lower half-life depending mainly on the organic matter content (from 1 to 60 days).
- Ecotoxicological testing is a complementary and interesting tool for the monitoring of bioavailable PAHs in soil materials. These techniques need a choice of appropriate tests battery for better hazard assessment data but are a unique method for the monitoring of bioavailability of pollutants in soils. Depending on the target organisms, the active pollutant fraction (inducing effects) is more or less important.
- The main degradation byproducts in aerobic environments (1-naphtol and catechol) are subjected to autoxidaton or polimerization processes which are close to humification. In anaerobic environment, these abiotic transformations cannot take place due to necessary oxygen and a biological degradation is observed.
- An indirect impedancemetric measurement of carbon dioxyde evolution has been developed and allows to study degradation processes. The mobility of bacterial cells seems to be strongly influenced by the non-stationnary hydrophobicity of cells. In a methanogenic environment, the mobility of this activity has been observed for less than 30 cm distances with a characteristic time of about 20 days.
- The bioavailability of PAHs for degradation is mainly limited by the existence of anaerobic zones and by organic matter content. In parallel, the bioavailability of PAHs for ecotoxicological effects is rapidly decreased in percolating water but only slowly for the less available fractions.

Starting date : 1st January 1993 **Duration : 30 months**

EVALUATION AND IMPROVEMENT OF THE BIOAVAILABILITY OF POLLUTANTS IN SOILS AND SEDIMENTS FOR BETTER REMEDIAL PRACTICES AND RISK ASSESSMENT METHODS

EVWA-CT92-0004
Coordinator : M. JAUZEIN

1 - INTRODUCTION

Concerning the bioavailability of pollutants in soil and sediments, the main objective of the research programme is to identify, understand and characterize the main processes involved. These processes influence both the acuteness of induced toxicity effects on organisms and the kinetics of biological degradation and thus the safety and efficiency of remedial practices. They include physico-chemical processes related to pollutants availability : mass transfer limitations and physico-chemical interactions between pollutants and stationnary phases. In addition, they also include processes related to organisms availability : microbial mobility limitations, physiological and ecological limiting factors. The expected achievement for this main task is the development of suitable concepts and associated numerical models which will be able to simulate the main processes governing the bioavailability of pollutants in soils or sediments. Then, with a development of adapted pilot-scale experiments, new remedial practices or risk assessment methods will be designed and tested at the pilot-scale with respect to the previous understanding of bioavailability processes.

One key problem encountered is that the hazards of contaminated sites as pollution potential sources, and the related risks for human health and the environment are not directly linked to the pollutant concentrations in soil materials. Thus, the present managing approach for contaminated lands, based on contamination level in soil materials, is not sufficient for a realistic risk assessment.

In the framework of this programme, PAHs contaminations were chosen as a case study. As a matter of fact, PAHs are critical hazardous substances present in many former industrial sites characterized by cokery installations, but the risk associated to these contaminations is difficult to assess due to low solubilization and potential evolution of these substances. Biological transformations of PAHs and specific interactions of PAHs and their byproducts with soil components are key processes governing their availability for potential impacts. Consequently, a detail study of the PAHs solubilization, transformation and retention by soil systems is necessary for predicting associated risks and enhancing remedial practices especially in the case of biological techniques.

2 - METHODOLOGICAL ASPECTS

Bioavailability has been studied through bioevolution processes and ecotoxicity effects. Different type of techniques has been developed for this study : physico-chemical characterization of soil fractions exhibiting different levels of PAHs bioavailability, monitoring methods to study the potential bioevolution of PAHs and their byproducts, ecotoxicological testing applied to soil materials and associated leachates, monitoring techniques for microbial colonization processes. The design of soil system simulators has allowed to understand bioavailability processes upscaling in less controlled conditions, in one hand for the mobility of biological activity, and in the other hand for the availability of PAHs for degradation and ecotoxicity potential effects.

The results presented in this paper have been obtained from the following main tasks involving different specific objectives and applied methods :

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- Physico-chemical, biological and ecotoxicological monitoring of the evolution of PAHs contaminated soils in pilot-scale soil simulator experiments (IRH).

3 - MAIN RESULTS OBTAINED

3 - 1. Characterization of non-available contaminants (DMT).

Four soils sampled in coke oven sites has been characterized. One was clayey (M5), an other was silty (TOL), a third one was anthropogenic and sandy (BUC), and a fourth one was constituted of filling materials (RE). All these soils were characterized by a PAHs contamination originated from tar oil. No heavy metals, phenols or BTEX contaminations have been detected. The performing of biodegradation experiments at the laboratory and at the pilot scale (airlift or fluidized bed bioreactors) demonstrates the existence of non available PAHs especially in the case of the filling material (RE). For all the soils, even for 2-4 rings PAHs known to be degradable, a significative fraction of the contamination is still non available for degradation after treatment. The initial range from 300 to 6000 mg/kg PAHs was reduced to a range from 200 to 500 mg/kg PAHs.

The separation and characterization of soil particle size fractions showed specific seggregation at the end of biological treatment. Particles having a size lower than 10 µm and greater than 1000 µm in the case of BUC material are enriched in PAHs. The other fractions are characterized by a PAHs content lower than 100 mg/kg. Consequently, between 7 and 30 % of the soil components contain 50 to 80 % of the total PAHs content. The surface load of PAHs in the contaminated soils were the highest in the fraction upper than 40 µm and then the fraction lower than 10 µm. After biotreatment, compared to other fractions, this surface load decrease only slightly for the fraction lower than 10 µm. In addition the non available PAHs content is correlated to the organic carbon content and specifically with the alkaline extractable humic and fulvic acids. In the cases where coal particles were present (BUC and RE), another part of non-available PAHs was associated to this fraction.

Thus, mass transfer limitation due to physico-chemical interaction with humic and fulvic acids in one hand and coal particles in the other hand, is the dominant factor determining the availability of PAHs in the investigated soils. Another point of interest is the increase of the alkaline extractable substances (AES) during biotreatment in soils giving a hint to the occurance of humification like processes (e.g. polymerization of reactive metabolites) during biotreatment of PAH-contaminated soils as confirmed by NMR-analyses of AES.

3 - 2. Bioevolution of PAHs in soil systems

3 - 2.1.Use of labelled compounds in a tar polluted soil (WQI).

The enhancement of degradation rates was studied through the use of surfactants. The main effects of surfactants has been observed only for highest concentrations (soil containing 3 to 4 g/kg of PAHs contaminated tar) indicating that for residual concentrations PAHs are not available for solubilization. Then, a selection of 3 over 70 strains of bacteria allows to select a specific consortia able to enhance the degradation of PAHs in soils. The use of such type of externally selected strains was tested (inoculation at the level of 10^6 cell per g) and it was only effective in the case of highest concentration with too high toxicity effect for inherent bacterial consortium. Using labelled compounds, it was possible to monitor the behaviour of carbon initially contained in PAHs rings. A major part of this carbon is integrated to the alkaline extractable fraction of organic carbon or to the non extractable humus. After 78 days of biological evolution, the 2-3 rings PAHs fraction was reduced to low availability fractions, the 4 rings PAHS fraction was subjected to minor reduction and the 5 rings PAHs fraction was persistent.

3 - 2.2. Biological degradation of Phenanthrene in soils (IRH).

The objective of these experiments was to study, quantify and understand the biological evolution of PAHs in soil systems. Five reference soils sampled in the Lorraine region in France has been selected due to their large range of properties (clayey, silty, sandy and acid, calcareous, organic). These soils has been contaminated by 800 ppm of phenanthrene in an inert oil (heptamethylnonane HMN : 150 ml / kg of soil). An inoculation at the level of 3.10^6 cells / g of soil was used for running the experiments.

Blanks with HMN but without phenanthrene at 25°C and duplication at 4°C has been performed to avoid interpretation problems. The biological evolution is studied in unsaturated conditions (80 % of water retention capacity) and surface ventilation with CO_2 free air. Phenanthrene degradation and CO_2 production are monitored.

For, the five soils, differences between 25 and 4°C are significative after about 10 days. After this delay, the biological degradation of phenanthrene is clearly observed. Volatilization of phenanthrene was verified to be non-significative compared to the degradation. The half-life of phenanthrene obtained for the five soils is ranged from 23 to 65 days. The maximum is obtained for the organic soil and the acidic one. The highest degradation is obtained for the calcareous soil. These results are thus completely coherent with the general biological activities of those soils. In addition, phenanthrene degradation is really correlated to the global respiration process. But, if the presence of phenanthrene is clearly linked to an excess of respiration, this excess is higher than expected and could be an indice of a cometabolism phenomenon.

3 - 3. Ecotoxicological testing and bioavailability assessment (DMT, WQI, IRH)

Ecotoxicological characterization of aqueous extracts of the soil fractions by standard toxicity test systems confirmed the results obtained by physico-chemical characterization of particle size fractions before and after biotreatment trials performed by DMT. Even residual PAHs remain in the treated soil, ecotocixity is reduced below the detection limits in aqueous extracts.

In the case of the biological evolution of a tar polluted soil studied by WQI, the reduction of toxicity is also effective over a period of 78 days. No transient toxicity events have been observed in the case of PAHs degradation and the decrease in toxicity in close to a linear process. This can be linked to the production of metabolites which are less bioavailable than the PAHs themselves. An another important result is related to the use of a tests battery including a bacteria (*Vibrio fisheri*), a crustacean (*Daphnia magna*) and a collembola (*Folsomia candida*). The bacteria is highly sensitive to the presence of contaminants in water and much more than the collembola. But after biotreatment, the collembola is more sensitive to less available fractions of contaminants than the bacteria. Consequently, the reduction in toxicity seems to be higher using the bacterial test (factor 10) than the collembola test (factor 2). The importance of using a battery is thus outlined here especially for the hazard assessment of low availability contaminants and the monitoring of remedial practice efficiency.

Different types of ecotoxicological tests have been tested by IRH for the monitoring of biological evolution experiments. The bacterial test Microtox on the aqueous phase of soils gives significative results indicating a detoxification of leachates. The half-life of the toxicity is generally lower than the half-life of phenanthrene in the soils indicating the presence of a non available fraction. This availability of toxicity is mainly related to the organic matter content : the half-life time is about 1 day in the organic soil, identical to the phenanthrene in the acidic soil (about 60 days) and the calcareous one (about 30 days), 2 to 3 times lower than the phenanthrene for the two other soils (about 15 days). The same test performed on a methanol extract is more sensible to less available fractions and can be an alternative to classic water extracts tests. A specific protocol is performed with a soil suspension with the same bacteria and seems to be extremely more sensitive. In the case of the organic soil, the toxicity is the highest before biological evolution but is completely reduced after 90 days. For the acidic soil, this toxicity indice is maintained at the same level during the same 90 days. Tests using plants (soja germination) or insects (*Colpoda aspera*) gave no significative response to the presence of phenanthrene in this reference soils.

3 - 4. Behaviour of degradation byproducts : 1-naphtol and catechol (UCL)

1-naphtol and catechol are known to be the main transient metabolites of PAHs degradation. But experiments in the soil systems with those compounds show generally a rapid dissapearance from the solution by abiotic reaction in aerobic conditions. These reactions have been studied to quantify their impact on the global process.

The results show that the naphtol does not undergo autoxidation (or only very slowly) when alone but is transformed quickly (autoxidised or polymerised) in the presence of catechol. From these first observations, we can assume that the presence of catechol or one of its reacting form, either enhances the rate of the 1-naphtol transformation reaction, or creates a new transformation pathway. The fact that catechol transformation rates seem to be equal when alone and in mixture suggests that catechol acts only as a catalyst in the 1-naphtol transformation reaction and do not combine with 1-naphtol.

These results confirm those obtained by the other partners of the project concerning the humification like process. If PAHs are oxydized to produce multiphenolic compounds, the presence of catechol enhance the process of condensation with the humic substances which are analogs for these metabolites. A major part of the carbon follows this particular route of transformation.

In anaerobic conditions, those reactions cannot take place but biological degradation is possible. Enhancement of this degradation is limited and gives average degradation rates of about 5 mg/l/day for the 1-naphtol compared to 8 mg/l/day obtained for 2,4,6-trichlorophenol and 2,4-chlorophenol inducing an accumulation of 4-chlorophenol. After more than 600 days, degradation of this compound was possible up to 4 mg/l/day.

3 - 5. Potential dynamics of degraders (UCL and UTC)

3 -5.1. Phenolic degraders in combined aerobic-anaerobic media (UTC).

For studying the acclimation of bacterial consortia to contaminants, a specific activity measuring system has been developed. This system is based on an indirect impedancemetric measurement able to monitor the CO_2 evolution. This system has been applied to the acclimation of aerobic and anaerobic bacteria to chlorinated phenols up to concentration of 10 to 500 mg/l. The complete degradation of 2,4,6-trichlorophenol has been obtained successfully combining an anaerobic dechlorination to 4-chlorophenol and a degradation of this metabolites by mixed cultures.

In addition, the influence of the hydrophobicity of cells during their life cycle has been studied to undertand the colonization processes. The use of diphasic media allows to create enhanced conditions for the colonization of multiphasic systems. Hydrophobicity of cells changes with time inducing mobility of new cells characterized by a lower hydrophobicity and an increased adhesion of cells with time due to an increase of their hydrophobicity. Consequently, hydrophobicity can be a key factor of selection when the main activity of microorganisms is expressed on interface locations. In addition, processes of mobility-adhesion of microbial population is enhanced by continuous changes in the hydrophobicity of cells.

3 - 5.2. Mobility of a microbial activity in the soil system (UCL).

A 0.5 m^3 pilot scale bioreactor has been developed in the laboratory. After a first period of validation and characterization, a bacterial displacement experiment has been performed in the model soil bioreactor filled with argex (expanded clay beads). The aim of this experiment is to quantify a specific bacterial activity moving horizontally from a colonised zone of the reactor to a sterilized zone. The specific activity chosen as the indicator of the bacterial displacement is the methanogenic activity. This activity is measured by sampling and incubation of about 15 g of soil with a feeding liquid in standardised conditions.

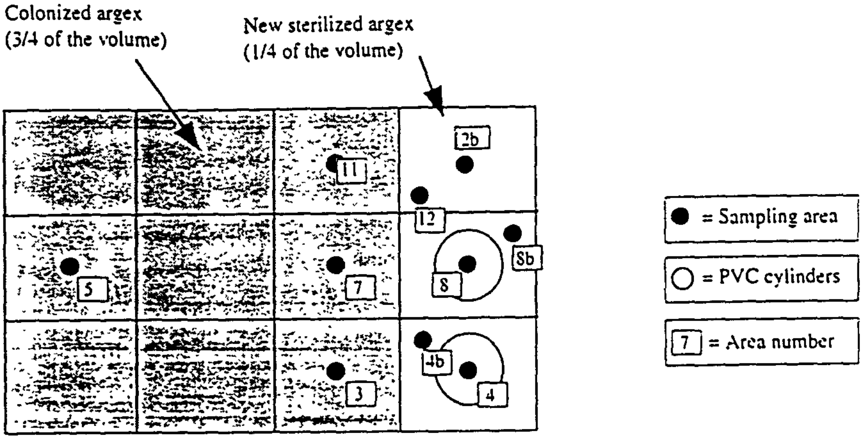


Figure n°1 : Top view of the reactor with the two zones (already colonized in dark grey and sterile in light grey), the two cylinders (isolated and sterile zones) and the sampling areas in these zones.

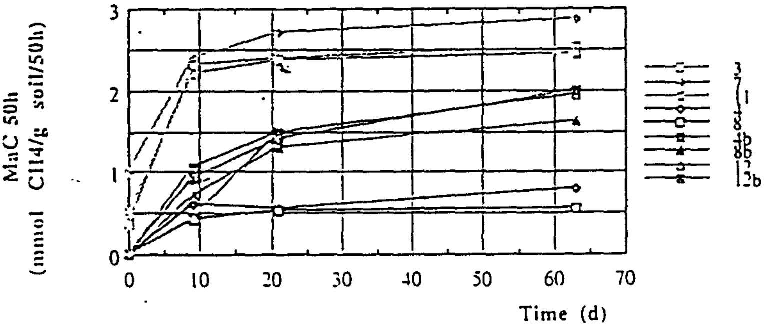


Figure n°2 : Evolution of the methanogenic activity at 8 locations in the reactor.

The already colonised part of the reactor recover quickly the normal activity. Then, this activity remains stable and constant during the whole experiment. The activity in the sterile part of the reactor is progressively colonized from the other part of the reactor. This activity increases and remains low for a long time period suggesting the necessity of a spatial reorganisation of the different bacterial population composing the methanogenic commmunity. This low activity can also be due to differential migration speed of the different populations. The activity in isolated and sterile part of the reactor, is very low compared to other zones. The only possibility of colonization is from bottom water fluxes and this demonstrates the limited extend of this route of colonization compared to transversal dispersion phenomena.

A second set of experiments as been performed using a real soil material. After a period of flow characterization, the same type of bacterial displacement experiment has been followed by the specific activity indicator. After 1320 hours (55 days), the basal methanogenic activity level is nearly recovered in the previously sterile volume. From these results obtained in a real soil material, a speed of migration of 0.3 cm per day has been computed.

3 - 5. Monitoring of the bioavailability during a pilot-scale experiment (IRH)

A specific experiment has been design to study the fate of PAHs and the related toxicity during the physico-chemical and biological evolution of contaminated soil in water unsaturated and saturated conditions. One soil L sampled in a coke oven site was silty and rich in small chain hydrocarbons. The second one N was also sampled in a coke oven site but was sandy and rich in oil tar material. A specific simulator hes been used for this purpose and for each soil L & N. Two columns having a 40 cm diameter and a 70 cm height are connected in a recycling loop. The first one is aerobic and unsaturated. The second is anaerobic and saturated by water. The presence of oxygen in the first reactor is enhanced by H_2O_2 and the degradation of PAHs is enhanced by the use of surfactants and nutrients added to the first column. 18 PAHs were monitored during 270 days by both soxlhet extraction and supercritical fluid extraction followed by an HPLC analysis.

In the two zones for the soil L, the PAHs content decreases from 430 to 150 mg/kg of dry matter. In addition, the evolution of concentrations in the two columns show a recycling wave with a period of 140 days. This wave is induced by the degradation of PAHs in the aerobic column and the related mobilization of PAHs with organic metabolites. An excess of PAHs is transfered in the anaerobic column were they accumulate up to two times their initial concentration. After one cycle of this wave, the concentration is reduced from 430 to about 350 mg/kg, and then the degradation activity is generalised to both columns for reaching 150 mg/kg in the whole system. Concerning PAHs types, 2-3 rings fraction decreases more rapidly than 4-5-6 ring compounds.

In the unsaturated zone for the soil N, the PAHs content decreases from about 5700 to a level of 3300 mg/kg of dry matter. In the saturated zone, the evolution is more influenced by the accumulation of PAHs up to 8100 mg/kg. Then the concentration is decreased to 4200 mg/kg of dry matter. A recycling wave is also observed with a similar period of 140 days. Concerning PAHs types, 2-3 rings fraction decreases also more rapidly than 4-5-6 rings compounds.

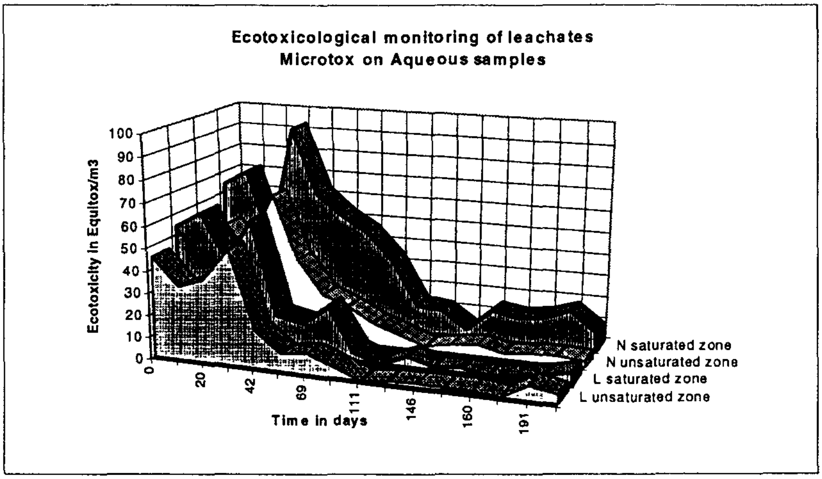


figure n°3 : ecotoxicological monitoring of leachates

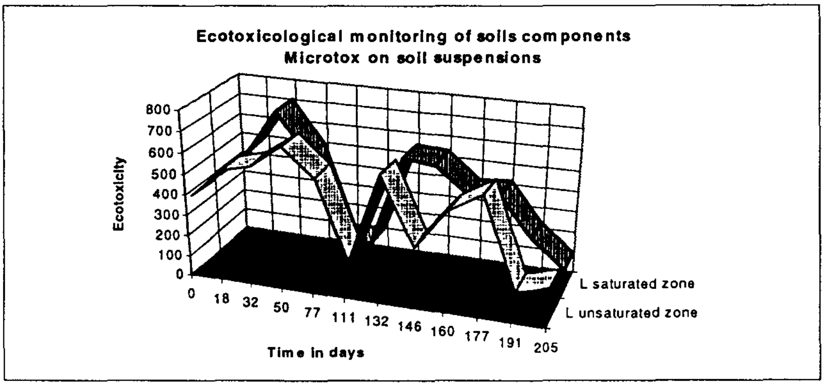


figure n°4 : ecotoxicological monitoring of soil L

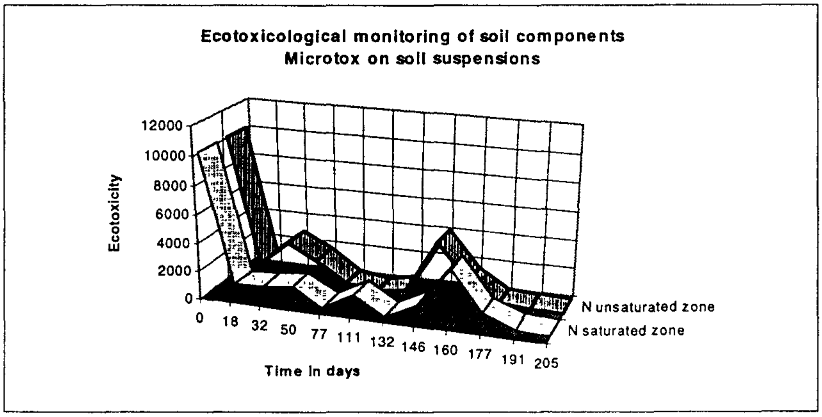


figure n°5 : ecotoxicological monitoring of soil N

In the two cases the ecotoxicity of the soil itself (solid phase Microtox) and of leachates has been monitored (see figures n°3, 4 and 5). As it was observed at the small scale, reduction of the toxicity of leachates is a rapid phenomenon. Nevertheless, the available toxicity measured in contact with a soil suspension is decreased more slowly then the toxicity of soluble fractions.

IV. CONCLUSIONS AND RESEARCH PERSPECTIVES

The main conclusions of this research programme are the following :

- PAHs in soils are mainly retained by an organic carbon fraction naturally occuring in < 10 µm particles size fraction and anthropogenically occuring in > 1000 µm particles (coal, coke, wood, ...). The non available fraction is close to 2.5 g of PAHs per 100 g of Total Organic Carbon.

- PAHs in soils are mainly transformed through biological processes in compounds accumulating in the alkaline extractable humic and fulvic acids fractions or in the non extractable humin fraction. These compounds are analogs of humus polymers, their availability for acute ecotoxicological effects is less important then initial PAHs. The half-life observed for phenanthrene is between 23 and 65 days for five different soils but the related acute ecotoxicological hazard exhibit lower half-life depending mainly on the organic matter content (from 1 to 60 days).

- Ecotoxicological testing is a complementary and interesting tool for the monitoring of bioavailable PAHs in soil materials. These techniques need a choice of appropriate tests battery for better hazard assessment data but are a unique method for the monitoring of bioavailability of pollutants in soils. Depending on the target organisms, the active pollutant fraction (inducing effects) is more or less important.

- The main degradation byproducts in aerobic environments (1-naphtol and catechol) are subjected to autoxidaton or polimerization processes which are close to humification. In anaerobic environment, these abiotic transformations cannot take place due to necessary oxygen and a biological degradation is observed.

- An indirect impedancemetric measurement of carbon dioxyde evolution has been developed and allows to study degradation processes. The mobility of bacterial cells seems to be strongly influenced by the non-stationnary hydrophobicity of cells. In a methanogenic environment, the mobility of this activity has been observed with a speed of migration of 0.3 cm per day.

- The bioavailability of PAHs for degradation is mainly limited by the existence of anaerobic zones and by organic matter content. In parallel, the bioavailability of PAHs for ecotoxicological effects is rapidly decreased in percolating water but only slowly for the less available fractions.

The main perspectives of research are :

- the integration of this knowledge in a single conceptual modelling tool for helping in the risk assessment procedures and for enhancing remedial practices through simulations. A computer code has been developed for taking into account the processes pointed out in this programme : water transfers, interactions with organic carbon phases, mass transfer limitations and bioreaction kinetics can be included on a flexible way. This computer code need further validations and adaptations to be incorporated in decision making helping systems developed in parallel in the member states. This validation was not possible on the basis of results obtained due to the non independance of available data for multiprocesses simulations.

- the development of an integrated method for the ecotoxicological hazards evaluation of contaminated soils and wastes based on tests battery adapted to the terrestrial and aquatic ecosystems. This method must integrate characterization parameters for evaluating potential generation, fate and effects of toxic substances and can be an alternative to the modelling approach for the evaluation of pollution sources.

- the study of the mobility of microorganisms in the soil system is also an important perspective of research for improving biological remedial practices and understanding the potential bioevolution of compounds percolating through soil systems.

Well-performing biodegraders for bioremediation

EV5V-CT92-0250

Coordinator: U. Karlson

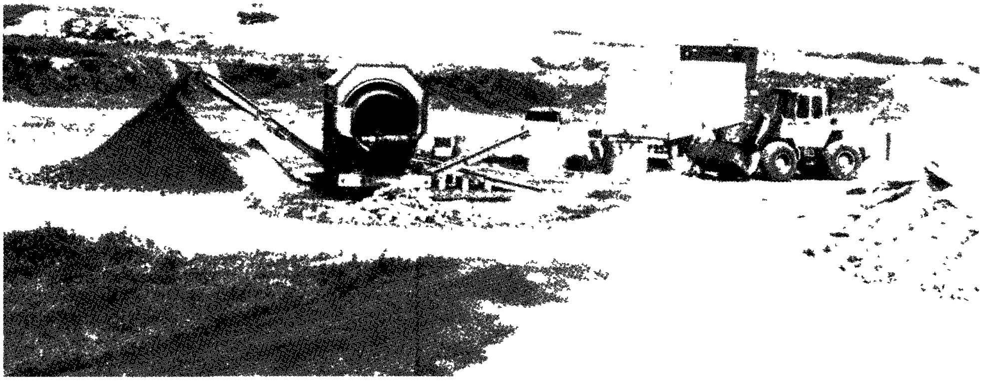
Danmarks Miljøundersøgelser
DK - 4000 Roskilde
Tel: +45-46301387
Fax: +45-46301216

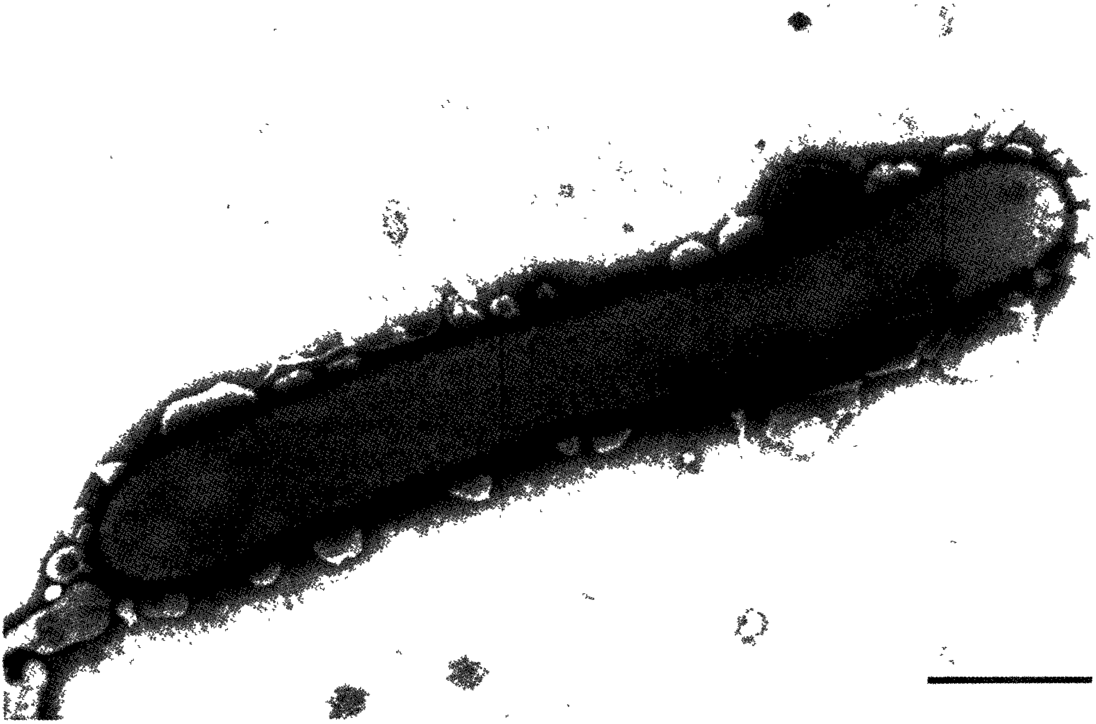
R&D PROGRAMME ENVIRONMENT AND CLIMATE
AREA II: ENVIRONMENT TECHNOLOGIES
TOPIC 2: Technologies for Protecting and Rehabilitating the Environment

Contract number EV5V-CT93-0250

Wellperforming Biodegraders for Bioremediation

1. Sept. 1993 – 31. Dec. 1995





PARTICIPANTS:

Partner 1 and coordinator:
Ulrich Karlson
Danmarks Miljøundersøgelser
Frederiksborgvej 399, P.O.Box 358
DK-4000 Roskilde, Danmark
Scientific staff: K. Schu, R. Miethling, M. Nielsen
Tel. +45-46301387
Fax +45-46301216 (brief)
or +45-46301114 (long)
ukarlson@hami1.dmu.dk

Partner 2:
Fernando Rojo
Centro Nacional de Biotecnología
C.S.I.C.
Campus de Cantoblanco, UAM
E-28049 Madrid, España
Scientific staff: J. Alonso, I. Canosa
Tel. +34-1-5854571
Fax +34-1-5854506
frojo@samba.cnb.uam.es

Partner 3:
Dick van Elsas
IPO-DLO
Binnenhaven 5, P.O.Box 9060
NL-6700 GW Wageningen, Nederland
Scientific staff: M. Briglia, A. Wolters
Tel. +31-8370-76210
Fax +31-8370-10113
J.D.vanElsas@ipo.dlo.NL

Partner 4:
Wolf-Dieter Deckwer
Bereich Bioverfahrenstechnik
GBF-Gesellschaft für Biotechnologische Forschung
Mascheroder Weg 1
D-38124 Braunschweig, Bundesrep. Deutschland
Scientific staff: A.-P. Zeng, S. Urstadt, C. Wittmann
Tel. +49-531-6181100
Fax +49-531-6181111
WDD@GBF-Braunschweig.DE

Partner 5:
Mirja Salkinoja-Salonen
Dept. of Appl. Chemistry & Microbiology
P.O.Box 56 (Biocenter 1 A, Viikinkari 9)
FIN-00014 University of Helsinki, Finland
Scientific staff: L. Nohynek, J.S. Uotila, G.M. Zaitsev, M. Briglia
Tel. +358-0-70859300
Fax +358-0-70859301
mirja.salkinoja-salonen@helsinki.fi

ABSTRACT:

This project attempted to determine the ecological rules for successfully isolating, maintaining and applying microorganisms for bioremediation of chemical spills. It was conducted as a comparative study of those pentachlorophenol (PCP)-degrading bacterial strains presently available, with PCP serving as a model compound for a bacterio-toxic persistent soil pollutant. The results demonstrated the necessity for taxonomic and genomic analysis of bioremediating bacterial strains, not only in the interest of public health, and revealed the narrow biodiversity of (potentially) bioremediating bacterial strains, in contrast to what was generally believed. The dominating role of the alpha-4 subclass members and the coryneform actinomycetes was demonstrated. The success of soil inoculation depends on the choice of the degrader strain, preferably from these two groups, with respect to its physiological properties in correspondence to the soil type and conditions.

