# steeluniversity

## SECONDARY STEELMAKING SIMULATION

### User Guide

*Version 2.0*

# CONTENTS

# 1 INTRODUCTION AND DISCLAIMER

This document has been prepared as a user guide to the **secondary steelmaking simulation**, available at http://www.steeluniversity.org. The interactive simulation has been designed as an **educational and training tool** for both students of ferrous metallurgy and for steel industry employees.

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Nothing contained in this document shall be deemed to be either any advice of a technical or financial nature to act or not to act in any way.

# 2 WHAT'S NEW IN THIS VERSION?

This simulation was originally released in August 2002 and underwent a significant revision in 2014.

## 2.1 Changes to the User Interface and Design

- The simulation rate can now be changed at any time during the simulation, instead of a fixed value being selected prior to the start. This allows you to slow the simulation down at critical decision-making points, and speed it at other times. However, the simulation rate automatically defaults to ×8 when equipment is in motion (e.g. BOF tilting, ladle car, crane movement, etc.). It is then restored to the original user-defined value on completion. The rate is selected via a drop-down menu near the top-left corner of the screen;

- The Steel Industry Foreman Level has been removed;

- Alloy additions: allows keyboard input via text field;

- The "Restart simulation" option now works more reliably;

- The Control Panel can now be opened by key presses;

- Changes to Ar stir, $O_2$ blowing, EAF power settings, etc. are now included in the event log. This makes it easier to analysis, diagnose and repeat simulation runs;

- At the end of the simulation, you can now view the Composition and Temperature 'flight paths' – i.e. how they changed with time over the duration of the simulation;

- Make your own steel grade. By copying and editing a data file onto your own computer or web-server, you can load your own values into the simulation. Of course we don't guarantee the results of unusual steel compositions, etc.

- The most recent chemical analysis can be accessed by a single key press. A second key press will initiate a new chemical analysis;

- Clashes between the Alert dialog box and Control Panel have been eliminated;

- Crane and ladle car designs have been altered;

- A screen giving the underlying assumptions and simplifications is provided;

- Equipment sounds added.

## 2.2  Technical Changes

- The Engineering steel grade has been changed to AISI 4140;

- The composition of the TiNb ultra-low carbon steel has been changed;

- The number of alloy additions has been reduced, with Cu and Sn components removed from all grades;

- A 100 tonne ladle is specified for grades delivered to the bloom and billet casters. Grades going to the slab caster continue to use 250 tonne ladles;

- For the Steel Industry Works Technical level, a change in the required delivery time at the caster can occur;

- The thermochemical model has been improved slightly;

- The recovery rate for Ca has been reduced to 15%.

# 3  INTRODUCTION TO SECONDARY STEELMAKING

Over the past couple of decades, major changes have taken place in steelmaking practice.

Traditional steelmaking involved the direct transfer of liquid steel via a ladle from the Basic Oxygen Steelmaking (BOS) vessel or Electric Arc Furnace (EAF) to the casting bay where the steel was cast into ingots. Only crude composition and temperature control were possible by this route.

In the 1950s the first attempts were made to remove hydrogen by **vacuum degassing**. More recently, vacuum degassers have been used to produce ultra-low carbon (ULC) steels with carbon contents less than 30 ppm (0.003 wt%). There are two main types of degasser: recirculating and non-recirculating. Recirculating systems include the **RH (Ruhrstahl-Heraeus) degasser**, in which the liquid steel is circulated through the unit by an argon lifting gas to lower the apparent density of the steel. In non-recirculating systems, such as the tank degasser, argon is used as a stirring gas.

The methods by which alloy and flux additions are made to trim the steel compositions and/or modify the inclusions has also expanded to include cored-wire feeding, powdered additions, etc. The **CAS-OB** process (Composition Adjustment by Sealed argon bubbling with Oxygen Blowing) provides a convenient way of making alloy additions in an inert environment, thereby improving the steel cleanness and the 'recovery rate' of the added components. The recovery rate is the amount of the added element that actually increases the steel composition rather than being lost to the slag, atmosphere, etc.)

Since many secondary steelmaking processes result in significant changes in temperature, it is very often necessary to reheat the ladle steel between processes and/or before casting. Two methods are commonly used: electrical reheating via a **ladle arc furnace**, and chemical reheating by the injection of oxygen and aluminum (or silicon), which react exothermically to generate heat.

Table 3-1. Summary of different secondary steelmaking processes.

| Process | Degassing | Reheating | Refining |
|---------|-----------|-----------|----------|
| RH degasser | Removal of C, O, H, (plus N if low O and S levels) | By Al+O$_2$ blowing | |
| Tank degasser | Removal of C, O, H, | | |

| | (plus N if low O and S levels) | | |
|---|---|---|---|
| CAS-OB | | By Al+$O_2$ blowing | Alloy additions in inert argon atmosphere |
| Ladle Arc Furnace | | Electrically | |
| Stir station | | | DeS of deoxidised steel by synthetic slag plus strong stirring/mixing |

Nowadays, a range of **secondary steelmaking** facilities is available for three main reasons:

- They permit wider range of steels to tighter and more demanding specifications;

- CC demands much tighter scheduling – secondary steelmaking acts as a buffer between BOS and CC;

- SS can provide financial benefits;

This interactive simulation aims to illustrate some of the key process controls in the secondary steelmaking.

