National Aeronautics and
Space Administration

**Investigative Report**

# Reactivity of alpha-Ketoglutaric Acid (AKGA) with Hydrazine and Monomethylhydrazine

**Lyndon B. Johnson Space Center**
**White Sands Test Facility**
**P.O. Box 20**
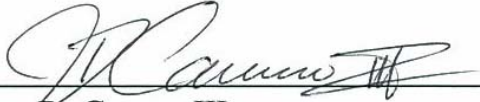**Las Cruces, NM  88004**
**(575) 524-5011**

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# Reactivity of alpha-Ketoglutaric Acid (AKGA) with Hydrazine and Monomethylhydrazine

Issued By
National Aeronautics and Space Administration
Johnson Space Center
White Sands Test Facility
Laboratories Office

Prepared By: _____
Dion J. Mast
NASA Test and Evaluation Contract

Prepared By: _____
Benjamin Greene
NASA Test and Evaluation Contract

Reviewed By: _____
John D. Caruso III
NASA Test and Evaluation Contract

Approved By: _____
Susana A. Harper
NASA Laboratories Office

# Abstract

A literature survey and laboratory investigations with alpha-ketoglutaric acid (AKGA), hydrazine, and monomethylhydrazine (MMH) were performed to characterize AKGA reactions with hydrazine and MMH. The use of AKGA to decontaminate hydrazine- and MMH-contaminated soft goods materials was evaluated. Investigations included reaction characteristics and rates under stoichiometric conditions, pH measurements, concentration effects, tests involving open beaker screening, spectral analysis, soft-goods material decontamination, and determination of corrosion rates of selected alloys commonly used in aerospace applications.

AKGA reacts with hydrazine to form 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (PCA) and water and with MMH to form l-methyl-1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (MPCA) and water. Stoichiometric reactions were performed, and concentrations of hydrazine and MMH with AKGA to form PCA and MPCA were monitored over time using two liquid chromatographic analytical methods developed at NASA White Sands Test Facility (WSTF), one for hydrazine and MMH and the other for AKGA, PCA, and MPCA. Simultaneous use of these methods allowed semi-continuous monitoring of reactant and product concentrations.

Reactions of 0.1 M and 1.0 M AKGA with 1000 ppm hydrazine and MMH were monitored over time, demonstrating that reaction rates depend upon the concentration and that 1.0 M AKGA reacted with over 99 percent of the hydrazine and MMH within 1 h. Experiments with hydrazine and MMH-contaminated poly(tetrafluoroethylene) were performed. Coupons that had been soaked in hydrazine were apparently not sufficiently permeated because they were equally decontaminated by soaking in AKGA and in a water control, determined by headspace vapor measurements taken after two days. MMH-contaminated coupons were not decontaminated by AKGA and a water control, as determined by measurements taken at intervals over 23 days, suggesting the rate of MMH decontamination is entirely dependent on its diffusion rate irrespective of the surrounding solution (AKGA or water). The pH values of different AKGA solutions were measured, and open beaker screening tests were performed with AKGA and hydrazine, and AKGA and MMH.

Attempts to confirm the PCA and MPCA identities and the presence of trace byproducts in reaction solutions were unsuccessful by the gas chromatography-mass spectrometry conditions employed; further work will be required to make mass spectral identifications. Fourier transform infrared spectra were obtained from reaction residues and compared to commercially obtained PCA; MPCA was not available commercially. Corrosion rates obtained for selected alloys used in aerospace applications were in low $\mu$in/yr ranges.

Because the reaction of AKGA with hydrazine and MMH is rapid and complete when a large stoichiometric excess of AKGA is used and the products are relatively benign, it is recommended that AKGA be evaluated as a spill control media at WSTF.

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# Tables

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# Abbreviations

AKGA    Alpha-Ketoglutaric Acid
DAD     Diode Array Detection
DI      Deionized (water)
FTIR    Fourier Transform Infrared
GC-MS   Gas Chromatography-Mass Spectrometry
HPLC    High Performance Liquid Chromatography
ICP-MS  Inductively Coupled Plasma Mass Spectrometry
KSC     Kennedy Space Center
LC      Liquid Chromatography
M       Mole, Molar
MMH     Monomethylhydrazine
MPCA    l-methyl-1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic Acid
NESC    NASA Engineering and Safety Center
NMHU    New Mexico Highlands University
PCA     1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic Acid
PPE     Personal Protective Equipment
PTFE    Poly(tetrafluoroethylene)
WJI     WSTF Job Instruction
WSTF    White Sands Test Facility

## 1.0     Introduction

This report presents the results of an investigation and evaluation at NASA White Sands Test Facility (WSTF) of the chemical reactions between alpha-ketoglutaric acid (AKGA) and hydrazine, and AKGA and monomethylhydrazine (MMH).

## 2.0     Objectives

The objectives of this work were to:

- Perform a literature search of AKGA reactions with hydrazine and with MMH
- Perform laboratory work to characterize AKGA reactions with hydrazine and MMH and to evaluate corrosion rates of selected alloys commonly used in aerospace applications with AKGA
- Evaluate hydrazine- and MMH-contaminated soft-goods material decontamination using AKGA
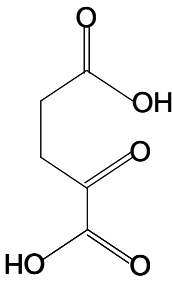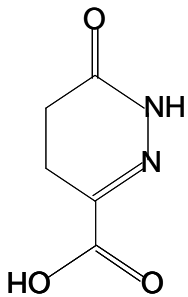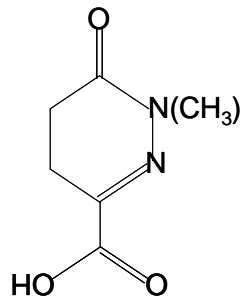
## 3.0     Background

WSTF initially became involved with AKGA in 2008, when the NASA Associate Administrator for the Space Operations Mission Directorate (Mr. William Gerstenmaier) requested an independent assessment of a process being developed at Kennedy Space Center (KSC) for the treatment of hydrazine- and MMH-contaminated hardware, hardware decommissioning, and reduction of hydrazine and MMH waste streams. The KSC process suggested cost and operational benefits to NASA. WSTF and the NASA Engineering and Safety Center (NESC) collaborated in the assessment and prepared a summary report (NESC Report RP-08-115). The NESC team found low technology readiness levels for all aspects of the work performed by KSC and associated work performed by New Mexico Highlands University (NMHU). However, WSTF anticipated that additional work would be forthcoming to further evaluate the potential for AKGA use in space shuttle and hardware decontamination or decommissioning, and therefore proposed the work presented in this report. It is also noteworthy that KSC and NMHU had not published any of their work in the technical literature at the time NESC Report RP-08-115 was prepared, so that report and its conclusions were partly based on verbal communications. It was not until April 2009, during the performance of this project, that KSC published results (Oropeza, Kahn, and Davis 2009a; Oropeza, Kosiba, and Davis 2009b) that clarified many issues the NESC team had, from lack of data, when NESC Report RP-08-115 was prepared.

## 4.0     Chemical Reactions in the Literature

WSTF performed a literature survey to understand the chemistry of AKGA reactions with hydrazine and MMH, and to prepare for laboratory investigations. The necessary background information follows.

Evans and Wiselogle (1945) were apparently the first to describe the reaction of hydrazine sulfate and AKGA (Table 1, a) to form 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (PCA) (Table 1, b). United States Patent 2873294 (Kline 1959) described the preparation of PCA and l-methyl-1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (MPCA) (Table 1, c) from hydrazine hydrate, MMH sulfate, and AKGA. A later report of the reaction of hydrazine hydrate and MMH sulfate with AKGA to form PCA and MPCA, respectively, was found in a 1961 publication (Kline and Cox 1961).