OBJECTIVES:

The aim of this project was to search for 'well-performing biodegraders' for bioremediation. It started off from the observation that in bioremediation only few of the isolated microorganisms perform well when utilised under field conditions, although in pure culture they appeared to be promising, this research intended to identify the reasons for this discrepancy. The objective of this work was to determine the ecological rules for successfully isolating, maintaining and applying microorganisms for bioremediation of chemical spills. The envisioned goal was to provide a systematic basis for predicting strain performance before soil application, and possibly before the isolation effort.

The project was designed as a comparative study of those pentachlorophenol (PCP)-degrading bacterial strains presently available (Table 1), with PCP serving as a model compound for a bacterio-toxic persistent soil pollutant.

Table 1: PCP-degrading strains available and used in this study (all), strains characterized in detail (+), strains chosen for studying strain performance in soil (x), and representative strains studied in larger detail for fermentor cultivation and ecological fitness (xx).

Strain	Source	Abbreviation	Studied
Mycobacterium chlorophenolicum PCP-1, DSM 43826	M. Salkinoja-Salonen	PCP1	+, x, xx
Mycobacterium chlorophenolicum CP-2	M. Salkinoja-Salonen	CP2	x
Mycobacterium chlorophenolicum CG-1	M. Salkinoja-Salonen	CG1	
Mycobacterium fortuitum CG-2	M. Salkinoja-Salonen	CG2	
*Flavobacterium** sp., ATCC 39723/53874	Ron Crawford	ATCC 39723	+
*Arthrobacter** sp., ATCC 33790	Stanlake, Edgehill & Finn	ATCC 33790	+
*Pseudomonas vesicularis** SR3	Resnick & Chapman	SR3	+, x
*Pseudomonas** sp. RA2, DSM 8671	Radehaus & Schmidt	RA2	+, x, xx

* new species designation, as a result of this study: *Sphingomonas chlorophenolica*

The PCP-degraders chosen served, in other words, as model organisms for bacterial strains with potential use in soil bioremediation. This model proved useful for the general objective of this study, because it combined two advantages: The bacterial strains were available and (seemingly) well-characterized in the scientific literature, and the contaminant to degrade is water-soluble and bacterio-toxic under prevalent soil conditions, i.e., the contaminant is bioavailable, but exerts a challenge to bacteria. We hypothesized that the physiological and genetic properties of these strains should correlate with their performance upon inoculation into contaminated soil. The approach of this study was to proceed with the phylogenetic, physiological and ecological characterization of all 8 strains as far as possible, but to concentrate on two strains, one Gram-positive and one Gram-negative, with respect to genetic characterization, cell cultivation/downstream processing and molecular detection methods. After the first 6 months, in reviewing the results obtained by that time, the choice of these two strains was finalized: PCP1 and RA2 (marked with xx in Table 1).

MAIN RESULTS:

The number of different PCP-degrading bacterial genera was recognized not to be 4, but 2: *Mycobacterium* and *Sphingomonas*. The importance of taxonomical research was clearly expressed in this work, introducing the genus *Sphingomonas* as a genus with several species capable of degrading various xenobiotic compounds, including PCP. Two new degrader species were found, covering many of the old 'species' of different assumed identities. On the basis of this study, the polychlorophenol-degrading strains KF1, KF3 and NKF1 represent a new species in the genus *Sphingomonas*, *S. subarctica* sp. nov. Additionally, the polycyclic aromatic hydrocarbon degrading strain *Beijerinckia* B1 should be reclassified as *S. yanoikuyae*, while *S. paucimobilis* EPA 505 was close to *S. chlorophenolica* on the basis of their 16S rDNA sequences and utilization capacity of different carbon sources. *Alcaligenes* sp. A175 and *Pseudomonas* sp. BN6 were identified as species of the genus *Sphingomonas* by similar criteria.

Our findings reveal the narrow biodiversity of (potentially) bioremediating organisms, in contrast to what was generally believed. Understanding of the specific bioremediater genera will be of value when searching for new degraders and when searching for methods to stimulate the indigenous degrader flora in soil or water to remediate the target. Our results, together with findings in our work published earlier, predict that it will not be useful to search or stimulate the general flora, but the action should be focussed on the alpha-4 subclass members (*Sphingomonas* and close relatives) or the coryneform actinomycetes (*Mycobacterium, Rhodococcus* and close relatives).

The assessment of the safety of degrader inocula intended for release into the open environment is much simplified by the comprehension of narrow biodiversity. Unfortunately, both of the bioremediater taxa exhibit features that will require careful study if the organisms are to be released into the environment, or if their habitat in soil or water is meant to be manipulated, so as to induce a large increase in their cell numbers.

Genomic analysis and serological typing of bacterial strains proved to be both a powerful tool for their taxonomic study and a useful tool for their detection and quantification in soil. One important lesson from this project is to have realized the necessity for genomic analysis prior to technological utilization of bacterial isolates.

Sphingomonas chlorophenolica RA2 and *Mycobacterium chlorophenolicum* PCP-1 were studied as representative members of the two genera mainly involved in microbial PCP-degradation. Significant differences in growth physiology and nutrient demand were observed. Under optimum cultivation conditions, RA2 grows more effectively. Strict inhibition effects can be observed under non-optimized conditions. RA2 possesses a high tolerance towards pentachlorophenol and an effective enzymatic mechanism for its mineralization. In contrast, PCP1 shows longer generation times and less PCP degradation activity under optimum conditions compared to RA2. However, the actinomycete performs better under unusual environmental conditions like low temperature, acidic pH value or autotrophic conditions. The ability of autotrophic growth provides an excellent survival potential since the substrates of autotrophic metabolism are ubiquitous in soil.

In conclusion, both bacteria pursue different strategies. RA2 as a kinetic strategist posesses higher activity under optimum conditions, whereas PCP1 acts as a survival strategist showing better surviving properties and generally less activity. Hence, the persistence of xenobiotics in the environment is often caused by incompatibility of the ecophysiological conditions with the physiological properties of the degraders. Depending on the soil conditions, high survival potential may be as important as a high degradation potential.

For optimal induction of PCP-degrading activity in strains RA2 and PCP1 during fermentor cultivation, inducer concentration and cell density are two important parameters. Adsorption effects of PCP to bacteria and several materials used in bioremediation for immobilization of degraders like polyurethane foam or sawdust were observed. These phenomona strongly influence bioavailability and toxicity of PCP also under field conditions and therefore play an important role in the effort of bioremediation processes.

For the cultivation of PCP1 and RA2 a cultivation strategy was developed. Using this strategy, large quantities of biomass of both degraders can be produced. As important stoichiometric and kinetic parameters of the production process were determined, it can be run with excellent reproducibility.

When inoculated into contaminated soil, the bacterial strains enhance PCP-degradation under certain minimum conditions. When these conditions are not met, the inoculation does not have an enhancing effect on PCP mineralization (compared with background activity attributable to the indigenous microbiota). Such conditions, which have a bearing on the choice of inoculum strain in the specific soil situation, were identified as:
(1) pH requirement of the inoculated bacterium (choice of strain depending on its pH optimum).
(2) Concentration of PCP in soil (pronounced effect of inoculation at high contamination level).
(3) Amendment with structural materials. (Enhancement of bacterial activity by providing a surface for temporary adsorption of PCP to avoid contaminant toxicity).
(4) Inoculum survival, surprisingly, turned out to not be a necessary requirement for biodegradation performance in all soil conditions.

Rhizosphere inoculation, i.e., inoculation of seeds of suitable plants, was invented in this project. In that it may be used to facilitate spreading of, and to enhance survival of, bacterial inoculants in soil, it potentially offers an alternative to traditional bioaugmentation by mixing of soil and bacteria. Because of the savings in machine power it should represent a major opportunity for the development of future bioremediation technology.

CONCLUSIONS:

A major conclusion from this project is that microbes capable of effectively degrading manmade xenobiotic residues do indeed exist, but that these microbes may simultaneously pose potential health hazards which will demand a high level of skill for their safe biotechnological and environmental use. Careful taxonomical analysis of bioremediating strains is, therefore, advisable before their massive use.

Genomic analysis of all bacterial strains and proper species identification should be required prior to their technological utilization.

Future efforts in finding or stimulating soil-borne bacterial biodegraders should focus on the alpha-4 subclass members (*Sphingomonas* and close relatives) and the coryneform actinomycetes (*Mycobacterium, Rhodococcus* and close relatives). The former group should provide kinetic strategists with higher activity under optimum conditions, high resistance to toxic contaminants and a capacity to degrade them rapidly, whereas the latter group contains survival strategists showing extreme properties and generally less activity.

The persistence of xenobiotics in the environment is often caused by incompatibility of the ecophysiological conditions with the physiological properties of the degraders. Depending on the soil conditions, degrader strains with high survival potential or with high degradation potential should be applied. The success of soil inoculation depends on the choice of degrader strain with respect to its physiological properties in correspondence to the soil conditions.

To reduce the machine cost in soil bioremediation, and to develop tools for *in situ* inoculation, the use of plants with inoculated rhizospheres provides a promising alternative.

PUBLICATIONS ARISING FROM THE PROJECT:

Patent applied for:

Karlson, U., J.S. Uotila, and C.S. Jacobsen. Use of plants with inoculated microorganisms for soil cleaning (in Danish). Patent Office, Copenhagen, 25 January 1995. Appl. No. 0088/95.

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Urstadt, S. (PhD thesis) Enzyme induction and PCP adorption behaviour of pentachlorophenol degrading bacteria. Universität Braunschweig, Germany (to be completed in 1997)

Wittmann, C. (PhD thesis) Strategies for cultivation of pentachlorophenol degrading microorganisms. Universitat Braunschweig, Germany (to be completed in 1996)

EXTENDED SCIENTIFIC ABSTRACT

Phylogenetic characterization (Partners 1, 2, 3, 4, & 5):

DNA extracts of all 8 PCP-degrading strains (Table 1) were prepared and two different analyses were performed: (1) The 16S rRNA was sequenced and the species affiliation of the strains was double-checked. Sequence information was also used for construction of probes in molecular detection methods (see there). (2) A probe for the ATCC 39723 type dehalogenase gene (pcpB) was constructed for use in hybridization assays against the different DNAs. The relatedness of the dehalogenase system of the different strains was inferred from those data.

The chemotaxonomic properties and the ultrastructure were studied for ATCC 33790, ATCC 39723, SR3 and RA2. Furthermore, specific antibodies (see "Immuno-fluorescent detection methods") were used to infer species relatedness by occurence of cross-reactions, and ERIC & REP PCR was employed to gain further evidence for the precise species affiliation of RA2, SR3, ATCC 33790 and ATCC 39723.

The results obtained proved that ATCC 33790 is in reality Gram-negative, belonging to the genus *Sphingomonas*, and ATCC 39723 and SR3 are also species of *Sphingomonas*. The genetic probe for ATCC 39723 *pcpb* gene strongly hybridized under stringent conditions with a 3 Kbp EcoRI DNA fragment of strains RA2, SR3 and ATCC 33790, which suggests that all these strains contain the same PCP-dehalogenase gene. The probe did not hybridize with the DNA of any of the the *Mycobacterium* strains (PCP1, CG-1, CG-2 and CP2), which suggests that their genes for PCP degradation are different from those of the strain ATCC 39723. The results strongly simplify future work on the comparison of the degradation efficiency of the different PCP degrading strains considered in the original proposal. They also strengthen the need for the isolation and characterization of the genes from PCP1, that could be a prototype for a new class of PCP-dehalogenases.

To assist in the generalization of these findings to 'well-performing biodegraders for bioremediation' of other contaminants, several more proposed chlorophenol- and other xenobiotic (aromatic and polyaromatic compounds) remediating organisms were examined, all of them gram-negative rods: In summary, we examined 14 different xenobiotic degrader strains, with good publishing records, described as members of 9 different genera or species, originally isolated from widely different environments from different continents, and found that all were *Sphingomonas*. Most of them were identical or close to one of the three species, *S. chlorophenolica*, *S. subarctica* and *S. yanoikuye*. The two first were new species, and therefore (as yet) without recorded knowledge of any pathogenic or opportunistic behaviour. *S. yanoikuyae* is a Class 2 pathogen in the German classification (Anon, 1992). All of them carry sphingolipids in their outer cell membrane, which has shown to be cytotoxic, similarly to the lipid A in the gram-negative bacterial outer membranes.

The sphingolipids of *Sphingomonas* and related bacteria contain cellular constituents of high reactivity towards mammalian cells. Both positive (inhibiting adherence of pathogens like *S. aureus*) or negative (cytotoxic to mammalian cells) effects may be expected, demanding attention to protect the staff involved in the biotechnology of cultivating or handling these bacteria. The cell wall components of the actinomycetal degraders are suspected to be immunoreactive, with continuous exposure potentially leading to auto-immune diseases. Especially the PAH degraders usually belong to this taxonomic group, but also several of the chlorophenol degraders, *M. chlorophenolicum* (Briglia et al., 1994) and *M. fortuitum* (Nohynek et al, 1993), *Rhodococcus percolatus* (Briglia et al., 1996) and chlorobenzene degraders (*Rhodococcus opacus*, Zaitsev et al, 1995). The pentachlorophenol-degrader strain PCP1 differed in its 16S rDNA sequence only by one nucleotide from *M. chubuense* which has been reported to be an (opportunistic) pathogen (Briglia et al.,1996b). So its seems clear that the possible biotechnical use of this group of organisms for remediation requires careful planning to avoid public health risks.

CONCLUSIONS:

Several of the chlorophenol degraders described in the literature and proposed for bioremediating organisms (Table 1), were not representing the genus nor the species under which they had been published in more than 20 publications in respectable journals. One of the achievements of this project was to show that they belong to only 2 genera, despite the different habitats of isolation at geographically distinct locations. These two genera utilize two distinct dehalogenase enzyme systems. Furthermore, a large number of new, or already known, degraders of various xenobiotics were shown to exclusively belong to one of two groups: The coryneform actinomycetes and the Sphingomonads. Such observations will be of importance for the future of bioremediation in many respects:
-- The two PCP-degrading genera (two types of dehalogenases) are likely to represent two fundamental eco-types. As was confirmed during this project (see "Ecological characterization"), bioaugmentation with PCP-degraders needs to

consider the soil conditions in accordance to the ecological requirements of these eco-types in choosing the degrader strain.

-- Evolution of the dehalogenase gene in PCP-contaminated environments may have been conservative, "re-using" already existing genes from other pathways, with only two possibilities for a new gene assemblage. With halogenated organic chemicals being at the frontline of today's environmental problems, it will be interesting to continue this comparative study focussing on other chlorinated pollutants. In the future we may discover that nature's answers to our problems follow a few simple patterns.

-- It appears that well-performing biodegraders should be looked for among species that colonize extreme habitats. Both and Sphingomonads are naturally found in most challenging physical environments, ranging from the surface of pine needles to acid nutrient-depleted soils.

-- Since all of the well-studied PCP-degraders appear to belong to genera which also contain pathogens or opportunistic pathogens, detailed knowledge on the physiological properties and bioreactiveness of the remediation strains is required, and their intense study is warranted.

It is a major finding of this work, that the biodiversity of xenobiotic degrading, potential bioremediator bacteria is much narrower than thought previously. It seems that there are two 'hot spots': The Gram negative *Sphingomonas,* belonging to the alpha-4 subclass of proteobacteria, as discussed above, and the cluster of coryneform actinomycetes (Gram positive bacteria), comprising *Rhodococcus, Mycobacterium* and a few other closely related genera.

Genetic characterization (Partners 1, 2 & 5):

The objective of this activity was the isolation and characterization of the *Mycobacterium chlorophenolicum* PCP-1 genes that code for the dehalogenases that participate in the degradation of PCP. In pursuing that goal, several steps have been undertaken:

1.- Construction of gene banks of total DNA from strain PCP1

Total DNA from strain PCP1 was purified and partially digested with endonuclease Sau3AI. The fragments ranging from 20 to 30 Kbp in length were isolated and cloned at the BamHI site of the cosmid vectors pLAFR3 and pJAR4. These vectors were selected because they are known to be stable and have been very useful in other projects. Cosmid pLAFR3, 21.6 Kbp in length, replicates in most Gram-negative bacteria and has a low copy number. We have isolated about 5,000 independent clones with DNA inserts about 20 Kbp in length or larger. It can be calculated that we need about 2,000 independent clones to have a 99.9% certainty of finding a given gene in the bank, assuming a genome size for PCP1 of about 10,000 Kbp (an overestimation). This gene bank was constructed in *E. coli,* and was mass-transferred to *Pseudomonas putida.* As it will be explained below, the screening of the PCP degrading genes was performed in both microorganisms. Cosmid pJAR4, 21.9 Kbp in length, replicates in *E. coli* and in *Streptomyces.* It has a moderate copy number in the former host and low in the latter host. We have isolated about 6,000 independent clones with insert sizes larger than 20 Kbp. Again we need about 2,000 independent clones to have a 99.9% certainty of finding a given gene in the bank. The gene bank was constructed in *E. coli,* and was transferred to *Streptomyces lividans.*

2.- Search for strategies to clone the PCP-degrading genes from strain PCP1

Once the gene banks were constructed, we have tested several strategies to find the genes coding for the PCP-degrading enzymes. Some procedures relied on the presumption that the genes would be expressed in one or several of the hosts in which the gene banks are kept: *E. coli, P. putida* and *S. lividans.* We performed the gene banks in three different hosts to maximize the possibility that the genes were expressed in at least one of the hosts. The use of *E. coli* for the initial construction of the gene banks was a must for technical reasons. The gene banks were transferred to *Pseudomonas* and *Streptomyces* because they have a high (*Pseudomonas*) or very high (*Streptomyces*) G+C content, as is the case for *Mycobacterium.* Even more, *Streptomyces* and *Mycobacterium* are both , which suggests that the genes from PCP1 have good chances of being expressed in *Streptomyces.* The other procedures used were based either on a forced transcription of the dehalogenase genes from a strong heterologous promoter, or on the purification of the enzymes.

a) Screening procedures based on a good expression of the dehalogenase genes in *E. coli, P. putida* or *S. lividans.*

Though many mycobacterial genes are poorly or not expressed in other hosts, some have been shown to be transcribed in hosts such as *E. coli.* The following assays presume that the genes for PCP degradation from strain PCP1 are expressed at detectable levels in either *E. coli, P. putida* or *S. lividans.*

i) Colorimetric assays
We have tested two different colorimetric assays for these enzymes, but none of them proved satisfactory.

ii) Resistance to the toxic effects of PCP or tetrachlorohydroquinone
The approach of using PCP or tetrachlorohydroquinone as antibiotics has given many false positives were also obtained. We suspect that the genes for the searched dehalogenases may not be expressed in the hosts used, and we have therefore turned to the more time consuming but safer indirect procedures described below.

iii) Direct assays for activity
Considering that the DNA inserts cloned in the gene banks have around 20-25 Kbp in length, it can be estimated that about 2,000 independent clones suffice to represent the whole bacterial genome. We made 200 groups of clones in each gene bank, each group consisting on 10 independent clones. After incubating the cells with a small amount of PCP or TCH, we measured by HPLC the ability of the cells to metabolize PCP of TCH. No group metabolized either compound. We infer that the TCH- and PCP-dehalogenases are not expressed or are not active in the gene banks.

b) Screening procedure based on a forced transcription of the TCH-dehalogenase gene from an *E. coli* promoter coupled to an *in vivo* colorimetric assay.

The previous screening methods suggested that the PCP degrading genes were either not properly expressed in the hosts harboring the gene banks, of that the genes were expressed but the enzymes were not functional. To circumvent a putative transcription problem, we designed a screening procedure based on the forced transcription of strain PCP1 genes from a strong heterologous promoter. More than 20,000 individual colonies were screened, but none was able to transcribe the dehalogenase. We conclude that the lack of expression of a functional TCH-dehalogenase in heterologous hosts is probably due to several problems, and not just to a poor transcription of the corresponding gene. It may be that the enzyme requires cofactors or additional protein components not present in the heterologous hosts used.

c) Screening based on the determination of the sequence of a stretch of amino acids of the enzymes of interest.

The goal was the purification of the dehalogenases involved in PCP degradation, sequencing of the amino terminus (or an internal fragment), and construction of a degenerated oligonucleotide complementary to the gene coding for each enzyme. The gene banks would then be screened for the presence of sequences complementary to the synthetic oligonucleotides. Although it is very time consuming, this method has been broadly used in the past as a tool to isolate genes of interest. We started purifying the second dehalogenase, a tetrachlorohydroquinone dehalogenase, for two reasons: i) there was some previous experience about the partial purification of this enzyme, and ii) the first dehalogenase is membrane bound and therefore probably more difficult to purify.

We have devised a purification protocol that allows to purify considerably the TCH dehalogenase from strain PCP1. In our best preparations we were able to purify the TCH dehalogenase to 5 major bands, but not further. Repeating the purification with noninduced cells should have in principle allowed to identify the band that corresponds to tetrachlorohydroquinone dehalogenase, but the low reproducibility of the purification protocol due to aggregation problems has rendered this approach useless. Our partially purified fractions are useful for biochemical analysis of the protein, but not for its sequencing.

In summary, we have done all possible efforts to isolate the genes coding for the dehalogenases that degrade PCP in *Mycobacterium* PCP1, but were not able to meet our ambitious goals within the time available. The isolation of these genes would have rendered interesting information. Nevertheless, we were able to coordinate the other parts of the project in such a way that the lack of this information did not compromise its overall conclusions.

Growth physiology and cell cultivation (Partner 4):

This activity pertained to the development of cell cultivation technology suitable for scale-up and to the technology of enzyme induction, and conservation of biomass and enzyme activity. Strains PCP1 and RA2 were studied.

Medium development:

Auxotrophic demand. For medium optimization the nutrient demands of PCP1 and RA2 were examined in shake flasks. It was found that PCP1 is only auxotrophic for thiamine. In contrast RA2 turned out to grow without any organic growth factor.

Medium optimization. Limited growth of RA2 was observed on tryptic soy broth (TSB) and mineral salt media described in the literature. Low biomass yields and slow growth rates are due to insufficient supply of nutrients in case of the mineral salt medium. When cultivated on TSB medium increase in ammonium and pH caused inhibition of the RA2 strain. These problems were overcome by optimization of medium components.

Growth physiological characterization:

pH and temperature optimum. Generally RA2 grows faster with a generation time of 3.5 h compared to 24 h for PCP1 on glucose. Both strains grow best at pH 7.0, with PCP1 showing good tolerance against acidic milieu and RA2 performing better under alkaline conditions. Both strains were found to be mesophilic with temperature optimum of 30 °C for PCP1 and 32 °C for RA2, respectively. However PCP1 is more resistant to high temperature (> 45 °C), whereas RA2 cannot grow at temperatures higher than 36 °C. Both strains were found to grow at 15 °C with similar specific growth rates.

Influence of oxygen. Both strains showed similar characteristics towards oxygen tension. Dissolved oxygen affects the growth rate of the strains only at pO_2 levels < 10 %. Both degrader strains can grow at pO_2 of about zero, altough the specific growth rates decreased significantly.

Influence of CO_2. Carbon dioxide clearly has a regulating effect on growth of PCP1 with optimum growth at 2%. Increase in specific growth rate was linked to slight increase in biomass yield from 0.43 to 0.51 g g^{-1} which may be caused by additional carbon dioxide fixation into the biomass. Towards higher carbon dioxide concentrations the specific growth rate was decreasing down to 30 % of maximum value at 7.4 % carbon dioxide. In comparison, only slight influence of carbon dioxide was observed on the growth of RA2. Already a concentration of 1 % carbon dioxide inhibits its growth. Nevertheless the specific growth rate remained at about 66 % of the maximum at 8 % CO_2.

Autotrophic growth. To study growth under autotrophic conditions cultures were incubated in chemolithotrophic medium under an atmosphere of 60 % hydrogen, 20 % nitrogen, 10 % carbon dioxide and 5 % oxygen. Autotrophic organisms *Alcaligenes eutrophus* H16 and *Hydrogenaphaga pseudoflava* were included in the experiment as positive control strains. PCP1 was found to grow under autotrophic conditions, whereas no growth of RA2 could be detected. The latter could nevertheless survive after 20 weeks of incubation. It appears that the facultative autotrophic metabolism is an important survival characteristic of well-performing biodegraders.

Metabolism. Concerning the consumption of different carbohydrates as carbon and energy sources both strains utilize only a restricted catalogue of substances. Glucose is preferred by RA2. In contrast PCP1 prefers fructose and polyols like sorbitol or mannitol that give 2-3fold higher growth rates compared to glucose, mannose and several pentose sugars like ribose, arabinose and xylose. Hence the catabolic pathways for consumption of sugars in *Mycobacteria* reported in the literature converge on fructose-bisphosphate, the reason for this may be based on different substrate uptake mechanisms. When grown on dual substrate mixtures like fructose and glucose, PCP1 shows clear diauxic behaviour, supressing effectively the utilization of glucose in the presence of the preferred fructose. Biomass yields on glucose are 0.43 g g^{-1} for PCP1 and 0.49 g g^{-1} for RA2, respectively. Both strains show an RQ value of 1.0 mol mol^{-1}. Under the conditions studied, PCP1 does not produce any metabolite. In contrast RA2 secrets pyruvate due to limited oxidative metabolism.

Cultivation strategies:

Inhibition by ammonium. Of particular importance for the cultivation of both strains is the observed strong inhibition by NH_4^+. Ammonium inhibition reduces both growth rate and biomass yield. Whereas RA2 performs better at low ammonium concentration, PCP1 shows better ability to tolerate higher amounts.

Mathematical modelling of the inhibition effects led to good quantitative description by the LUONG model for RA2 and the AIBA-SHODA kinetic for PCP1, respectively. In case of PCP1 inhibition is mainly due to the ammonium ion, although at high pH ammonia acts inhibitory. More importantly PCP-degradation activity is also inhibited at higher ammonium concentrations.

Ammonium feeding strategy. Based on the observation that pH decrease in the culture is stoichiometrically linked to the ammonia consumption a pH-controlled ammonium feeding strategy was developed for effective cultivations of both degrader strains.

Biomass production. Using the developed feeding strategy a cell density of PCP1 of 30 g l^{-1} could be achieved in one-week batch culture with glucose as carbon source. The cells grew with maximum specific growth rate over the whole process. During the cultivation ammonium concentration remained constant in the range of 0.1 to 0.3 g l^{-1}. Compared to normal batch cultivation the ammonium-fed process showed increased biomass yield, biomass concentration and shortened process time, thus leading to 240 % increased productivity. The developed strategy was demonstrated for RA2 in 130 l stirred tank reactor. After 3 days of cultivation, a final concentration of 40 g l^{-1} biomass was achieved. The developed strategy allows the production of large quantitaty of biomass for both field research and remediation of contaminated sites.

Induction and degradation:

Inducibility of PCP-degradation activity. The PCP-degrading enzymes in many bacterial strains need to be induced. Strain PCP1 cells without pre-induction do not degrade PCP in the presence of protein synthesis inhibiting streptomycin in contrast to induced ones, indicating a *non-constitutive expression* of PCP-degrading enzymes. The PCP degrading enzymes of RA2 are also *inducible.*

Induction and degradation kinetics. Experiments with non-induced cultures of strain PCP1 show that the PCP-degradation activity can be induced at a PCP-concentration below 0.1 µmol l^{-1}. Optimum degradation activity was observed at an inducer concentration (first induction) of about 10 µmol l^{-1}. In contrast, RA2 is more tolerant to PCP. At initial PCP-concentrations of 200-800 µmol l^{-1} a maximum degradation rate q_{PCPmax} of 600 µmol g^{-1} h^{-1} was achieved, representing a 100-fold higher degradation activity compared to PCP1. Nevertheless, PCP mainly affects the duration of the lag-phase (time of reaching q_{PCPmax}).

Adsorption and Desorption of PCP:

An observed cell density effect on enzyme induction and toxicity was determined to be largely due to PCP adsorption on the cell wall. Thus, the adsorption and desorption behaviour of PCP on strain PCP1 and RA2 was studied in more detail. To inhibit degradation activity during the experiments cells were pre-treated with protein synthesis inhibitor. The adsorption revealed a fast kinetic nature and is *partly irreversible.* The pH was found to strongly affect both, the adsorption and desorption process. The adsorption-capacity and the amount of irreversibly adsorbed PCP on strain PCP1 cells is much higher under acidic conditions. Similar results were found for strain RA2.

Therefore, the adsorption equilibrium leads to lower effective PCP concentrations at high cell densities and at basic pH. Induction and toxicity are therefore less effective under these conditions.

Thus, *PCP-sorption* should be always considered when investigations of *enzyme-induction, toxicity* and *degradation* are made. Studies for revealing these relations are important for understanding the whole fate of PCP. Such investigations are further in preperation for setting up a combined adsorption-reaction model.

CONCLUSIONS:

Significant differences in growth physiology and nutrient demand were observed. Under optimum cultivation conditions, RA2 grows more effectively. Strict inhibition effects can be observed under non-optimized conditions. RA2 possesses a high tolerance towards pentachlorophenol and an effective enzymatic mechanism for its mineralization. In contrast, PCP1 shows longer generation times and less PCP degradation activity under optimum conditions compared to RA2. However, the actinomycete performs better under unusual environmental conditions like low temperature, acidic pH value or autotrophic conditions. The ability of autotrophic growth provides an excellent survival potential since the substrates of autotrophic metabolism are ubiquitous in soil.

In conclusion, both bacteria pursue different strategies. RA2 as a kinetic strategist posesses higher activity under optimum conditions, whereas PCP1 acts as a survival strategist showing better surviving properties and generally less activity. Hence, the persistence of xenobiotics in the environment is often caused by incompatibility of the ecophysiological conditions with the physiological properties of the degraders. A high survival potential should be regarded as important as a high degradation potential.

For optimal induction of PCP-degrading activity in RA2 and PCP1, inducer concentration and cell density are two important parameters. Adsorption effects of PCP to bacteria and several materials used in bioremediation for immobilization of degraders like polyurethane foam or sawdust are observed. These phenomona strongly influence bioavailability and toxicity of PCP also under field conditions and therefore play an important role in the effort of bioremediation processes.

For the cultivation of PCP1 and RA2 a cultivation strategy was developed. Using this strategy large quantities of biomass of both degraders can be produced. As important stoichiometric and kinetic parameters of the production process were determined, it can be run with excellent reproducibility.

Environmental fate of inocula (Partners 1 & 3):

Immuno-fluorescent detection method:

In order to have a tool for rapid enumeration and in situ detection of the bacterial strains, polyclonal antibodies were generated in rabbits. Strong specific binding was observed with all Gram-positive cells (with the Mycobacteria cross-reacting), and weak specific binding with all Gram-negatives. Improvement of the quality of the RA2 antibodies was achieved by repeated injection at higher doses of the immunized rabbit. Nevertheles, all 4 antisera for the Gram-negative strains, although they provide a usable detection tool, do not generate the intense reaction (and easy-to-read fluorescent image) as we observe with the Gram-positive strains. In the meantime, we understand this to be a limitation of the bacterial species: Since all 4 Gram-negatives were discovered to be *Sphingomonas* spp., which possess no O-antigens, but only sphingolipids, we just cannot expect a better result than we already achieved. The antisera were also used to aid in the phylogenetic characterization of strains (see there), and to calibrate the DNA-based detection methods (see there).

Soil extraction for enumeration of bacterial cells was refined for the experimental soils used in this study. Cell recoveries are 100 ±20% for PCP1. The detection limit for PCP1 and RA2 is 10^5 cells/g soil by immuno-fluorescence microscopy. Lower detection limits are achievable with the new DNA-based detection methods (see there).

DNA-based detection methods:

This activity pertained to the development of detection and quantification techniques in soil for two selected well-performing PCP degraders, *Mycobacterium chlorophenolicum* PCP-1 and *Sphingomonas chlorophenolica* strain RA2. The detection was intentionally based on naturally occurring DNA sequences, to avoid using genetic markers which would result in unnecessary regulatory complications when planning releases. Since the method was based on extraction of soil microbial DNA (followed by PCR and molecular detection via hybridization) and had to be applicable to a wide variety of soil types, we first aimed for the development of a "universal" flexible DNA extraction protocol which would serve this purpose.

A direct DNA extraction protocol previously developed in our laboratory was tested on five different soils, i.e. a Danish sandy low organic, a Finnish sandy high organic, a Dutch sandy high organic, a Finnish organic and a Dutch clay soil. Cell lysis was shown to be optimal with the bead beating procedure used, as evidenced by checking lysis of total indigenous bacteria, and of selected inoculants, hereunder strain PCP1. Small adaptations in the purification procedure allowed for adequate extraction of high quality DNA from all five soils (Van Elsas et al., 1996a).

To more specifically detect target DNA in bacterial cells, rather than in overall DNA extracts (hence avoiding possible biases of the direct lysis approach), a standard protocol (Jacobsen and Rasmussen, 1992) was unlashed on three soils. However, poor DNA recovery values were found in all three soils. We therefore developed a new method based on sodium pyrophosphate dispersion of soil followed by bead beating lysis and purification steps. This novel method resulted in greatly enhanced DNA recovery values. In addition, selected inoculant bacteria like strain PCP1 ran through at high rate, showing the efficacy of the method in recovering the DNA of inoculants (Van Elsas et al., 1996a).