# 4  SIMULATION OBJECTIVES

The aim of the simulation is to take charge of a ladle of molten steel from the Basic Oxygen Furnace (BOF), and deliver it to the **appropriate caster** at the **specified time**, **composition**, **temperature** and **inclusion content**.

You should also aim to **minimise the cost** of the whole operation.

# 5  PLANT LAYOUT AND DESCRIPTION
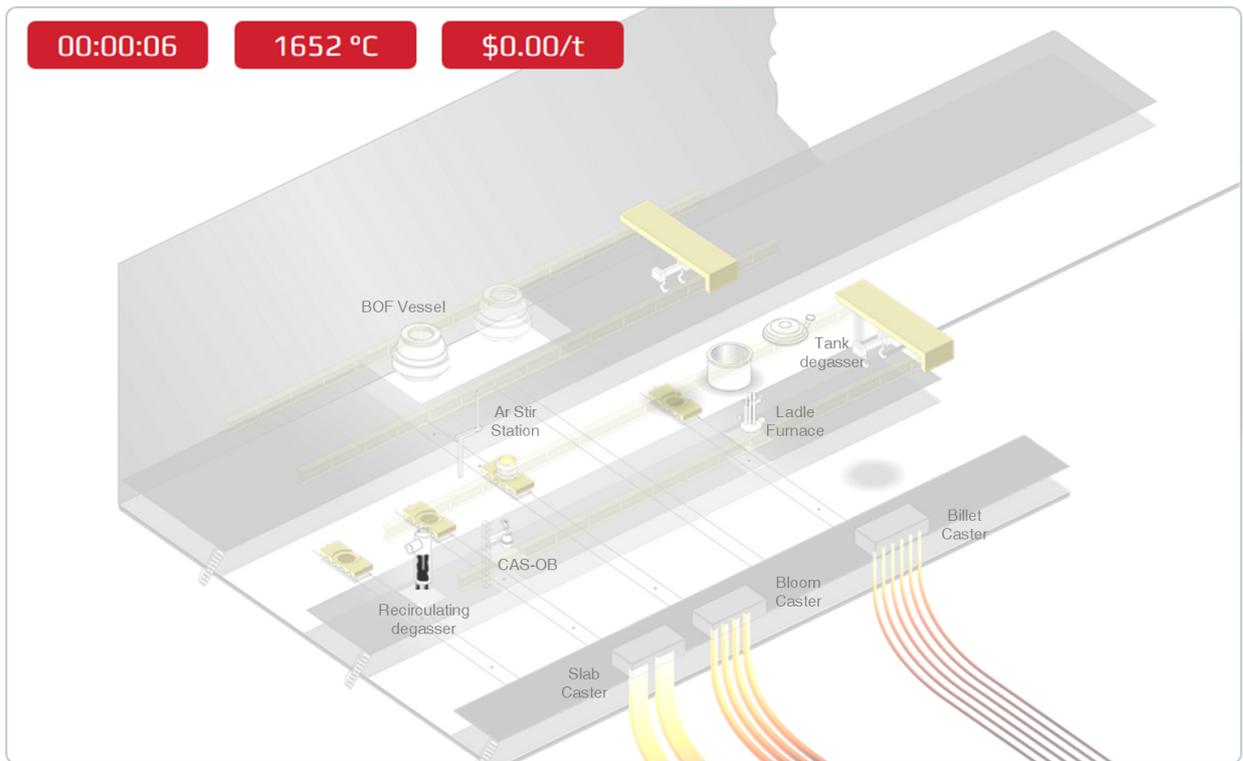
**Figure 5-1**. Screenshot showing the plant layout used in the simulation.

Ladle transporter cars run on a series of parallel tracks running from the BOF to the casting bays. Two cranes, one in each bay, are used to lift the ladle between cars.

The plant in the simulation is laid out as shown in the Figure. At the start of the simulation, the steel is tapped into the ladle from the active **basic oxygen furnace**, or BOF. The other, shaded BOF, is inactive.

The ladle is moved away from the BOF on a **transporter car**. The first stop is the **Ar stir station**, where Ar can be injected into the ladle in order to homogenize the composition and temperature.

The **recirculating degasser**, **CAS-OB** and **ladle arc furnace** are all situated above their own tracks, such that the ladle can be positioned beneath them on a transporter car. A crane is required to lift the ladle between the cars.

The **tank degasser** is accessed by lowering the ladle directly by crane 1.

The three casting machines are situated at the front of the works and the ladle is delivered to them using crane 2. You must ensure that you deliver the ladle to the specified casting unit.

# 6  SIMULATION OPTIONS

## 6.1  User Levels

The simulation has been developed for use by two different user groups:

・University students of metallurgy, materials science and other engineering disciplines, and

・Steel industry works technical.