**Table 1**
Structures of AKGA, PCA, and MPCA

| a) alpha-Ketoglutaric acid (AKGA) | b) 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (PCA) | c) l-methyl-1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (MPCA) |
|---|---|---|

Evans and Wiselogle (1945) prepared PCA for the purpose of determining its absorption spectrum, and Kline (1959) and Kline and Cox (1961) prepared and characterized PCA and MPCA for investigations into the preparation of other organic compounds, not for purposes of hydrazine or MMH decontamination. In their work, PCA and MPCA were synthesized, purified, and isolated in laboratory preparatory scale, then characterized. The high concentrations employed by Evans and Wiselogle (PCA), Kline (PCA and MPCA), and Kline and Cox (PCA and MPCA) were not representative of anticipated space shuttle and hardware decontamination or decommissioning conditions, although they did establish that the corresponding reactions of hydrazine and MMH with AKGA to produce the pyridazines do occur. More recently, Kaupp and Schmeyers (2000) examined the solid state reactivity of a hydrazine-hydroquinone complex with AKGA; however, little relevance of this solid state work to aqueous chemistry was apparent.

The reactions of AKGA with hydrazine and MMH are shown in Equations (1) and (2) respectively.

Equation (1). Reaction of AKGA with Hydrazine
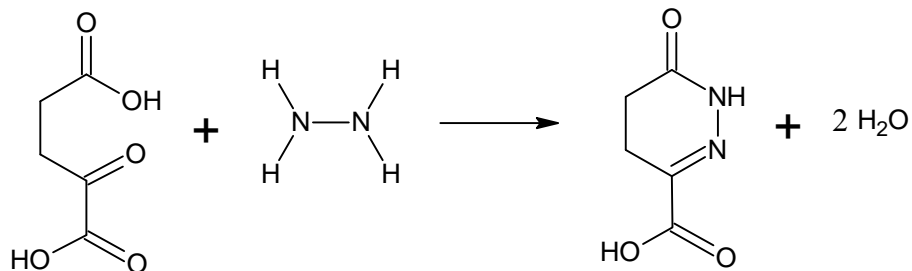
Equation (2). Reaction of AKGA with MMH
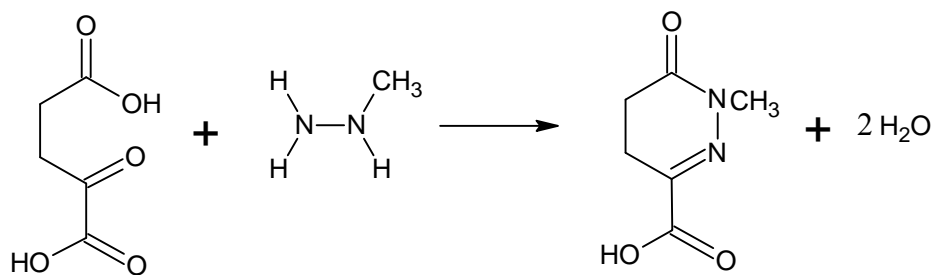


The utility of the AKGA reactions for hydrazine and MMH spill control or neutralization was apparently not recognized in the literature until U.S. Patent 7,074,959 B2, *Methods and Systems for Remediating Hydrazine-Contaminated Equipment and/or Surfaces* (Helvenston et al. 2006), made numerous claims regarding the use of AKGA for hydrazine and MMH decontamination. Reaction and rate data were presented, but under pseudo first-order conditions in which there was a large stoichiometric excess of AKGA with respect to hydrazine or MMH. Under these conditions, the amount of AKGA consumed by the reactions with hydrazine and with MMH did not measurably vary and remained essentially constant. Patent 7,074,959 B2 appeared to be based largely on the work of Kaupp and Schmeyers (2000), which, as stated previously, had little relevance to aqueous AKGA treatability studies with hydrazine and MMH.

The Helvenston et al. U.S. Patent 7,074,959 B2 (2006) described a microbial digestion process for decomposition of PCA and MPCA, which appeared to be based on speculation derived from a single 30-year-old reference in which one pseudomonas species, studied under controlled laboratory conditions, degraded PCA (LaRue and Child 1979). Microbial digestion was one of the options reported for decomposing PCA and MPCA for in-situ spill remediation. No results for the microbial digestion of MPCA were reported by LaRue and Child (1979), nor were found elsewhere in the literature.

The Helvenston et al. (2006) patent also claimed that PCA and MPCA had potential commercial use for producing commercially used chemicals such as glutamic acid or glutamine. PCA is currently commercially available from a number of sources; however, MPCA is not. The commercial use of PCA and MPCA is of some interest because, if its use as product can be demonstrated, this has bearing on its disposition as hazardous waste or as commercial chemical product.

Because AKGA might be used to decontaminate hydrazine and MMH in metallic systems such as spacecraft or spacecraft components, corrosion of metals was of interest in the literature work. Based on molecular structure (carboxylic acid and ketone functional groups), AKGA can be expected to form stable complexes with metal ions; and in combination with its acidity, corrosion of metals should be considered if AKGA is used to decontaminate hardware. Yang et al. (2003) examined the complexation of AKGA with metal ions including aluminum, and referred to other studies on the complexation of copper, cobalt, nickel, zinc, iron, calcium, and strontium with AKGA.

Kennedy Space Center has taken the lead for investigating the use of AKGA for space shuttle and hardware decontamination or decommissioning (NESC 2008). More recently, Oropeza, Kahn, and Davis (2009a) presented baseline characterization of AKGA for hydrazine- or MMH-contaminated component decontamination and Oropeza, Kosiba, and Davis (2009b) reported the use of AKGA as a hydrazine and MMH scrubbing liquor. Although positive results were achieved with scrubbing vapors and decontaminating metallic hardware, AKGA did not permeate into or decontaminate soft-goods materials. Decontamination of soft-goods materials was strictly dependent on the rate of hydrazine or MMH diffusion out of the materials.

A review reported by Greene, Mast, and Maes (2009) indicated that derivatization reactions are not often used for spill control of hydrazine fuels.

## 5.0 Approach

The work by Evans and Wiselogle (1945), Kline (1959), Kline and Cox (1961), Kaupp and Schmeyers (2000), Oropeza, Kahn, and Davis (2009a), and Oropeza, Kosiba, and Davis (2009b) provided an excellent baseline for the work performed at WSTF. In anticipation of the interest in space shuttle and hardware decontamination or decommissioning and the need for a basic understanding of reaction chemistry and characteristics, WSTF performed multiple experiments designed to provide a fundamental understanding of AKGA-hydrazine and AKGA-MMH reaction chemistry not found in the literature. Experiments included pH measurements, reaction characteristics and rates under stoichiometric conditions, concentration effects, open beaker screening tests, and additional vapor measurements on AKGA-treated hydrazine- and MMH-contaminated soft-goods material. Studies were also performed to determine corrosion rates in 1.0 M AKGA of selected alloys commonly used in aerospace applications.

## 6.0 Experimental

The analysis of AKGA, PCA, and MPCA in reaction mixtures, and the reaction conditions, are discussed in this section, followed by a description of the experiments performed. Results of testing and pertinent discussion are presented in Section 7.0.

### 6.1 Analysis of AKGA, PCA, and MPCA in Reaction Mixtures

Concentrations of reactants (hydrazine, MMH, and AKGA) and products (PCA and MPCA) were monitored using liquid chromatography (LC). An LC method with diode array detection (DAD) was developed to monitor AKGA, PCA, and MPCA concentrations. An existing method (WSTF Job Instruction (WJI) CHEMLAB-0268[1]) was used for the determination of hydrazine and MMH.

The LC method for the simultaneous determination of AKGA and PCA or AKGA and MPCA was developed using a Hewlett Packard[®2] High Performance LC (HPLC) 1100 Series instrument with DAD. A wavelength of 210 nm was used for analyte detection. AKGA and PCA/MPCA in reaction solutions were chromatographically separated using a 250 by 4.6 mm Phenomenex Luna[®3] SCX (strong cation exchange) column (Part #00G-4401-E0). The LC mobile phase consisted of a phosphate buffer solution described in WJI-CHEMLAB-0268. Calibration standards were prepared using commercially available AKGA (Fluka[®4] α-Ketoglutaric acid, puriss, ≥ 99.0 %, Cat. No. 75890-500G) and PCA (Alfa Aesar[®5] Item #B20289 1,4,5,6-tetrahydro-6-oxopyridazine-3-carboxylic acid, 97 %). Because no authentic sample of MPCA was commercially available for calibration, the results for MPCA were quantitated using the PCA calibration curve assuming a 1:1 response factor. Based on the mode of detector response at 210 nm, this was a reasonable assumption because both PCA and MPCA contain the α,β-unsaturated carboxylic acid functionality responsible for absorption at the selected wavelength. Calibration curves for AKGA

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[1] In-house document. WSTF Job Instruction. WJI-CHEMLAB-0268.D. *Determination of Propellant Hydrazines in Aqueous Solution Using Hewlett Packard HPLC 1100 Series with Amperometric Detection.* March 17, 2008.