To obtain a specific detection method for strains PCP1 and RA2, their 16S rDNA sequences were analyzed via database comparisons for the occurrence of strain-specific regions. The characteristics of one sequence, that of strain PCP1, served to move this strain from *Rhodococcus* into the new taxon *Mycobacterium chlorophenolicum* (Briglia et al., 1994). The sequence of strain RA2 formed a basis to propose the inclusion of this strain together with three other PCP degrading strains, in the genus *Sphingomonas*, as outlined before (Karlson et al., 1995). For both strains, strain-specific regions were found, and PCR amplification/DNA probing detection systems were based on the selection of two PCR primers and one (internal) oligonucleotide probe. The detailed primers and probe sequences, and the alignments to closest relatives are shown in Briglia et al (1996) and Van Elsas et al. (1996a; 1996b). For strain PCP1, the initially selected PCR amplification system was found to produce inadequate results on further testing in one soil, due to lack of specificity of the forward primer. Hence, in later work, this primer was substituted by a newly-defined primer with enhanced specificity for PCP1 (Van Elsas et al. 1996b). The application of several refinements in the PCR (hot start, touch-down PCR, addition of primer annealing adjuvants to PCR mix) resulted in clear-cut detection of PCP1 in all soils under study (Van Elsas et al., 1996b).

For strain RA2, the PCR primers were based on two highly variably regions of the 16S rRNA gene. Testing with a limited number of strains and with soil showed high specificity of the system for RA2. The application of probing with the specific probe supported this contention.

To get an insight in the population dynamics of the inoculants in soil, quantitative PCR was developed for detection of inoculant strains. Two different strategies were followed for strains PCP-1 and RA2, respectively. Thus, most-probable-number (MPN) PCR was used for strain PCP1, and competitive PCR, using an internal standard, was developed for strain RA2. MPN-PCR correlated well with immunofluorescence (IF) counts in four soils, showing the applicability of this method for PCP1 detection. In two soils over a 14 day period, the dynamics of strain PCP1 was shown to be roughly stable, i.e. strain PCP1 was a good survivor. This was backed up by IF data, and good stability of the inoculant populations was also found in two other soils using IF (Van Elsas et al., 1996a). MPN-PCR, albeit feasible, is a time-consuming and expensive method, and therefore an alternative method was developed for strain RA2 detection. Strain RA2 was detected in soil using competitive PCR with an internal standard (competitor). An approx. 480 bp competitor fragment was constructed using MIMICS (Van Elsas et al., 1996b); in this strategy, primer annealing sites are introduced into a heterologous DNA fragment, which is then cloned. The vector/insert combination is then used as competitor DNA to be added to the PCR reaction mixes. Amplification of target and competitor in the same reaction mix and presumably at similar efficiency would result in an estimation of the initial target copy number by comparison to the competitor. The competitive PCR worked well in RA2 genomic DNA/ competitor mixes in vitro, and the principle was shown to work in a soil DNA extract background. Quantitative results have been obtained and served to calibrate the method for soil, at high inoculum densities. Calibration of the method for low inoculum densities is in progress. This work has been written up in a publication (Van Elsas et al., 1996b).

CONCLUSION:

Quantitative PCR is now operational for detection of strain PCP1 down to approx. 10^2 to 10^3 cells per g soil, whereas 10^4 to 10^5 RA2 cells per g can be well quantified using competitor PCR.

Physiological characterization (Partner 5):

Cell physiology of PCP degraders:

The cell physiology pertaining to the performance of strains ATCC 33790, ATCC 39723, PCP1, SR3 and RA2 was studied. This part of the study is based on the hypothesis that well-performing biodegraders have cell physiological properties designed to allow the cells to be active under nutrient stress, to survive adverse conditions through cell attachment, to interact with organic contaminants through a lipophilic cell surface, to solubilize organic chemicals by excreting emulsifiers, and to preserve their mineralization genes through generations of living on natural substrates.

The activity and viability of the strains was tested during starvation. The contents of ATP in cultures decreased to the same level in all strains during starvation. Judged from colony forming units there were 10 to 100 times more viable cells of PCP1 after starvation for 130 days than of the other species.

The PCP degradation activity of the 5 strains was studied under starvation. All 5 strains retained their degradation activity, although the degradation rate slowed down during 90 days. The choice of growth medium for PCP1 is important to keep the degradation rate constant during starvation, whereas with other strains the degradation rate was not significantly affected by the growth medium. This is noteworthy, because the growth medium of choice for PCP1 according to these results is not DSM-65 (as recommended in the DSM catalog), but minimal medium plus 0.2 g/L yeast extract.

Hydrophobicity of the cells was measured by the contact angle method, and attachment was measured by adherence of the bacterial cells to n-octane. These tests showed, that the cell surface of PCP1 is very hydrophobic, whereas the cell surfaces of the other strains are show low hydrophobicity. Starvation of the cells increased the hydrophobicity of ATCC 33790, ATCC 39723 and RA2 cells grown in minimal medium.

The emulsification capacity of fresh colonies and starvation cultures were tested in a suspension of minimal salts medium and hexadecane. Both fresh and starved liquid cultures, as well as cells collected from plates of ATCC 33790, RA2, SR3 and ATCC 39723 were capable of emulsiying hexadecane. PCP1 did not enhance emulsion formation.

The maintenance of PCP-degradation activity was tested by following the ability of the strains to degrade PCP after repeated cultivations in the absence of PCP. After three transfers at 10% dilution, and recultivation for 11 days after the last transfer, PCP was degraded in the cultures of ATCC 33790, RA2 and PCP1, but the activity was lost in the ATCC 39723 and SR3 cultures.

Ultrastructure and extracellular products of biodegraders in general:

The ultrastructure and extracellular products of *Sphingomonas* and the other alpha 4-subgroup strains of proteobacteria was studied to see, whether explanations could be found for the unique degrader capacities of these strains. Furthermore, the emulsification capacity of different xenobiotics degrading *Sphingomonas* strains was tested to predict their ability to produce biosurfactants. Only two strains out of 15 tested xenobiotics degrading *Sphingomonas* strains (*Sphingomonas* spp. B1 and HH69) did not emulsify hexadecane. The emulsification capacity increased with increasing incubation time. Based on electron microscopic findings (see Fig. on cover page) we assume that the emulsifying agent originated from the blebbing outer membrane, and contained sphingolipids. It is likely that such emulsifiers will increase the bioavailability of hydrophobic, poorly water soluble substrates, such as PAH and other hydrocarbons, and therefore contribute to biodegradation. Furthermore, we consider it possible that the unique membranous blebs, reversibly attaching/detaching from the cell surface pits, are instrumental in the uptake of large molecular substances from the environment into the cell.

The cell surface of the *Sphingomonas* strains was quite hydrophilic. This may explain why these bacteria need a specific mechanism to improve bioavailability of hydrophobic substrates - in contrary to the coryneform actinomycetes, like *Mycobacterium* and *Rhodococcus*, which possess an extremely hydrophobic cell surface.

Ecological characterization (Partner 1):

Bioaugmentation by direct soil inoculation:

Mineralization performance of inoculated PCP-degraders was measured in the laborarory by artificial contamination of experimental soil with ^{14}C-PCP and capture of $^{14}CO_2$. Later, gas chromatographic (GC) analysis was used to double-check the degradation estimates. GC analysis was used for a field experiment in bioremediation of a contaminated site. Inoculum survival was followed by immunofluorescent microscopy and 16S rDNA PCR amplification.

The results of the ecological characterization are summarized as follows (Miethling et al., 1996; Nielsen et al., 1996).

Inoculation with RA2 had a strongly enhancing effect on PCP removal from this soil. PUF affects the PCP degradation rate of RA2 negative. Sawdust is the best additive at higher PCP concentrations and increases the mineralization rate.

PCP1, although a very good survivor, is not suitable for bioremediation in this soil. The reason might be a loss of activity caused by the pH of 7 - 8 which is outside the optimum range for PCP degradation (Wittmann et al., 1994). Under these conditions an application of PCP1 on PUF may result in mineralization rates over the background level, particularly at high PCP concentration.

Soil without a long history of contamination benefits the most from bioaugmentation.

Strain RA2 does not perform well in low pH soil.

Application of SR3 together with a carrier causes a strong stimulation of PCP-mineralization, in particular at high PCP concentration. At low concentration, SR3 without a carrier also had a positive, but not so strong effect. Without carrier, SR3 does not survive over longer periods (survival with carrier was not determined).

In a field experiment (see Fig. on cover page) with ca. 30 mg/kg PCP-contamination, inoculation with CP2, a close relative of PCP1, on polyurethane foam at $5*10^6$ cells/g soil resulted in disappearance of PCP to ca. 5 mg/kg within 10 days and to ca. 0.5 mg/kg in 120 days (by GC analysis). The uninoculated control reached ca. 0.5 mg/kg in 1 year, but it did not reveal those high initial degradation rates. Cells of CP-2 were detected in the inoculated field soil throughout the experiment. After an initial drop in bacterial numbers, cell counts stabilized between 10^5 and 10^6 g^{-1} soil, which parallels the findings from the laboratory study.

Delivery of bacterial inoculants for *in situ* soil bioremediation using plant roots:

Plant root delivery systems for soil inoculation with contaminant-degrading bacteria were developed at bench scale. Strains PCP1, ATCC 33790, ATCC 39723, RA2 and SR3 were screened for their ability to colonize the root zones of 7 different agricultural plants and to simultaneously express their dehalogenase genes. Among all combinations tested, only one scored positive: Strain PCP1 with alfalfa (*Medicago sativa* L. var. Vela). The colonization of this bacterial strain in the rootzone of alfalfa allowed it to be transported over a distance of ≥20 cm and to mineralize PCP after transport. Furthermore, inoculation of alfalfa roots with strain PCP1 resulted in enhanced root and shoot growth. In further experiments, the other PCP-degrading *Mycobacterium* strains were determined to share the alfalfa root-colonization capabilities of strain PCP1. In a field experiment, alfalfa seeds inoculated with strain PCP1 developed into normal seedlings after being sown into PCP-contaminated soil. Non-inoculated seeds, and seeds inoculated with strain ATCC 33790, did not produce viable seedlings.

GENERALIZATION:

Generally, our results indicate that bioaugmentation of contaminated soil enhances PCP-degradation under certain minimum conditions. When these conditions are not met, the inoculation does not have an enhancing effect on PCP mineralization (compared with background activity attributable to the indigenous microbiota). Such conditions are being identified as:

(1) **pH requirement** of the inoculated bacterium. It appears that PCP1 should be used in acid soil, and RA2 in neutral to basic soil.

(2) **Concentration of PCP** in soil. Inoculation seems to be most beneficial at high (> 30 mg kg^{-1}) concentration. At low (≤ 30 mg kg^{-1}) concentration the contaminant is mineralized by the indigenous microbiota (provided it is stimulated by some physical disturbance, comparable to the mixing action in connection with inoculation).

(3) **Amendment with structural materials.** Early in this work we thought that immobilization of the bacterial cells on a carrier (polyurethane foam, wood chips, bentonite) would enhance their activity by protecting them from predation or contaminant toxicity. Immobilization had been described as the appropriate technology for microbial cleaning of PCP-contaminated water, and evidence was cited that this might also apply to soils. Our findings question that assertion. However, addition of the carrier to soil as "structural amendment" prior to inoculation seems to yield the same activity enhancing effect as using the carrier to carry the "immobilized" inoculum. It needs to be emphasized that such activity enhancing effects seem to be limited to high PCP concentrations. The best explanation for these observations is alleviation of PCP toxicity due to temporary adsorption of PCP to the structural materials.

(4) **Inoculum survival.** Specific cell counts revealed a decrease of both PCP1 and RA2 with time, unaffected by the amount of degraded PCP. After an intial decrease of strain PCP1 within the first 3 months, a level of ca. $5*10^6$ cells/g was maintained over a period of 4 months at 30 and 100 mg/kg PCP. Polyurethane amendment had no effect on the inoculum survival. Although strain RA2 degraded PCP much more effectively, the bacteria died off at a higher rate than strain PCP1. In most experiments at 30 mg/kg PCP in non-amended soil, strain RA2 was no longer detectable after 7 months ($<10^5$ cells/g). These observations suggest that survival and degradation performance are not necessarily correlated in biodegraders.

Well-performing Biodegraders for Bioremediation: Microbial Growth and Degradation Strategies of Pentachlorophenol-degrading bacteria

C. Wittmann, S. Urstadt, A.-P. Zeng, W.-D. Deckwer
GBF, Biochemical Engineering Division, Mascheroder Weg 1, 38124 Braunschweig, Germany

Within the framework "Well-performing biodegraders for bioremediation" the Pentachlorophenol-degraders *Sphingomonas chlorophenolica* RA2 and *Mycobacterium chlorophenolicum* PCP-1 have been examined to evaluate their potential for application in bioremediation.

Concerning physiological characteristics RA2 grows generally faster, but shows strict loss of vitality towards non-optimum conditions. On glucose specific growth rates of 0.21 h^{-1} for RA2 and 0.02 h^{-1} for PCP-1 are obtained. In comparison RA2 prefers slightly alcaline conditions, whereas PCP-1 grows best at pH 6.5-7.0. Growth of both strains is inhibited at pO_2 of < 10 %. PCP-degradation activity of RA2 is about 30fold higher compared to PCP-1. Nevertheless PCP-1 performs much better under extreme conditions like acidic pH or low temperature.

Ammonium was detected as "key substrate" during the development of production strategies in bioreactors. It is essential for growth but exhibits strict inhibition of growth and PCP-degradation for RA2 and PCP-1. 4 g/l ammonium totaly inhibit PCP-degradation by RA2. However, the actinomycete PCP-1 posesses 80 % of its optimum activity under these conditions.

Studies on bioavailability and toxicity of PCP revealed high affinity of PCP towards bacterial cell walls. The observed adsorption has a fast kinetic nature and is partly irreversible. The pH was found to strongly affect both, the adsorption and the desorption process. Adsorption capacity and the amount of irreversible adsorbed PCP are much higher under acidic conditions, resulting in higher toxicity.

In conclusion, the physiological characterization of the two PCP-degrading strains led to different strategies of growth and PCP-degradation:

- RA2 can effectively exploit optimum conditions and shows a powerful degradation system, but low survival capacity
- PCP-1 has a low metabolic activity, but an excellent potential of surviving under "environmental conditions"

The observed sorption processes influence bioavailability of PCP as well as toxicity and therefore significantly affect bioremediation.

Well-performing biodegraders for bioremediation: Microbial strategies of growth and degradation

C. Wittmann, S. Urstadt, A.-P. Zeng, W.-D. Deckwer

Introduction

Because of their broad spectrum of antimicrobial properties Pentachlorophenol (PCP) and its salts have been one of the most widely used pesticides in the world Although production and use of PCP are banned in several countries the actual world production is still around 30,000 metric tons This extensive use caused serious pollution of the environment

Bioremediation technology using natural microorganisms for the cleanup of polluted sites turns out as an effective tool especially for the treatment of large sites Often the effort of bioremediation is due to compability of environmental parameters with the physiological demand of the degrading organisms (Fig 1)

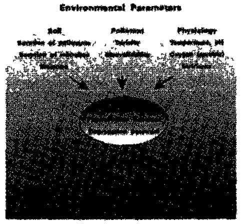

Fig 1 Environmental impact on bioremediation

Within the framework of the EU-research projekt "Well-performing biodegraders for bioremediation" two of the most representative PCP-degraders have been examined to evaluate their potential for application in bioremediation (Fig 2)

Physiological Parameters

Physiological optima of PCP-1 and RA2 are presented in Tab 1 RA2 grows generally faster, but shows strict loss of vitality towards non-optimum conditions

Parameter	PCP-1	RA2
pH	6 0-7 0	7 0-7 5
T (°C)	30	32
pO_2 (%)	> 10	> 10
$\mu_{max, Glc}$ (1/h)	0 02	0 21
$q_{max, PCP}$ (µmol/g/h)	25	600

Tab 1 Physiological optima of *M chlorophenolicum* PCP-1 and *S chlorophenolica* RA2

Concerning PCP-degradation RA2 shows 30-fold higher activity Nevertheless PCP-1 performs much better under extreme conditions like acidic pH or low temperature

Fig 2 PCP-degraders *Mycobacterium chlorophenolicum* PCP-1 and *Sphingomonas chlorophenolica* RA2

Ammonium was detected as "key" substrate during the development of production strategies in bioreactors [1] It is essential for growth, but exhibits strict inhibition of growth and PCP degradation for RA2 and PCP-1 (Fig 3)

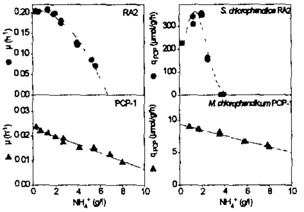

Fig 3 Influence of ammonia on growth and PCP-degradation activity of *S chlorophenolica* RA2 and *M chlorophenolicum* PCP-1

Using the developed cultivation strategy large quantities of biomass of both degraders can be produced

Pollutant Parameters

RA2 can tolerate 180 mg/l PCP which is 40-fold more compared to PCP-1 The PCP-degradation was found to be strongly affected by cell density

PCP shows high affinity towards bacterial cell walls The adsorption revealed a fast kinetic nature and is partly irreversible The pH was found to strongly affect both, the adsorption and desorption process (Fig 4)

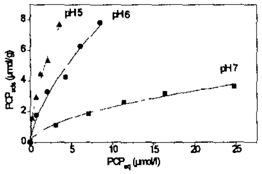

Fig 4 Isotherme of PCP-adsorption by *M chlorophenolicum* PCP-1 cells at different pH values (30 °C, 4 7 g/l bdm)

The adsorption-capacity and the amount of irreversible adsorbed PCP are much higher under acidic conditions, resulting in higher toxicity

Soil Parameters

Degradation studies in soil also performed in the EC-project show that the success of bioremediation is closely related to the observed physiological demands of the degaders [2]

Conclusion

The physiological characterization of the two PCP-degrading strains led to different strategies of growth and PCP degradation

- RA2 can effectively exploit optimum conditions and shows a powerful degradation system, but low survival capacity
- PCP-1 has a low metabolic activity, but an excellent potential of surviving under "environmental conditions"

The observed sorption processes influence bioavailibility of PCP as well as toxicity and therefore significantly affect biodegradation

Literature

[1] C Wittmann et al (1995) Appl Microbiol Biotechnol 44 419-425

[2] R Mietling et al (1996) Appl Env Microbiol (submitted)

Methods for determining degradation rates of organic chemicals in land-filled waste and groundwater

EV5V-CT92-0229

Coordinator: T.H. Christensen

Danmarks Tekniske Høskole
DK - 2800 Lyngby
Tel: +45-4525.1603
Fax: +45-4593.2850

Title: **Methods for determining degradation rates of organic chemicals in landfilled waste and groundwater**

Contract no.: EV5V-CT92-0229

Starting date: 1-1-93

Duration 36 months

Scientific coordinator: Thomas H. Christensen
Institute of Environmental Science and Engineering
Technical University of Denmark
DK-2800 Lyngby
Tel: +45 4525 1603
Fax: +45 4593 2850
E-Mail THC@IMT.DTU.DK

Group leader: Geoffrey M. Williams
Fluid Process Group
British Geological Survey
Keyworth, Nottingham NG12 5GG, UK
Tel: +44 1159 363 100
Fax: +44 1159 363 261
E-Mail G.Williams@BGS.ac.UK

GENERAL OBJECTIVES:

To measure in situ degradation rates of organic chemicals in waste disposal sites and in aquifers, and to compare these actual rates to rates measured in corresponding but simpler laboratory systems in order to form a basis for assesing the fate and environmenntal risk of organic compounds disposed to landfill or relased from the landfill into groundwater.

MAIN RESULTS

In situ measurements have been performed by *in situ* microcosm in aquifers, borehole microcosms in consolidated or coarse aquifers, or artificial borehole microcosm for use in landfilled waste. In the laboratory various batch experiments and column experiments have been performed. The organic chemicals have includede aromatic-and- nitroaromatic compounds, and chlorinated aliphatic compounds, which represent priority chemicals found in polluted groundwater and in waste disposal sites.

It seems crucial to include solids in such experiments, preferably aquifer sediment or fines from aquifer sediment or at least quartz sand in those cases where sediment is not available (existing wells, landfills). It is very important to account for the loss of the organic chemicals from the water phase by sorption onto the solids. Also, monitoring of the redox conditions is critical, and changes may be a problem over time, especially in *in situ* microcosms with long experimental periods. The various methods have advantages and disadvantages, and the choice of methods will depend on scope and resources available

In aerobic aquifers, all aromatic compounds and most phenoliccompounds were degradable within a few months. However, for some chemicals the degradation was not complete. There was no systematic differences between rates determined in *in situ* microcosms and those determined in batch systems, which suggests that batch methods will be appropriate for experimental work.

In anaerobic aquifers the degradation of organic chemicals is less extensive and the degradation rates of those chemicals that do degrade are slow. Exceptions are the chlorinated aliphatic compounds tetrachloromethane and trichloroethane and also toluene. Both in situ microcosm and laboratory experiments yield comparable results. However for slowly degradable chemicals final conclusions on their degradation potential cannot be drawn from the current project.

In landfills, leachate reactors with quartz sand seem to be useful tools to determine the degradability of organic chemicals. The experiments indicate that only chlorinated or nitro aromatic compounds degrade in the landfill environments within the experimental periods. However, in both cases daughter products were formed (e.g. vinyl chloride, anilines).

Local variability (e.g. in an aerobic aquifer, among landfills) and very slow rates of anaerobic degradation of organic chemicals create methodological difficulties in estimating degradation rates. These results demonstrate that at a specific site, degradation rates should be categorized fairly broadly, and that for general regulatory purposes, degradation rates should be categorized in very broad terms in order to account for the variability between sites.

LIST OF JOURNAL PUBLICATIONS

Albrechtsen, H.-J., Smith, P.M.; Nielsen, P & Christensen T.H. (1996): Significance of biomass support particles in laboratory studies on microbial degradation of organic chemicals in aquifers Accepted for publication in Water Research.

Albrechtsen, H.-J , Smith, P.M.; Nielsen, P & Christensen T H (1996): Microbial degradation potentials for organic chemicals in different size-fractions of aerobic aquifer sediment Submitted for publication in Water Research

Albrechtsen, H -J.; Smith, P M.; Nielsen, P.; Christensen, T.H. (1996) Importance of sediment fines in laboratory studies on the degradation of organic chemicals in aquifers Submitted for publication in Water Research.

Bjerg, P.L.; Brun, A., Nielsen, P.H., Christensen, T.H (1996) Application of a model accounting for kinetic sorption and degradation to in situ microcosm observations on the fate of aromatic hydrocarbons in an aerobic aquifer Water Resources Research. In Press

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Kromann, A., Ejlertsson, J.; Ludvigsen, L., Albrechtsen, H.-J ; Svensson, B. H.; Christensen, T H. (1996) Degradability of chlorinated aliphatic compounds in methanogenic leachate sampled at eight landfills. Submitted to Waste Management and Research.

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Nielsen, P.H ; Christensen, T.H., Albrechtsen, H.-J.; Gillham, R W. (1996): Performance of the in situ microcosm technique for measuring the degradation of organic chemicals in aquifers. Ground Water Monitoring and Remediation, 16, (1), 130-140.

Methods for determining degradation rates of organic chemicals in landfilled waste and groundwater

Thomas H. Christensen, Poul L. Bjerg &Hans-Jørgen Albrechtsen
Institute of Environmental Science and Engineering,
Bldg 115, Technical University of Denmark, DK-2800 Lyngby

Geoffrey M. Williams & Jenny J.W. Higgo
Fluid Process Group, British Geological Survey,
Keyworth, Nottingham NG12 5GG, UK

Background and objectives

One of the major obstacles to identifying the fate and evaluating the risks from organic chemicals in landfills and groundwater is the difficulty of determining field degradation rates. For those chemicals and redox environments where rates have been determined in the laboratory, substantial concern exists as to the applicability of these rates to actual field conditions. In-situ determination of degradation potentials and rates has been performed only in very few cases, partly because of the extensive resources needed to perform such experiments and partly because of the difficulties in interpreting such experiments.

The in situ microcosm (ISM) technique originating from the University of Waterloo, Canada has been developed to determine degradation potentials and degradation rates in sandy aquifers. The ISM consists of a 2 L semi-open column that is pushed into the aquifer and loaded from the ground surface with the chemicals to be studied. The installation of an ISM in a sandy aquifer is shown in Fig. 1. For landfill bodies and for aquifers in fractured rock a "borehole-microcosm" was developed containing appropriate solids mimicking the solid surfaces needed for supporting microbial growth.

The objective of the research programme was to measure in-situ degradation rates of organic chemicals in landfilled waste, waste disposal sites and in aquifers, and to compare these actual rates to rates measured in comparable, but simpler, laboratory systems.

The research programme included 5 projects:

A. Significance of particle surfaces in degradation experiments.
B. Correlation of degradation rates with microbial activity.
C. Comparison of degradation rates in groundwater determined in-situ and in laboratory experiments (aerobic as well as anaerobic redox environments).
D. Development of a "borehole microcosm" for non-sandy situations.
E. Determination of degradation rates in a methanogenic landfill by an "artificial borehole microcosm" and by laboratory experiments.

The project has focused on aromatic and nitroaromatic compounds as wells as chlorinated aliphatic compounds in trace levels.

General results

The research programme has been completed and the final report submitted to EC in March 1996. Publications prepared by the project are listed in the back of this extended abstract. Details about the activities can be found in the scientific papers; here only a general summary is provided.

Methods to determine degradation rates for organic chemicals should include solids, preferably aquifer sediment or fines from aquifer sediment or at least quartz sand in those cases where sediment is not available (existing wells, landfills). It is very important to account for the loss of the organic chemicals from the water phase by sorption onto the solids. Also, monitoring

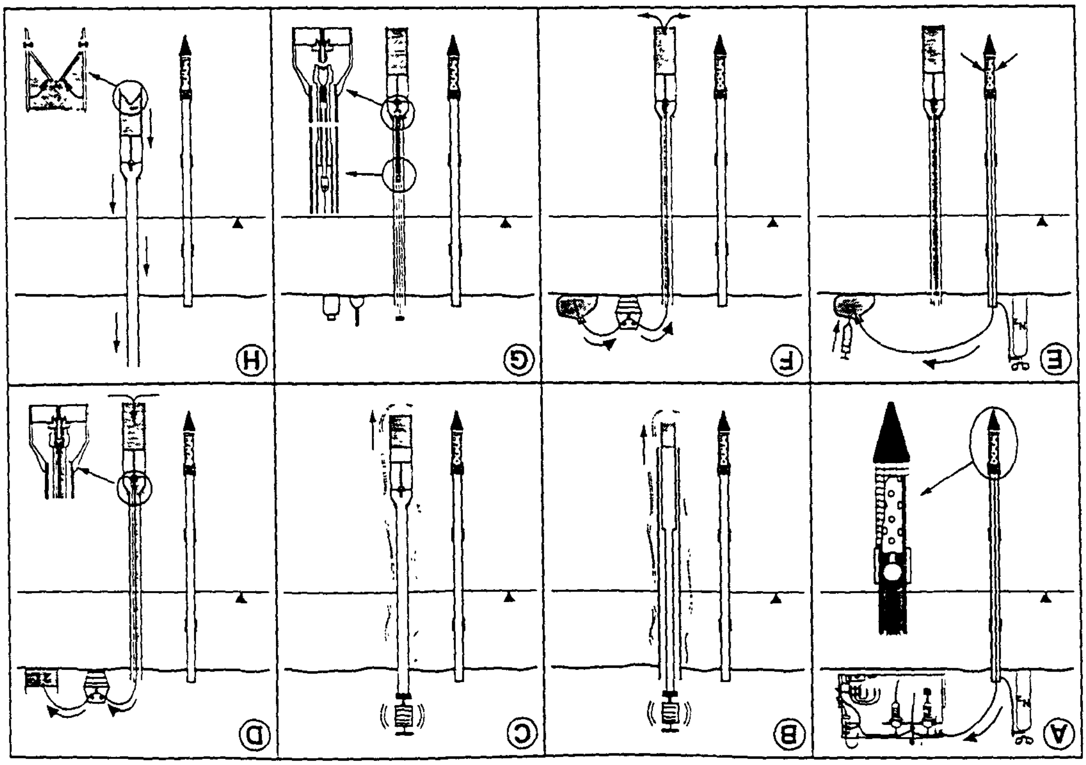

Figure 1: Sketches showing how ISM experiments were performed: (a) initial characterization of groundwater; (b) sediment sampling prior to experiment; (c) installation; (d) development; (e) collection and spiking of groundwater for loading; (f) loading; (g) sampling groundwater; (h) sampling of sediment after experiment.

of the redox conditions is critical, and changes may be a problem over time, especially in *in situ* microcosms with long experimental periods. The various methods (batch, column, *in situ* microcosm) have advantages and disadvantages, and the choice of methods will depend on scope and resources available. The use of the *in situ* microcosm is illustrated in Figure 1.

In aerobic aquifers, all aromatic compounds and most phenolic compounds were degradable within a few months. However, for some chemicals the degradation was not complete. There was no systematic differences between rates determined in *in situ* microcosms (ISM) and those determined in batch systems (LBM), which suggests that batch methods will be appropriate for experimental work (Table 1).

In anaerobic aquifers the degradation of organic chemicals is less extensive and the degradation rates of those chemicals that do degrade are slow. Exceptions are the chlorinated aliphatic compounds tetrachloromethane and trichloroethane and also toluene. Both in situ microcosm and laboratory experiments yield comparable results. However for slowly degradable chemicals final conclusions on their degradation potential cannot be drawn from the current project.

Table1: Sorption parameters and first order degradation rate constants determined in an *in situ* microcosms (ISM) and in laboratory batch microcosms (LBM). **Nielsen et al., 1996a).**

		location A		location B			
compound		ISM A[b]	LBM A[c]	ISM B1	ISM B2	LBM B1	LBM B2
benzene	F						
log K_{ow} = 2.1[d]	K_d	0.08		<0.05	<0.05		
	k_1	0.5	0.07	0.2	0.3	0.2	0.2
	lag phase	6	0	5	1	5	5
toluene	F	0.25					
log K_{ow} = 2.6	K_d	0.13		0.07	0.07		
α = 0.2	k_1	0.4	0.09	0.1	0.2	0.2	0.2
	lag phase	5	0	7	1	3	5
o-xylene	F	0.22		0.17			
log K_{ow} = 3.0	K_d	0.24		0.10	0.09		
α = 0.2	k_1	0.1	0.02	0.04	0.04	0.03	0.03
	lag phase	7	0	0	0	3	0
nitrobenzene	k_1	na[e]	–[f]	na	na	–	–
naphthalene	F	0.29		0.19	0.19		
log K_{ow} = 3.4	K_d	0.43		0.17	0.16		
α = 0.09	k_1	0.8	0.4	0.2	0.9	0.9	0.9
	lag phase	6	10	12	6	8	9
biphenyl	F	0.19		0.17	0.29		
log K_{ow} = 4.1	K_d	1.50		0.43	0.54		
α = 0.05	k_1	0.2	0.4	0.09	0.2	0.9	0.09
	lag phase	0	15	0	0	8	10
o-dichlorobenzene	F	0.29		0.28	0.24		
log K_{ow} = 3.4	K_d	0.37		0.17	0.15		
α = 0.2	k_1	0.06	0.02	0.04	0.02	0.02	0.02
	lag phase	13	0	20	0	0	0
p-dichlorobenzene	F	0.28		0.29	0.24		
log K_{ow} = 3.4	K_d	0.41		0.18	0.15		
α = 0.2	k_1	0.05	0.01	0.03	0.02	0.01	0.01
	lag phase	22	0	14	9	0	0
1,1,1-trichloroethane	k_1	–	–	–	–	–	–
tetrachloromethane	k_1	–	–	–	–	–	–
trichloroethene	k_1	–	–	–	–	–	–
tetrachloroethene	k_1	–	–	–	–	–	–
phenol	F						
log K_{ow} = 1.5	K_d	0.06		<0.05	<0.05		
	k_1	0.5	0.4	0.2	0.4	0.5	0.4
	lag phase	0	0	0	0	0	0
o-cresol	F						
log K_{ow} = 2.0	K_d	D[g]		D	D		
	k_1	0.2	0.4	0.2	0.4	0.4	0.4
	lag phase	0	0	0	0	1	2
2,4-dichlorophenol	F	0.30			0.48		
log K_{ow} = 3.1	K_d	0.20		<0.05	0.12		
α = 0.05	k_1	0.1	0.09	0.02	0.06	0.4	0.4
	lag phase	0	50	0	0	25	20
2,6-dichlorophenol	F	0.30					
log K_{ow} = 2.8	K_d	0.11		<0.05	0.08		
α = 0.05	k_1	0.03	–	0.02	0.02	–	–
	lag phase	0		0	0		
4,6-*o*-dichlorocresol	F						
log K_{ow} unknown	K_d	D		D	D		
	k_1	0.2	–	0.2	0.04	–	–
	lag phase	0		0	0		
o-nitrophenol	F	0.30					
log K_{ow} = 1.8	K_d	0.11		<0.05	0.07		
α = 0.05	k_1	0.05	–	0.01	0.01	0.05	0.02
	lag phase	0		0	0	42	30
p-nitrophenol	F						
log K_{ow} = 1.9	K_d	<0.05		<0.05	<0.05		
	k_1	0.2	0.4	0.09	0.4	0.5	0.4
	lag phase	0	7	2	0	6	7

[a] Units: log K_{ow}, dimensionless; α, day^{-1}; F, dimensionless, K_d, L kg^{-1}; k_1, day^{-1}; lag phase: day. [b] In ISM experiments, sorption kinetic parameters (α and F) were not estimated for K_d < 0.1 L kg^{-1}, and first-order degradation rate constants (k_1) were determined without taking sorption into account. [c] In LBM experiments, the solid/water ratio was low, and no significant sorption of any compounds was observed. [d] Log K_{ow} values were selected from ref 27 except for biphenyl (*29*) and 2,6-dichlorophenol (*29*). [e] Not analyzed due to analytical difficulties. [f] Compound not degraded during experiment. [g] No sorption parameters determined because compound degraded during sorption experiment.