### 6.1.1  University Student Level

At this level the user will be expected to approach the problem scientifically, using the relevant thermodynamic and kinetic theories to make decisions on the various processing options.

For example, the user will need to calculate the amount of alloy additions to make, degassing times, temperature fluctuations, etc.

At this level there will be no operational problems to overcome and the scheduling will be relatively straightforward.

### 6.1.2  Steel Industry Works Technical Level

At this level you will be expected to approach the problem scientifically. However, you may also experience a range of operational problems that will require you to make adjustments to your planning and use your experience to make rapid decisions.

Typical examples of the operational problems you might encounter are changes to the time required at caster, malfunctions or non-availability of certain steelmaking units, malfunctions or non-availability of ladle transporters, delays in chemical analysis results, and so on.

## 6.2  Simulation Speed

The simulation can be run at a range of different speeds between ×1 and ×32. The rate can be changed at any time during the simulation. However, when plant is in motion (BOF tilting, cranes, ladle cars, etc.) the simulation will automatically default to ×8. Upon completion, the rate will return to the previously set value.

## 6.3  Target Steel Grade

The simulation includes a few different steel grades to illustrate a range of different processing options.

The general-purpose **construction steel grade** is a relatively undemanding grade that requires minimal processing, and is therefore recommended for the **novice user**. Your main job will be to ensure the correct levels of alloy additions.

The **TiNb ultra-low carbon steel** for automotive body parts has a carbon specification of less than 0.0035%C in order to optimize formability. This is around one-tenth of the carbon levels typically present at the end of primary steelmaking. Your main priority therefore is to select and control the appropriate secondary steelmaking unit to efficiently remove the excess carbon.

The **linepipe steel** for gas distribution is a very demanding grade as the combination of high strength and high fracture toughness demands extremely low levels of impurities (S, P, H, O and N) and inclusions. Only more experienced users are recommended to attempt this grade.

The **engineering steel** is a heat-treatable low alloy grade. It contains significant Cr and Mo additions, and also requires a low hydrogen content.

**Table 6-1**. Compositions for the four target steel grades available in the simulation.

| Element | General purpose Construction beam steel | TiNb ULC steel for car bodies | Linepipe steel | Engineering steel |
|---------|-----------------------------------------|-------------------------------|-----------------|-------------------|
| C | 0.1450 | 0.0030 | 0.0700 | 0.4150 |
| Si | 0.2000 | 0.2100 | 0.1800 | 0.4000 |
| Mn | 1.4000 | 0.7500 | 1.0500 | 0.7500 |
| P | <0.0250 | 0.0650 | <0.0120 | 0.0350 |
| S | <0.0200 | <0.0120 | <0.0030 | 0.0350 |
| Cr | <0.1000 | <0.0500 | <0.0600 | 1.0500 |
| Al | 0.0350 | 0.0450 | 0.0300 | 0.0225 |
| B | <0.0005 | 0.0030 | <0.0050 | 0.0050 |
| Ni | <0.1500 | <0.0800 | <0.0500 | 0.3000 |
| Nb | 0.0500 | 0.0200 | 0.0150 | 0.0000 |
| Ti | <0.0100 | 0.0300 | <0.0100 | 0.0000 |
| V | <0.0100 | - | <0.0100 | 0.0100 |
| Mo | <0.0400 | <0.0100 | <0.0100 | 0.2250 |
| As | - | <0.0010 | - | 0.0000 |
| Ca | - | - | <0.0050 | 0.0000 |