[2] Hewlett Packard[®] is a registered trademark of Hewlett-Packard Company, Palo Alto, California.

[3] Luna[®] is a registered trademark of Phenomenex, Inc., Torrance, California.

[4] Fluka[®] is a registered trademark of Fluka AG, St. Gallen, Switzerland.

[5] Alpha Aesar[®] is a registered trademark of Johnson Matthey Public, Ltd., London, United Kingdom.

and PCA were generated using laboratory-prepared standards. The calibration curves for AKGA and PCA were found to be linear from 1 to 1000 ppm and were used for all AKGA, PCA, and MPCA quantitation.

Hydrazine and MMH concentrations were monitored on a second Hewlett Packard 1100 HPLC. Chromatography was achieved using the same column and mobile phase as used for AKGA and PCA/MPCA. The detector for hydrazine and MMH was a Hewlett Packard 1049A electrochemical detector.

## 6.2    Reaction Conditions

Initial reaction conditions used a 0.00704 M (1028 ppm) AKGA solution and 0.00704 M (225 ppm) hydrazine or 0.00704 M (324 ppm) MMH. The AKGA solution concentration was chosen to be ~ 1000 ppm partially for convenience, because the anticipated corresponding product PCA concentration would remain in solution and also the chromatographic peaks would be well resolved. The hydrazine and MMH concentrations were the corresponding stoichiometric equivalent of the AKGA concentrations.

## 6.3    Stoichiometric Reaction Characteristics and Reaction Rate Determinations

Stoichiometric reactions were performed by combining known amounts of hydrazine or MMH and AKGA in a stirred beaker, then withdrawing two aliquots of each of the reaction mixtures and placing them in autosampler vials (one vial for hydrazine or MMH analysis and a second vial for AKGA and PCA or MCPA analyses). The autosampler vials were loaded into the appropriate LC instrument, and data were collected over similar times by sequential injections over the course of the reactions. The concentrations of hydrazine, MMH, AKGA, PCA, and MPCA were tabulated as a function of time, and data plots and calculations were made accordingly (see Section 7.1 for results and discussion).

## 6.4    pH Values of AKGA Solutions

The pH values of 0.00704 M (1028 ppm), 0.01 M (1461 ppm), 0.10 M (14,610 ppm), 1.0 M (146,100 ppm), and 4.0 M (584,400 ppm) AKGA solutions were measured with a pH electrode. The pH values of these AKGA solutions are shown and discussed in Section 7.2.

## 6.5    Effect of AKGA Concentration

Experiments were performed using 0.10 M (14,610 ppm) and 1.0 M (146,100 ppm) AKGA solutions reacted with 1000 ppm of hydrazine (0.0312 M) and MMH (0.0217 M). To each 50 mL Erlenmeyer flask containing 25.0 mL of the respective AKGA solution was added 24.9 μL hydrazine or 28.6 μL MMH to produce a solution that would have a nominal concentration of 1000 ppm of hydrazine or MMH in the absence of reaction with AKGA. The initial time was recorded and the flasks were rapidly swirled before aliquots were withdrawn and crimped into autosampler vials for hydrazine or MMH analysis by LC. Results for hydrazine and MMH are given in Section 7.3.

## 6.6    Test 15 Open Beaker Screening Test

To determine if a violent and potentially dangerous reaction would occur if solid AKGA was combined with undiluted hydrazine or MMH, a NASA Standard 6001 screening (beaker) test was performed with AKGA and hydrazine, and AKGA and MMH. In accordance with NASA-STD-(I)-6001A Test 15 (2008) (Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia), hydrazine or MMH in 10 mL aliquots were added to

0.25 g of crystalline AKGA in an open beaker, and observations were recorded over a 2-h period. Results are discussed in Section 7.4.

## 6.7  Spectral Characterization of Reaction Products

AKGA-hydrazine and AKGA-MMH reaction products were analyzed by gas chromatography-mass spectrometry (GC-MS) and by Fourier transform infrared (FTIR) spectroscopy to identify reaction products. Prior to FTIR analysis, stoichiometric reaction mixtures were evaporated to dryness, then the residues were compressed in a diamond anvil cell. Results are given in Section 7.5.

## 6.8  PTFE Coupon Decontamination Evaluation and Vapor Measurements

Experiments were performed to evaluate the efficacy of AKGA solutions to decontaminate hydrazine- or MMH-contaminated poly(tetrafluoroethylene) (PTFE) coupons. The PTFE coupons, having a surface area of 25 cm$^2$, were first weighed then immersed in hydrazine or MMH in 40 mL amber glass vials. After 48 days immersion in hydrazine and 69 days immersion in MMH, the coupons were removed, rinsed briefly with water, and patted dry. They were then re-weighed to determine the mass of absorbed hydrazine or MMH. One set of hydrazine-contaminated coupons and one set of MMH-contaminated coupons were then immersed in a 1.0 M AKGA solution and the others in controls of deionized (DI) water. The coupons were removed from the 1.0 M AKGA solution and the DI water at 1, 2, 9, and 23 day intervals, then placed in a headspace analysis container for vapor measurements using a Dräger[®1] PAC III[®2] hydrazine vapor monitor. The headspace analysis container, which has an internal volume of approximately 40 mL, was slip-fitted to the Dräger sensor head for vapor measurements. If measurable amounts of MMH or hydrazine were observed, the coupons were returned to their respective solutions, and vapor measurements were repeated after specified time intervals. Results of the PTFE decontamination studies are discussed in Section 7.6.

Figures 1 and 2 show the headspace analysis container and Dräger PAC III hydrazine vapor monitor side-by-side and slip-fitted together. The apparatus is a valuable tool for determining offgassed hydrazine or MMH in small samples such as coupons. The headspace analysis container was designed and manufactured at WSTF. Being constructed of 304L/304 stainless steel, it is inert to hydrazine and MMH vapors, and is therefore suitable for vapor containment. The tolerances for the slip-fit connection between the Dräger sensor and the headspace analysis container are vapor tight. The design of this slip fit connection is similar to that used by McClure, Mast, and Maes (2009) in the determination of permeability of personal protective equipment (PPE) materials by hydrazine, MMH, and dinitrogen tetroxide. Because the Dräger PAC III hydrazine vapor monitor is programmable to the frequency and number of vapor measurements it records, experiments can be designed to measure the rate and concentration of hydrazine and MMH offgassed from soft-goods materials over a period of days or weeks without having to remove it from the headspace analysis container. This allows the uninterrupted accumulation and measurement of offgassed hydrazine or MMH vapors, which will be required for soft-goods materials decontamination testing, and will be employed in future work.

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[1]  Dräger® is a registered trademark of Dragerwerk AG, Lubeck, Fed. Rep. Germany.
[2]  PAC III® is a registered trademark of National Draeger, Inc., Pittsburgh, Pennsylvania

**Figure 1**
Headspace Analysis Container and Dräger PAC III Hydrazine Vapor Monitor

**Figure 2**
Headspace Analysis Container Fitted to Dräger PAC III Hydrazine Vapor Monitor

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### 6.9 Corrosion of Selected Alloys in 1.0 M AKGA

The corrosivity of 1.0 M AKGA was studied by immersing selected alloys commonly used in aerospace applications. The alloys were stainless steel (SS) 304, SS 316, 17-4, MP35, Inconel[1] 718, and Ti 6-4. Except for SS 304, which were small coupons, the only samples of these alloys that were readily available and traceable in composition were cylindrical electrodes. All samples were resurfaced prior to immersion to ensure clean, fresh surfaces. Up to three samples of each alloy, having surface areas of ~ 2.5 to 5.5 cm$^2$, were completely immersed in 1.0 M AKGA, with one from each type immersed in DI water as a control. The volume of AKGA in each alloy test was sufficient to immerse the entire surface but was kept to a minimum to assure maximum posttest detection of dissolved metals in solution. After 35 days, aliquots of each immersion solution were analyzed for alloy constituents by inductively coupled plasma mass spectrometry (ICP-MS). These data were used to calculate corrosion rates in microinches per year (µin/yr). The corrosion rates of these alloys in 1.0 M AKGA are discussed in Section 7.7.