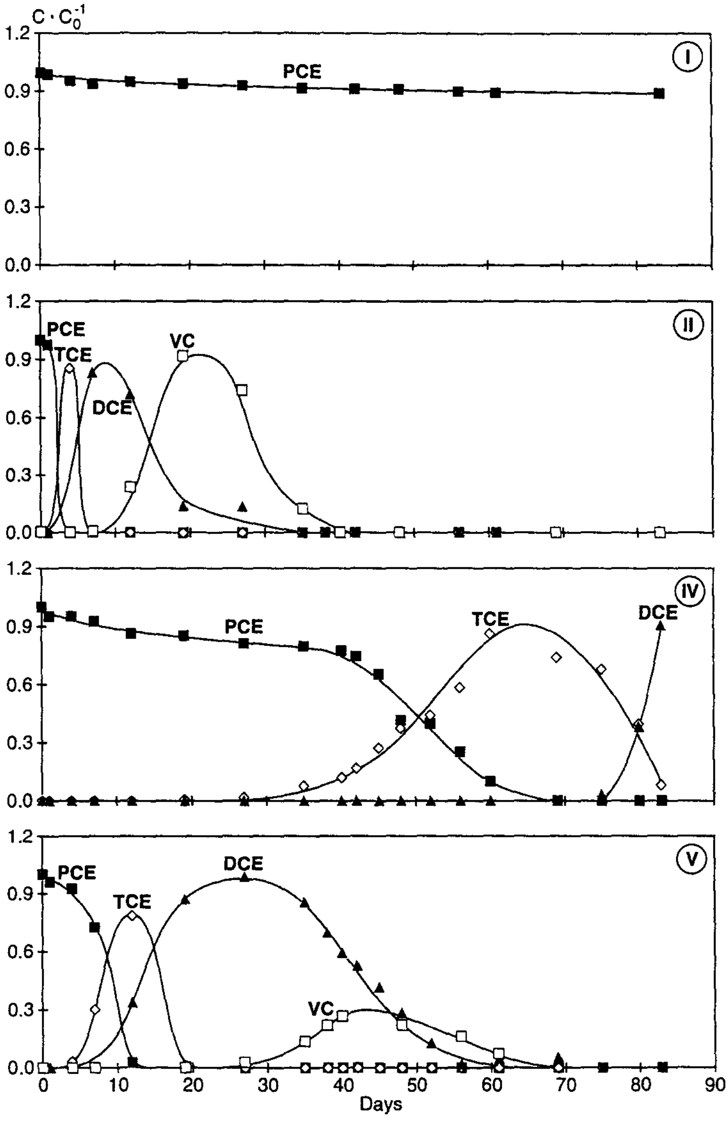

Figure 2: Fate curves for PCE and its transformation products TCE, DCE and VC in leachates from four landfills: Relative concentrations versus time (**Kromann et al., 1996**).

In landfills, leachate reactors with quartz sand seem to be useful tools to determine the degradability of organic chemicals. The experiments indicate that only chlorinated or nitro aromatic compounds degrade in the landfill environments within the experimental periods. However, in both cases daughter products were formed (e.g. vinyl chloride, anilines) (Figure 2).

Local variability (e.g. in an aerobic aquifer, among landfills) and very slow rates of anaerobic degradation of organic chemicals create methodological difficulties in estimating degradation rates. These results demonstrate that at a specific site, degradation rates should be categorized fairly broadly, and that for general regulatory purposes, degradation rates should be categorized in very broad terms in order to account for the variability between sites.

Publications

Christensen, T.H.; Bjerg, P.L.; Albrecthsen, H.-J: Williams, G.M.; Higgo, J.J.J.W. (1996): Methods for determining degradation rates of organic chemicals in landfilled waste and groundwater. Final Report. European Commission, pp. 30 + appendix.

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Degradation of xenobiotics: an investigation of microbiological events occurring within polluted sites with emphasis on those undergoing bioremediation

EV5V-CT94-0539

Coordinator: P. Williams

School of Biological Sciences
University of Wales
UK - Gwynedd LL57 2UW
Tel: +44-1.2483.51151
Fax: +44-1.2483.70731

Project N° EV5V-CT94-0539

Degradation of xenobiotics: an investigation of microbiological events occurring within polluted sites with emphasis on those undergoing bioremediation.

Coordinator:

P.A. Williams
School of Biological Sciences
University of Wales, Bangor
UK - Gwynedd LL57 2UW
Tel: +44-1.2483.51151
Fax: +44-1.2483.70731

Partners:

J.G. Van Andel
Laboratory of Waste Materials and Emissions
National Institute of Public Health and Environmental Protection
P.O. Box 1
NL - 3720 BA Bilthoven
Tel: +31-30.74.3063
Fax: +31-30.29.3651

J.L. Ramos
Consejo Superior de Investigaciones Científicas
Estacion Experimental del Zaidin
1, Prof. Alberada
E - 18008 Granada
Tel: +34-5812.1011
Fax: +34-5812.9600

PROJECT: EV5V-CT94-0539

DEGRADATION OF XENOBIOTICS: A COMPARISON OF SOIL BACTERIA OCCURRING IN POLLUTED SITES WITH EMPHASIS ON THOSE UNDERGOING BIOREMEDIATION

Juan L. Ramos, M. Barnes, W. Duetz, S. Marqués and P. Williams

Introduction.

This project is aimed at filling two major gaps in the knowledge surrounding biodegradation of the monoaromatic hydrocarbons - benzene, toluene, ethylbenzene, and the xylenes - the so-called BTEX compounds: 1) the environmental factors that determine the prevalence of different types of BTEX degraders (different genera, different pathways) and 2) the role and characteristics of the Gram-positive BTEX degraders.

The experimental programme was divided into two parts:

A. Competition experiments between a selected number of representative strains of different environmental conditions in both chemostat cultures and soil microcosms.

B. Characterisation of xenobiotic-degrading strains by genetic and biochemical analysis of their catabolic pathways.

To fulfil these aims a number of different organisms have been chosen for study. The core organisms chosen for this study were *Pseudomonas putida* F1, *Pseudomonas putida* T1 and *Rhodococcus* sp. PWD1. In addition to these, a number of other organisms have been studied in respect to the above targets.

A. - Comparison of different strains with respect to their competition behaviour:

Gram-positive and Gram-negative toluene-degrading strains were compared with respect to their competition behaviour in chemostat cultures and soil microcosms.

A.1 Competition between Gram-positive and Gram-negative strains in chemostat culture.

The strains were competed in one-to-one competition experiments at different growth rates in the following way. The strains were pregrown individually in axenic chemostat cultures under carbon and energy limitation with toluene as the sole source of carbon and energy, and supplied with mineral medium at the appropriate dilution rate. During an adaptation period of 1 to 3 weeks the axenic cultures were allowed to reach steady-state conditions. Then, a new, sterile, chemostat was started, using samples from the steady state cultures of the axenic cultures as inoculants. Subsequently, the relative proportion of the two strains was followed in time. The relative proportion of the two strains was determined by plating diluted samples from the chemostat on non-selective peptone-agar plates.

In order to mimic the natural conditions with respect to low growth rates as for as possible we have chosen to perform the competition experiments at relatively low dilution rates: 0.05 and 0.005 h^{-1}. The growth yields of the three strains at a dilution rate of 0.05 h^{-1} were not significantly different. At the lowest dilution rate (0.005 h^{-1}), however, *Rhodococcus* PWD1 was found to have a 2.5 times higher growth yield than both Pseudomonas strains. This is in accordance with the general assumption that Gram-positive bacteria are specialized at growing at low rate in nutrient-poor environments.

In all competition assays, the *P. putida* strains progressively dominated the chemostat cultures. Mathematical analysis showed that the growth rate of the *P. putida* cells was more than 10 times greater than the growth rate of the *Rhodococcus* cells. Apparently the specific affinity for toluene of the *P. putida* cells is larger than that of *Rhodococcus* PWD1. As mentioned above, the growth yield on toluene is larger for *Rhodococcus* PWD1 but apparently (the strain lost all competition experiments) this advantageous feature is not sufficient to compensate for the lower specific affinity.

A.2 - Competition between and among Gram-positive and Gram-negative strains in soil microcosms.

The competition behaviour of BTEX degrading soil bacteria dependent on the prevailing environmental conditions. When the BTEX compounds are present at high concentrations, the resistance to toxic effects will be the main factor determining the thriving of the different strains. On the other hand, when the BTEX are present at low concentrations, the affinity for the BTEX compounds determine the relative growth of the different sub-populations.

Therefore two kind of competition experiments between different toluene-degrading strains in soil microcosms were performed.

1) Competition experiments between *Rhodococcus* and *P. putida* strains at low, growth limiting concentrations of toluene.
2) Competition experiments among different *Pseudomonas* strains at saturating concentration of toluene.

A.2.1. - Competition experiments between *Rhodococcus* and *P. putida* strains at low, growth limiting concentrations of toluene.

Soil microcosms were inoculated with toluene-degrading bacterial cultures of *Rhodococcus* PWD1 and *P. putida* F1 that were pregrown under toluene-limiting conditions in chemostat. One soil microcosm was supplied with an air flow of 2 l/h containing 2.5-4 μM toluene. The other microcosm was supplied with an air flow without toluene. Subsequently, the development of the cell numbers of the two strains was followed in time by extracting bacteria from soil samples taken at regular time intervals and plating them on non-selective agar-media. In the absence of toluene conditions, the viable counts of both strains decreased in time at about the same rate. When low concentrations of toluene were supplied the cell numbers of both strains increased slowly by a factor of only 2 to 3.

A.2.2 - Competition experiments among *Pseudomonas* strains with different degrees of tolerance to high concentrations of toluene.

In order to select the strains for competition experiments, a series of assays was carried out to study the survival and establishment of different *Pseudomonas* strains in soil microcosms supplemented or not with 10% (vol/wt) toluene.

For these experiments, four strains were selected. *Pseudomonas* *putida* DOT-T1 that tolerates in liquid medium high concentrations of toluene, up to 90% toluene (vol/vol). The second strain, *Pseudomonas putida* F1, is able to degrade toluene via 3-methylcatechol, and can tolerate relatively high concentrations of this compound, although to a lower degree than T1. The third strain, *Pseudomonas putida* EEZ15 bears the mutant TOL plasmid pWW0-EB62 that confers the ability to grow on *p*-ethyltoluene via toluene monooxygenase. The fourth strain, *Pseudomonas mendocina* KR1, is able to degrade toluene via the *p*-cresol pathway.

In the absence of toluene, the four strains could stably survive in the microcosm, reaching a density of about 10^6 CFU/g of soil, that was maintained during at least two months. Previous experiments had shown that several indigoneous bacterial strains were present in this soil microcosm at a maximal density of about 10^5-10^6 CFU/g of soil.

In the presence of 10% (vol/wt) toluene, only strains T1 and F1 could survive and establish, while EEZ15 and *Pseudomonas mendocina* could not be detected after a few days. We therefore chosed the two tolerant strains for further assays.

In order to distinguish and follow the presence of the two populations in competition experiments, the two selected strains were labelled with a mini-Tn5 transposon bearing a different antibiotic resistance.

Two sets of competition experiments were carried out: 1) The first was designed to estimate the competition ability of the strains.

2) The second set was designed to determine the effect of the precolonization of the soil by one of the strains on the ability of the second strain to became established in this soil.

In the first series, soils were inoculated with equal cell densities of both strains (10^4 or 10^6 CFU/g) soil. In soils in which both strains were introduced at 10^4 CFU/g soil strain, T1 grew and was maintained at higher levels than F1. In soils in which both strains were introduced at high cell density, no difference was observed between the two strains, probably because they both had reached their maximum soil capacity and were maintained stably.

When the same set of experiments was carried out in the presence of

10% (vol/wt) toluene, strain T1 proved to be better maintained in the microcosm, in detriment of strain F1, that disappeared from the soil.

For the second set of experiments, survival of either strain was followed in conditions in which one of the strains had previously been allowed to establish in the microcosm. A series of soil microcosms were inoculated at day 0 with one of the strains at an initial cell density of 10^6 CFU/g soil, and the same concentration of the second strain was added to the microcosm 1, 5 or 14 days after. The numbers of both strains were followed for a month thereafter. Results shows that the fact that one strain had been colonizing the soil for a certain time gave it a considerable advantage in competition. However, when the experiment was done in the presence of 10% (vol/wt) toluene, strain T1 was always the winner in competition.

B. - Pathways of Gram positive toluene-degraders

The Gram positive *Rhodococcus* sp. strain PWD1 and *Brevibacterium* sp. MTB5 were chosen for biochemical characterisation. Biochemical assays indicated that *Rhodococcus* degraded toluene via cis-glycol and 3-methylcatechol, followed by extradiol (*meta*) cleavage by a catechol 2,3-dioxygenase. This route is similar to the pathway found in *Pseudomonas* sp. F1.

Shotgun clones of genomic DNA were screened for toluene dioxygenase and catechol 2,3-dioxygenase activities. This yielded three separate *Bgl*II fragments (ranging between 9-21 kb), carrying three distinct *meta*-cleavage dioxygenases, two 2-hydroxymuconic semialdehyde hydrolases and a putative toluene dioxygenase (indicated by conversion of indole to indigo). Southern hybridisations located all of these genes to the chromosome.

The 9 kb *Bgl*II shotgun clone, pPWD1-2, was sequenced over a 4.2 kb region. Three open reading frames were identified. Sequence homologies to these ORFs suggested the presence of a catechol 2,3-dioxygenase, a 2-hydroxymuconic semialdehyde hydrolase and an ORF with similarities to both phenol and *p*-hydroxybenzoate hydroxylase. Homologies to genes in the databanks were rarely above 60%, although amino acid alignments indicated common ancestry with similar genes in Gram negative organisms. Attempts were made to confirm the role of these genes, by the construction of insertion mutants in the wild type *Rhodococcus* strain.

A Brevibacterium strain isolated from agricultural soil was shown to exhibit a pWW0-like pathway but metabolism seemed to be restricted to unsubstituted toluene.

Degradation of xenobiotics by thermophilic microorganisms

EV5V-CT94-0540

Coordinator: R. Müller

Technical University Hamburg-Harburg
D - 21149 Hamburg
Tel: +49-40.7718.3118
Fax: +49-40.7718.2127

Degradation of Xenobiotics by Thermophilic Microorganisms

EV5V-CT94-0540

Starting Date: 1. July 1994 Duration: 3 Years

Thermophilic Degradation
Cl
of Xenobiotics

Participants:

Coordinator:
Prof. Dr. R. Müller
Technical University Hamburg-Harburg,
Biotechnology II, Denickestraße 15,
D 21149 Hamburg, Germany
+49-40-7718-3118
+49-40-7718-2127

Prof. Dr. G. Antranikian
Technical University Hamburg-Harburg,
Biotechnology I, Denickestraße 15,
D 21149 Hamburg, Germany
+49-40-7718-3117
+49-40-7718-2909

Prof. Dr. R. Sharp
Centre for Appl. Microbiol.& Research
Division of Biotechnology
Porton Down, Salisbury SP4 0JG, UK
+44-1980-612443
+44-1980-611320

Prof. Dr. W. M. de Vos
Wageningen Agricultural University
Microbiol., Hesselink van Suchtelenweg 4
6703 CT Wageningen, The Netherlands
+31-83-8059558
+31-83-7083829

Main objectives:

The aim of this research project is to exploit the potential of thermophilic microorganisms for the degradation of xenobiotic compounds under conditions, which occur in many waste streams of production plants that are so far considered not to be treatable biologically. For that purpose thermophilic microorganisms shall be enriched, the degradation pathways shall be elucidated and the relevant enzymes in the degradation pathways shall be isolated and characterized.

Main results:

In all the laboratories involved a screening has been conducted for new microorganisms with the ability to degrade various xenobiotics. This screening is still continuing and shall be conducted till the end of the project. Several problems due to the high temperatures were solved.

The screening of known extreme thermophilic microorganisms with temperature optima above 80°C did not reveal any degradation potential with the xenobiotics tested.

Under aerobic conditions in the temperature range up to 75°C several thermophilic bacilli have been isolated showing degradation of alkanes, phenols, cresols, chlorophenols, benzoate, naphthalene, biphenyl and different permethrins. The organisms have been characterized physiologically. They all belong to the thermophilic bacilli. In some cases the degradation pathways have been elucidated. In general the degradation pathways were identical to those seen at lower temperatures. In some cases, however, the instability of intermediates in the degradation pathways resulted in a rapid formation of polymers, toxic to the bacteria, a reaction not seen at ambient temperatures.

Several enzymes have been detected and some of them were purified to homogeneity and characterized. In addition the genes encoding the enzymes involved in the initial steps of phenol and cresol degradation at 70°C have been cloned and sequenced.

Under anaerobic conditions reductive dehalogenation of tetrachloroethene to dichloroethene via trichloroethene at 60°C and the dechlorination of 3-chlorobenzoate to benzoate were observed so far.

For several enrichment cultures the isolation of pure cultures is still in progress.

Degradation of Xenobiotics by Thermophilic Microorganisms

Commisison of the European Communities

Programme Environment

Project No. EV5V-CT94-0540

Extended Abstract:

During the last years public concern about pollution of soil water and air has increased continously. The public has become aware of many problems associated with the production and use of various chemicals. Waste water streams that contributed to the contamination of lakes rivers and the sea are no longer tolerated. This situation lead to an intensive search for possibilities to abate or at least reduce the amount of chemicals released into the environment. One possibility to degrade environmental pollution is the use of microorganisms. Many bacteria have been isolated from soil and water samples which show a surprising potential for the degradation of xenobiotics. The degradation pathways have been elucidated and the enzymes involved in these pathways have been studied. This knowledge has been used to create new or to improve existing treatment facilities for waste water and for contaminated soil. Even for the treatment of contaminated exhaust air biofilters have become a valuable option. All of these existing facilities are operated at ambient temperatures.

On the other hand during the last decade many bacteria have been discovered which can grow at high temperatures up to 110°C. These organisms have

gained a lot of interest from biotechnological companies and are now exploited for their potential in new biotechnological processes. However, it remained unclear, whether these organisms have a potential for the degradation of xenobiotics. If this would be the case, such organisms could be used to treat hot waste streams or exhaust gases as they occur in many production plants. At the same time it would be expected, that such organisms would have an advantage in degrading especially such compounds, that are poorly water soluble at ambient temperature and are therefore poorly biodegradable. The solubility of such compounds is much better at high temperatures. For example the solubility of anthracene in water increased by about tenfold on shifting the temperature from 30°C to 70°C. The same temperature dependence was seen in the extraction of soils contaminated with diesel oil. Therfore the cleaning of such soils should be facilitated at higher temperatures.

Often oxygen is considered to be a limiting factor in aerobic degradation reactions at high temperatures. Although oxygen solubility is much lower at higher temperatures, the diffussion and thus the transport of fresh oxygen from the gas phase into the liquid phase is accelerated. In a stirred tank reactor it was shown that this effect completely neutralized the effect of the lower solubility of oxygen. Even higher oxygen transfer rates were obtained at higher temperatures.

These considerations prompted us to set up this research project for the exploitation of the potential of thermophilic microorganisms to degrade xenobiotics. In this project four groups from the Centre for Applied Microbiology and Research, Porton Down (CAMR) from the Technical

University Hamburg-Harburg (TUHH) and from the Agricultural University Wageningen (WAU) are involved. In the initial stage of the project a screening was conducted in all four laboratories using known extreme thermophilic microorganisms from different culture collections, which might possess a potential for xenobiotic degradation. However, none of the extreme thermophilic bacteria from culture collections which were tested for their degradative potential did show any activity with the substrates used.

In contrast, in all institutions involved, enrichment cultures for the degradation of various xenobiotics from environmental samples could be set up successfully. Under aerobic conditions from these enrichment cultures pure microbial strains for the degradation of phenol, all isomers of cresol, benzoate, naphthaline, biphenyl and different permethrins have been isolated. These strains were characterized according to their morphological, physiological, biochemical and genetic properties. All aerobic bacteria obtained so far in this project belong to the thermophilic bacilli.

So far, all degradation pathways elucidated corresponded to those observed with mesophilic microorganisms. Thus, all thermophilic organisms transforming phenol or substituted phenols degraded phenol via *meta*-cleavage pathway. In the degradation of naphthalin several metabolites were detected, which do not correspond to those observed in mesophilic strains. The identification of these metabolites is now in progress. In the conversion of 2-chlorophenol, 3-chlorocatechol was detected as an intermediate (Figure 1). However, it was demonstrated, that 3-chlorocatechol was not converted by the bacteria, but was degraded chemically at the high temperatures used (Figure

2). Thus the degradation of 2-chlorophenol by the thermophilic bacilli is a cometabolic process, in which the bacteria do not gain any energy or carbon from the conversion of this substance. Therfore as seen in figure 1 the conversion of this substrate comes to a stop as soon as additional carbon sources are no longer present in the culture fluid.

Figure 1: Cometabolic conversion of 2-chlorophenol by a thermophilic bacillus at 70°C.

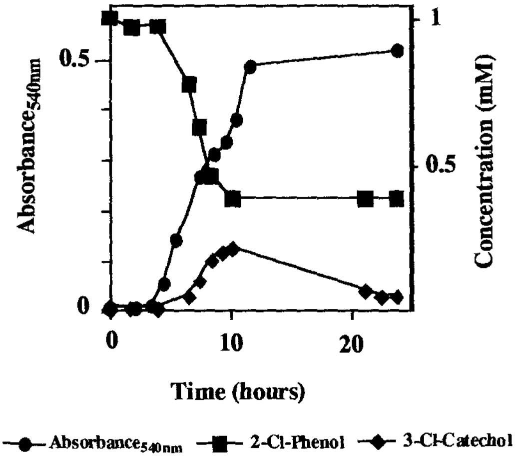
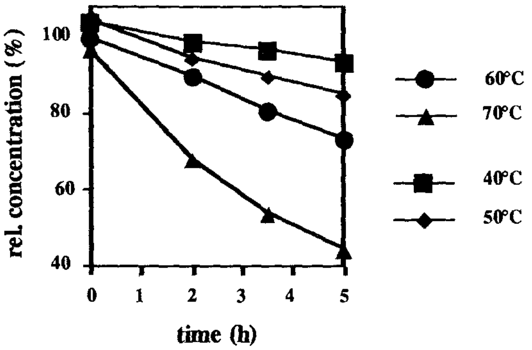


Figure 2: Decomposition of 3-chlorocatechol at different temperatures.



From one of these organisms the catechol 2,3-dioxygenase has been purified to homgeneity and the purification of the phenol hydroxylase is in progress. The genes for both enzymes have been cloned in *E. coli* and sequenced. The evaluation of the sequence data is in progress.

Under anaerobic conditions reductive dechlorination was found at elevated temperatures. Thus the conversion of tetrachloroethylene to dichloroethylene via trichloroethylene was demonstrated at 65°C. In the anaerobic degradation of 3-chlorobenzoate at 75°C unsubstituted benzoate was found as major metabolite after about 3 weeks of incubation, which disappeared after additional 2 weeks of incubation. 2- and 4-chlorobenzoate were not dehalogenated by the same enrichment samples. The anaerobic enrichments contained Clostridia and non-spore forming obligate anaerobes.

Five synthetic pyrethroid insecticides were detoxified microbially by a mixed culture from a geothermal source growing anaerobically at 75°C. These pyrethroids were hydrolyzed to non-insecticidal products within a period of four weeks. Of these five pyrethroids the *trans* isomer of permethrin was the most readily transformed and Fastnac the most persistent.

Conclusions and Outlook:

In this project so far several new microorganisms have been isolated, illustrating the potential of microorganisms to degrade various xenobiotics at elevated temperatures. The range of xenobiotics attacked seems to be similar to that under ambient temperatures although the microorganisms are much more difficult to isolate. However, when more insight into the special properties of these newly isolated microorganisms has been gained, these organisms should provide a valuable tool for the decontamination of hot waste streams and hot exhaust gas streams.

Microbial adaptation to degradation of organohalogens: effects on Ecosystems Adaptation and Bioremediation of polluted sites

ENV4-CT95-0086

Coordinator: D.B. Janssen

Biochemical Laboratory
Groningen Biomolecular Sciences and Biotechnology Institute
University of Groningen
NL - 9747 AG Groningen
Tel: +31-50.3634.209
Fax: +31-50.3634.165

PROJECT DATA SHEET ENV4-CT95-0086

Microbial Adaptation to Degradation of Natural and Synthetic Organohalogens: Effects on Ecosystem Acclimation and Natural Bioremediation of Polluted Sites

1. Project Participants

Prof. D.B. Janssen (coordinator)
Biochemical Laboratory, Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
Fax: (31)50-3634165; Tel: (31)50-3634209; E-mail: d.b.janssen@chem.rug.nl
Prof. K.H. van Pée
Institute of Biochemistry, Technical University Dresden, D-01062 Dresden, Germany
Fax: (49)351-4635506; Tel: (49)351-4634494; E-mail: chr@ctch02.chm.tu-dresden.de
Dr. A.J. Weightman
School of Pure and Applied Biology, University of Wales College of Cardiff,
PO Box 915, Cardiff CF1 3TL, Wales, UK
Tel: (44)1222-874309; Fax: (44)1222-874305; E-mail: weightman@cardiff.ac.uk
Dr. M.J. Larkin & Prof. D.B. Harper
The Questor Centre, David Keir Building, The Queens University of Belfast
Belfast BT9 7BL, Northern Ireland
Fax: (44)1232-236505; Tel: (44)1232-254133. E-mail: m.larkin@queens-belfast.ac.uk

2. Starting date and duration

February 1, 1996. 3 year project.

3. Project goal

The objective of the project is to understand how aerobic microorganisms develop the capacity to degrade synthetic halogenated aliphatic compounds that occur as soil and groundwater pollutants and to develop generic methods for stimulation of indigenous microbial populations to effect the removal of such pollutants from contaminated soil and groundwater.

4. Project approach and activities

The project approach is to carry out laboratory research aimed at establishing the relationship between dehalogenation mechanisms for natural and synthetic organohalogen compounds. Subsequently, it will be investigated which genetic processes (mutation, gene transfer) occur during adaptation under selective conditions, and how these processes are influenced by environmental conditions. The activities include:

- isolation of organisms that degrade halogenated substrates, using as inocula samples obtained from unpolluted areas and contaminated sites

- physiological and biochemical studies to determine dehalogenation and halogenation mechanisms in newly isolated strains
- analysis of the genetic organization of organisms that degrade xenobiotic halogenated compounds
- examination of genetic processes that occur in chemostats or biofilm systems and that lead to an expansion of the substrate range of the organisms. Organisms known to degrade natural or synthetic organohalogens will be used as the starting material, and the relationship between gene transfer and adaptation of the community will be established
- testing the effect of environmental conditions on the development of dehalogenating organisms and community adaptation, and establishing the relevance to bioremediation strategies.

5. Results

Previous work of the groups involved in this project has led to the identification of bacterial dehalogenases for chloroalkanes, chloroalkanoic acids and chloroalcohols in a wide range of bacteria. The group in Groningen has unraveled the catalytic and kinetic mechanism of haloalkane dehalogenase of *Xanthobacter.* The organism is now used at full scale for the removal of 1,2-dichloroethane from groundwater. The group in Dresden has discovered various halogenating enzymes that have structural and mechanistic similarities to the haloalkane dehalogenase studied in Groningen. The Cardiff laboratory has discovered that dehalogenase genes may be located on transposable elements, and that they can be mobilized via transferable plasmids to other organisms. The Belfast laboratory has wide experience on halogenating organisms, and recently also studied the genetics of a novel group of haloalkane dehalogenases.

7. Selected publications of the participants

Pries, F., A.J. van den Wijngaard, R. Bos, M. Pentenga, & D.B. Janssen (1994). The role of spontaneous cap domain mutations in haloalkane dehalogenase specificity and evolution. J. Biol. Chem. 269: 17490-17494.

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Microbial Adaptation to Degradation of Natural and Synthetic Organohalogens

Effects on Ecosystem Acclimation and Natural Bioremediation of Polluted Sites

D.B. Janssen[1], K.H. van Pée[2], A.J. Weightman[3], & M.J. Larkin[4]
[1]Biochemical Laboratory, Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, [2] Institute of Biochemistry, Technical University Dresden, D-01062 Dresden, Germany, [3] School of Pure and Applied Biology, University of Wales College of Cardiff, Cardiff CF1 3TL, Wales, UK, [4]The Questor Centre, David Keir Building, The Queens University of Belfast, Belfast BT9 7BL, Northern Ireland

Project summary

The objective of the project is to understand how aerobic microorganisms adapt to degrade synthetic halogenated aliphatic compounds that occur as soil and groundwater pollutants and to develop generic methods for stimulation of indigenous microbial populations to effect the removal of such pollutants from contaminated soil and groundwater.

The underlying hypothesis is that organisms that degrade industrial chlorinated chemicals can evolve from bacteria that degrade naturally produced organohalogens. It is investigated how natural organohalogens are formed and degraded, how adaptation of microbial communities to synthetic compounds in polluted environments proceeds by mutations and genetic exchange, and how this can be influenced by modifying environmental conditions.

Introduction: background information and description of scope

Chlorinated chemicals: environmental toxicants and natural products. Chlorinated organic compounds are one of the most important classes of environmental pollutants. Their widespread occurrence as contaminants of soil and groundwater, surface water, air, drinking water and waste water poses a serious health risk due to their toxic characteristics and bioaccumulation properties. Most synthetically produced organochlorine compounds have a xenobiotic structure, which is not recognized by microbial enzymes and therefore degradation may be extremely slow. During the last few years it has become more apparent that there is also substantial natural production of halogenated organic compounds. Plants, seaweeds, fungi, and bacteria produce a variety of chlorinated, brominated and fluorinated chemicals including halogenated methanes, haloalkanoic acids, chlorinated phenols, and chlorinated antibiotics. It is likely that organisms which can degrade such compounds do occur at locations where production of natural organohalogens takes place.

Genetic adaptation. The recalcitrance of synthetic chlorinated compounds is mainly caused by the limited substrate specificity of dehalogenating enzymes that must cleave off the halogen atoms. However, microorganisms can slowly adapt to synthetic compounds, and thereby evolve new degradative abilities. The extent and rate of genetic adaptation of dehalogenases thus are of key importance since they determine whether or not a certain synthetic compound will be degraded in an ecosystem. Furthermore, the spread of newly developed genetic information to other organisms allows new combinations of catabolic genes to be formed, leading to evolution of new pathways for the degradation of chlorinated compounds. How genetic processes such as gene transfer and the occurrence of specific adaptive mutations in catabolic genes are influenced by the conditions and to what extent these can be stimulated is unknown, however.

Description of the scientific problem. New degradation activities may develop in a wide range of microorganisms, but there is very little information as to how this development proceeds. Questions central to this issue and on which this proposal focusses are:

- can naturally produced organohalogens be degraded by microorganisms, and if so, by what physiological mechanisms?

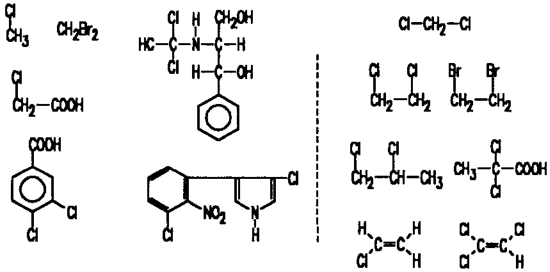

Fig. 1. Naturally produced halogenated compounds (left), and halogenated aliphatic compounds that occur as important environmental pollutants (right).