| N | <0.0050 | <0.0040 | <0.0045 | 0.0050 |
|---|---|---|---|---|
| H | <0.0005 | <0.0005 | <0.0002 | 0.0002 |
| O | <0.0010 | <0.0005 | <0.0007 | 0.0005 |
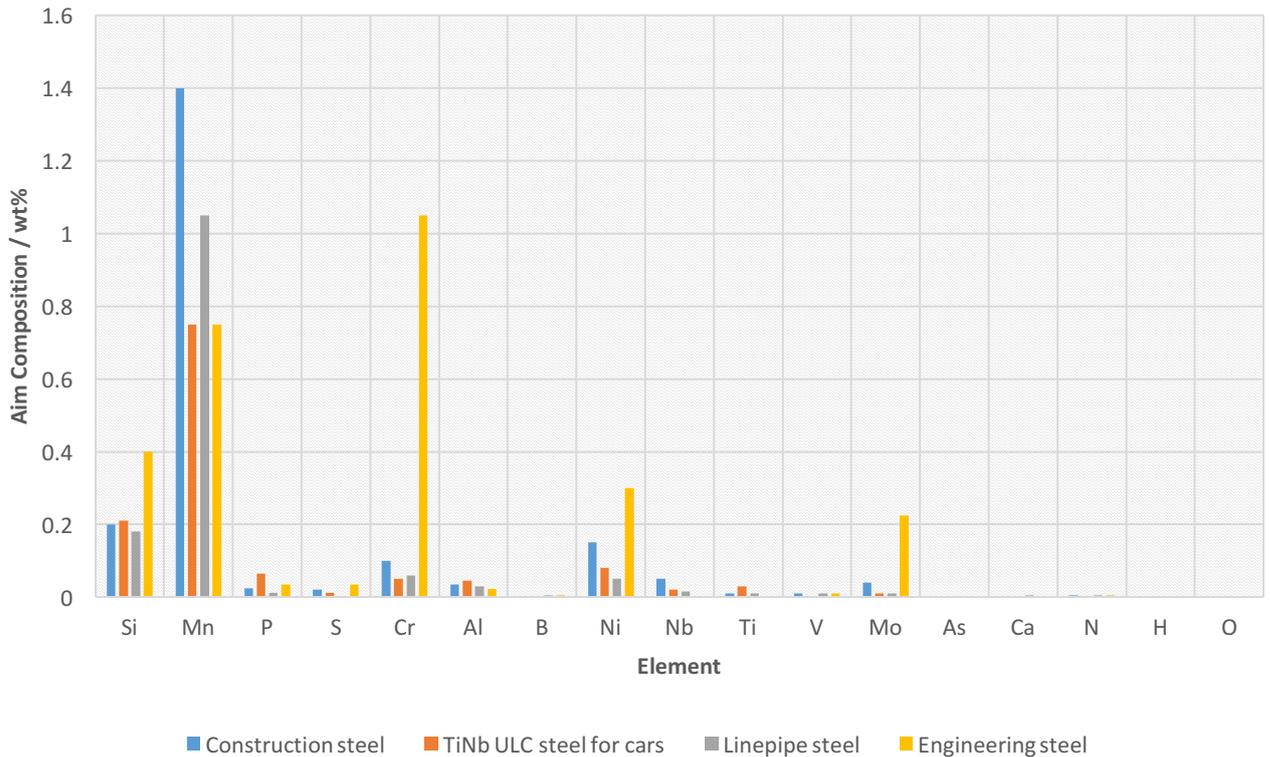


**Figure 6-1**. Graphical comparison of the four target steel grade compositions.

# 7 PLANNING YOUR SCHEDULE

Before you start the simulation, it is important that you plan ahead. The first thing to do is to compare the steel composition and temperature at tap to the aim values required at the caster.

You then need to think how to achieve the aim values within the required time.

**Table 7-1.** Example Tap and Aim Compositions. Carbon, manganese, silicon and aluminum compositions must all be increased, whereas oxygen must be removed.

| Element | Tap / wt% | Aim / wt% | Difference / wt% |
|---|---|---|---|
| C | 0.05 | 0.145 | +0.095 |
| Mn | 0.12 | 1.4 | +1.28 |
| Si | 0 | 0.2 | +0.2 |
| Al | 0 | 0.035 | +0.035 |
| O | 0.04 | 0.001 | -0.039 |
| Temperature | 1650°C | 1535°C | -115°C |

## 7.1 Composition

Some elements will have to be added in order to meet the aim composition. Here are the key questions you will need to answer:

- Which additive(s) can be used to achieve this?

- How much additive (in kg) will be required?

- Will this additive affect other elements too and if so, how much?

- Where and when should you make the addition?

- How will the additions affect cost, temperature and steel cleanness?

For further help in calculating alloy additions, see Section 9.1 "Calculating Alloy Additions".

**Table 7-2**. Compositions and costs of available additives.

| Additive | Composition | Cost per tone |
|---|---|---|
| Recarburiser | 98%C + Fe bal. | $280 |
| High C Ferro-Manganese | 76.5%Mn, 6.7%C, 1%Si, 0.03%S, 0.3%P + Fe bal. | $490 |
| Low C Ferro-Manganese | 81.5%Mn, 0.85%C, 0.5%Si, 0.1%S, 0.25%P + Fe bal. | $840 |
| Ferro-Manganese, high purity | 49%Mn + Fe bal. | $1820 |
| SiMn | 60%Mn, 30%Si, 0.5%C, 0.08%P, 0.08%S + Fe bal. | $560 |

| | | |
|---|---|---|
| Ferro-Silicon 75 | 75%Si, 1.5%Al, 0.15%C, 0.5%Mn, 0.2%Ca + Fe bal. | $770 |
| Ferro-Silicon 75, high purity | 75%Si, 0.06%Al, 0.2%Mn, 0.02%C + Fe bal. | $840 |
| Ferro-Silicon 45 | 45%Si, 2%Al, 0.2%C, 1%Mn, 0.5%Cr + Fe bal. | $630 |
| Aluminum wire | 98%Al + Fe bal. | $2100 |
| Aluminum pebbles | 98%Al + Fe bal. | $1400 |
| Ferro-Boron | 20%B, 3%Si, 0.2%P + Fe bal. | $3780 |
| Ferro-Chrome | 66.5%Cr, 6.4%C + Fe bal. | $1260 |
| Ferro-Molybdenum | 70%Mo + Fe bal. | $16800 |
| Ferro-Niobium | 63%Nb, 2%Al, 2%Si, 2%Ti, 0.2%C, 0.2%S, 0.2%P + Fe bal. | $9800 |
| Ferro-Vanadium | 50%V + Fe bal. | $8400 |
| Ferro-Phosphorus | 26%P, 1.5%Si + Fe bal. | $630 |
| Ferro-Sulphide | 28%S + Fe bal. | $700 |
| Nickel | 99%Ni + Fe bal. | $7000 |
| Titanium | 99%Ti + Fe bal. | $2800 |
| CaSi powder | 50%Ca, 50%Si | $1218 |
| CaSi wire | 50%Ca, 50%Si | $1540 |