# 7.0 Results and Discussion

NESC Report RP-08-115 acknowledged the relative insolubility of PCA compared to MPCA in AKGA solutions. Because the goal of the initial experiments was to develop analytical methods for the determination of AKGA, PCA, and MPCA and to characterize the reactions, concentrations of reactants were selected so as not to experience PCA precipitation (Oropeza, Kahn, and Davis 2009a; Oropeza, Kosiba, and Davis 2009b) and to lie within the analytical range of the HPLC instruments. Initial experimentation with PCA and water indicated that approximately 0.1 percent (1000 ppm) PCA would remain in solution at room temperature, although mild heating (hot water bath) was required for initial dissolution.

### 7.1 Stoichiometric Reaction Characteristics and Reaction Rate Determinations

Figure 3 shows a typical reaction of AKGA and hydrazine and the simultaneous formation of PCA under stoichiometric conditions, and Figure 4 shows a reaction rate plot using the reciprocal of AKGA and hydrazine reactant concentrations plotted versus time. Figure 5 shows a typical reaction of AKGA and MMH and the simultaneous formation of MPCA under stoichiometric conditions, and Figure 6 shows a reaction rate plot using the reciprocal of AKGA and MMH reactant concentrations plotted versus time. These results correspond well to the balanced reactions (see Equations 1 and 2), and show that for every molar equivalent decrease in either AKGA or hydrazine, and AKGA or MMH, there is a corresponding increase in the molar equivalent of PCA and MPCA, respectively. These reaction rates increase with AKGA concentration, as discussed in Section 7.3. Stoichiometric concentrations would not be employed for decontamination purposes, but were necessary to determine the basic chemical reaction characteristics and the rate constant for the reaction.

A linear plot of the reciprocal of reactant concentration versus time is characteristic of a second order rate with respect to reactants, and the slope of the line is the reaction rate constant in units of 1/M·s.
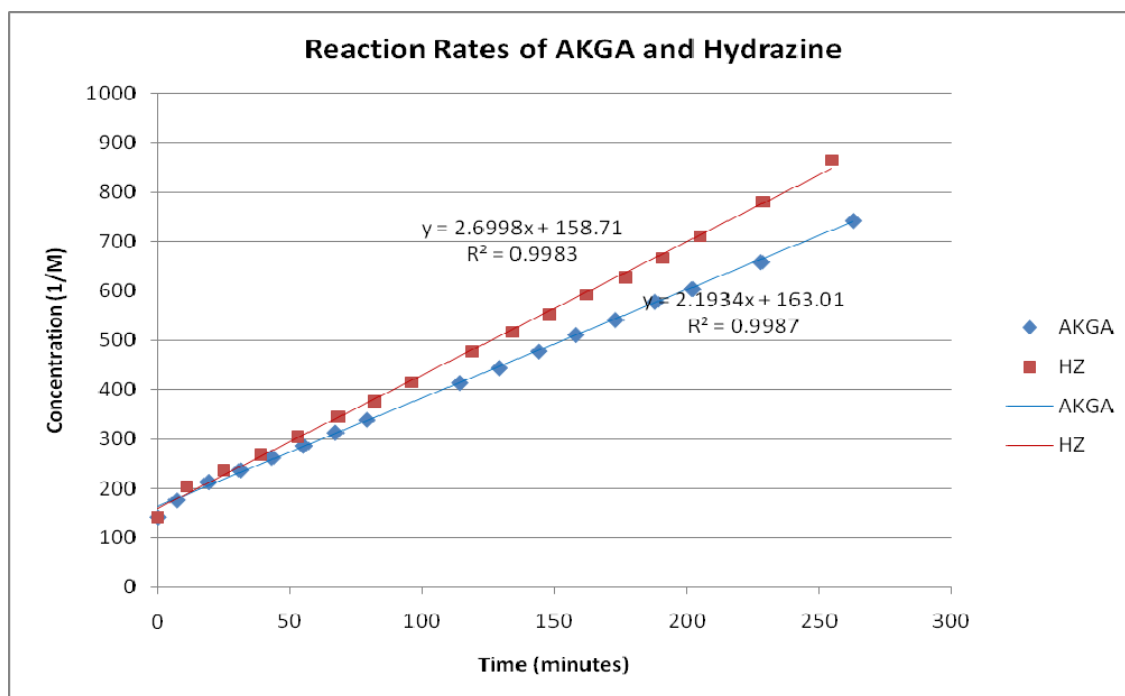
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[1] Inconel® is a registered trademark of Inco Alloys International, Inc., Huntington, West Virginia.
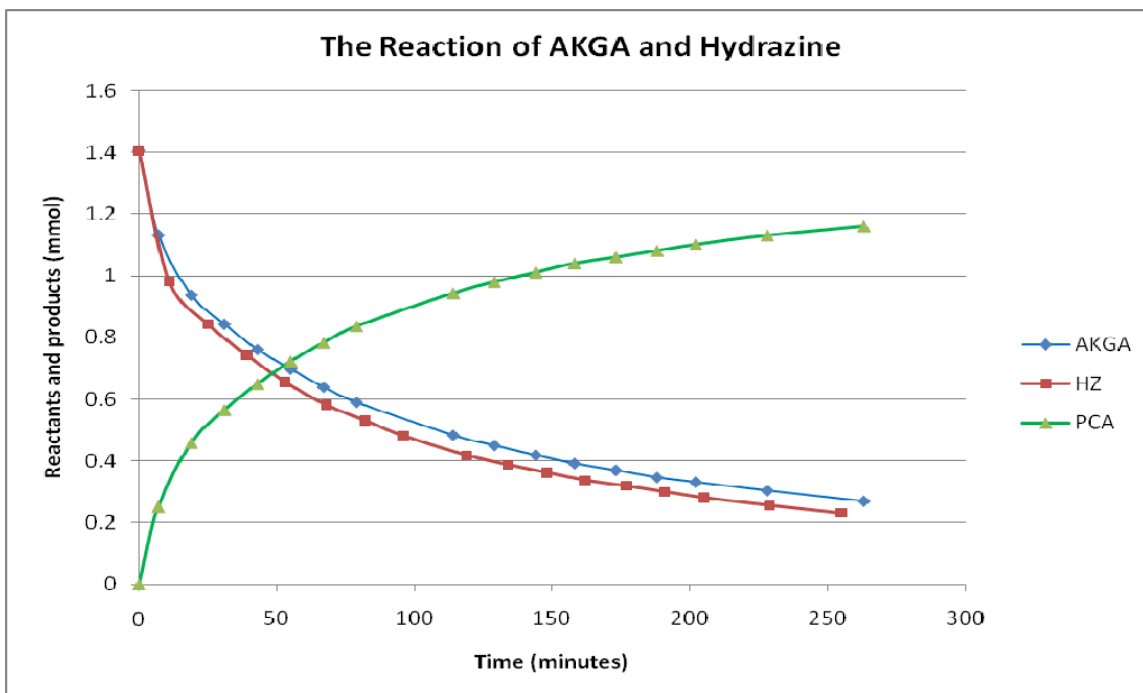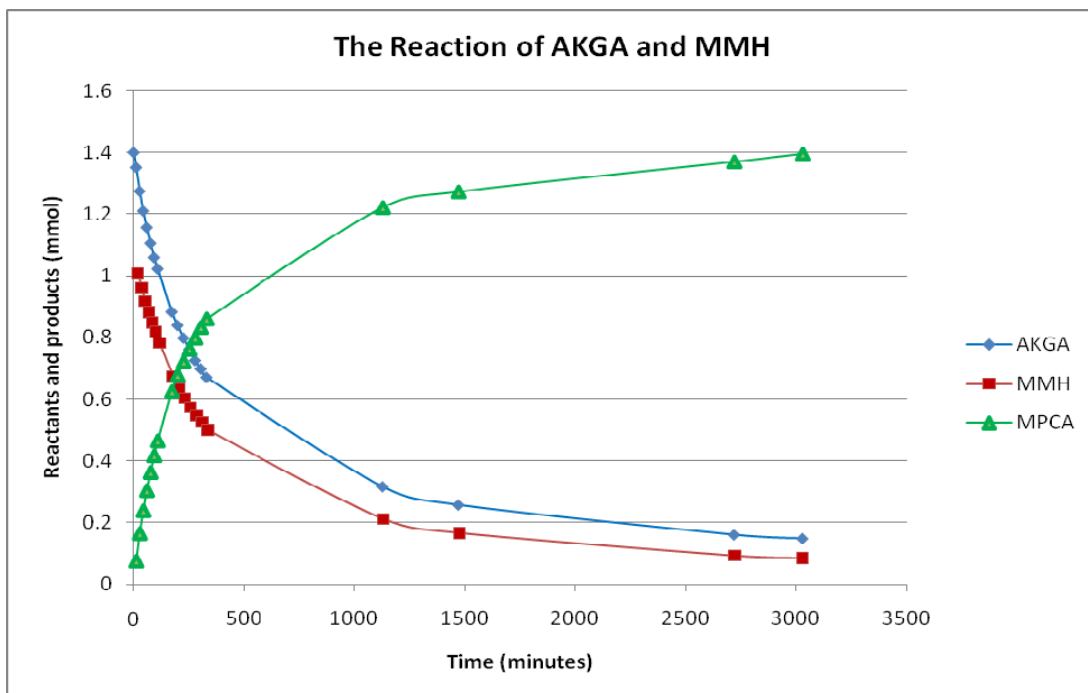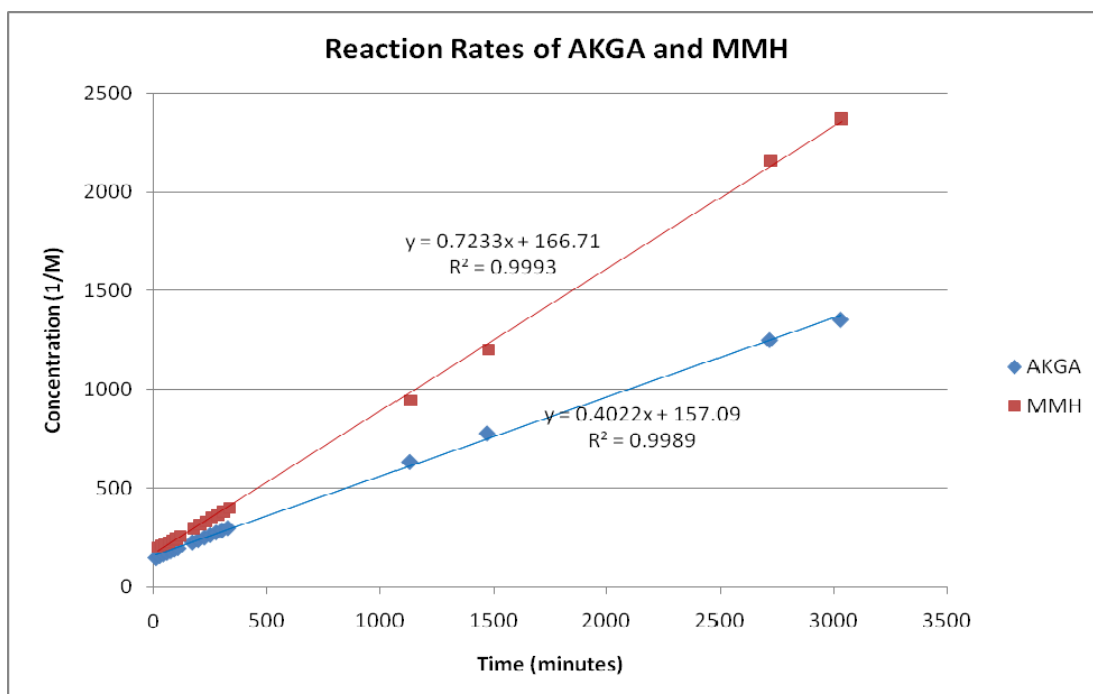
**Figure 3**
The Reaction of AKGA and Hydrazine