- what is the distribution of dehalogenase genes for the degradation of synthetic halogenated aliphatics in pristine and polluted environments, and do elevated numbers of dehalogenating organisms occur at sites with natural production of organohalogens or contamination by synthetic pollutants?
- what are the genetic changes that allow improved conversion of halogenated aliphatic compounds which occur as pollutants and how do genetic processes contribute to the diversity and spread of organisms that can degrade xenobiotics?
- how can we use the natural capacity to adapt for predicting the feasibility of bioreclamation and for stimulating bioremediation processes?

Project approach and activities. The project approach is to carry out laboratory research aimed at establishing the relationship between dehalogenation mechanisms for natural and synthetic organohalogen compounds. Subsequently, it will be investigated which genetic processes (mutation, gene transfer) occur during adaptation under selective conditions, and how these processes are influenced by environmental conditions. The activities include:

- isolation of organisms that degrade halogenated substrates, using as inocula samples obtained from unpolluted areas and contaminated sites
- physiological and biochemical studies to determine dehalogenation and halogenation mechanisms in newly isolated strains
- analysis of the genetic organization of catabolic genes in organisms that degrade xenobiotic halogenated compounds
- examination of genetic processes that occur in chemostats or biofilm systems during adaptation. Organisms known to degrade natural or synthetic organohalogens will be used as the starting material, and the relationship between gene transfer and adaptation of the community will be established
- testing the effect of environmental conditions on the development of dehalogenating organisms and community adaptation, and establishing the relevance to bioremediation strategies.

The target compounds for the project are halogenated aliphatic compounds including 1,1- and 1,2-dichloroethane, 1,1,1- and 1,1,2-trichloroethane, dichloropropa(e)nes, 1,2-dibromoethane, mono- and dihalomethanes, and chlorocarboxylic acids. These compounds are ubiquitous environmental pollutants in Europe.

Results

The project started by February 1, 1996. Results from the ongoing project are not yet available. However, in each participating laboratory, the contribution to the EC project is part of a larger research program aimed at understanding formation or degradation of organohalogens. Some of the results obtained from these research programs that are of relevance for the current project are listed below.

Similarity of haloalkane dehalogenase and haloperoxidase. The Dresden group has previously investigated haloperoxidases from a 7-chlorotetracyclin producing *Streptomyces* sp. It is striking that the three dimensional structure of the enzyme is similar to the hydrolytic haloalkane dehalogenase from *Xanthobacter autotrophicus* GJ10 studied in Groningen. The similar 3D structures and conserved positions of the active site residues point to an evolutionary relationship.

Role of mobile genetic elements. In Cardiff, previous work has shown that the dehalogenases produced by *Pseudomonas putida* PP3, an organism selected on the herbicide Dalapon, are encoded by cryptic genes which are switched on and off by association with *DEH*, an unusual transposon carrying one of the dehalogenases and its cognated regulatory gene. Under laboratory conditions, *DEH* can be transferred on plasmid vectors to a broad range of Proteobacterial species which, as a result of dehalogenase gene expression, acquire the ability to degrade halocarboxylic acids (Thomas *et al.*, 1992a,b,c; Topping *et al.*, 1995). Also the *X. autotrophicus* strain studied in Groningen contains insertion elements that can stimulate gene expression and transfer.

The mechanisms by which catabolic transposons evolve and the processes which stimulate transposition and horizontal gene transfer remain unknown, however, and an objective of this proposal is to improve our understanding of this important aspect of microbial adaptation.

Degradation of natural organohalogens: methylchloride. In Belfast, a number of microbial enrichment cultures have been obtained which exhibit growth on chloromethane as the sole carbon and energy source. The cultures have been obtained using inocula from local soils where there is no record of haloalkane contamination but from which there is likely to be the natural evolution of chloromethane. These soils include field, woodland and soils associated with potato crops. All of the cultures used methanol for growth but none were supported by methane as carbon and energy source and they are currently under investigation to determine if a hydrolytic route for dehalogenation is present.

Identification of novel haloalkane dehalogenases. The complete nucleotide sequence of the hydrolytic dehalogenase from *Rhodococcus* sp. NCIMB 13064 has been determined in Belfast and made available to the other collaborators involved in the project. There is considerable similarity between the *Rhodococcus* enzyme and the related enzyme in *X. autrophicus*, for which the catalytic mechanism was studied in Groningen by X-ray crystallography. However, although each enzyme employs a hydrolytic mechanism they exhibit very different substrate ranges. The *Rhodococcus* enzyme is plasmid encoded and its expression is regulated by chloroalkanes. This could mean that it has further evolved than the dehalogenase system from *X. autotrophicus*.

Using PCR amplification based on the sequence obtained from Belfast, the Groningen group demonstrated the occurrence of a closely related haloalkane dehalogenase in a number of the dehalogenating organisms obtained from various geographic areas (Japan, US, Switzerland, Netherlands). Furthermore, the gene was cloned in a site-directed mutagenesis and expression vector that allows large scale purification of enzyme suitable for kinetic analysis.

Degradation of 1,3-dichloropropene. The nematocide 1,3-dichloropropene has been used on a large scale in agriculture. Such large scale uses may contribute to the spread of dehalogenases genes in the environment. Therefore, the presence of dehalogenase genes in a *Pseudomonas* strain that degrades 1,3-dichloroethane was investigated in Groningen. The results showed that the organism produces a dehalogenase that has sequence similarity to the *Rhodococcus* enzyme studied in Belfast. The organisms also produces chloroacrylic acid dehalogenase activity, suggesting that dichloropropene is degraded via chloroallylalcohol and 3-chloroacrylic acid.

Kinetics of haloalkane dehalogenase. Steady-state and transient kinetic measurements on haloalkane dehalogenase from *X. autotrophicus* were carried out in Groningen. This provided answers to a number of questions concerning the substrate specificity and kinetics of conversion of chloro- and bromoalkanes. The main rate-limiting step in the conversion of dichloroethane and dibromoethane appeared to be a conformational change that is necessary for halide release from the enzyme at the end of the catalytic cycle. This explains that dichloroethane and dibromoethane are converted at similar rates, although the K_m values are very different and bromine is a much better leaving group that chlorine. With poorly converted substrates, however, the rate of carbon-halogen bond cleavage is the main rate limiting step. This explains that for poor substrates, the alkylbromide is always converted much faster than the alkylchloride.

Conclusions

Based on previous research, a great amount of knowledge on the biodegradability of haloaliphatics has been obtained. Thus, it is known that several of these compounds can be degraded hydrolytically by existing enzymes and that many other compounds are recalcitrant since they are not hydrolyzed. Furthermore, it is known that organisms can genetically adapt to new substrates. This may be related to overexpression and/or modification of enzyme specificity.

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Processes underlying remediation of creosote contaminated groundwater in fractured sandstone

EV5V-CT94-0529

Coordinator: D.N. Lerner

University of Bradford
Dept. of Civil & Environmental Engineering
UK - BD7 1DP Bradford
Tel: +44-1274.385470
Fax: +44-1274.383888

Project: Processes underlying remediation of creosote contaminated groundwater in fractured sandstone

Number: EV5V - CT94 - 0529

Starting date 1st October 1994 Duration: 36 months

Participants

Prof D N Lerner
University of Bradford
Department of Civil and
Environmental Engineering
Bradford
BD7 1DP
United Kingdom
Tel. 44 1274 385470
Fax: 44 1274 383888
E-mail D.N.Lerner@bradford.ac.uk

Dr C Mouvet
Bureau des Reserches Geologiques
et Minieres (BRGM)
Department Geochimie
BP6009 Avenue de concyr
45060 Orleans
Cedex 2
France
Tel. 33 3864 3908
Fax 33 3864 3711
E-mail C.Mouvet@dr.brgm.fr

Prof E Arvin
Institute of Environmental Science
& Engineering
Technical University of Denmark
Bygning 115
DK 2800 Lyngby
Denmark
Tel: 45 45 25 1471
Fax: 45 45 93 28 50
E-mail: E.Arvin@imt.dtu.dk

Research team members

Laurence Amalric
Owen Baines
Mette Broholm
Paul Cannon
Ruth Davison
David Hay
Dr Huang
Ian Jones
Sophia Nema
Calvin Packwood
Daniel Tortensson

Steering group

Prof J Barker, Waterloo
Mr R C Harris, Environment Agency
Prof W Kinzelbach, ETH, Zurich
Mr R Rodgers, Severn Trent Water

Objectives The project goal is to decide where remediation of groundwater contaminated by the coal gassification process is feasible in fractured sandstone

The main objectives are.

1 Determine the rate and extent to which the rock can be flushed, or degrading agents delivered to all contaminated zones, i.e hydrogeological characterisation
2 Assess the extent of natural attenuation (degradation, sorption and dilution) of the contaminants seen in the field, by characterising the contaminant plume in the field, and conducting laboratory experiments
3 Assess the scope for degradation of typical coal tar related contaminants, chemically or biologically, based on laboratory experiments
4 Determine the interactions between contaminants and rock, by geochemical characterisation of cores from the field site and laboratory study

5. Review and assess the viability of remedial technologies, using the knowledge of the fundamental process developed during the project, and numerical simulations

Results

- Efficient analytical techniques have been developed for a wide range of coal tar organics in both water and sandstone cores
- Sroption characterisation of a range of coal tar organics have been evaluated in column experiments
- Drilling with air-mist has been found to recover cleaner cores than use of drilling mud
- Design of a multi-level sampler for sandstone has been improved Geophysical surveys have proved useful in understanding the site and delineating polluted areas. The field site has a more complex hydrogeology and pollution history than expected
- Changes in groundwater flow patterns over time have been major and affect the chemical behaviour of the plume.
- Hydraulically significant fractures are present
- No non-aquous coal tar has been observed
- Organic contamination of groundwatert is less severe than expected, and than was present in 1986
- Significant ammonium pollution (up to 400mg N/L) has been observed Active nitrification is taking place.

INTRODUCTION

Coal gassification has polluted many thousands of sites throughout Europe with complex mixtures of organic and inorganic chemicals The biochemical behaviour and movement of these pollutants must be well understood if clean up is to be reliably and economically achieved Fractured sandstones and important sources of groundwater for water supply and the environment in many regions, characterising the movement of groundwater and solutes in such systems remains a problem. The project objectives (given in detail above) have been designed to lead to conceptual and technical descriptions of pollutant behaviour, and hence lead to an assessment of the feasibility of restoration of groundwater quality

A particular field site has been chosen as a basis for the study, so that the complexity of real problems are taken into account The site is a format coal gasification plant near Mansfield (UK) which closed in 1974 Significant phenol and other pollution was detected 1000m downgradient in 1986 In 1994, the site was excavated to a depth of 5-10m, capped and refilled The aquifer consists of approximately 80m of Triassic Sherwood Sandstones, overlying Permian marls, which form an effective base to the aquifer

METHODOLOGY

The research activities are organised in three themes, F-field studies, L-laboratory studies and S-synthesis

Field Studies has five sub-tasks which are

F1 - a reconnaissance survey of the field site to locate the pollution plume, groundwater flow direction and other features.
F2 - hydraulic characterisation of fracture and matrix flow systems, to be achieved by borehole testing and core testing
F3 - Characterisation of the pollution plume by detailed sampling and analysis, linked to hydrochemical and modelling interpretation.
F4 - a forced gradient, radial flow, tracer experiment to understand solute transport processes in the aquifer.
F6 - geophysical surveys to assist with delineation of the plume and siting of boreholes

A sixth task (F5 - natural gradient tracer experiment) has been deleted from the programme in the light of preliminary results and the absence of a suitable location

Laboratory studies has six sub-tasks, as follows:

L1 - establishment of suitable analytical techniques
L2 - geochemical characterisation of the aquifer.
L3 - assessment of the leaching of non-aqueous phase (NAP) coal tar into groundwater, particularly under the influence of surfactants as a possible remedial technology
L4 - assessment of the mobility of contaminants in the dissolved phase (principally sorption studies)
L5 - biodegradation studies of the organic contaminants, particularly the potential for degradation of dissolved compounds and the effects of mass-transfer rates on NAP coal-tar degradation (a separate sub-task, L6, on diffusion characterisation has been combined into these studies).
L7 - behaviour of ammonium during infiltration and groundwater flow, an additional task introduced in the light of actual field conditions

Synthesis includes both modelling and other integrating activities in four sub-tasks

S1 - modelling of groundwater flow, both at regional and plume scale, and expanded to include modelling of reactions within the plume
S2 - simulation of tracer experiments using a radial flow model.
S3 - simulation of remedial options
S4 - review and assessment of remediation technologies

INTERIM RESULTS

L1 - Analytical technologies

A protocol for measuring bromide in sandstone was developed in order to test whether borehole covers were contaminated during the drilling process. Sandstone is manually crushed, mixed with Ca Cl_2 solution, centrifuged and filtered. Recovery is 97 0±10.5% Field trials showed that use of mud as a drilling medium was unsatisfactory, but that air-mist returned much cleaner cores

A single extraction step analytical technique was developed for a large number of organic coal tar compounds in water Target organic coal-tar compounds from the five main groups of soluble compounds (mono-aromatic hydrocarbons, phenols, N-,S- and O-heterocyclic compounds, naphthalenes and polyaromatic compounds) were selected The technique includes a single extraction with an ether-pentane mixture followed by gas-chromatography with flame ionization detection Extraction efficiencies for target phenolic compounds range between 38 and 85 %, for target N-heterocyclic compounds (quinolin) 40 %, and for all other target compounds > 80 % 37 compounds were separated by the technique. Detection limits for the majority of the compounds were < 10 ppb, for some of the higher boiling point compounds the detection limits were in the 10 to 60 ppb range The technique developed provides the possibility of analysing a large number of samples for a large number of compounds within a reasonable time-frame and with a limited consumption of solvents. The effect of groundwater pH and ionic strength variations at the site were found to be of little significance for extraction of the target compounds Very high ionic strength improves extraction efficiencies for phenols and quinolin but also changes the partitioning of ether resulting in higher detection limits for almost all target compounds. Extracts could be stored for > 65 days at -12, 4 and 22 °C

A technique is under development to analyse for organic and coal tar compounds in saturated sandstone cores, as published methods are based on dry samples Soxtec extraction (USEPA method 3540) was not satisfactory. Sonication of crushed core in dichloromethane gave satisfactory recoveries, and further refinement of the method is underway

L4 - Contaminant mobility

An aqueous solution of bromide, phenol, carbazole, dibenzofurane, dibenzothiophene and phenanthrene was percolated through a non-contaminated sandstone core to determine (i) the retardation factors (Rf) and (ii) whether this system could produce saturated and artificially contaminated cores

Compared to bromide, the organic compounds eluted in the following order phenol, carbazole, dibenzofurane, dibenzothiophene and phenanthrene (Figure 1). The retardation factors determined for outlet concentration/inlet concentration = 50 %, were 1 2, 1 3, 4 1, 5 and 5 6 for phenol, carbazole, dibenzofurane, dibenzothiophene and phenanthrene, respectively. The resulting sorption coefficients, Kd, calculated by the equation [1] . $Rf = 1 + \rho Kd/\theta$, were 0 02, 0 03, 0 28, 0 36 and 0.42 for phenol, carbazole, dibenzofurane, dibenzothiophene and phenanthrene, respectively (ρ = 2.55 g/cm^3, θ = 0 23 cm^3/cm^3) The retardation factors can be calculated either with methods using sorption isotherm data or by analysing the column breakthrough curve (BTC) data Dual calculation enables a comparison of sorption behaviour measured under static conditions (batch isotherms) with that characterised under dynamic flowing conditions (BTC data). For dibenzothiophene, Kd literature values determined with batch experiments vary from 4 1 to 304 8, depending on the soil and sediments tested [2] with values between 4 1 and 4 5 for organic carbon contents 0 15 and 0 11 % , similar to these of the sandstone cores studied (0 23 - 0 25 %) For dibenzofuran, a Kd value of 53 has been reported [3] Our values are much lower than those literature values The difference between our values and these literature data could proceed from the method used, sorption isotherm and column BTC data

Other studies on the sorption of phenanthrene [4] and phenol [5] showed these molecules to have log K_{OC} (normalized organic carbon sorption coefficient) of 4.3 and 1 4, respectively The log K_{OC} for dibenzothiophene was 4 0 [2] These studies suggest the following decreasing sorption order phenanthrene > dibenzothiophene > phenol Our retardation factors results phenanthrene > dibenzothiophene > dibenzofuran > carbazole > phenol are in agreement with these literature values

The number of pore volumes required for the concentration of organic compounds at the outlet to equal the concentration at the inlet was about 9-11.5 for carbazole, dibenzofurane, dibenzothiophene and phenanthrene The saturation was maintained over percolated volumes of 220 to 650 mL, after which the concentrations of organic compounds decreased in the inlet flask solution and similarly in the outlet samples. The outlet phenol concentration at the end of the experiment was only about 10 % of the initial inlet value. This may have been due to an erratic sorption in the system, or a pH change of the water which modified the extraction yield, or an adsorption in the core or a modification of the molecule within the solid. First control experiment showed that the phenol decrease was at least partly due to a sorption in the pump flushing the aqueous solution.

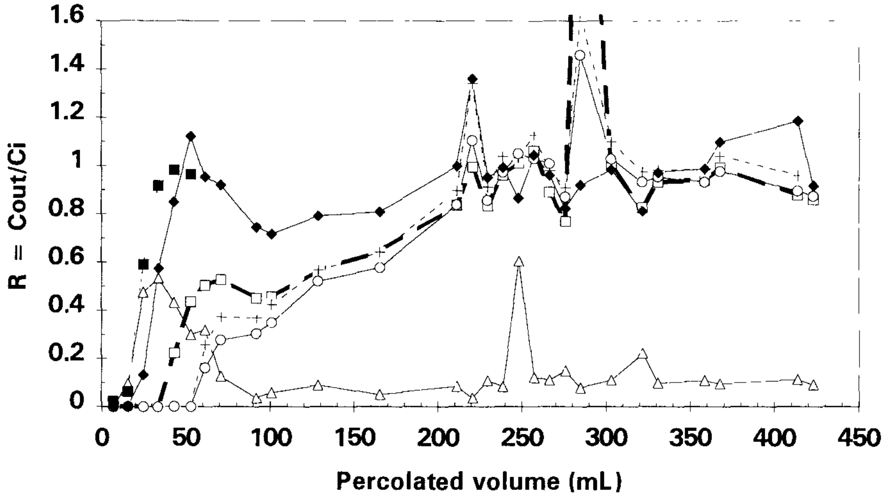

Figure 1 : Breakthrough curves of bromide (19.4 mg/L) and various organic compounds (initially 0.2 mg/L) during the percolation (0.15 mL/min) through the sandstone core ; black square = bromide, diamond = carbazole, triangle = phenol, square = dibenzofurane, cross = dibenzothiophene and circle = phenanthrene.

F6 - Geophysical surveys

An initial geophysical survey covering all the areas of interest (0.6km^2) used six electromagnetic methods and revealed a series of anomalies. These are related to mine waste heaps, lithological variations, the coal gasification plant and groundwater pollution plumes and have assisted in understanding the context and history of the site A second survey in the vicinity of the plant has been correlated with borehole data and used to identify the plume location and position further boreholes.

F1 - Reconnaissance survey

Twenty boreholes have been drilled on the field site to (a) measure groundwater levels, (b) collect samples for location and preliminary characterisation of the pollution plumes, (c) test drilling and coring methods, (d) test multi-level sampling technologies The site is more complex than expected and substantial additional effort has been invested in this task than originally planned

Drilling with a mud flush, designed to minimise intrusion into the cores, was found unsatisfactory Br tracer placed in the mud was found in similar concentration in the core pore fluid as in the mud. However, use of air mist was satisfactory, with little contamination or displacement of porefluids. This result has lead to reduced involvement of the British Geological Survey in the project.

The design of the multipoint sock sampler [6], intended to provide multiple sampling levels in a single borehole in a consolidated, deep, aquifer has been extensively simplified and improved. Ten sampling intervals in 20m of borehole can be provided for 2000 ecu, and a further six samplers are planned for the detailed plume characterisation.

In general the concentrations of specific organic compounds in the groundwater at Mansfield were insignificant, for most samples lower than or of the same order of magnitude as the detection and quantification level for the compounds. This was verified by analysis at independent laboratories. Elevated NVOC concentrations were encountered in the plume. The NVOC content appear to consist primarily of humic-like substances

A plume of ammonia with concentrations of up to 352 mg/L has been located emanating from the drain or from the part of the site east of the access-road along the Toray factory access road. The plume could also originate from the part of the site located west of the road and have been snapped off after the reclamation of the site The distribution of ammonia in the aquifer is illustrated in Figure 2 The high concentrations of ammonia in the groundwater strongly indicate that the source of the contamination is the aqueous ammonia liquor (wash-water) from the Rexco process The results of organic analysis has revealed that no significant contamination is present in the plume defined by the ammonia This means that either the compounds have been degraded/transformed in the aquifer or have been separated from the source and the ammonia plume, or a significant plume of organic coal-tar compounds in the groundwater reservoir has never evolved from the plant The potential for degradation of organic coal-tar compounds in the groundwater reservoir will be studied in microcosm tests

The aquifer is aerobic Within the ammonia plume depletion of oxygen is observed indicating reduced conditions in the plume. Nitrification is indicated at the perimeter of the plume. Dissolved (reduced) iron is present in the centre of the plume, possibly a result of NVOC degradation.

The reconnaisance survey has provided no evidence of the presence of NAP coal tar, although such pollution is known to have entered the ground

Fractures have been observed in several boreholes, from surface to aquifer base, and preliminary tests show them to be hydraulically important.

The groundwater level and chemical data from the reconnaissance have provided an overview of conditions on the site, and identified several areas of pollution An area for hydraulic characterisation has been selected, and a plume identified for further characterisation (Fig 2)

S1 Groundwater flow

A transient, regional groundwater flow model has been successfully calibrated, providing a basis for future modelling of the site and movement of the plume. The model demonstrates that groundwater flow has changed several times in magnitude and direction within the period of interest This is due to the changing patterns of groundwater abstraction and industries come and go in the area. These results are significant for (a) design of site investigations, (b) increasing dispersion, (c) altering the reactive zones of the plume

PLANS FOR COMING YEAR

F2 - Core and packer testing of aquifer properties.
F3 - New boreholes, some cored, sampling and analysis
F4 - Plan tracer experiment
L1 - Continued development of analysis of coal tar compounds in cores.
L2 - Study hetrogeneity of transport controlling parameters (organic carbon, calcite, oxidative capacity) Investigate speciation of ireon minerals in areas of the plume
L3 - Review literature on surfactant flushing of coal tar
L4 - Continue sorption studies in batch and column models
L5 - Initiate microcosm studies on degradation of coal tar compounds by local groundwater Plan mass-transfer experiment.
L7 - Conduct feasibility experiments on ammonium behaviour
S1 - Develop plume scale model. Incorporate simple biodegradation reactions.
S2 - Finalise radial flow model of tracer experiment
S4 - Initiate review of remedial options.

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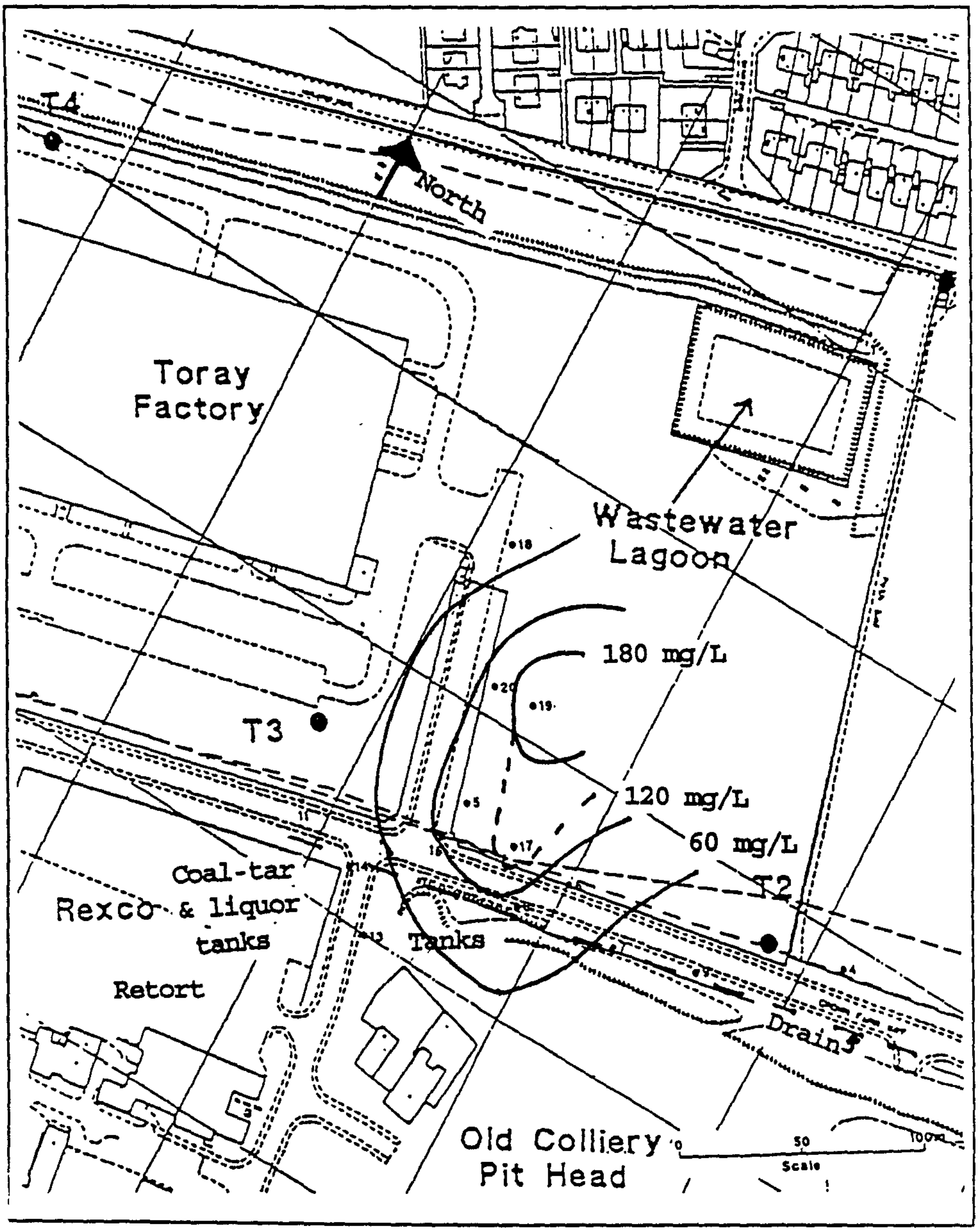

Figure 2 The site and the distribution of ammonia in the plume

Biorehabilitation of acid mine drainage phenomenon by accelerated bioleaching of mine waste incorporating metal from leachate

EV5V-CT93-0248

Coordinator: N. Gray / A. Kontopoulos

Environmental Sciences Unit
IR - Dublin 2
Tel: +353-1.702.1639
Fax: +353-1.671.8047

TITLE: BIOREHABILITATION OF THE ACID MINE DRAINAGE PHENOMENON BY ACCELERATED BIOLEACHING

CONTRACT No **EV-5V-CT93-0248**
STARTING DATE: August 1993
DURATION: 30 months

PARTICIPANTS:

1 Prof. Nick Gray (Project Coordinator) Environmental Sciences Unit, 188 Pearse Street Trinity College Dublin 2, Ireland Tel.: +353-1-702-1639 Fax: +353-1-671-8047 E-mail: nfgray@mail.tcd.ie	*5. Prof. David J. Vaughan* Dept. of Geology and Geoscience Research, University of Manchester, Manchester M13 9PL U.K. Tel.: +441-61-275-3801 Fax: +441-61-275-3947
2. Dr Hans Doddema Instituut voor Milieuwetenschappen TNO, Schoemakertraat 97 P.O Box 6011 2600 JA Delft, The Netherlands Tel.: +31-1569-6022 Fax +31-1569-6057	*6. Dr Phil Parsonage (Scientific Coord)* *Roger Dunn* AEA Technology, National Environmental Technology Centre, 353 Harwell, Didcot, Oxfordshire OX11 0RA U.K. Tel.: +441-235-463542 Fax: +441-235-463030 .
3. Prof. Piet Bos Dept. Microbiology and Enzymology, Technical University of Delft, P.O. Box 5057, 2600 GB Delft, The Netherlands Tel.: +31-1578-2359 Fax: +31-1578-2355	*7. Prof. Antonios Kontopoulos* Laboratory of Metallurgy, National Technical University of Athens GR-157 80 Zografos, Athens, Greece Tel.: +30-1-7722167 Fax: +30-1-7722168 E-mail: kontop@metal.ntua.gr
4. *Dr Claire Sahut* Commissariat a L' Energie Atomique, Cen Cadarache DCC/DSD/SEP/SEATN 13108 St Paul Lez Durance, Cedex France Tel.: +33-42-257-423 Fax: +33-42-254-274	*8. Dr Pat O' Connor* Geological Survey Ireland Beggars Bush Haddington Road Dublin 4, Ireland Tel.: +353-1-660-2276 Fax: +353-1-668-1782

OBJECTIVES:

- Development of characterisation methodologies for acid mine drainage (AMD) sites
- Development of enhanced leaching techniques for control of AMD
- Development of a preliminary protocol for the rehabilitation of AMD sites

MAIN RESULTS:

- Development of detailed methodology for sampling and environmental characterisation of mine waste
- Development of reliable and robust techniques for assessing the impact of AMD on aquatic and terrestrial ecosystems
- Identification of the main mechanisms and kinetics involved in AMD generation due to bacterial oxidation.
- Development of accelerated bioleaching techniques for waste.
- Elaboration of a rehabilitation protocol.

LIST OF PUBLICATIONS:

A. Papers in peer reviewed journals

1. K. Adam, A Kourtis, B. Gazea, A. Kontopoulos. "Prediction of acid rock drainage in polymetallic sulphide mines", Submitted Trans. *IMM.*
2. K. Komnitsas, A. Xenidis, K. Adam: Oxidation of pyrite and arsenopyrite in sulphidic spoils in Lavrion. *Minerals Engineering*, Vol. 8 (1995), pp 1443-1454.
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16. Herr, C. and Gray, N F. (1996) Sampling riverine sediments impacted by acid mine drainage: problems and solutions. Environmental Geology, (In press)
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2. E Mylona: Preventive techniques for acid mine drainage.
3. A Kourtis. Treatment of acid mine drainage from polymetallic sulphide mines
4. E Gazea: Environmental management in polymetallic sulphide mines.
5. S. Tampouris· Remediation of lead contaminated soils by leaching techniques.

EC Workshop Recycling technologies, treatment of waste and contaminated land
Hannover, 20-24 May 1996

EV5V-CT93-0248

BIOREHABILITATION OF THE ACID MINE DRAINAGE PHENOMENON BY ACCELERATED BIOLEACHING

Extended abstract

INTRODUCTION

Polymetallic sulphide mining results in the formation of huge tailings and waste rock dumps containing sulphidic minerals. Under the synergistic action of water, oxygen and sulphur oxidising bacteria, the sulphide minerals oxidise to produce acidic waters with high concentrations of heavy metals and other toxic elements (acid mine drainage, AMD) The surface and underground mining works constitute additional AMD sources. AMD causes widespread environmental pollution, severely affecting groundwaters, rivers and estuaries, as well as the soils around mining sites. The phenomenon is persistent, being active for tens or even hundreds of years after mine closure.

The aim of the current project is the elaboration and evaluation of a practical protocol for the environmental characterisation and risk assessment of the sulphidic tailings and the development of environmentally robust technology for rehabilitation.

The project is of a generic nature and the techniques and processes developed will be of a wide applicability; two specific sites have been selected as case studies: the Avoca copper mines in Ireland and the Lavrion lead-silver mines in Greece.

Pursuing the original work programme, the following tasks have been completed:

1. CHARACTERISATION

1.1 Definition of experimental areas

Two experimental areas have been defined and used as case studies: Avoca and Lavrion. A multi-disciplinary approach was adopted for comprehensive site characterisation. Geographical, morphological and geological maps of the dumps and the affected areas have been collected and inputted to an Arc-Info GIS system.

Avoca mines, Ireland

This is a abandoned copper mine located in the County Wicklow southeast Ireland . Active copper mining took place from about 1720 to the 1980's. Pyrite and silver have also been produced during this period. The sulphide mineralisation is predominantly pyrite with lesser amounts of chalcopyrite, galena and sphalerite. The host rocks are volcanics with little buffering capacity. Exploitation was carried out by underground and open pit mining methods. Mining has resulted in the creation of surface deposits of tailings and waste spoils that produce AMD with high levels of toxic metals; considerable AMD flow is also observed from the underground mining works; AMD is ultimately discharged into the Avoca river, severely affecting river water quality and biota.