**Table 7-3**. Typical recovery rates for elements added in air (e.g. at the BOF or stir station) and under partial vacuum or argon (e.g. in degasser, ladle furnace or CAS-OB).

| Element | Average Recovery Rate when added at degasser, ladle furnace or CAS-OB* | Average Recovery Rate when added at BOF or stir station* |
|---|---|---|
| C | 95% | 66% |
| Mn | 95% | 66% |
| Si | 98% | 69% |

| | | |
|---|---|---|
| S | 80% | 56% |
| P | 98% | 69% |
| Cr | 99% | 69% |
| Al | 90% | 63% |
| B | 100% | 70% |
| Ni | 100% | 70% |
| Nb | 100% | 70% |
| Ti | 90% | 63% |
| V | 100% | 70% |
| Mo | 100% | 70% |
| As | 100% | 70% |
| Ca | 15% | 10% |
| O | 100% | 70% |
| N | 40% | 28% |
| H | 100% | 70% |
| Fe | 100% | 70% |

* Note that these are average values only, and are will vary from batch to batch.

TIP: Recovery rates are higher when additions are made under vacuum (as in the degassers) or a protective Ar environment (ladle furnace, CAS-OB), thereby reducing the amount (and cost) of the addition. **However**, there is a cost associated with using this equipment that must be offset against the higher recovery rates. As a general rule, the more expensive additions, such FeNb, FeMo, etc. will be made under protective environments.

Other elements, such as carbon, oxygen, sulfur, hydrogen, phosphorus and nitrogen may need to be removed in order to meet the aim composition.

- Which process, or sequence of processes is most effective at removing the element of interest?

- What are the main process variables (such as stirring power, slag chemistry and weight, oxygen blowing, etc.) and how do they affect the removal?

- Does the current composition and/or temperature of the steel affect the kinetics, and if so how?

## 7.2 Temperature

To ensure the ladle arrives at the caster at the correct temperature, it is important to be able to calculate the effects of different processes on the ladle temperature.

1. Tapping: the steel temperature will decrease by around 60°C during the tapping process. (Note that this is accelerated in the simulation to save time.)

2. Under normal conditions, such as ladle hold and transport times, the steel cools at around 0.5°C min-1.

3. For most alloy additions, each tonne (1,000 kg) added results in an additional temperature drop of about 6°C.

4. Aluminum de-oxidation is highly exothermic. For every 100 kg of aluminum that reacts[1] with oxygen, expect a 12°C temperature **increase**. Aluminum can also be added with injected oxygen in the recirculating degasser or CAS-OB to achieve **chemical reheating**. Again, expect a 12°C temperature increase for every 100 kg of aluminium that reacts with oxygen.

5. The ladle steel can also be **electrically reheated** in the ladle arc furnace. At full power, the reheating rate is about 3°C min-1.

6. Stirring the ladle by Ar bubbling increases the cooling rate to around 1.5°C min-1.

By carefully calculating the overall time from BOF to caster, the temperature loss due to alloy additions, plus any reheating (electrical or chemical), it should be possible to compute the steel temperature at the caster.

### 7.2.1 Calculation of Liquidus Temperature

It is imperative to prevent the steel bath temperature falling below the liquidus temperature (i.e. the temperature at which the steel starts to solidify). The liquidus temperature, $T_{liq}$, is very dependent on composition and can be calculated from the following equations:

For C < 0.5%:

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[1] Note however that not all of the aluminum added will react with oxygen – you must include the aluminum recovery rate in any calculation.

$$T_{liq} = 1537 - 73.1\%C - 4\%Mn - 14\%Si - 45\%S - 30\%P - 1.5\%Cr - 2.5\%Al$$
$$- 3.5\%Ni - 4\%V - 5\%Mo$$

**7-1**

For C > 0.5%:

$$T_{liq} = 1531 - 61.5\%C - 4\%Mn - 14\%Si - 45\%S - 30\%P - 1.5\%Cr - 2.5\%Al$$
$$- 3.5\%Ni - 4\%V - 5\%Mo$$

**7-2**

# 8  USER INTERFACE

This section describes the basic 'mechanics' of running the simulation (e.g. how to move the ladle, how to make alloy additions, how to control the various pieces of equipments, etc.).

The underlying scientific relationships (chemistry, thermodynamics, reaction kinetics, etc.) that you will need to use in order to calculate alloy amounts, process parameters, etc. are presented in Section 9.