**Figure 4**
Reaction Rates of AKGA and Hydrazine

**Figure 5**
The Reaction of AKGA and MMH



**Figure 6**
Reaction Rates of AKGA and MMH

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Figures 4 and 6 use the same AKGA and hydrazine or AKGA and MMH data shown in Figures 3 and 5, respectively, but show reaction rate plots using the reciprocal of AKGA and reactant concentrations plotted versus time. The plots are linear for all reactants, which indicate the reaction of AKGA with hydrazine and with MMH are second order. From Figure 4, the rate constant for hydrazine was 2.6998/M s and the rate constant for AKGA was 2.1934/M s. From Figure 6, the rate constant for MMH was 0.7233/M s and the rate constant for AKGA was 0.4022/M s. The rate constants for AKGA and hydrazine and for AKGA and MMH ideally should be identical for a second order reaction; typically, rate constants are determined under more exacting experimental conditions and using the mean of multiple data points. In this case, only a single determination of the rate constants was made for each reaction; replicates would be required to gather data that could be treated statistically. Sources of error are typically experimental, and include deviation of determined concentrations from their true values and the times at which the values were obtained.

Results of AKGA, hydrazine, and MMH reactions performed in studies reported by Oropeza, Kahn, and Davis (2009a) and Oropeza, Kosiba, and Davis (2009b) were obtained under pseudo first order conditions, in which AKGA was present in such excess that there was no appreciable change in its concentration as the reactions proceeded. A large excess of AKGA is preferred for hydrazine and MMH decontamination purposes, however, because the excess provides assurance that there is sufficient AKGA present to completely consume the hydrazine or MMH. Also, excess AKGA solutions can be reused because their concentrations remain relatively constant until bulk concentration depletion occurs; there is a faster reaction rate than under stoichiometric conditions; and more complete reactions occur because higher AKGA concentrations drive the chemical equilibrium between AKGA and hydrazine or MMH to favor the product PCA or MPCA, respectively.

## 7.2    pH Values of AKGA Solutions

Table 2 shows the pH values of various AKGA solutions. Increasing concentrations of AKGA yield lower pH values. AKGA is a fairly strong organic acid. For comparison, the pH of 1.0 M AKGA is 1.6, and the pH of 1.0 M acetic acid is 2.4. Because pH is a logarithmic function, AKGA is a considerably stronger acid than acetic acid. The acidity of AKGA solutions must be factored into safe handling procedures as well as containment. The appropriate PPE must be worn for protection against organic acid exposure. Corrosive solutions can corrode or dissolve flesh, metal, and other materials. The corrosivity of AKGA to hardware being decontaminated must also be considered if hardware integrity is to be maintained and if AKGA is damaging to metals. Many aerospace soft-goods materials used for hydrazine and MMH service, including PTFE, are inert to acids in the range of the AKGA solutions tested; however, soft goods are normally removed and replaced during component and hardware refurbishment. For decontamination and decommissioning purposes, the users should ensure that residual AKGA is removed, to eliminate potential hazards to personnel and hardware integrity issues associated with residual acid.