Lavrion mines, Greece

This is a abandoned lead-silver mine located in Lavrion, 60 km S of Athens. Mining started in the 7th century BC; intensive modern era mining and smelting took place from mid-19th century up to 1980. The mineralisation consists mainly of pyrite, argentiferous galena and sphalerite and is found as hydrothermal emplacements along contacts between marble and schist Exploitation was carried out by underground mining only. Mining, processing and smelting activities resulted in the creation of huge tailings spoils deposited both terrestrially and in the sea. Rain water oxidises the spoils producing highly contaminated AMD which causes widespread soil pollution.

1.2 Characterisation of geological and geotechnical nature of mines and waste dumps

The geology of the Avoca and Lavrion mines has been assessed based both on existing data and data generated during this project. A methodology for the environmental characterisation of the wastes has been established and tested.

Avoca

A protocol for the definition of the experimental area has been proposed and applied, three areas were defined for study: the *source zone,* the *contaminated zone* and the *uncontaminated zone.* The protocol examines ways of managing data and presents a data management system using GIS technology, and also requires a preliminary definition of the impacts. Using this protocol, the Avoca mine site has been fully characterised A detailed examination of the catchment and the mines has also been completed The metal content of soil and vegetation around the eastern mining area was determined 50% of the soils showed elevated Cu and Cd concentrations, but non of the herbage species had elevated metal contents.

Lavrion

The environmental characterisation of the sulphidic tailings and wastes in Lavrion included the following steps·

Definition of a sampling campaign where undisturbed core samples were taken from drillholes placed into the wastes; the samples were analysed chemically and their mineralogical constitution was determined; their acid production capacity was established using both static (acid-base accounting) and dynamic (column leaching) tests; their toxicity was determined according to the EPA TCLP test, the speciation of the heavy metals was established using a 5-stage sequential extraction method (determination of the exchangeable, carbonate, oxidizable, reducible and residual fraction); the bioavailable fraction of the heavy metals was determined by EDTA extraction Several important geotechnical parameters of the spoils, such as density and permeability, were measured *in situ*; Piezometers were installed in the boreholes and the pore water quality and level were monitored over a 12 months period.

1.3 Evaluation of AMD flow and chemical composition

Avoca

A large number of surface streams and springs exist in the Avoca mine area, ultimately draining into the Avoca river A hydrogeological study revealed that most of the AMD generated originates from the underground works, with only about 40% generated from spoil and surface workings

An *objective index* has been developed and fully evaluated for the assessment of AMD contaminated waters

A large number of surface water sites were monitored, including mine and spoil leachates, Avoca river and streams. The results show that the Avoca mine is an active AMD producing site causing severe surface water pollution Total contaminated discharge to the river is estimated to be between 1266-7430 m^3/day, containing (in kg/day) 169-1738 Fe, 69-535 Zn, 1.5-35.4 Cu

Lavrion

Climatic conditions dictate that only limited surface water flows are observed in Lavrion, moreover, water outflow from the underground mining works is alkaline and with low concentrations of heavy metals; this is attributed to the fact that water entering the mine passes through the marble host rock that behaves like a huge limestone drain adding alkalinity to the water; upon contact with sulphides, the rate of oxidation is expected to be very low, as at this high pH the reaction will not be catalysed by *thiobacilli*. The alkalinity of the water will also neutralise the acid produced; it is stipulated that neutralisation products (gypsum, ferric oxides and oxy-hydroxides) will precipitate onto the pyrite surface, hindering further oxidation.

Severe AMD generation is observed in the sulphide tailings heaps after rainfall; water collected from basins on and around the heaps has pH=1.9 and contains 0.5-0 7 ppm Pb, 500-1100 ppm Zn, 2-4 ppm Cd and 40-800 ppm As. This acidic water is considered to be the worst environmental problem in Lavrion as it provides the main mobilisation and transport route for polutants. Some of the acidic water, especially the discharge originating from heaps deposited on, or close to the beach, finds its way into the sea.

1.4 Environmental impact of AMD

AMD is a multi-factor pollutant It affects both aquatic and terrestrial ecosystems via a number of direct and indirect pathways In the present project, the major impact on Avoca appears to be on the aquatic ecosystem of the Avoca river downstream of the mine area. In Lavrion the major impact is terrestrial, with major effects on soils and plants, and secondary on ground and coastal waters.

Avoca

Due to its complexity, the impact of AMD is difficult to quantify and predict in lotic systems. Its major effects have been classified as chemical, physical, biological and ecological.

For the *field assessment of AMD contamination* sulphate analysis of affected samples is suggested as an indicator, with either direct or indirect conductivity measurements. For *toxicity assessment* a number of tests has been considered; the activated sludge inhibition test was found suitable, while Microtox proved to be a rapid but expensive toxicity screening test. *Fish toxicity* and *field toxicity tests* were carried out. Routine *biological surveillance* of the Avoca river downstream of the input of AMD consistently showed a significant impact on both diversivity and productivity; while all quantitative indices demonstrated the impact, use of taxa numbers in riffle areas was found to have the greatest discriminatory power and has been recommended as a simple and effective index. The *impact on the Avoca river biota* as well as *sediment contamination* have been studied in detail. A simple descriptive index based on the degree of deposition of ochre on the river substrate and the level of floc formation has been derived for the rapid *field assessment of impact* and has been related to the biological impact that can be expected. The *toxicity of the discharged AMD* has been calculated using the 96 h LC_{50} values for Cu and Zn on Atlantic Salmon *Fish migration* (salmonids) upstream the river has been considered. At Avoca the toxicity of AMD varies seasonally due to fluctuations in the Zn:Cu ratio, with the concentration of Zn remaining constant but the concentration of Cu varying widely due to secondary sulphate mineralization and dissolution. A model has been developed for the prediction of the toxicity of the river caused by AMD with 95% precision

Lavrion

The major environmental impact of AMD at Lavrion is on the surrounding soils and vegetation. The phenomena involved are very complex and difficult to quantify and predict. Essentially, AMD provides the migration route for the mobilisation of the toxic elements that are contained in the tailings and for their transportation and deposition in soils In the course of its downward migration, AMD comes in contact with the subjacend rocks and soils and metal deposition occurs through neutralisation-precipitation reactions or through adsorption on the clay fractions. Besides AMD, physical transport mechanisms (wind transport of the fine sulphide grains) are also active in the Lavrion site.

Severe soil pollution by heavy metals has been detected and studied in detail over an area 2x6 km around the mines. 600 soil samples were collected and analysed Total elemental concentrations of Pb, Zn, Cd and As were found to be extremely high compared to accepted soil standards (Netherlands "C" values, Canadian standards for agricultural, residential or industrial areas). It was decided therefore to determine the "bioavailable fraction" of these elements with EDTA leaching and apply this criterion against the standards. The bioavailable fraction of Pb in 75% of the area examined was over the 600 ppm set limit for total Pb by the NL regulations. 25% of the values were in the 2100-6200 ppm range. Smaller deviations were established for Zn and Cd, while As was mostly non-bioavailable

Elevated heavy metal content in grapes and olives grown on the contaminated land was also measured.

2. BIOLEACHING

2.1 Identification of the main mechanisms and kinetics

The critical factors that control the generation of AMD are oxygen, water, temperature, bacterial activity. The rate of oxidation of pyrite and arsenopyrite in the sulphidic spoils in Lavrion has been studied in the lab; the results were correlated to actual field conditions in the Lavrion sulphide spoils.

The main conclusions of the study are: (a) Oxidation of pyrite and arsenopyrite in sulphidic spoils generates acidic solutions which accelerate mineral phase dissolution and result in mobilisation of heavy metals which migrate and pollute the surrounding areas, (b) Arsenopyrite is the first phase to oxidise; pyrite oxidation commences at a later stage, when sufficient concentrations of ferric ions and high Fe^{3+}/Fe^{2+} ratios are established in solution. (c) The critical factors controlling oxidation are availability of oxygen and water, temperature, permeability, enhanced bacterial activity and the rate of oxygen diffusion through the pores of the upper zones of spoils A crucial factor for AMD generation is the absence of alkaline minerals that neutralise acidity. (d) The main oxidation products in the upper zones of spoils are hydrated ferrous sulphate compounds and gypsum, produced by precipitation reactions following dissolution of sulphide phases. In the lower zones, hydrous ferric sulphate compounds and jarosites are produced while no oxidation is observed The depth of the oxidation zone depends on the permeability of the tailings which controls oxygen diffusion and water infiltration. The original permeability of the tailings is modified due to the precipitation reactions, which may contribute to "hard pan" formation

Anaerobic processes to reduce leaching have been studied; it was concluded that it will not be sufficient to reduce the access of oxygen to prevent leaching and environmental damage because, even under anaerobic conditions microbial activity of *Thiobacillus ferrooxidans* and perhaps other microorganisms will lead to acidification and release of metals Increased ionic strength of water might inhibit microbial activity; therefore Lavrion wastes might safely be disposed of into the sea to prevent further environmental damage, although this alternative will probably meet strong opposition from the public and regulatory authorities. Inhibition with increased ionic strength of water is not a viable option for Avoca.

Laboratory tests have shown that the Lavrion tailings, upon contact with rain water generate fairly quickly acidic leachates; application of impervious dry covers is a viable solution for the Lavrion and Avoca tailings spoils. however, a complete rehabilitation scheme for Avoca must include treatment of the AMD from the underground works.

Extensive laboratory tests showed that AMD generation from sulphidic spoils can be effectively inhibited using alkaline additives to increase their net neutralisation potential Addition of ground limestone to pyritic tailings at a ratio much lower than the stoichiometric requirement will effectively reduce AMD, provided that the two materials are completely mixed; in this case iron precipitation products are formed around the pyrite grains, hindering further oxidation In case of incomplete mixing, hot spots are formed and acid is produced; iron migration takes place and neutralisation-precipitation occurs around the limestone particles, causing armouring and hindering its effective utilisation for further neutralisation.

2.2 Bioleaching of mining wastes

The rationale in using bioleaching as a treatment technology for mine waste is that by accelerating the rate of natural bacterial leaching in a controlled fashion the subsequent environmental impact of the waste can be drastically reduced. The leachate produced from the controlled oxidation will mobilise toxic metals, this leachate can be collected and treated either for metal recovery or as an effluent.

Bulk samples of spoils have been collected and subjected to accelerated bioleaching under laboratory conditions. Both stirred reactor and column leaching experiments have been performed Conditions in column leaching were designed so as to simulate field-like conditions (i.e. low temperature, leachate flow based on rainfall), to accelerate bioleaching (addition of nutrients and microbial mass, higher temperature and flows), and to decelerate bioleaching (recirculation of leachate, inhibition of microbial growth, stimulation of precipitation).

The results were critically assessed for the selection of the optimum rehabilitation strategy

3. REHABILITATION PROTOCOL DEVELOPMENT

The AMD phenomenon is widely considered to be the worst environmental problem associated with sulphide mining due to its serious impact on aquatic and terrestrial ecosystems Its effects are spatial and temporal, as the phenomenon remains active for decades after mine closure.

Rehabilitation of the AMD phenomenon involves complex and interrelated factors. Simple, robust and cost-effective processes have to be developed and applied on a large scale These must aim both at arresting further pollution from the AMD sources and rehabilitating the damage already caused (restoration of aquatic systems, soil rehabilitation).

The present project is addressing the first issue A working protocol is required to help develop cost-effective and environmentally sound strategies for the management of AMD discharges from active and abandoned mines.

The specific finding of the research, based on the results from the sites in Ireland and Greece, are being used to develop a more general methodology for managing the environmental problems associated with acid mine drainage and mining wastes. Collection and selection of standard procedures relating to the multi-disciplinary investigation, characterisation and treatment of mine waste and associated waters have been completed Surveys of contaminated soil treatment and metal recovery techniques have been carried out. An outline structure for a handbook or protocol has been prepared. The aim is to produce a management tool as a guide to assist in the development of an action plan for abandoned mining sites, as well as an environmentally reliable mine closure strategy for operating mines

A spin-off of the present project is the full-scale application of a rehabilitation scheme for a 150000 t sulphidic tailings dam in Lavrion; the acid generation capacity of the tailings was neutralised with limestone sand addition and a soil cover was applied on top of the tailings.

Impact assessment of acid mine drainage on a lotic systems: a case study

N.F. Gray

Environmental Sciences Unit, Trinity College, University of Dublin,
Dublin 2, Ireland.

Acid mine drainage (AMD) is a major environmental pollutant of both surface and ground waters[1,2]. *Intensive sampling of drainage from mine adits has revealed a seasonal variation in the Zn:Cu ratio. This is linked to secondary sulphate mineral formation due to wetting and drying cycles within the mine workings and surface spoil heaps, leading to an annual cycle of formation and dissolution causing a predictable fluctuation in the Cu concentration only. The variation in the Zn:Cu ratio leads to extreme variations in the toxicity of drainage, and linked with increased adit flows and surface runoff during wetter months, results in higher river toxicity, even at high river discharge rates. This seasonal variation in toxicity of AMD from underground workings, or from mines with exposed surface spoil, has important ramifications for its control to surface waters.*

The ores at the abandoned copper and sulphur mines at Avoca, south-east Ireland, are volcanic massive sulphide deposits of Ordovician age. The principal minerals of economic significance in the Avoca region are chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS) and pyrite (FeS_2)[3]. The concentration of lead in the sulphate rich waters are low due to the limited solubility of anglesite ($PbSO_4$). So the cations of greatest environmental concern at this site are Cd, Cu, Zn and Fe.

The Avoca mining area is principally drained by two major adits. The Deep Adit drains the eastern side of the disturbed site while the Ballymurtagh Adit drains the western side. There are secondary inputs of AMD such as small contaminated streams, groundwater discharge and bank infiltration. All the AMD from the mining area (Fig. 1) drains into the River Avoca. `The rate of discharge from the adits follows a seasonal cycle being high in the winter and spring, declining through summer to reach lowest flows in autumn and rising again in the winter. The discharge rate in the Deep Adit varies from 8.51 to 42.6 l/s compared to 6.1 to 43.4 l/s in the Ballymurtagh Adit. This represents a total discharge rate for the two adits of between 1266 - 7430 m^3/d. The discharge rates from the two main adits are significantly correlated ($p<0.001$), and as the regression equation shows ($y = -1.01+1.045x$) there is no significant difference ($p>0.05$) between discharge rates, although the discharge rate in the Ballymurtagh Adit recovers more slowly in winter than the Deep Adit. Significant weights of cations are discharged from the two adits, ranging from 169-1738 kg/d for Fe, 69-535 kg/d for Zn, 1.5-35.5 kg/d for Cu and 0.167-0.875 kg/d for Cd, with the Deep Adit contributing on average 40.4, 70.4, 66.7 and 80.9% of each metal respectively over the period of May 1994 to May 1995. This confirms the Deep Adit to be more polluting overall in terms of metal toxicity than the Ballymurtagh Adit.

During the sampling period, the concentration of Zn in the Deep Adit varied very little (mean 70 mg/l, sd 0.5), while the Cu concentration fell steadily from 8.2 to 1.0 mg/l up to October and then began to rise again reaching a peak of 9.5 mg/l in February. This results in a predictable fluctuation in the Zn:Cu ratio. A similar phenomenon, although much less well defined, was also identified in the Ballymurtagh Adit. The variation in the Zn:Cu ratio corresponds closely to the height of the water table within the mine, being correlated to adit flow rate. The ratio is high during low water table periods and *vice versa* (Fig 2). This variation in the Zn:Cu ratio corresponds closely to seasonal variation in expected rainfall, with highest Zn:Cu ratios recorded towards the end of the dry season (Fig 3).

The reason for this variation appears to be due to secondary sulphate mineral formation within the mine workings, being more pronounced on the east side due to the more complex nature of the workings (shafts and adits) and the highly fractured nature of the bed rock through which mine water freely moves, offering more potential for secondary sulphate formation. In contrast, the western side has been more extensively mined being deeper with fewer shafts and adits with vast underground stoops which were never backfilled. Among the more important secondary sulphate minerals formed are chalcanthite ($CuSO_4.5H_2O$) and melanterite ($(Fe^{II},Zn,Cu)SO_4.7H_2O$). Both minerals may be major contributors to this phenomenon. Melanterite is of particular interest as it is commonly formed in iron rich AMD and has a propensity to incorporate Cu in preference to Zn. The formation and dissolution of these minerals can have a significant effect on the characteristics of AMD discharged from adits, responding to seasonal cycles of wetting and drying. The effect appears related to available surface area for sulphate formation.

The variation in Cu in relation to Zn has profound effects on the toxicity of AMD discharged in to the river. The toxicity of the AMD can be calculated using the 96h LC_{50} values for each individual and combination of key metals were calculated using Atlantic Salmon. The River Avoca is extremely soft (hardness 15 mg $CaCO_3$/l) and so the calculated toxicity threshold concentrations for Cu and Zn are 0.036 and 0.479 mg/l respectively[4]. It can be seen from Fig. 4 that while the toxicity exerted by the Zn remains constant over the period at about 150 toxicity units per litre (TU/l) except for March 1995 during very high adit flows, the toxicity exerted by the copper varies from <50 to >250 TU/l. When earlier, less intensively sampled, data is re-examined then a similar seasonal pattern of toxicity emerges. With riverine concentrations of Cd below detection limits (0.001mg/l), just zinc and copper were used for toxicity assessment purposes. The total toxicity of the leachate varied from 177 toxicity units per litre (TU/l) in the late summer to 431 TU/l in late winter due to the variation in Cu concentration.

The overall adit flow increased by up to 500% over the same period, while total toxicity (Cu+Zn) discharged from the two adits varied from 2.86×10^8 to 2.10×10^9 TU/d; so that during high flow periods the impact of the adits is 7.4 times greater than at low flow periods. This does not include the effect of surface runoff which is significantly more acidic and contains higher concentrations of most metals than the leachate discharged from the adits, as well as a high solids content comprising of fines from the spoil heaps. This results in higher toxicity concentrations being frequently recorded during the winter period compared to summer low flow periods when minimum dilution is available.

Using the equations below then the toxicity in the river water caused by the AMD can be predicted, with 95% precision, if the river discharge rate is known as well as the discharge rates in the two main adits. The total toxicity of the drainage from the Deep Adit is closely linked (logarithmic) to discharge rate due to the predictable nature of the Zn:Cu ratio with discharge rate (Fig. 5). In contrast, due to the different hydrological nature of the west Avoca mining area the total toxicity of the discharge is more complex to model. There is a similar seasonal relationship between discharge rate and the Zn:Cu ratio, although less defined due to a lower surface area underground for secondary sulphate formation. However, at higher discharge rates, and during short period afterwards, the Cu concentration is reduced due to dilution (Fig. 6). This is not apparent with either the Zn or Fe which continue to increase in strength with increasing adit discharge rate. For predictive purposes the contribution of metals and so toxicity from the Ballymurtagh Adit have to be calculated separately using linear regression for Zn and a second order polynomial relationship for Cu.

To predict the toxicity of the river water below the mixing zone then:

I. Calculate toxicity emanating from the Deep Adit (β^{DA}):

$$(\beta^{DA}) = -228.6 + 424.3\log(f^{DA})\ \text{TU/l}$$

II. Calculate toxicity emanating from the Ballymurtagh Adit (β^{BA}):

$$(\beta^{BA}) = (32.9 + 2.11f^{BA}) + (16.4 + 3.23f^{BA} - 6.26\text{e-}2f^{BA\wedge 2})\ \text{TU/l}$$

III. Calculate contribution of main adits to overall AMD discharge to river ($\emptyset$). This is done by using the sulphate ion as a conservative tracer and mass balance analysis. Values of $\emptyset$ are given below and are estimated from the discharge rate from the Deep Adit.

Flow rate in Deep Adit (l/s)	Value of $\emptyset$
0-10	0.9
11-20	0.8
21-30	0.7
31-40	0.6
>41	0.5

IV. Toxicity of adit discharges. At this point the total toxicity from the two main adits is $((\beta^{DA}) + (\beta^{BA}))$, while the total toxicity of AMD discharged into the river is $((\beta^{DA}) + (\beta^{BA}) / \emptyset)$.

V To calculate the toxicity after complete mixing within the river in TU/l (Ω) then the following mass balance equation is used:

$$\Omega = \frac{(((\text{ß}^{DA}) + (\text{ß}^{BA}) / \text{Ø}) \text{ x } ((f^{DA}) + (f^{BA}) / \text{Ø})) + ((\text{ß}^{R}) \text{ x } (f^{R}))}{((f^{DA}) + (f^{BA}) / \text{Ø}) + f^{R})}$$

VI. To include the effect of surface runoff during an intense and prolonged storm the calculation to estimate the toxicity after complete mixing within the river in TU/l (Ω) is modified as follows:

$$\Omega = \frac{(((\text{ß}^{DA}) + (\text{ß}^{BA}) / \text{Ø}) \text{x} (f^{DA}) + (f^{BA}) / \text{Ø})) + ((\text{ß}^{SR}) \text{x} (f^{DA} + f^{BA})) + ((\text{ß}^{R}) \text{x} (f^{R}))}{((f^{DA}) + (f^{BA}) / \text{Ø}) + (f^{DA} + f^{BA}) + f^{R})}$$

Field measurements have shown that the rate of storm water is approximately equal to the adit discharge rate and so can be taken as ($f^{DA} + f^{BA}$). The annual mean total toxicity (Cu + Zn) of the surface runoff (ß^{SR}) has been measured as 525 TU/l, which should be taken for modelling purposes. During a typical prolonged period of heavy rain resulting in surface runoff the toxicity will vary from 86 to 1,748 TU/l, the variation due to dilution and flushing of stored acidity from spoil.

The Avoca mining area is situated in the lower part of the Avoca-Avonmore catchment (652 km^2), which is of the highest water quality. The catchment is bordered on all sides by EU salmonid designated rivers[5]. However, the AMD discharged from the mines eliminates all biological life from the last 9 km stretch of the river to the sea, thus providing an effective barrier for salmonid migration to spawning areas upstream. In the River Avoca, dilution is often poor and ephemeral due to the discharge characteristics of the catchment, making the river extremely spatey. However, from the current study it is apparent that even at higher flow rates it is unlikely that toxicity levels will be low enough for sufficient periods to permit migration of fish. Salmon tend to mass off shore and attempt to swim up river during a spate. During the early period of these spates there is a very high sediment load in the river, so it is probable that the salmon only attempt their migration once the water begins to clarify,dur to cessation of surface runoff, and the river discharge rate is stabilised or on the decline. Maximum toxicity in the river occurs prior to the peak of the spate due to surface runoff and the period when the river discharge rate has returned to its base flow rate. It is during these critical periods for fish migration that the river is at its most toxic. Leaving fish with a very small opportunity during the spate-time series to successfully past the mining area up into the unpolluted catchment. While it only takes 24 hours for salmonids to swim from the estuary up river past Avoca mines during a spate, migration of young fish downstream over the same distance takes several weeks as they need to constantly feed. To fully restore the catchment as a salmonid fishery, it would require the removal of Fe from the AMD in order to restore the biota to the riverine substrate which is eliminated due to orche deposition resulting in habitat loss[6].

Acknowledgements

This work has been funded by the European Union under the Environment Programme (EU Contract EV5V-CT93-0248).

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Figure 1. The Avoca-Avonmore River catchment area showing the location of the mining strip.

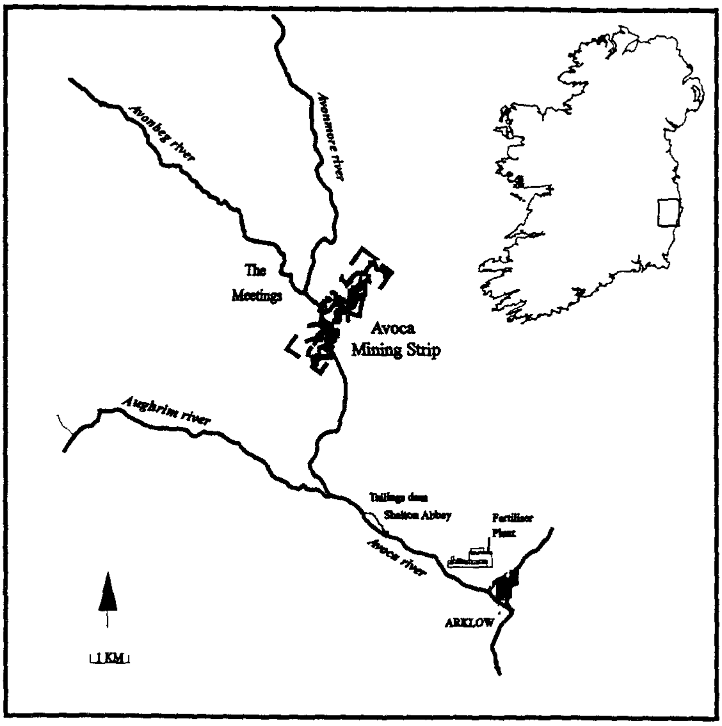


Figure 2. Variation of the Zn:Cu ratio in the AMD discharged from the Deep Adit with discharge rate.

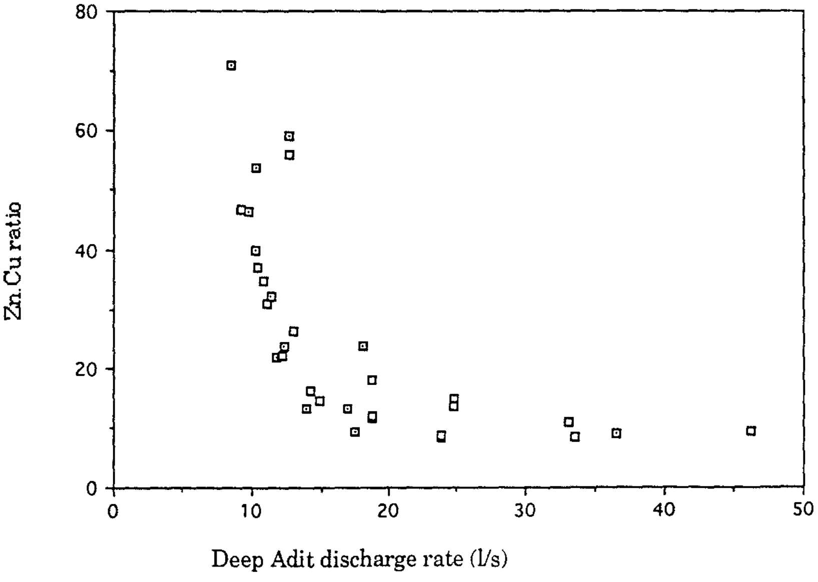


Figure 3. The variation in the Zn:Cu ratio in Deep Adit AMD showing the increase during the dry periods and rapid decline once the wet season becomes established. Values are mean monthly ratios

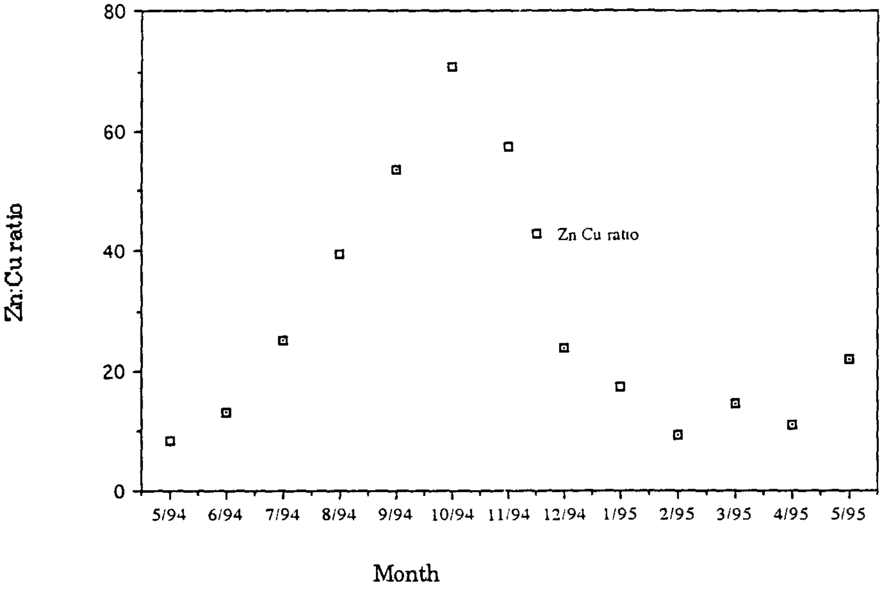


Figure 4. Total toxicity of AMD discharged from the Deep Adit into the Avoca River caused by Zn and Cu toxicity units per litre (TU/l). Values are monthly means.

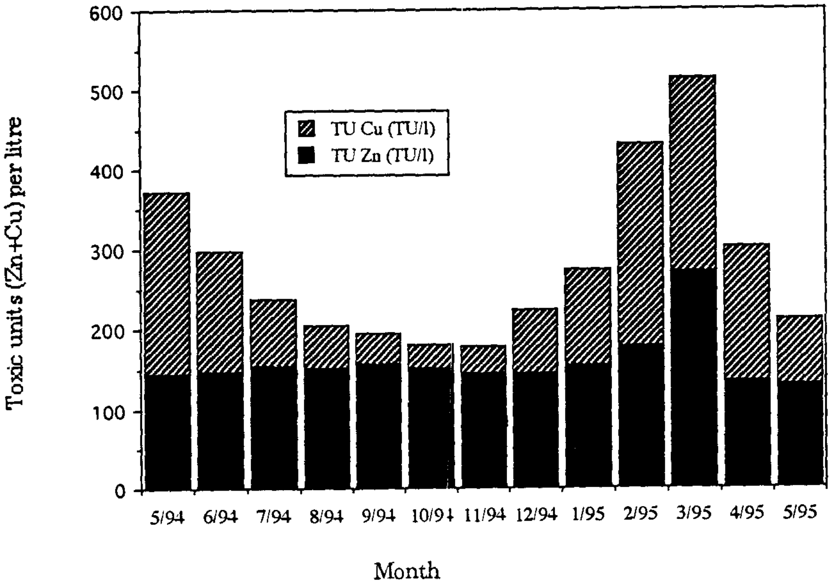


Figure 5. The toxicity of the AMD discharged from the Deep Adit in toxic units per litre (TU/l) can be estimated from the adit flow rate using the equation:

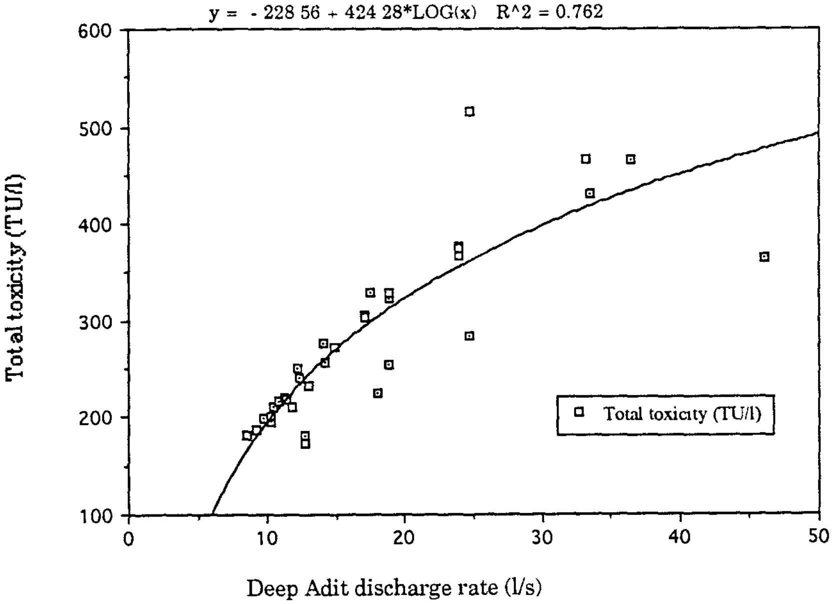
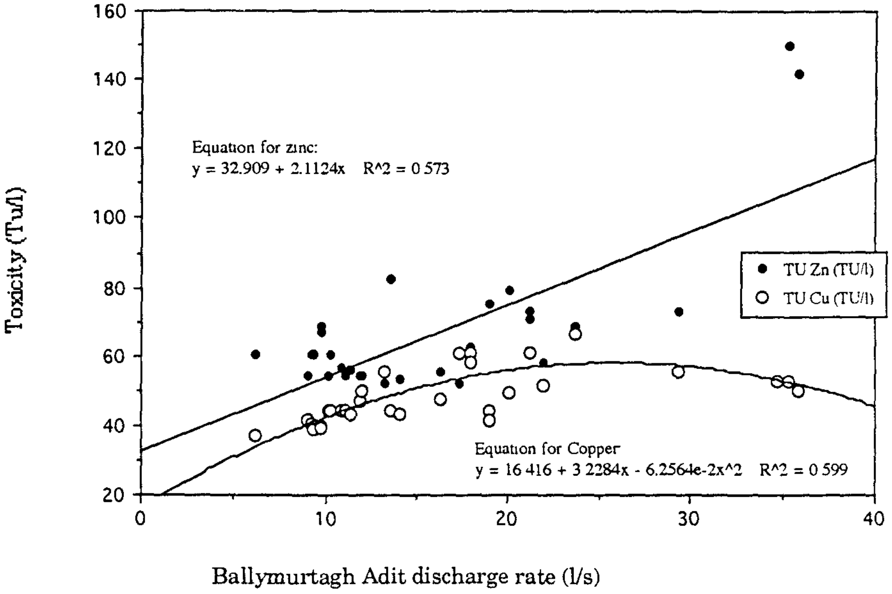


Figure 6. The toxicity of Cu and Zn must be calculated separately for the AMD discharged from the Ballymurtagh Adit, as the Zn:Cu ratio is independent of flow due to the different hydrological nature of the west mining zone.