## 8.1  Transporting the Ladle

The ladle is moved around the works by a system of **transporter cars** running on parallel tracks between the BOF and casting 'bays', and a pair of **cranes**, one in each bay. There is no cost penalty associated with any of the ladle transporters.

### 8.1.1  Ladle Cars

Each ladle car is moved along its track automatically when you select a destination in "Go to". The cars stops automatically at set points along each track – there is no need for user intervention.
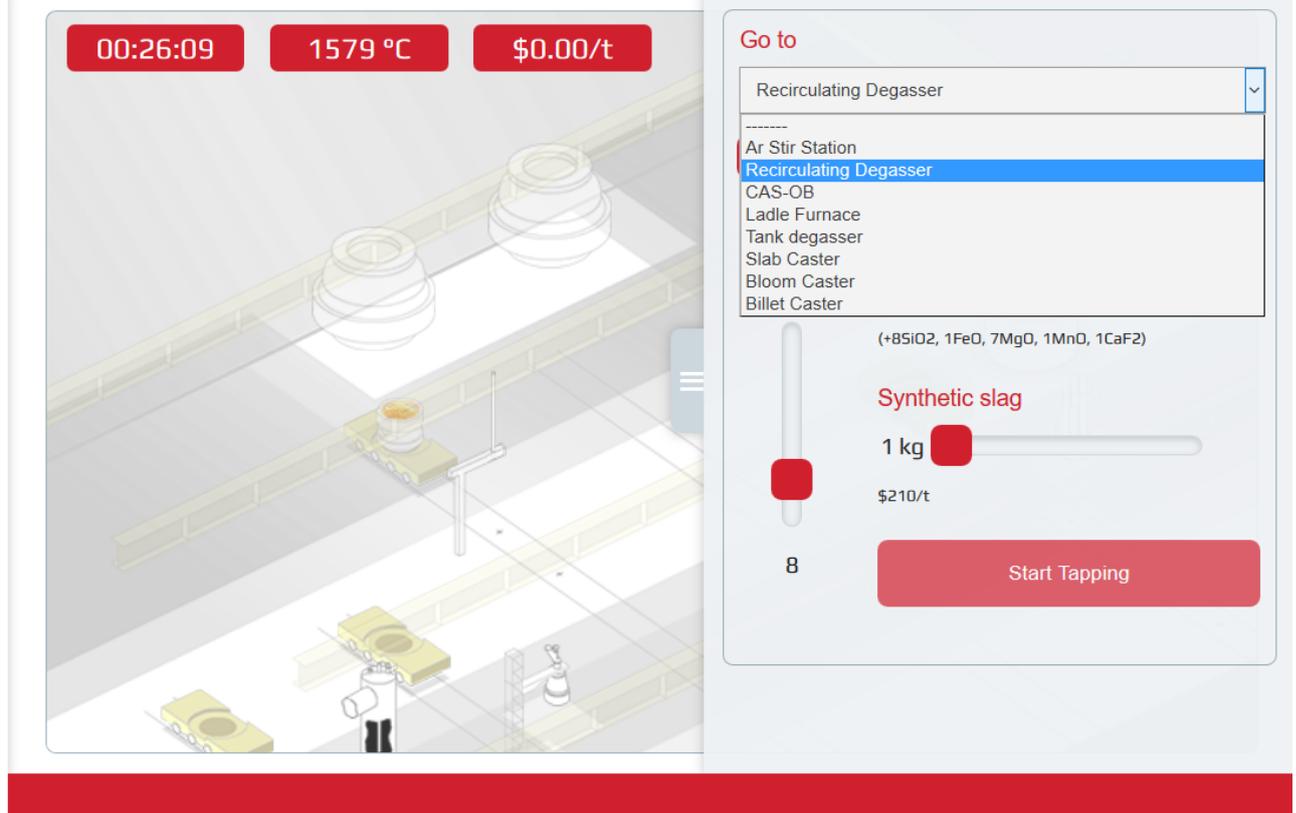
**Figure 8-1:** Screenshot illustrating the "Go to" options.