**Table 2**
pH Values of Various AKGA Solutions

| AKGA Concentration (M) | pH |
|---|---|
| 0.00704 | 2.4 |
| 0.010 | 2.3 |
| 0.10 | 1.7 |
| 1.0 | 1.6 |
| 4.0 | 1.2 |

## 7.3    Effect of AKGA Concentration

Figures 7 and 8 illustrate reactions of 1000 ppm hydrazine and MMH with two different
AKGA concentrations (0.1 M AKGA (14,610 ppm) and 1.0 M AKGA (146,100 ppm)) as a function of
time. The concentration dependence of AKGA is clearly seen by the faster reaction rates at the higher
AKGA concentrations. The hydrazine concentration remaining in 0.1 M AKGA solution after 55 min.
was 2.1 ppm (99.79 percent reacted); after 97 min. it was 0.016 ppm (99.999 percent reacted). The
hydrazine concentration remaining in 1.0 M AKGA solution after 40 min. was 0.6 ppm (99.94 percent
reacted); after 96 min. it was 0.015 ppm (99.999 percent reacted). The MMH concentration remaining in
0.1 M AKGA solution after 53 min. was 190 ppm (81 percent reacted); after 96 min. it was 69 ppm
(93.1 percent reacted). The MMH concentration remaining in 1.0 M AKGA solution after 39 min. was
0.25 ppm (99.975 percent reacted); after 82 min. it was 0.0084 ppm (99.999 percent reacted). These data
indicate the hydrazine and MMH reactions do not go to completion instantaneously at either
AKGA concentration, but higher concentrations of AKGA yield faster and more complete reactions.
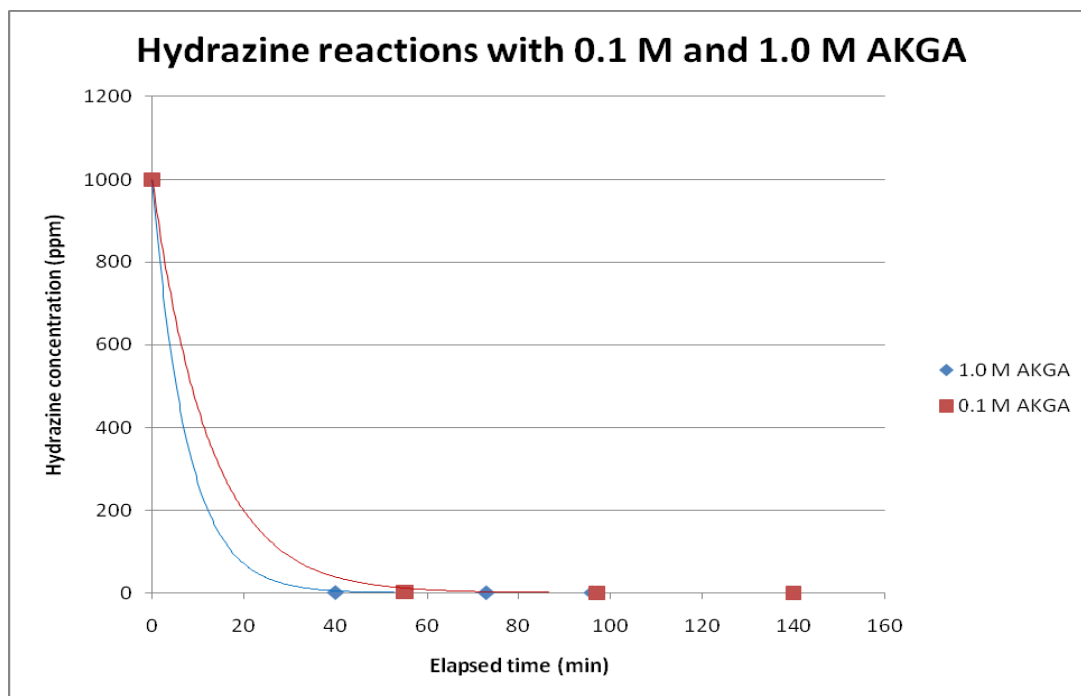


**Figure 7**
Hydrazine Reactions with 0.1 M and 1.0 M AKGA
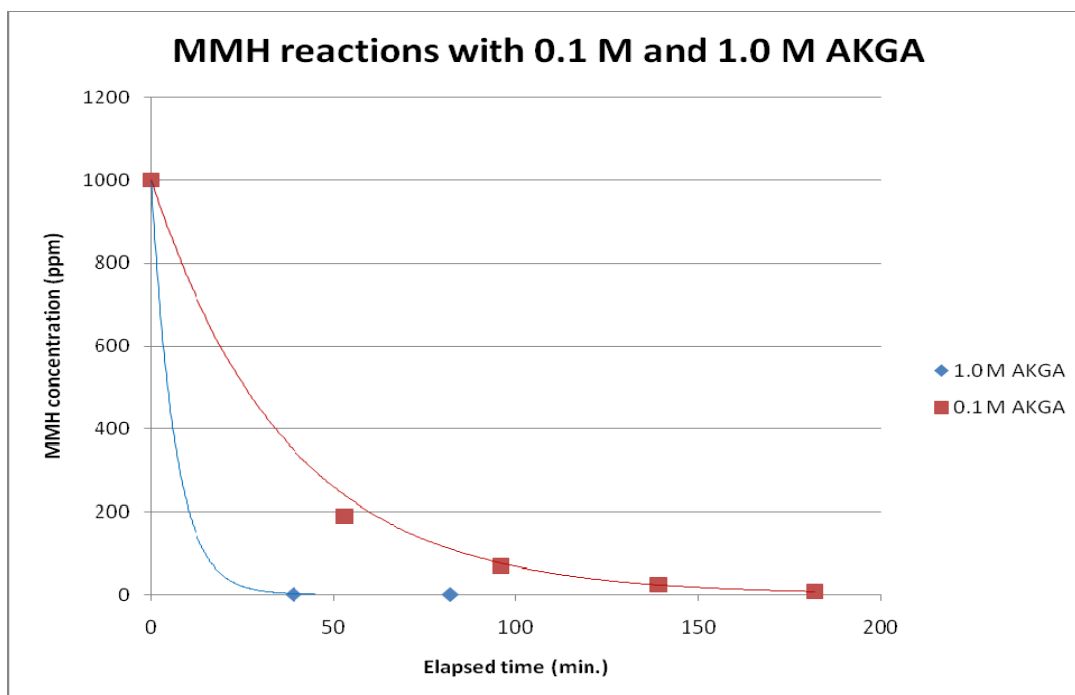
**Figure 8**
MMH Reactions with 0.1 M and 1.0 M AKGA

## 7.4    Test 15 Open Beaker Screening Test

A screening (open beaker) test is a NASA standard test performed with a small amount of material and fluid to screen materials and aerospace fluids for gross reactivity (NASA-STD-(I)-6001A Test 15). This test was performed to determine if a violent and potentially dangerous reaction would occur if solid AKGA was combined with undiluted hydrazine or MMH. AKGA is a white crystalline material. At the beginning of addition of hydrazine to AKGA in a beaker, there was an apparent rapid evolution of gases, observed as smoke or steam wisps, which stopped before 10 mL of hydrazine was added. After the hydrazine addition was complete, the beaker was slightly warm to the touch with a gloved hand. The AKGA dissolved in the hydrazine within 10 min. According to Equation 1, AKGA reacts with hydrazine to produce PCA and water. The reaction is exothermic, and it is possible the apparent evolution of gases was either heated water (steam) or hydrazine vapors evolving from the hot reaction mixture reacting with carbon dioxide in air. AKGA dissolved in MMH within 30 min. of immersion, and the MMH became light yellow within 5 min. of the immersion. No apparent change in temperature was evident to the touch of the beaker with a gloved hand. Oropeza, Kahn, and Davis (2009a) observed spattering and emission of hydrazine vapors from AKGA neutralizing solution upon contact with anhydrous hydrazine and suggested it is possible for a high temperature "hot spot" to occur upon addition of hydrazine to AKGA solution, allowing hydrazine release to the atmosphere.

These observations indicate that, at least with hydrazine, precautions should be taken to avoid contact of solid and probably high concentrations of aqueous AKGA with undiluted or inadequately diluted fuel. Producing heat without a sufficient heat-sink and with evolving vapors is not desirable under any conditions, as airborne contamination is created; and in cavities, tubing, hoses, or tanks, localized heating and pressure buildup could occur with potentially hazardous consequences. Further work with MMH would be required to determine if similar hazards exist.