Soil and vegetation contamination from a disused sulphur and copper mine in southeast Ireland

EV5V-CT93-0248

N.F. Gray, C. O'Neill and C. Herr

Environmental Sciences Unit, Trinity College, University of Dublin,
Dublin 2, Ireland.

Metal content was determined in soil and vegetation around the eastern zone of the disused Sulphur and Copper mines at Avoca (south-east Ireland). A 250 x 250 m grid survey was conducted covering a total area of 4 km^2. The mining belt was in the centre of the investigated site and was sampled separately. Iron, Zn, Cu and Cd concentrations in soil and plant material were determined in addition to soil organic matter content and soil pH. Soil samples taken from the spoil showed elevated Cu and Cd concentrations, low soil pH and organic matter contents. At least 50 % of the agricultural sites examined surrounding the East Avoca Mine, showed elevated Cu and Cd concentrations, whereas Zn and Fe concentrations were within the range for unpolluted soils. However, none of the vegetation analysed had elevated Zn, Cd, Fe or Cu concentrations. Overall there is no indication of serious metal contamination either in soils or vegetation surrounding the mine in spite of extensive dust deposition during open pit mining activity 20-50 years ago. There is however a plume of elevated Cu in the soil originating from a large spoil heap for some 2.0 km spread by the prevailing wind.

INTRODUCTION

Open pit mining of pyrite ores can lead to the contamination of the local environment and cause severe environmental impact to aquatic and terrestrial ecosystems (Soldevilla *et al.*, 1992). Historical mining activities and bare spoil heaps from previous mine workings are often a source of metal contamination to surrounding agricultural land. In the UK the most extensive areas of contaminated soils are caused by mining and are associated with mineral processing activities (Thornton, 1980). Wind-blown dust containing high metal concentrations from unvegetated spoil heaps may be deposited on soil and plants, and can enter the food chain. Avoca Mines are situated in County Wicklow in south-east Ireland (Fig. 1). The ores are volcanic sulphide deposits of Ordovecian age. The principal minerals of economic importance are chalcopyrite ($CuFeS_2$), pyrite (FeS_2), sphalerite (ZnS) and galena (PbS). Mining of copper ore (chalcophyrite) began in 1720 in East Avoca in underground mining operations. During the nineteenth century pyrite was also mined and processed. Up until the mid twentieth century all sulphide mining operations were subsurface. As mining in Avoca became more economical due to new mining and processing techniques, the excavation of open pits and the processing of lower grade ore deposits was encouraged. Platt (1975) reported that open-pit operations at Avoca created substantial amount of dust and in exposed situations the spoil was prone to continuous wind erosion. However no large scale dust control programme was implemented since the dust was only periodically problematic and was primarily related to the east mining area only. It was felt that rainfall alone was sufficient as dust suppressant (Platt, 1975). Despite this, severe deposits of dust over a prolonged period were a cause of complaint and legal action during the operation of the mine. A number of large unvegetated spoil heaps are still present in the East Avoca mining district and are subject to wind erosion. The residents of the area feel that metal contamination in soils has led to localized toxicity problems.

Since the closure of the Avoca Mine in 1982 large unvegetated spoil heaps mark the area surrounding the Avoca Mines. They are predominant at the East Avoca mining district and are still subject to wind erosion. A survey to investigate metal enrichment of soil and vegetation in the vicinity of the East Avoca mines was conducted during June and July, 1995. The principal soils surrounding the mines are brown podzolics; the agricultural land is principally used for grazing of cattle and sheep and tillage production. Soil and vegetation samples were also taken from the spoil heap at Mount Platt. All samples were analysed to determine metal content of Fe, Zn, Cu and Cd, soil organic matter and soil pH in the 4 km^2 area surrounding the East Avoca mining district (Fig.1).

RESULTS AND DISCUSSION

Soils surrounding the mines

The sites with high organic matter content were located on the edge of the mine (Table 1). The high concentrations may indicate inhibition of the breakdown of organic matter by the soil microflora. A significant correlation between cultivated and uncultivated soils was found for Cu ($p<0.05$) and pH ($p<0.01$) indicating that land use affects soil chemistry.

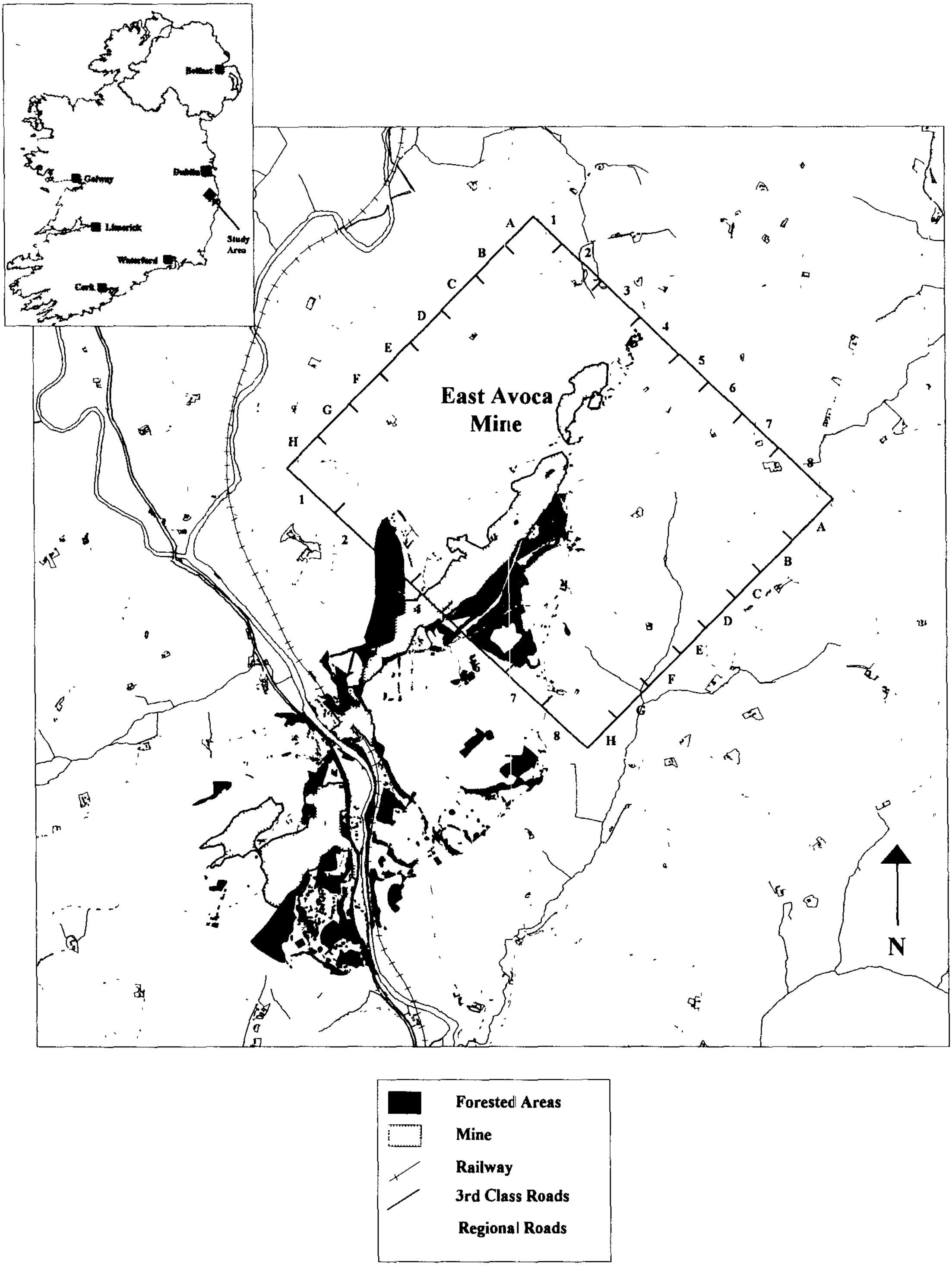


Figure 1: Map showing the location of East Avoca Mines and Sampling Grid

Table 1. Summary statistics for soil parameters measured in soil samples from pastures in the vicinity of the mine (n=54)

	Mean	SD	Median	Min	Max	normal range for mineral soils (µg/g) (Allan,1989)
Cu (µg/g)	145	159	77	15	769	5-80
Zn (µg/g)	131	68	113	39	342	20-300
Cd (µg/g)	0.9	0.6	1.0	0.0	2.6	0.03-0.3
Fe (%)	2.8	1.2	2.7	0.3	6.8	0.5-10
pH	6.2	0.9	6.3	3.5	7.9	
LoI (%)	16.2	10.5	13.2	6.1	61.2	

Some of the soils surrounding the Avoca Mines showed elevated Cu and Cd concentrations. Approximately 50 per cent of Cu concentrations of the investigated sites surrounding the mines exceeded the normal range indicating contamination from the mines has spread to the surrounding area. High Cu concentrations were mainly detected on sites which lay in a south-westerly direction, and also on the southern site of the mine (Fig. 2). Soils to the south of the mine were mainly uncultivated land used for sheep grazing. Merrington and Alloway (1994) in an investigation of deposition rates and retention parameters of metals in mined polluted soils found that Cu accumulated in soils to a greater degree than Zn and Cd per unit input. This, combined with the fact that copper was the main element mined in the region is most probably the reason for the widespread contamination of Cu.

It is unlikely that the elevated Cd concentrations are due to wind blow from the mine spoil as Cd concentrations in spoil itself are low in comparison to the surrounding agricultural land. Singh and Steinnes (1994) reported that maximum concentrations of some elements (As, Cd, Cu and Zn) in fertilizers such as N, P, NPK and liming material exceed background levels for soils, although cases of soil contamination from these sources have only been linked to Cd, and not to Cu and Zn. The agricultural land in the Avoca Region has been subject to heavy and continuous applications of fertilizers indicating that Cd contamination may be due to fertilizer application.

Vegetation sampled comprised mainly grass species. Increased metal content in grass species due to soil-plant transfer is not evident as plant metal content was not correlated to soil metal content. The trace element

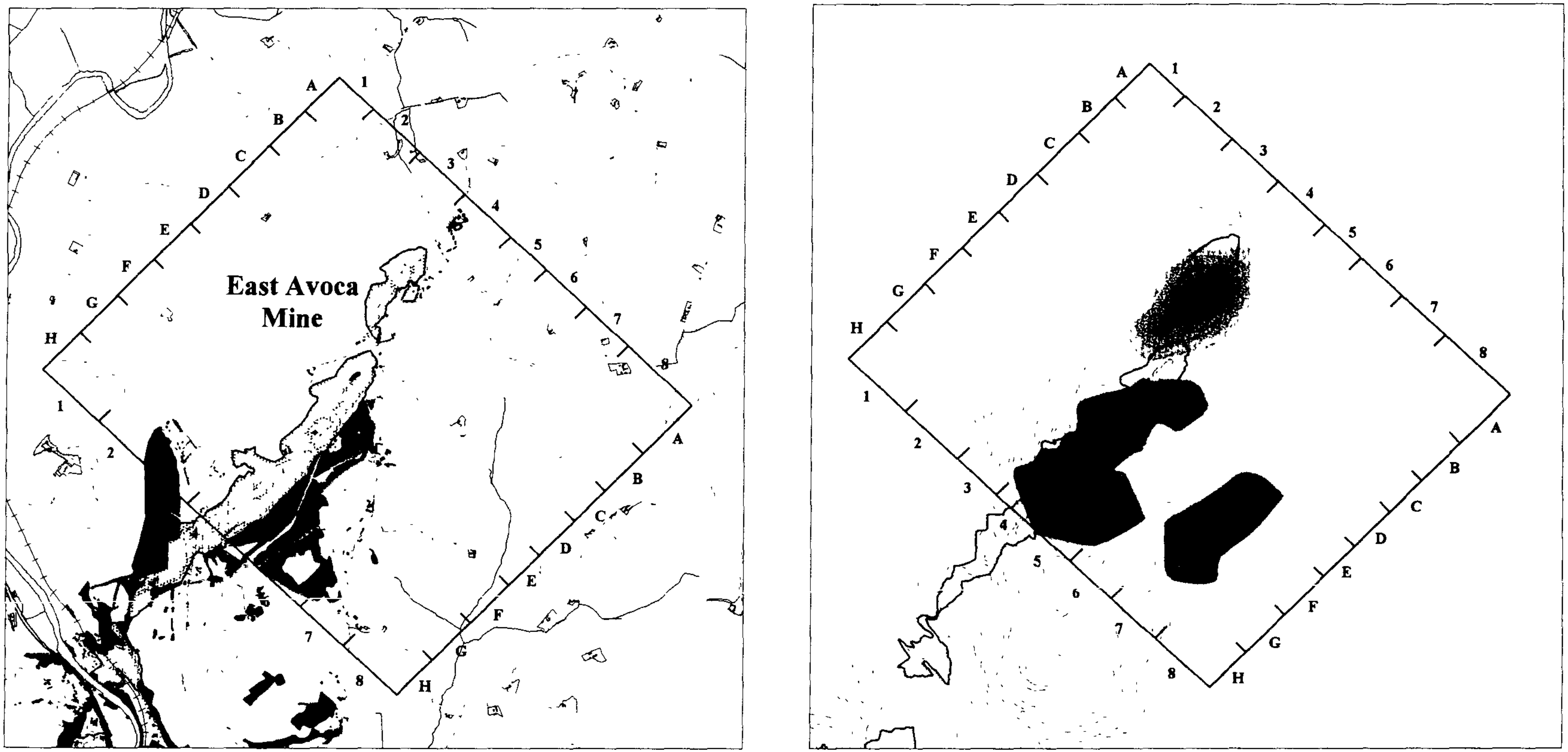


Figure 2: Contour plot of Cu concentration (µg/g) on spoil and surrounding agricultural land

concentration of the above ground portion of plants reflect only to a small degree large amounts present in soil due to limited uptake and translocation of these elements (Abrahams and Thornton, 1994). Only mean Cd concentrations were above the normal range of 0.03-0.3 μg/g for *Pinus* needles and Juvenile *Pinus*. Evidence of increased cadmium uptake at low pH was found. The concentration of elements found in species in Avoca as compared to the normal range can be seen in Table 2. Phytotoxic concentrations of elements found in plant leaves are also given. It can be seen from the summary data that although the metal concentrations exceed the normal range in some cases they are not at phytotoxic concentrations (Table 2). However, species in individual sites showed some phytotoxic levels of copper and zinc .

Table 2. Mean concentrations and standard deviation (SD) of Cu (μg/g), Zn (μg/g), Cd (μg/g) and Fe (μg/g) measured in plant species growing on pastures in the vicinity of the mine.

	n	Copper (SD)	Zinc (SD)	Cadmium (SD)	Iron (SD)
Juvenile *Pinus*	3	12	46	0.33	33.6
		(6.3)	(12.5)	(0.29)	(9.1)
***Pinus* needles**	4	3.5	64	0.48	69
		(0.8)	(16)	(0.41)	(32)
Grass species	56	11.7	44	0.08	171.4
		(4.7)	(37)	(0.19)	(126)
Calluna vulgaris	4	13	47	0	139
		(6.3)	(31)	(0)	(15)
Erica cinerea	6	9.1	42	0	118
		(2.7)	(17)	(0)	(40)
Toxic range (μg/g) (Alloway & Ayres, 1993)		20-100	100-400	1-4	
Normal range (μg/g) (Allan, 1989)		2.5-25	15-100	0.03-0.3	40-500

Soil and grass species examined for Cu, Fe and Cd concentrations at agriculture sites within the Hayle-Camborne-Redruth mining province of south-west England, principally important for mining of Sn and Cu, are compared with results gained in this study (Table 3). Soils in Southwest England compared to soils in Avoca show similar Cu, Zn and Fe concentrations, while herbage samples from the Avoca sites indicate a wider range in Cu and Zn concentrations.

Metals in soils and plants from spoil

Vegetation samples were only collected at about half of the mine sites, as others did not support any vegetation. The absence of vegetation over much of the mine area may be due to toxicity of the substrate which is a product of the low pH, lack of soil structure and elevated Cu and Zn concentrations in some of the spoil (Tables 4 and 5). Phytotoxicity was apparent on some pine trees growing at the edge of spoil. The damage observed could be a product of low pH or poor nutrient conditions in the substrate, and may not necessarily be linked to metal toxicity. The main problem areas were found to be sites at the edge of the spoil possibly due to extensive runoff. Toxic symptoms are said to be usually only found in plants when the total concentration of individual metals in soils exceeds 1,000 µg/g (Bradshaw and Chadwick, 1980). In this study a few of the mine sites showed concentrations exceeding this for both Cu and Zn.

Table 3. Soils and herbage species examined for Cu (µg/g), Zn (µg/g), Cd (µg/g) and Fe (%) in agricultural land in a metalliferous in Southwest England, (Abrahams and Thornton, 1994) compared with Avoca.

	Soil			Herbage	
	S.W. England	Avoca. Ireland	North Somerset	S.W. England	Avoca Ireland
	(n=12)	(n=55)	(n=174)		
Cu (µg/g)	12-319	15-342	2.8-145	8-23	4-25
Zn (µg/g)	29-365	39-342	14-8344	25-62	0-199
Cd (µg/g)	-	0-2.6	0.5-127	-	0-0.8
Fe (%)	1.1-5.9	0.3-6.8	-	42-1224 µg/g	52-413 µg/g

Table 4. Summary statistics for soil parameters measured in soil samples from mine spoil (n=14).

	Mean	SD	Median	Min	Max	normal range for mineral soils (µg/g) (Allan,1989)
Cu (µg/g)	658	317	566	261	1235	5-80
Zn (µg/g)	342	344	179	86	1184	20-300
Cd (µg/g)	1.14	1.06	0.83	0.00	3.62	0.03-0.3
Fe (%)	5.5	2.4	4.9	2.6	9.9	0.5-10
pH	3.5	0.68	3.6	2.6	4.5	
LoI (%)	3.52	0.97	3.52	1.55	4.94	

Analysis of soil samples showed that organic matter content and pH were lower at all spoil sites compared to the surrounding agricultural farmland sites. As expected all of the mine sites contained high concentrations of copper (Table 4). The material on the mine sites consists mainly of spoil, overburden and waste material and therefore probably lacking in cation exchange sites. This, along with the low organic matter content means that little binding of metals is likely to take place and combined with the low pH there is great potential for leaching of essential nutrients.

Considerable quantities of acid mine drainage are generated within the spoil with pore water highly acidic (pH < 2.5) and rich in metals, making conditions for plant growth extremely difficult.

Table 5. Mean concentrations and standard deviation (SD) of Cu (µg/g), Zn (µg/g), Cd (µg/g) and Fe (µg/g) measured in plant species growing on the spoil

	n	Copper (SD)	Zinc (SD)	Cadmium (SD)	Iron (SD)
Juvenile Pinus	4	16.3 (2.8)	42.3 (7.0)	0.09 (0.17)	115.8 (59.6)
Pinus needles	6	7.2 (2.2)	100.7 (22.6)	0.23 (0.29)	248.3 (153.1)
Grass	4	27.8 (5.3)	196.8 (208.5)	0.17 (0.34)	1022.3 (617.0)
Calluna vulgaris	1	15	363	0	946
Erica cinerea	2	14 (4.2)	49.5 (4.95)	0	501.5 (113.8)
Ulex europaens	1	11	39	0	194
Normal range (µg/g) (Allan,, 1989)		2.5-25	15-100	0.03-0.3	40-500

A comparison between the metal content of spoil in other abandoned mines in the UK and the Avoca spoil can be seen in Table 6. It can be seen that the Avoca spoil is within the range found for copper at four of the above sites and for zinc at all but one of the sites examined. Therefore the spoil is comparable with a range of spoil types found in the U.K., and is in fact less toxic than many others.

Table 6. Copper, lead and zinc in spoil from abandoned mines in Britain as compared to Avoca (mg/kg air-dried substrate) (after Johnson et al., 1994).

Mining region	Counties	No. Sites	Copper surveyed	Zinc
S.W. England	Devon, Cornwall	16	65-6140	26-1090
W. and N.W. England	Shropshire Cheshire	12	15-7260	980-21000
N. Pennines	N. Yorkshire Durham	8	20-140	470-28000
S. Pennines	Derbyshire	17	23-97	12700-42000
Lake district	Cumbria	7	77-3800	4690-7370
Mid-Wales	Powys, Dyfed	10	67-195	475-8000
N. Wales	Clwyd, Gwynedd	19	30-5750	11300-12700
S. Scotland	Dumfries, Galloway	6	125-657	1600-31400
Ireland	Avoca	14	261-1235	86-1184

ACKNOWLEDGEMENTS

This work has been funded by the European Union under the Environment Programme (EU Contract EV5V-CT93-0248).

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Strategies for rehabilitation of metal polluted soils: in situ phytoremediation, immobilization and revegetation. A comparative study

ENV4-CT95-0083

Coordinator: J.A.C. Verkleij

Vrije Universiteit Amsterdam
Vakgroep Oecologie en Oecotoxicologie
NL - 1081 HV Amsterdam
Tel: +31-20.444.7000
Fax: +31-20.444.7123

STRATEGIES FOR REHABILITATION OF METAL POLLUTED SOILS: IN SITU PHYTOREMEDIATION, IMMOBILIZATION AND REVEGETATION. A COMPARATIVE STUDY. (PHYTOREHAB)

project number: ENV4-CT95-0083

Starting Date: February 1996
Duration: 36 months

Coordinator:
Vrije Universiteit Amsterdam, VUA
Vakgroep Oecologie en Oecotoxicologie
De Boelelaan 1087
1081 HV Amsterdam, The Netherlands
Tel. +31 20 4447000
Fax +31 20 4447123
Verkleij, Jozeph A.C. (Dr.)
Tel. +31 20 4447054
E-Mail: verkleij@bio.vu.nl

Schat, H. (Dr.)
Tel. +31 20 4447052
E-Mail: hschat@bio.vu.nl

Partners:
Limburgs Universitair Centrum, LUC
Universitaire Campus, B-3590 Diepenbeek, Belgium

Vangronsveld J.C.H.M. Dr.
Tel: +32 11 268331
Fax: +32 11 268301
E-mail: jvangron@luc.ac.be

Institut National de la Recherche Agronomique, INRA
Avenue Edouard Bourleaux 71, FR-33883
Villenave D'Ornon, France
Mench, Michel Dr.
Tel: +33 56843055
Fax: +33 56843054
E-mail: MENCH@bordeaux.inra.fr

University of Kuopio U. Kuopio
Savilahdentie 9, FIN-70211 Kuopio, Finland

Karenlampi, Sirpa O. Dr.
Tel: +358 71 163069
Fax: +358 71 2811510
E-Mail: Sirpa.Karenlampi@uku.fi

Universidade de Iras-os-Montes e Alto Douro, UTAD
Apartado 202, Quinta de Prados PT-5001 Vila Real, Portugal
De Koe, Tjarda Dr. Ir.
Tel: +351 59 320239
Fax: +351 59 25058

Subcontractor of LUC
Vlaams Instituut voor Technologisch Onderzoek (VITO)
Boeretang 200, B-2400 Mol, Belgium
Mergeay, Max Prof.
Tel. +32 14 335511
Fax. +32 14 320372
E-mail: MERGEAYM@VITO.BE

Objective

In this project work programme an evaluation/comparison will be made of two 'soft' strategies which can be used for rehabilitation of metal polluted soils . Both strategies are based on phytoremediation:

(1) Metal/metalloid immobilization by means of metal/metalloid binding soil additives, either with or without
(2) revegetation and
(3) metal bioextraction by means of accumulator plants. For moderately polluted soils a comparison will be made of metal immobilization and bioextraction by metal accumulating plants. For highly polluted, bare and/or scarcely vegetated areas a combination of pollutant immobilization and revegetation (using plant ecotypes with increased metal tolerance) is proposed to limit the environmental impact of these areas.

1. Brief description of the Project Programm:

The following research tasks will be carried out during the project:

1. Study of the mechanism and molecular genetics of metal tolerance, metal uptake and plant internal metal transport, in order to develop plant material with more valuable characteristics for bioextraction.
2. Laboratory trials on immobilization and bioextraction: physico-chemical characterization of the substrates, evaluation of efficiency of substrate treatments or immobilizing heavy metals, study of effects of revegetation on percolation of pollutants and study of efficiency and feasibility of bio-exportation of metals from polluted substrates, study of metal accumulation capacity of transgenic plants used for bioextraction, study of stress-tolerance of plants which can be used for revegetation.
3 Field experiments: revegetation experiments, bioextraction experiments and evaluation of possibilities of recuperation of extracted metals. The field trials will take place in 4 countries: Portugal, France, Belgium (near the border with the Netherlands) and Finland.

2. PROPOSAL SUMMARY

Cadmium, zinc, lead, copper and other elements can be responsible for toxic responses in plants, animals and man when they are assimilated in increased amounts. Local soil accumulations of these elements are found in the vicinity of (former) mine sites and old non-ferrous smelters and refineries. In the highly contaminated zones, the substrate often is that phytotoxic that vegetation is scarce or even absent. These heavily polluted areas constitute a severe environmental risk for air, water and soil. In the zones with moderate to low contamination, pollution is not or less visible and soils are often used for agriculture and private kitchen gardens. The agricultural use causes increased riscs of transfer of metals to man and animals.

It is clear that the highly polluted sites as well as the lesser contaminated land need to sanitated. Classical (hard) sanitation techniques are very costly, and often their efficiency is limited. In some cases (e.g. acid extraction of metals) the mobility and by consequence the bio-availability, toxicity and environmental impact of the low amount of metals left are even higher after performing the "sanitation" measures.

In this project, an evaluation/comparison will be made of two "soft" strategies which can be used for the rehabilitation of metal polluted soils. The two strategies are based on phytoremediation. The first "soft" strategy is applied for moderately polluted soils, by which a comparison is made with metal immobilization using soil additives and bioextraction by metal accumulating plants.

To limit the environmental impact of the bare and scarcely vegetated areas (highly contaminated soils) a combination of pollutant immobilization and revegetation (using plant ecotypes with increased metal tolerance) is proposed as a second "soft" strategy. This revegetation strategy has ecological and economical benefits.

The main objective of the project proposal is: reclamation and consists of 3 steps:

(1) Study of the mechanism and genetics of metal tolerance, metal uptake and plant internal metal, transport in order to develop plant material with better valuable characteristics for bioextraction.

(2) Laboratory trials on immobilization and bioextraction: physico-chemical characterization of the substrates, evaluation of efficiency of substrate treatments or immobilizing heavy metals, study of metal accumulation capacity of transgenic plants used for bioextraction, study of stress-tolerance of plant which can used for revegeation, study of effects of revegetation on percolation of pollutants and study of efficiency and feasibility of bio-exportation of metals from polluted substrates.

(3) Field experiments: revegetation experiments, bioextraction experiments and evaluation of possibilities of recuperation of extracted metals. The field trials will take place in 3 countries: Portugal, Belgium (near the border with the Netherlands) and Finland.

The project proposal is a solid multidisciplinary collaboration between institutional and university research groups, most of them with a long experience and expertise in the area of heavy metals, plants and soil and combining various disciplines from molecular genetics and plant physiology to soil science and more applied research.

Keywords: Phytoremediation, immobilization, revegetation, bioextraction, heavy metal contamination, metal tolerance, environmental biotechnology

3. Major project milestones:

- Development of an effective (i.e. reliability, cost-benefit effects,..) in situ 'soft' sanitation strategy for heavily and moderately to low metal contaminated soils.
- Isolation of metal tolerance gene(s) from Silene.
- Expression of pro- and eukaryotic genes in tobacco.

4. Role of Participants

1) Vrije Universiteit Amsterdam, The Netherlands (VUA)
   - Coordinating department. Participates in the objectives: revegetation and bioextraction, particularly in the mechanisms of heavy metal tolerance, selection of plant ecotypes and "in situ" field experiments.

2) Limburgs Universitair Centrum Diepenbeek, Belgium (LUC).
   Contractor, participates in the objectives: biological test immobilization, revegetation and bioextraction with emphasis on laboratory tests of soil additives, and "in situ" trials and field experiments. A special task is reserved for VITO (subcontractor of LUC) transfering Cd-accumulating genes from yeast to tobacco.

3) Institut National de la Recherche Agronomique, Bordeaux, France (INRA).
Contractor, participates in the objectives: biological test characterization of metal-contaminated soils and immobilisation of metals, particularly laboratory tests of soil additives; revegetation (in situ field experiments) and follow up including changes in metal mobility in soil, plant availability and metal bioextraction by the microorganisms-plant systems

4) University of Kuopio, Kuopio, Finland (U. Kuopio)
Contractor, contribution - Revegetation: In isolation and characterization of tolerant ecotypes, our primary contribution is in birches. The field experiments are done in collaboration with Professor Lauri Kärenlampi, Department of Ecology and Environmental Science, University of Kuopio.
Bioextraction: Mechanism of metal tolerance is approached by several molecular biological tools, our primary approach being the isolation of metal tolerance genes from Silene by functional complementation in fission yeast. Our second major contribution is in the production of tobacco plants transformed with genes affecting metal tolerance and/or accumulation.

5) Universidade de Tras-os-Montes e Alto Duro, Vila Real, Portugal (UTAD)
Contractor, participates in the objectives immobilization and revegetation, particularly in in situ immobilization trials, selection of plant ecotypes and in situ field experiment.
The Plant Eology and Ecotoxicology Lab. has knowledge of and experience in arsenic tolerance in grasses from SW Europe.

Other poster contribution

"Hydrocarbon detection by means of Ground Penetrating Radar (GPR)"

Technological innovation from MAP Environmental Research BV, The Netherlands

By Ing P.B.van der Roest and Drs D.J.S.Brasser (+31-26-3778730).

The Netherlands is one of the leading countries in the world in the field of environmental legislation, resulting in constantly evolving environmental industry and on-going research aimed at finding methods for lowering environmental clean-up costs.
In response to that need, MAP Environmental Research BV has developed an innovative site investigation method. Current methods utilizing soil borings and groundwater wells are useful tools for analyzing contamination, but are both ineffective and costly in providing detailed information on the location and the extend of a contamination. This often leads to uncertainty in estimating clean-up costs or even worse, unsuccesful clean-ups.
To increase quality and reduce cost of such site investigations MAP Environmental Research BV has combined Ground Penetrating Radar with the in-house developed software "EnviScan" to locate and define the extent of the hydrocarbon contamination (mineral oil, aromats, poly-aromatic HC's, chlorinated HC's).

The theoretical background has been studied by several well-know research institutes, foremostly in North America. MAP has now developed software which is able to put this academic knowledge into a pratical tool. In the beginning of 1994 several test were done to prove the basic use. Comparision of the GPR-data with data collected through the conventional method showed a good correlation. Since then this method has been applied to nearly 100 projects in the Netherlands for the public and private sector, like Shell (30 projects), BP, Texaco and Akzo Nobel. All these projects have been checked by conventional sampling. The experiences gained from all these (commercial) projects has led to further improvements of the methods.

To execute the method, a systematic GPR survey is done to collect the necessary data. This data is then processed by the EnviScan program. The collected data are then analyzed partly by utilizing the principle that the electrical resistance of hydrocarbons varies considerably from that of groundwater and soil in the environment, resulting in a variation in radar reflection. The method provides a interesting amount of data. For example at a gasoline station of around 1.000 m2, around 15,000 reference points are collected versus maybe 20-30 refenrence points by the conventional method. An average investigation will reach depths of around 30 feet, but in some cases, depending on the soil conditions, contamination has been detected at depths of more then 90 feet.

The GPR-data is then used to generate a computer image (3-D) of the contamination in relative values. Based on experience minimum detection levels are in the range of 200-500 milligrams per kg/dm in ground and 10-50 micrograms per liter in groundwater.
The comprehensive information forms the basis for a targetted and effective drilling plan, which then delivers information on absolute values and the type of contamination. This additional information may then be used into the relative model to give it an absolute character.
This absoluut mobel may then again be used for various applications like volume calculations and monitoring of an remediation proces.