## 8.2  The Control Panel

Once the simulation begins, you can control the individual pieces of steelmaking plant using the Control Panel. The first step is start the tapping process. You can control the Simulation rate, Slag composition and Synthetic slag. The button Make Additions and Chemical Analysis will be explained in the next sections.
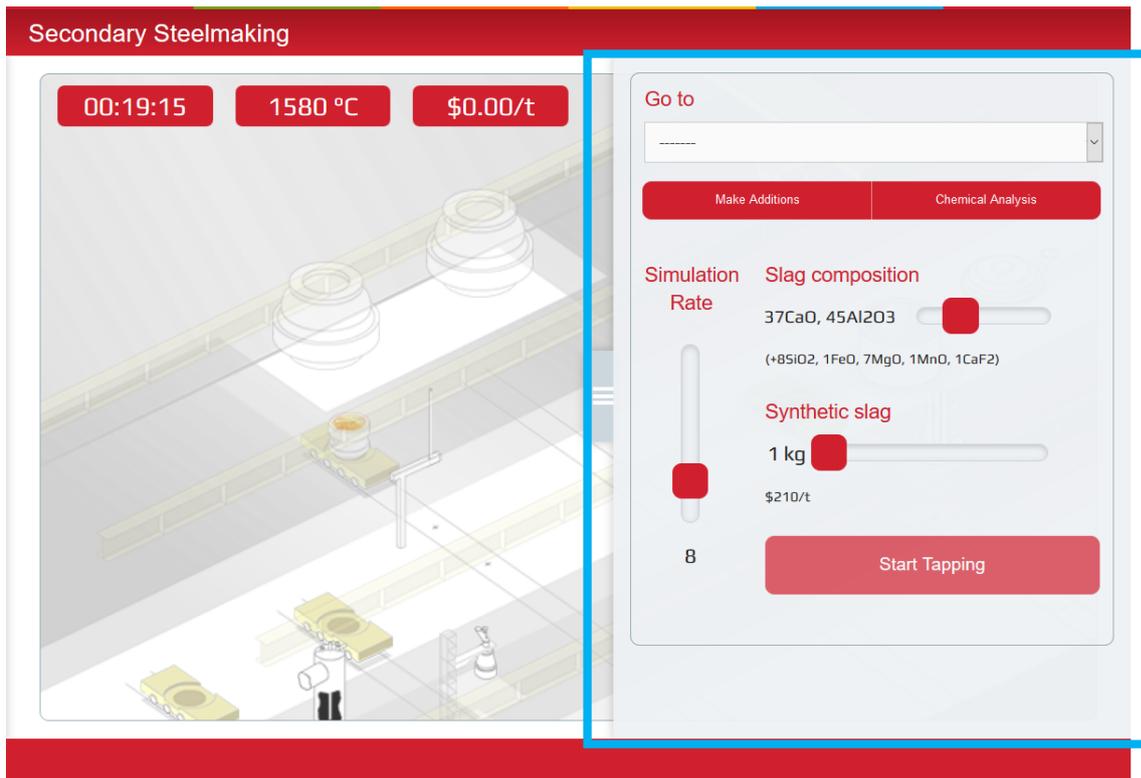
**Figure 8-2:** Screenshot illustrating the Control Panel interface.

### 8.2.1    Make Alloy Additions

A range of different additives can be added to the ladle using the "Make addition" control panel.
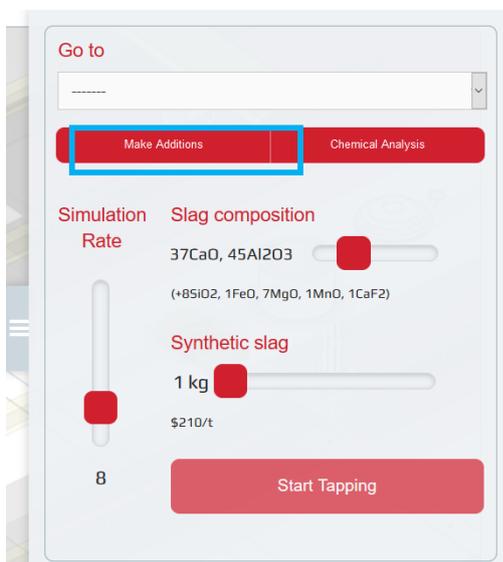


**Figure 8-3**. Button to "Make Additions".

Each individual additive has a slider to control the amount to be added. By default all sliders are initially set to zero. The unit cost of each additive is displayed, together with the calculated cost for the selected amount.

**Figure 8-4**. Screenshot of "Make additions" interface.

Additives are divided into "major" and "micro" categories. Major additives include ferromanganese and ferrosilicon, and can be added in amounts up to 5,000 kg. Micro additives include aluminum, chromium, nickel, ferroniobium, etc. and can be added in amounts up to 500kg.

> **TIP**: Hover the cursor over the addition labels on the left for information about their composition and typical recovery rates.

Click on the **Order** button when you are ready.



**Figure 8-5**. Screenshot illustrating the Order button and information about composition.

Note that that alloy additions made to the ladle **do not** result in instantaneous changes to the steel composition, but take a finite time to dissolve. In the simulation, be sure to allow sufficient time for alloy additions to dissolve by observing the following trends:

- Powders, wires and fine particle additions dissolve faster than coarse pebbles or bars;

- Stirring the ladle (i.e. by argon bubbling) accelerates the dissolution process and is also essential for homogenizing the liquid steel composition;

- Mixing times will increase as the temperature decreases.

You can expect well-stirred powder additions made at higher temperatures to dissolve fastest. Pebbles added at lower temperatures without stirring will take many minutes to dissolve and the ladle steel may not be homogenized by the time it arrives at the casting unit.

### 8.2.2 Ar Stir Station Control Panel

Once the ladle is in position, a dialog box automatically pops up, allowing you to control the Ar flow rate. You can press the power button ⏻ to start the flow of Ar. The costs associated with the Ar Stir Station are as follows:

- $0.60 per N m$^3$ for Ar. (i.e. 1 minute at 1.0 N m$^3$ min$^{-1}$ will cost $0.60);

- $5.70 per minute for lance wear.