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## 7.5 Spectral Characterization of Reaction Products

Attempts to identify the components in AKGA-hydrazine and AKGA-MMH reaction mixtures by GC-MS were unsuccessful; it is speculated that the high molecular weight non-volatile products, PCA and MPCA, are not amenable to GC-MS determinations under the conditions employed. The FTIR spectroscopy gave the only data that could be used for identification. Spectral overlays are shown in Figures 9 and 10.

The spectral overlays shown in Figure 9 show the residue from a stoichiometric AKGA-hydrazine reaction and commercially obtained PCA. The residue and the commercially obtained PCA did not give identical spectra, so it cannot be concluded the reaction product is pure PCA. There is a fair but inconclusive spectral overlap suggesting the residue may contain more than one species. A speculative explanation would be that the residue might contain unreacted hydrazine and AKGA, water, and/or intermediate reaction products such as hydrazine-AKGA salts, hydrazides, and/or hydrazones.

Similar considerations apply to MPCA (for which a commercially obtainable product was not available) if compared to an AKGA-MMH reaction mixture residue. As PCA was the closest pyridazine available in pure form, a spectral overlay with PCA is shown in Figure 10. There is a fair but inconclusive spectral overlap. Further work with GC-MS will be required to conclusively identify the reaction products. However, Oropeza, Kosiba, and Davis (2009b) definitively identified PCA and MPCA in AKGA-hydrazine and AKGA-MMH reaction mixtures, respectively.
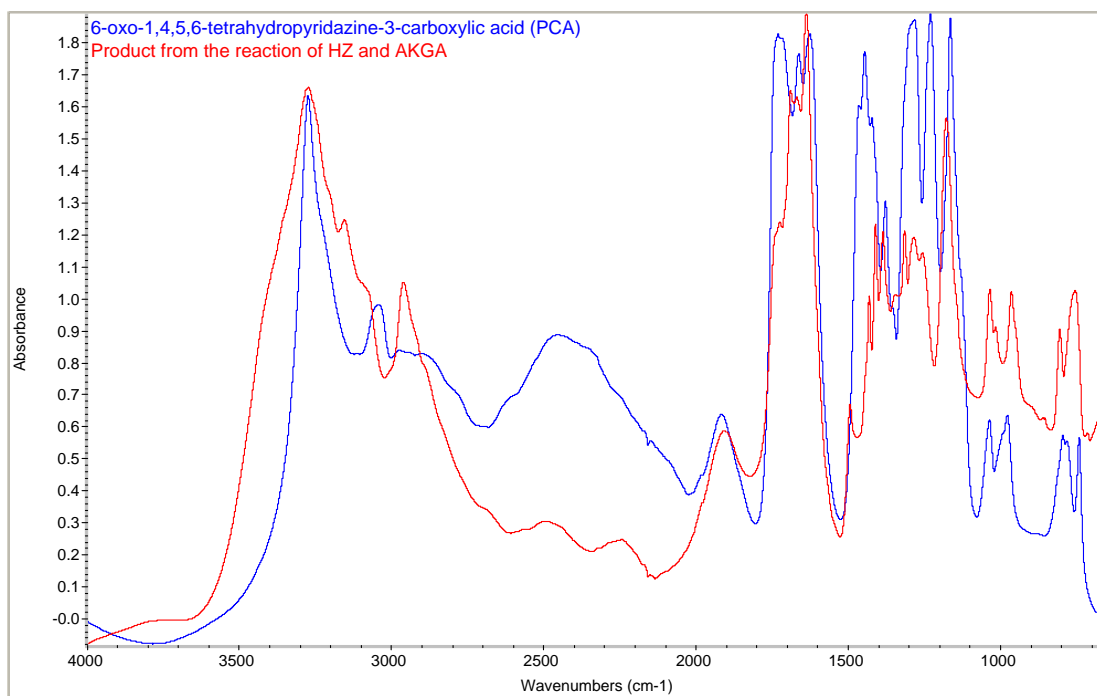


**Figure 9**
FTIR Spectral Overlay of PCA and the Hydrazine-AKGA Reaction Product

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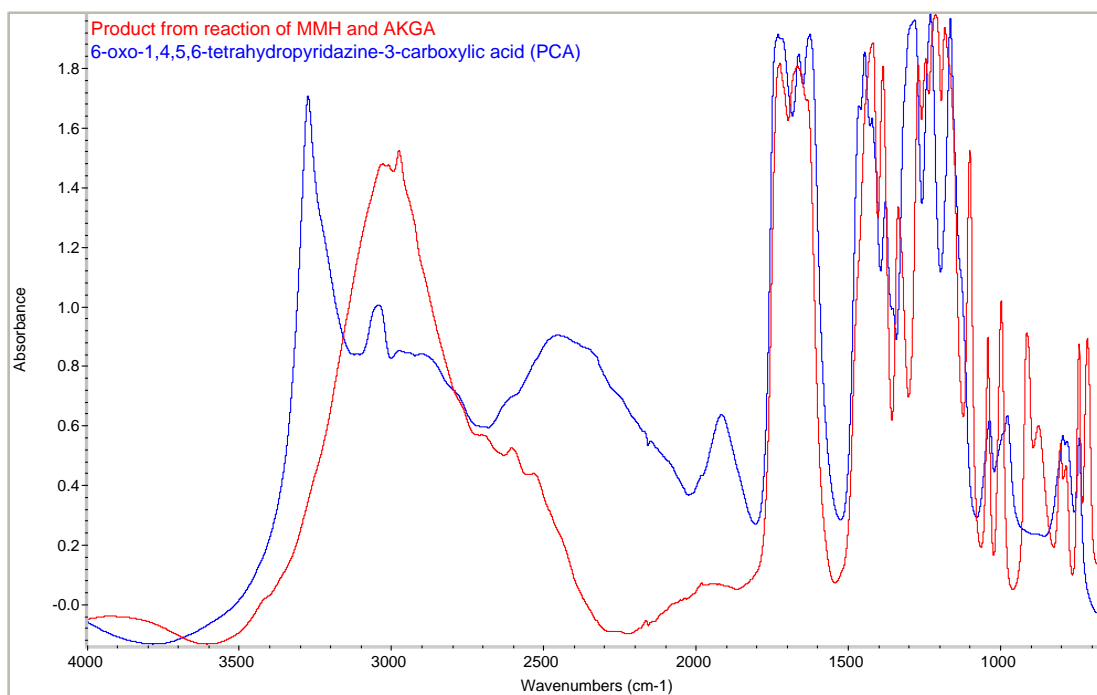
**Figure 10**
FTIR Spectral Overlay of PCA and the MMH-AKGA Reaction Product

## 7.6 PTFE Coupon Decontamination Evaluation and Vapor Measurements

Table 3 shows that PTFE coupons soaked for 48 days in hydrazine absorbed 3.0 to 3.4 mg hydrazine, but that after 2 days of soaking in 1.0 M AKGA or DI water gave no detectable vapor readings in the headspace analysis container fitted with a Dräger PAC III hydrazine vapor monitor. These data suggest that, because hydrazine is a polar molecule, it does not rapidly absorb into PTFE. The increase in coupon weight may indeed have been due to absorbed hydrazine, but it may have been close enough to the surface that it was readily rinsed off by AKGA or water, or that outward diffusion of hydrazine from the PTFE surface was rapid. The results of this experiment are not conclusive, and longer hydrazine exposure times would be required to obtain sufficiently contaminated coupons to evaluate. However, AKGA and water gave similar results for the decontamination tests.

Table 4 shows that coupons soaked for 69 days in MMH absorbed 2.4 mg for the AKGA decontamination test and 5.3 mg for the DI water control test. The PTFE gave measurable vapor readings for both the AKGA- and water-soaked coupons at four intervals over 23 days. The trend in data suggests that MMH is diffusing from the coupons into the respective soak solutions; that lower vapor readings are observed with increasing soak times; and, furthermore, that successively longer coupon residence times in the headspace analysis containers were required to allow sufficient vapor accumulation for the hydrazine vapor monitors to give measureable readings.