MAP currently seeks international joint-ventures with partners who are interested in this innovative method; essential is access to environmental and geophysical know-how.

Short-term research priorities identified by three concerted actions

LCANET

European Network for
Strategic Life-Cycle Assessment
Research and Development

Short-term strategy paper establishing links between LCA and waste management and cleaner technologies

LCANET short-term research and development priorities

Objective

The objective is to develop LCA in cooperation with stakeholders and in connection to specific applications in the field of waste management and cleaner technology.

Research tasks

Development of different Life cycle approaches

- Analysis of the specific features and uses of different analytical decision-support techniques, and how LCA and other techniques can complement each other. The analysis should consider which tools to use in specific situations and specification of methodological implications in relation to different LCA application domains. Including principles for use of LCA for the definition of Best Available Technology (BAT).
- Development of simpler LCA methods, considering principles for a tiered LCA approach and screening techniques, providing less detailed but robust outcomes still satisfying stakeholder expectations.

Life cycle inventory modelling

- System boundaries and allocation on both system level and process level of environmental inputs and outputs of recycling systems and waste treatment processes to economic inputs and outputs like specific flows of waste-to-be-processed, energy generation and production of secondary materials.
- Development of models for systems in which materials are recycled through cascades of use, allowing for dynamic and non-linear system behaviour by local linearisation, and accounting to the balance between materials conservation, energy recovery and pollution prevention.

Life Cycle Impact assessment

- Allocation and quantification of environmental inputs and outputs in landfill processes, providing a basis for the impact assessment, giving due attention to background concentrations and the time horizon of the processes.
- Development of equivalency factors for biotic and abiotic resources, taking into account scarcity, renewability, present rate of use and regional characteristics of the resources.
- Development of equivalency factors for human and ecotoxicity, taking all aspects in the cause-effect chain from emission up to effect into account. A differentiation into sub-categories, taking also subsequent valuation requirements into account, should be considered.
- Development of generic weighting factors for ranking and priority setting of environmental impact categories on an European level and in accordance with EU policy, considering different application domains and different rationales.

SCIENTIFIC PROGRAMME OF THE CONCERTED ACTION CARACAS

Six CARACAS TOPIC GROUPS have been set up to address specific aspects of Contaminated Land Risk Assessment (CLaRA). TOPIC GROUP 1 deals with **Human Toxicology** and will focus on issues such as appropriateness of primary data (exposure conditions, mode of delivery, chemical form); extrapolation from high to low doses and from animal to man; mechanisms of toxicity; exposure to mixtures; and bioavailability of contaminants in a soil matrix.

Ecological risk assessment (TOPIC GROUP **2**) involves characterising exposure and effects in various organisms and biological systems, including issues of bioconcentration, bioaccumulation and biomagnification. There are particular problems in interpreting multispecies exposure to mixtures of components, not all of them known or well characterised.

Fate and Transport of Contaminants (TOPIC GROUP **3**) is concerned with many issues relevant to removal, attenuation, phase transfer and bioavailability of contaminants, especially in complex mixtures. Processes include speciation, bio- and photo-degradation, plant uptake, sorption/desorption, dissolution, diffusion and volatilisation.

The **Site Investigation/Analysis Group** (TOPIC GROUP **4**) is concerned with reviewing national approaches to sampling and analysis, and identifying the most crucial parameters for risk assessment. It will seek to make recommendations on data quality needs and good scientific practice to ensure appropriate statistically valid, and cost effective data.

The many **models** available in the CLaRA community, including priority setting models and exposure/risk assessment models, will be reviewed by TOPIC GROUP 5. Models will be classified according to purpose of application, targets of concern, scientific basis and use status. An important area will be to improve the validation and applicability of models.

The role of **screening/guideline values**, and the scientific and policy basis for them, will be addressed by TOPIC GROUP 6. The Group will compare and contrast different soil policy approaches, and the role of guideline values in soil management frameworks. Various protocols for deriving these values will be examined including basic assumptions and methodological aspects.

A **seventh Topic Group (Methods for Risk Assessment)** is charged with reviewing and making recommendations on methods to integrate the basic elements of risk assessment such as soil, sediment and groundwater sampling, exposure modelling and measurement, effects assessment and risk evaluation.

Some overlaps between the Topic Group briefs are inevitable and intentional, and many CARACAS participants are member of more than one Topic Group.

Article by Prof. Colin FERGUSON, Nottingham Trent University, Speaker of the scientific CARACAS CORE GROUP. Prof. Ferguson can be reached at
+44-1159-486 510 (fax), +44-1159-486 888 (phone), e-mail: cbe3nathacp@ntu.ac.uk

CARACAS NEWSLETTERS can be obtained from the
CARACAS Office at +43-1-804 93 194 (fax), e-mail: 101355.1520@compuserve.com

NICOLE

A Network for Industrially Contaminated Land in Europe

(co-funded by the CEC)

In the opinion of NICOLE, an industry-led network of companies, technology developers and research performers, research and development is needed to significantly improve the efficiency and cost effectiveness of the way contaminated soil and groundwater at industrial and abandoned waste sites is identified, assessed and dealt with. There are five broad areas where research and development should be focused -

i) Improved methodologies and techniques for non-invasive investigation of potentially contaminated sites

More effective reconnaissance survey techniques are needed to establish the presence of contamination and enable detailed sampling and analysis to be better targeted. There is scope to develop and adapt existing techniques such as airborne remote sensing and surface geophysical techniques and indicative / semi-quantitative on-site analytical methods.

ii) Improved understanding of the behaviour of contaminants in the ground

Better understanding of the physical, chemical and biochemical behaviour of contaminants in the saturated and unsaturated zones and improved methods for modelling and measuring the parameters which describe this behaviour. This includes:

- improving the understanding of the conditions and processes under which contamination is attenuated naturally
- addressing the issue of heterogeneity of man-made ground at industrial sites
- quantifying the effect and impact of the interactions between contaminants

As far as practicable, such research should include 'field' measurements and analysis of site samples where the results can be applied generically.

iii) Improved methodologies for human and ecological risk assessment

Risk assessment is becoming increasingly recognised and often a preferable alternative to the use of prescriptive threshold values when determining contaminated land clean up criteria. However, to widen the acceptability and applicability of the technique further research and development is needed to provide

- improved methods for determining and establishing the effect of contaminant speciation and bioavailability
- updated ecological dose-response data which overcome the difficulty of linking and extrapolating data from a variety of *in vitro* toxicological tests with ecological effects using relatively untested assumptions and safety factors
- more information to enable consistent application of factors of safety and interpretation of toxicological data
- improved ways of communicating the results of risk assessment to interested third parties and the general public

Nicole Coordination:
Dr Dale A Laidler
ICI Research & Technology Centre
P.O Box 8, The Heath, Runcorn,
Cheshire, WA7 4QD, UK
Tel +44-1928-511521, Fax. +44-1928-581864

Nicole Secretariat:
H.J van Veen and M. Euser
TNO-MEP
P.O. Box 342, 7300 AH Apeldoorn, NL
Tel. +31-55-5493 927, Fax. +31-55-5493 410
E-mail. m.euser@mep.tno.nl

iv) Sustainable, low intensity *in situ* treatment processes

Development and validation of simple relatively inexpensive remediation and containment techniques which do not require sophisticated controls are needed Research should focus on *in situ* processes and include

- developing new techniques for improving accessibility to contamination at depth
- exploring the potential of natural attenuation as an acceptable control method
- seeking improvements in the performance and longevity of containment systems and reductions in their costs
- developing in-ground barriers and zones which promote *in situ* treatment of dissolved contaminants as groundwater percolates through
- exploring the potential for hybrid or integrated *in situ* treatment systems

These activities should involve field demonstrations which address the practicalities of carrying out remediation

v) Long term remote monitoring of the fate of contaminants

Research is needed to develop techniques (eg biosensors) for *in situ* remote monitoring of small changes in low levels of contamination over long periods to verify that natural attenuation is taking place or assess its release

Participants within NICOLE would welcome the opportunity to discuss ideas for research in the context of the topics outlined above (see below for contact details)

D A Laidler
NICOLE Co-ordinator

INDEX OF PROJECT NUMBERS

LIST OF PARTICIPANTS

AGATHOS, S.N.
Catholic University of Louvain
Unit of Bioengineering
Place Croix du Sud 2/19 (UNITE GEBI)
B - 1348 Louvain-La-Neuve
Tel: +32-10.47.36.44/47.36.55
Fax: +32-10.47.30.62

AGUIRRE, P.
INASMET
Camino de Portuetxe 12
E - 20009 San Sebastian
Tel: +34-43.21.80.22
Fax: +34-43.21.75.60

ALTER, H.
Resources Policy Department
U.S. Chamber of Commerce
1615 H Street, N.W.
USA - Washington D.C. 20062
Tel: +1-202.463.5531
Fax: +1-202.887.3445

ARRIBAS-QUINTANA, J.
European Commission
DG XI/E-3
Rue de la Loi 200
B - 1049 Brussels
Tel: +32-2.296.23.14
Fax: +32-2.299.10.68

BARNES, Michael
University College of North Wales
School of Biological Sciences, Memorial Building
UK - LL57 2UW Bangor
Tel: +44-1248-351.151
Fax: +44-1248.370.731

BARTON, J.
University of Leeds
Dept. of Civil Engineering
Woodhouse Lane
UK - Leeds LS2 9JT
Tel: +44-113.233.22.78
Fax: +44-113.233.22.43

BAUMBACH, J.I.
Inst. für Spektrochemie & Angewandte Spektroskopie
Bunsen-Kirchhoff-Str. 11
D - 44139 Dortmund
Tel: +49-231.13.92.238
Fax: +49-231.13.92.120

BECKERS, W.

BILITEWSKI, B.
Technische Universität Dresden
Lehrstuhl Abfallwirtschaft
George-Bähr-Str. 1-3
DE - 01069 Dresden
Tel: +49-351.463.7020
Fax: +49-351.463.7288

BIVER, C.
Solvay S.A.
310, rue de Ransbeek
B - 1120 Brussels
Tel: +32-2.264.27.93
Fax: +32-2.264.34.75

BOCARD, Christian
Institut français du pétrole
Direction biotechnologie et environnement
1-4 Avenue de Bois-Préau
B.P. 311
FR - 92506 Rueil-Malmaison CEDEX
Tel: +33-1.47.52.64.03
Fax: +33-1.47.52.70.01

BÖCKLE

BOGON, H.
GfL Planungs- und Ingenieurgesellschaft
Friedrich-Mißler-Str. 42
D - 28211 Bremen
Tel: +49-421.2032.729
Fax: +49-421.2032.747

BOWDEN, Richard
BLC The Leather Technology Centre
Leather Trade House
Kings Park Road
UK - Northampton
Tel: +44-1604.49.41.31
Fax: +44-1604.64.82.20

BRACH, J.
Celabor S.C.R.L.
Zoning de Petit-Rechain
Avenue du Parc 38
B - 4650 Chaineux
Tel: +32-87.32.24.54
Fax: +32-87.34.13.87

BRASSER, D.J.S.
MAP Benelux B.V.
Lovinklaan 1
NL - 6821 HX Arnhem
Tel: +31-26.3778.730
Fax: +31-26.3892.272

BROMAN, D.
University of Stockholm
ITM
S - 106 91 Stockholm
Tel: +46-8.16.4018
Fax: +46-8.16.7715

BUEKENS, A.
Vrije Universiteit Brussel
Dienst Chemische Ingenieurstechniek & Industriële Scheikunde
Pleinlaan, 2
B - 1050 Brussels
Tel: +32-2.629.32.44
Fax: +32-2.629.33.33

BÜSING, J.H.
European Commission
200 rue de la Loi
DG XII/D-1
B - 1049 Brussels
Tel: +32-2.295.56.25
Fax: +32-2.296.30.24

CARSTEN, C.
ISAH
Inst. für Siedlungswasser-Wirtschaft & Abfalltechnik
Universität Hannover
Welfengarten 1
D - 30167 Hannover
Tel:
Fax:

CAMPBELL, R.

COCHAUX, Alain
Centre Technique du Papier
Domaine Universitaire B.P. 251
F - 38044 Grenoble
Tel: +33-76.15.40.65
Fax: +33-76.15.40.16

DARMENDRAIL, D.
BRGM
C.T. DEFIS
Fort de Lezennes
F - 59260 Lezennes
Tel: +33-20.19.15.40
Fax: +33-20.67.05.56

DECWER, W.-D.
GBF mBH
Mascherode Weg 1
D - 38124 Braunschweig
Tel: +49-531.6181.100
Fax: +49-531.6181.111

DETTWILER, B.
SULZER CHEMTECH AG
P.O. Box 65, ER 0662
CH - 8404 Winterthur
Tel: +41-52.262.43.61
Fax: +41-52.262.01.79

DIELS, Ludo
VITO
Boerentang, 200
BE - 2400 Mol
Tel: +32-14.33.5100
Fax: +32.14.32.0372

DITZE
Metallurgie & Werkstoffwissenschaften
Robert-Koch-Str. 42
D - 38678 Clausthal-Zellerfeld
Tel: +49-5323.72.22.77
Fax: +49-5323.72.23.24

ECCLES, H.
BNFL
6 Riversway Business Village
Navigation Way
Ashton on Ribben
UK - PR2 2YF Preston-Lancashire
Tel: +44-1772.732.713
Fax: +44-1772.733.184

EHLE, M.
BASF AG
Farbenlaboratorium, ZDH/S - M 311
Carl-Bosch-Str. 38
D - 67056 Ludwigshafen
Tel: +49-621.60.79232
Fax: +49-621.60.79398

EISENREICH, N.
Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V.
Institut für Chemische Technologie
Postfach 12 40
Joseph-von-Fraunhofer-Straβe 7
D - 76327 Pfinztal (Berghausen)
Tel: +49-721.4640.138
Fax: +49-721.4640.111

FERGUSON, C.
The Nottingham Trent University
Burton street
UK - NG1 4BU Nottingham
Tel: +44-1159.486888
Fax: +44-1159.486510

FELDHOFF, R.

FOUREST, E.
CEA/DTA/BEM
17, Av. des Martyrs
F - 38054 Grenoble Cedex
Tel: +33-76.88.98.26
Fax: +33-76.88.46.66

FRANK, H.

FRANKE, M.

FREGO
Enel Societa per Azioni
R&D Dept. Residuerization & Treatment
Research Center
Via Dalmazia 21/c
I - 72100 Brindisi
Tel: +39-831.5173.51
Fax: +39-831.5173.05

FRENZEL, M.

HALL, S.
University of Nottingham
Institute of Environmental Eng.
University Park
UK - NG7 2RD Nottingham
Tel: +44-115.951.4088
Fax: +44-115.951.4115

HERR, C.
Institut WAR, TH Darmstadt
Petersenstr. 13
D - 64287 Darmstadt
Tel: +49-6151.164.662
Fax: +49-6151.163.739

HEYDE, M.
Fraunhofer Institute for Food Technology & Packaging
Steinerstr. 15
D - 81369 München
Tel: +49-89.72485.126
Fax: +49-89.74290.611

HIGGO, J.
British Geological Survey
Keuworth
UK - NG2 5GG Nottingham
Tel: +44-1159.363.131
Fax: +44-1159.363.261

HOLLAND, F.
Electrochemical Techniques Ltd
5 Castletown Road, Hazelgrove
UK - SK7 6LB Stockport
Tel: +44-161.483.6665
Fax: +44-161.456.8542

HUTH-EEHRE, T.

IVANOVICH, Miro
RMC Environmental Ltd
Suite 7, Hitching Court
Abingdon Business Park
Abingdon
UK - OX14 1RA Oxfordshire
Tel: +44-1235.555755
Fax: +44-1235.525143

JACKSON, D.V.
6, Grange Road
Saltwood, HYTHE
UK - KENT CT 21 4QS
Tel: +44-303.261.383

JAUZEIN, M.
Institut de Recherches Hydrologiques
Génie de l'Environnement
11 bis, Rue Gabriel Péri B.P.286
FR - 54515 Vandoeuvre Les Nancy
Tel: +33-83.50.36.99

JAVIER GUTIERREZ F.
Instituto de Fisica Aplicada - CSIC
Serrano 144
E - 28006 Madrid
Tel: +34-1.561.88.06
Fax: +34-1.411.76.51

JENSEN, A.A.
dk-Teknik. Energy & Environment
Gladsaxe Moellevej 15
DK - 2860 Copenhagen Soeborg
Tel: +45-39.696.511
Fax: +45-39.696.002

JØRGENSEN, K.S.
Finnish Environment Agency
Hakuninmaantie 4-6
FIN - 00430 Helsinki
Tel: +358-0.403.00851
Fax: +358-0.403.00890

KARLSON, U.
NERI
Dept. of Marine Ecology & Microbiology
Frederiksborgvej 399
P.O. Box 358
DK - 4000 Roskilde
Tel: +45-46.30.13.87
Fax: +45-46.30.12.16

KASAMAS, H.
CARACAS-Office
Breitenfurterstr. 97
A - 1120 Vienna
Tel: +43-1.804.93.19
Fax: +43-1.804.93.194

KEIJZER, H.
Wageningen Agricultural University
P.O. Box 8005
NL - 6700 EC Wageningen
tel: +31-317.483641
Fax: +31-317.483766

KELLER, H.
Forschungszentrum Karlsruhe - IAI
P.O. Box 3640
D - 76021 Karlsruhe
Tel: +49-7247.82.5756
Fax: +49-7247.82.5730

KOCH, F.
Austrian Research Centre Seibersdorf
A - 2444 Seibersdorf
Tel: +43-2254.780.2657
Fax: +43-2254.780.2652

KÖGEL-KNABNER, I.
Lehrstuhl für Bodenkunde
TU München
D - 85350 Freising-Weihenstephan
Tel: +49-8161.71.36.77
Fax: +49-8161.71.44.66

KONTOPOULOS, A.
National Technical University of Athens
Laboratory of Metallurgy
P.O. Box 64056
GR - 157 80 Zografos, Athens
Tel: +30-1.772.2167
Fax: +30-1.772.2168

KREJSA, P.
Forschungszentrum Seibersdorf GmbH
Austrian Research Centre Seibersdorf
AU - 2444 Seibersdorf
Tel: +43-2254.780.2652
Fax: +43-2254.74060

KRISTENSEN, P.
VKI
Agern Alle 11
DK - 2970 Hørsholm
Tel: +45-42.86.52.11
Fax: +45-42.86.72.73

KÜNZER, F.

LARKIN, M.
The Questor Centre
The Queen's University of Belfast
David Keir Building
Stranmillis Road
UK - BT9 5AG Belfast
Tel: +44-1232.33.55.77
Fax: +44-1232.66.14.62

LEBEAULT, J.-M.
Université de Technologie de Compiègne
B.P. 649
F - 60206 Compiègne
Tel: +33-44.23.44.56
Fax: +33-44.23.19.80

LEIPNITZ, Y.

LERNER, D.N.
University of Bradford
Dept. of Civil & Environmental Engineering
West Yorkshire
UK - BD7 1DP Bradford
Tel: +44-1274.385470
Fax: +44-1274.383888

LESCHONSKI, K.

LOUW, R.
Rijksuniversiteit Leiden
Center for Chemistry & the Environment
P.O. Box 9502
NL - 2300 RA Leiden
Tel: +31-71.52.74.289
Fax: +31-71.52.74.488

LUBINA, C.
Max-Planck-Institute for Chemistry
Airchemistry Dept.
P.O. Box 3060
D - 55020 Mainz
Tel: +49-6131.305.461
Fax: +49-6131.305.436

LUDWIG, J.-M.
Sony Deutschland GmbH
Stuttgart Technology Center
Stuttgart Str. 106
D - 70736 Fellbach (Stuttgart)
Tel: +49-711.5858.467
Fax: +49-711.5858.140/142/144

MADSEN, T.
VKI
Agern Alle 11
DK - 2970 Hørsholm
Tel: +45-42.86.52.11
Fax: +45-42.86.72.73

MARKS, T.
Centre for applied .... and Research
Porton Down
UK - SP4 OJ4 Salisbury
Tel: +44-1980.612.455
Fax: +44-1980.611.320

MASSIANI, C.
Université de Provence
Laboratoire de Chimie et Environnement
3, Place Victor Hugo
FR - 13331 Marseille Cedex 3
Tel: +33-91.10.6374
Fax: +33-91.10.6377

MATIS, K.
Aristotle University
Chemistry Dept.
GR - 540 06 Thessaloniki
Tel: +30-31.99.77.43
Fax: +30-31.99.77.43

MAUSER, N.
Ind. für Physikalische Chemie
Egerlandstr.3
D - 91058 Erlangen
Tel: +49-9131.85.8312
Fax: +49-9131.85.8307

McCARTHY, A.
University of Liverpool
Department of Genetics & Microbiology
Life Sciences Building - P.O. Box 147
UK - Liverpool L69 3BX
Tel: +44-1517.94.4413
Fax: +44-1517.94.4401

MELSSEN, W.
KUN Analytical Chemistry
Toernooiveld 1
NL - 6525 ED Nijmegen
Tel: +31-24.365.2512
Fax: +31-24.365.2653

MICHELFELDER, B.
Fraunhofer-Institut für Chemische Technologie (ICT)
Joseph-von-Fraunhofer-Str. 7
D - 76327 Pfinztal
Tel: +49-721.464.0236
Fax: +49-721.464.0111

MÜLLER, B.
Forschungszentrum Karlsruhe IAI
P.O. Box 3640
D - 76021 Karlsruhe
Tel: +49-7247.82.57.82
Fax: +49-7247.82.57.30

MÜLLER, R.
Technical University Hamburg-Harburg, Biotechnology II
Denickestr. 15
D - 21071 Hamburg
Tel: +49-40.7718.3118
Fax: +49-40.7718.2127

NAVEAU, H.
Catholic University of Louvain
Unit of Bioengineering
Place Croix du Sud 2/19 (Unité GEBI)
B - 1348 Louvain-La-Neuve
Tel: +32-10.47.36.46/47.36.55
Fax: +32-10.47.30.62

NICKEL, U.
Ind. für Physikalische Chemie
Egerlandstr. 3
D - 91058 Erlangen
Tel: +49-9131.85.7334
Fax: +49-9131.85.8307

NILSSON, J.
University of Linköping, IKP
S - 581 83 Linköping
Tel: +46-1328.2447
Fax: +46-1328.2798

NOGUEIRA, C.

NORRTHON, P.
Linköping University
IFM/Miljöteknik
S - 581 83 Linköping
Tel: +46-1328.2785
Fax: +46-1312.2587

NOWAK, D
DNU Berlin
Pfalzburger Str., 82
DE - 10719 Berlin
Tel: +49-30.883.61.92
Fax: +49-30.881.71.02

O'CONNOR, P.
Geological Survey of Ireland
Dept. of Energy
Beggars Bush
Haddington Road
IE - Dublin 4
Tel: +353-1.604.1416
Fax: +353-1.668.1782

OPPENLÄNDER, K.
BASF AG
Farbenlaboratorium, ZDH/S - M 311
Carl-Bosch-Str. 38
D - 67056 Ludwigshafen
Tel: +49-621.60.54137
Fax: +49-621.60.79398

PANZNER, G.
Umweltschutztechnik in der Deutschen Forschungsanstalt für Luft- und Raumfahrt
125, Südstrasse
DE - 53175 Bonn
Tel:
Fax:

PAPAMELETIOU, D.
EC-SRC-IPTS
WTC, Isla de la Cartuja
E - 41092 Sevilla
Tel: +34-5.448.82.89
Fax: +34-5.448.82.79

PARKES, J.
Faraday Center
Green Road
IE - Carlow
Tel: +353-503.42795
Fax: +353-503.41392

PRONE, A.
Université de Provence
Laboratoire de Chimie et Environnement
3, Place Victor Hugo
FR - 13331 Marseille Cedex 3
Tel: +33-91.10.6374
Fax: +33-91.10.6377

RAMOS, J.L.
CSIC - EEZ
Apdo 419
E - 18008 Granada
Tel: +34-58.121.011
Fax: +34-58.129.600

REINIGER, P.
European Commission
200 rue de la Loi
DG XII/D-1
B - 1049 Brussels
Tel: +32-2.295.95.86
Fax: +32-2.296.30.24

RODHE, J.

RYDIN, S.
Danish Technological Institute
Department of Environmental Technology
PO Box 141
DK - 2630 Taastrup
Tel: +45-43.50.4601
Fax: +45-43.50.7150

SAHUT, C.
Commissariat à l'Energie Atomique
Centre de CADARACHE - Bât. 352
F - 13108 St. Paul
Tel: +33-42.25.78.25
Fax: +33-42.25.42.74

SALKINOJA-SALONEN, M.
University of Helsinki
Dept. of Appl. Chemistry & Microbiology
Viikki, P.O. Box 56
FIN - 00014 Helsinki, Suomi
Tel: +358-0.708.59300
Fax: +358-0.708.59301

SARDIN, M.
Lab. des Sciences du Génie Chimique - CNRS
ENSIC, 1 rue Grandville, BP 451
F - 54001 Nancy
Tel: +33-83.17.52.59
Fax: +33-83.32.29.75

SCHMITZ U.

SCHOONE, M.
University of Bochum
Soil Science Group, NA 6/131
D - 44780 Bochum
Tel: +49-234.700.3661
Fax: +49-234.709.4180

SCHRAA, G.
Dept. of Microbiology
Wageningen Agricultural University
H.V. Suchtelenweg 4
NL - 6703 CT Wageningen
Tel: +31-317.483620
Fax: +31-317.483829

SCHWARZ, N.
Österreichisches Forschungszentrum Seibersdorf GmbH
Department of Automation
AT - 2444 Seibersdorf
Tel: +43-2254.780/2216
Fax: +43-2254.74060/74061

SCHWERDTFEGER, K.
Allgemein Metallurgie / TU-Clausthal
Robert-Koch-Str. 42
DE - 38678 Clausthal-Zellerfeld
Tel: +49-5323.72.2385
Fax: +49-5323.72.3184

SPANINKS, F.
Institute for Environmental Studies
De Boelelaan 1115
NL - 1081 HV Amsterdam
Tel: +31-20.44.49.555
Fax: +31-20.44.49.553

STEINBERG, K.-H.

STIETZEL

SUNDERLAND, J.-G.
EA Technology Ltd
Capenhurst
Chester
UK - CH1 6ES Cheshire
Tel: +44-151.347.2411
Fax: +44-151.347.2138

SURFLEET, B.
EA Technology Limited
Capenhurst
UK - Chester CH1 6ES
Tel:
Fax: +44-51.347.2305

TACKE, A.

TEMMINGHOFF, E.
Agricultural University Wageningen
Dreyenplein 10
NL - 6703 HB Wageningen
Tel: +31-317.482357
Fax: +31-317.483766

TENNISON, S.
MAST International Ltd
62, Farleigh Road, New Hawy
UK - KT15 3HR Addlestone, Surrey
Tel: +44-1932.336.892
Fax: +44-1932.336.892

UJMA, H.J.
Abteilung Forschung & Entwicklung
Preussag AG
Karl-Wiechert-Allee, 4
D - 30625 Hannover
Tel: +49-511.566.1135
Fax: +49-511.566.1159

URSTADT, S.
GBF mBH
Mascherode Weg 1
D - 38124 Braunschweig
Tel: +49-531.6181.100
Fax: +49-531.6181.111

URZELAI

VAN DEN BROEK, W.
KUN Analytical Chemistry
Toernooiveld 1
NL - 6525 ED Nijmegen
Tel: +31-24.365.3186
Fax: +31-24.365.2653

VAN DER ROEST

VAN VEEN, H.J.
TNO/MEP
P.O. Box 342
NL - 7300 AH Apeldoorn
Tel: +31-55.549.3922
Fax: +31-55.549.3410

VEGTER, J.J.
TCB
Technical Soil Protection Committee
P.O. Box 30947
NL - 2500 GX The Hague
Tel: +31-70.339.3034
Fax: +31.70.339.1342

VERKLEIJ, J.
Vrij Universiteit Amsterdam
De Boelelaan 1087
NL - 1081 HV Amsterdam
Tel: +31-20.444.7054
Fax: +31-20.444.7123

VIGLIANESI, G.

VON DOSSOW, A.

WELTIN, D.
TU-Dresden
Institut für Abfallwirtschaft und Altlasten
George-Bähr-Str. 1-3
DE - 01069 Dresden
Tel: +49-351.463.2238
Fax: +49-351.463.7288

WINTER, F.
ICB Münster
Mendelstr. 7
D - 48149 Münster
Tel: +49-251.980.1968
Fax: +49-251.980.1999

WITTICH, R.

WITTMANN, C.
GBF mBH
Mascherode Weg 1
D - 38124 Braunschweig
Tel: +49-531.6181.100
Fax: +49-531.6181.111

WRISBERG, N.
Center for Environmental Science
Leiden University
P.O. Box 9518, Einsteinweg, 2
NL - 2300 RA Leiden
Tel: +31-71.527.7477
Fax: +31-71.527.7434

LIST OF POSTER CONTRIBUTIONS

NAMES	TITLE OF THE POSTERS
AGATHOS, Naveau	Introduction and Monitoring of De Novo Reductive Dechlorination Activity into Anaerobic Soil Microcosms
BALIS, Constantine	Bioremediation of olive mill wastes for use as fertilizers (poster+video)
BARNES, Michael	Aromatic hydrocarbon catabolism in rhodococcus sp PWD1
BAUMBACH, J.I.	Multi-capillary column GC coupled to ion mobility spectrometry
BRASSER, D J.S.	Hydrocarbon detection by means of Ground Penetrating Radar
BUEKENS, Alfons	Preliminary pilot plant design Heavy metal recovery from fly ashes.
DECWER, WITTMANN, URSTADT	1. Well-performing biodegraders for bioremediation: microbial growth and degradation strategies of pentachlorophenol-degrading bacteria. 2 Microbial strategies of growth and degradation.
DIELS, Ludo	1 Dry solid reactors for the biodegradation of organic pollutants in soil. 2. Dechlorination of highly chlorinated PCBs: Chemical and microbial solutions 3. Mineralization of lower chlorinated biphenyls by aerobic microorganisms
GRAY, Nick	1. Impact assessment of acid mine drainage on a lotic system: a case study. 2. Soil and vegetation contamination from a disused sulphur and copper mine in South-East Ireland
JAUZEIN, Michel	1. Evaluation and improvement of the bioavailability of polluants in soil and sediments for better remedial practices and risk assessment methods 2. Multicomponent multiphase pollutant transport in contaminated soils Chemical and spatial heterogeneity. 3 Measurement and modelling of VOC mobility in soils and groundwaters for environmental risks assessement assessment.
JAVIER GUTIERREZ	Analysis of VOC's with a semiconductor sensor array.
JORGENSEN, Kirsten	Bioremediation of chlorophenol-contaminated soil by composting in full scale.
KASAMAS, Harald	Concerted action on risk assessment for contaminated sites - CARACAS
KEIJZER, Henriette	Fundamentals of in-situ redediation technology
KELLER, Hubert	Neural nets for combustion process simulation

NAMES	TITLE OF THE POSTERS
KÔGEL-KNABNER,I	Fate of PAH in soils Effect of organic matter composition in bulk and aqueous phase.
KONTOPOULOS, A	1. Rehabilitation of a sulphidic tailings dam in Lavrion 2 Soil rehabilitation in Lavrion.
LARKIN, Michael J	A comparison of haloalkane dehalogenase DWA and amino acid sequences
LOUW, Robert	Catalytic combustion of organo chlorine compounds
MADSEN, Torben	PAH degradation by addition of bacteria and surfactants.
MATIS Konstantine A.	Recovery of heavy metals from effluents by sorption (or biosorption) and flotation
MICHELFELDER, B., EISENREICH, N.	Combined SCF-SCWO to Degrade Organic Wastes
MYFTIU, Gene	Recycling of fly ashes for the production of ceramic materials
PAPAMELETIOU, D	Technology water activities at the EC-IPTS in the area of Environment, Recycling and LCA.
PURI, Annemarie	Inertization capacity and hardening properties of blended cements containing MSW ashes.
RAMOS, Juan L.	Degradation of xenobiotics in soils.
SALKINOJA-SALONEN, M	Ultrastructure and phylogeny of xenobiotic degrading sphingomonads.
SARDIN, Michel	1. Transport of phenanthrene through soil columns. experiments and modelling 2. Transport of volatile organic compounds in saturated media experiments and modelling
SCHRAA, Gosse	Microbial and chemical dechlorination of highly chlorinated PCBs
SPANINKS, Frank	Development of a combined methodology to evaluate recycling processes based on the life cycle assessment (LCA) and economic valuation analysis (EVA)
STICHER, H.	Binding and transport of simple ions in laboratory soil columns
TEMMINGHOFF, E.	Availability, mobility and spatial variability of heavy metals in soil.