**Table 3**
Vapor Data for PTFE soaked in Hydrazine

| Coupon Weight Gain after 48 Days | Decontamination Fluid | Dräger PAC III Readings[a] |
|---|---|---|
| | | 2 days |
| 3.0 mg | 1.0 M AKGA | None detected |
| 3.4 mg | DI water | None detected |

[a]Vapor detection limit = 10 ppb

**Table 4**
Vapor Data for PTFE soaked in MMH

| Coupon Weight Gain after 69 Days | Decontamination fluid | Dräger PAC III Readings[a] | | | |
|---|---|---|---|---|---|
| | | 1 day | 2 days | 9 days | 23 days |
| 2.4 mg | 1.0 M AKGA | 100 ppb (5 min) | 100 ppb (6 min) | 50 ppb (120 min) | 20 ppb (5 h) |
| 5.3 mg | DI water | 100 ppb (8 min) | 100 ppb (15 min) | 20 ppb (120 min) | 10 ppb (5 h) |

[a]Vapor detection limit = 10 ppb

Soft-goods material decontamination is dependent on the rate of diffusion of contaminants out of the material. For chemical decontamination, unless the decontaminating agent can be absorbed and react with the contaminant within the material, its presence serves only to react with the contaminant that diffuses outward. Oropeza, Kahn, and Davis (2009a) established that AKGA did not permeate into soft-goods materials and, therefore, decontamination of soft-goods materials was strictly dependent on the rate of hydrazine or MMH diffusion outward of the material. While hydrazine or MMH diffusing into an AKGA solution form PCA or MPCA, respectively, and hydrazine and MMH diffusion into water form weakly basic hydrazine or MMH solutions, respectively, there is essentially no driving force to increase the rate of diffusion of hydrazine or MMH from the soft-goods material. The water control (water soak) provided a baseline for AKGA decontamination efficacy. The vapors detected from the coupons, soaked in water for the same times as the coupons soaked in MMH, prove conclusively that AKGA offers no advantage over water as a decontaminating medium for soft-goods materials contaminated with MMH. As stated earlier, longer hydrazine exposure times would be required to obtain sufficiently contaminated coupons to evaluate.

### 7.7 Corrosion of Selected Alloys in 1.0 M AKGA

Corrosion rates of the selected alloys are shown in Table 5. While the raw analytical data for the metallic species in solution were on the order of 2 to 10 ppm, which are relatively large concentrations as determined by the sensitive ICP-MS instrument, the reduced data show the corrosion rates were relatively low µin/yr values. However, measurable corrosion rates were obtained for all the alloys tested in 1.0 M AKGA as determined from the concentrations of iron, nickel, chromium, molybdenum, manganese, cobalt, titanium, vanadium, aluminum, and niobium found in the solution after 35 days. These data demonstrate that 1.0 M AKGA is measurably corrosive at varying rates with selected alloys commonly used in aerospace applications. As with any fluid exposure process, corrosion should be considered for applications of AKGA to hardware and to the use of the hardware. For example, corrosion may be acceptable for decommissioned hardware but not for reusable hardware.

The ability of AKGA to complex with transition metal ions, as evidenced by the solution concentrations of iron, nickel, chromium, molybdenum, manganese, cobalt, titanium, vanadium, aluminum, and niobium detected in this work, is consistent with the work of Yang et al. (2003) and their references.

**Table 5**
Corrosion Rates of Selected Alloys in 1.0 M AKGA

| Alloy | Corrosion Rate (µin/yr) | | | | |
|---|---|---|---|---|---|
| | Replicate 1 | Replicate 2 | Replicate 3 | Avg. | Control (DI Water) |
| SS 304 | 1.2 | 1.4 | NA | 1.3 | ND |
| SS 316 | 1.1 | 0.94 | 1.1 | 1.0 | 0.026 |
| MP35N | 0.47 | 0.42 | 0.55 | 0.48 | 0.18 |
| Ti-6Al-4V | 1.8 | 2.3 | 2.0 | 2.0 | ND |
| 17-4 | 1.6 | 2.2 | 2.2 | 2.0 | ND |
| Inconel 718 | 0.25 | 0.044 | 0.16 | 0.15 | ND |

NA = Not applicable; only two replicates
ND = None detected

## 8.0 Conclusions and Recommendations

Relatively little data on the reaction of AKGA with hydrazine or MMH were found in the literature. The work performed prior to 2006 focused primarily on synthesis and characterization of PCA or MPCA to obtain spectral data or to serve as chemical intermediates in the synthesis of other compounds. The Helvenston et al. U.S. Patent 7,074,959 B2 (2006) came forth with numerous claims regarding the utility of AKGA for hydrazine and MMH decontamination, many of which were speculative and not supported by data. WSTF gained considerable insight into the proposed use of AKGA at KSC for hydrazine and MMH waste stream reduction as a result of participation in the team that prepared NESC Report RP-08-115. Anticipating that NASA interest in AKGA would continue in many of the areas KSC was investigating, WSTF proposed to perform the investigations described in this report in order to be prepared for further testing.

The data presented in this report conclude that the reactions of AKGA with hydrazine and MMH produce PCA and MPCA. Reaction rates and completeness of reactions are concentration dependent. AKGA solutions are acidic and must be handled using appropriate safety precautions. When pure hydrazine and

AKGA were combined, the reaction of hydrazine evolved gas and was sufficiently exothermic that the fuel must be diluted for safety reasons. Similar precautions should be applied to MMH although no heating or gas evolution was observed. MMH-contaminated PTFE was not decontaminated by AKGA.

Corrosion rates were obtained for SS 304, SS 316, 17-4, MP35, Inconel 718, and Ti 6-4 in 1.0 M AKGA and were in low μin/yr ranges. However, the low corrosivity may be acceptable for decommissioned hardware but not for reusable hardware. If hardware is reused, the corrosive nature of AKGA must be considered during the refurbishment process to ensure that surface characteristics, compositions, and tolerances are acceptable. Corrosion rates must also be taken into account for the determination of AKGA soak times so as not to corrode hardware beyond acceptable limits.

WSTF recently researched and prepared a review paper on propellant hydrazine spill mitigation (Greene, Mast, and Maes 2009). That paper included various methods for treating hydrazine and MMH spills, including absorption, catalytic decomposition, oxidation, reduction, and derivatization. Absorption on an inert media, then containerization, can be a problem with hydrazine due to its potential to air oxidize and generate sufficient heat to ignite; and absorbed hydrazine or MMH still requires chemical treatment or incineration. Catalytic decomposition, such as use of supported copper oxide, is only suited for hydrazine, and fire can result if the hydrazine is not sufficiently diluted. Dilution and chlorination with hypochlorite was found to be the most widely used method for treatment of hydrazine spills. MMH is typically absorbed and containerized (although hypochlorite oxidation is used to a limited extent). Reductive methods appear most suited to controlled laboratory conditions and after the hydrazine or MMH is collected in a container. Derivatization reactions are not often used for spill control.

AKGA may be well suited to the control of hydrazine and MMH spills because it is relatively non-toxic, does not ignite, does not produce volatile halogenated products, and forms stable products. When a stoichiometric excess of AKGA is used, it favors rapid and complete reactions. It is strongly recommended that AKGA be examined as a spill control agent for hydrazine and MMH at WSTF, and that experiments, both lab-scale and field-scale, be performed to establish optimum fuel dilution and AKGA concentrations and to develop written spill procedures. WSTF Environmental Management should also consider the use of AKGA as a potential means for eliminating the existing hydrazine and MMH waste stream. This was one of the primary reasons for KSC interest in AKGA.

The applicability of AKGA to decontamination and decommissioning of hydrazine- and MMH-contaminated flight hardware is being examined, and KSC has taken the lead on that effort. Tests at WSTF are planned using MMH-contaminated articles removed from the Space Shuttle Fleet Lead Forward Reaction Control System. Results will be reported when that work is completed.

None of the experiments encountered the PCA precipitation problems observed by KSC (Oropeza, Kahn, and Davis 2009a; Oropeza, Kosiba, and Davis 2009b). This was because PCA had not reached its solubility limit in the solutions produced by testing. PCA precipitation must be kept in mind, however, for future work.

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