Expect the steel cooling rate to increase to ~1.5°C min-1. Click again on the lance to terminate the process.



**Figure 8-6**. Screenshot of control panel of Ar Stir Station.

### 8.2.3 Recirculating Degasser Control Panel

Once the ladle is in position press the power button ⏻ to start. Then you can use the toogle button to blow on and off (off by default) the oxygen. The costs of running the degasser are ~$7.75 per minute, and the steel cooling rate increases to ~1.0°C min$^{-1}$. Click on the degasser again to terminate the process.
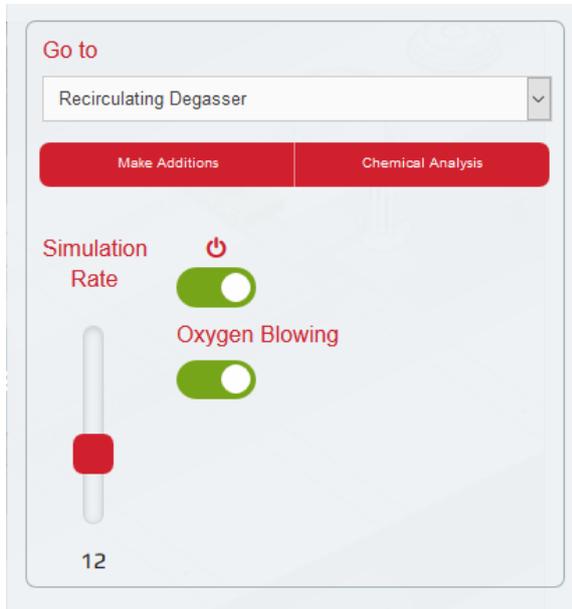


**Figure 8-7**. Screenshot of control panel of Recirculating Degasser.

### 8.2.4 CAS-OB Control Panel

Once the ladle is in position press the power button ⏻ to start. In the control panel, you can control the Ar flow rate by a slider control. The costs associated with the CAS-OB are as follows:

- $30 per minute for wear and other consumables;

- $0.60 per N m$^3$ for Ar. (i.e. 1 minute at 1.0 N m$^3$ min$^{-1}$ will cost $0.60).

Expect the steel cooling rate to increase to ~1.5°C min$^{-1}$.

**Figure 8-8**. Screenshot of control panel of CAS-OB.

### 8.2.5 Ladle Furnace Control Panel

Once the ladle is in position press the power button ⏻ to start. In the control panel, you can control the electric power and Ar flow rate via two slider controls. The costs associated with the ladle furnace are as follows:

- $16.60 per minute for electricity at the maximum power of 20 MW (proportionately lower cost for lower power settings);

- $5.90 per minute for electrode wear at maximum power (again proportionately lower cost for lower power settings);

- $0.60 per N m$^3$ for Ar. (i.e. 1 minute at 1.0 N m$^3$ min$^{-1}$ will cost $0.60).
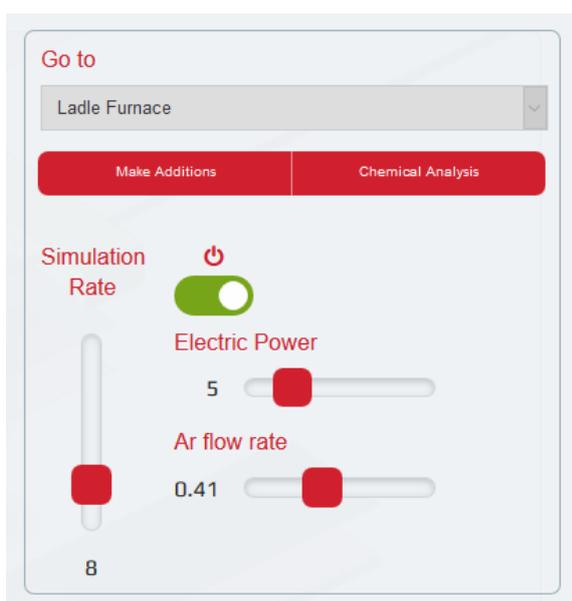
**Figure 8-9**. Screenshot of control panel of Ladle Furnace.

### 8.2.6  Tank Degasser Control Panel

Unlike all the other secondary steelmaking units, which are accessed by ladle car, the ladle must be lowered into the tank degasser directly from crane 1 (this is doing automatically). Once the ladle is in position press the power button ⏻ to start. In the control panel, you can set the desired vacuum level and Ar flow rate via two slider controls. The costs associated with the tank degasser are as follows:

- $10 per minute for vacuum, refractory wear and other consumables;

- $0.60 per N $m^3$ for Ar. (i.e. 1 minute at 1.0 N $m^3$ $min^{-1}$ will cost $0.60).

Expect the steel cooling rate to increase to ~1.0°C $min^{-1}$.
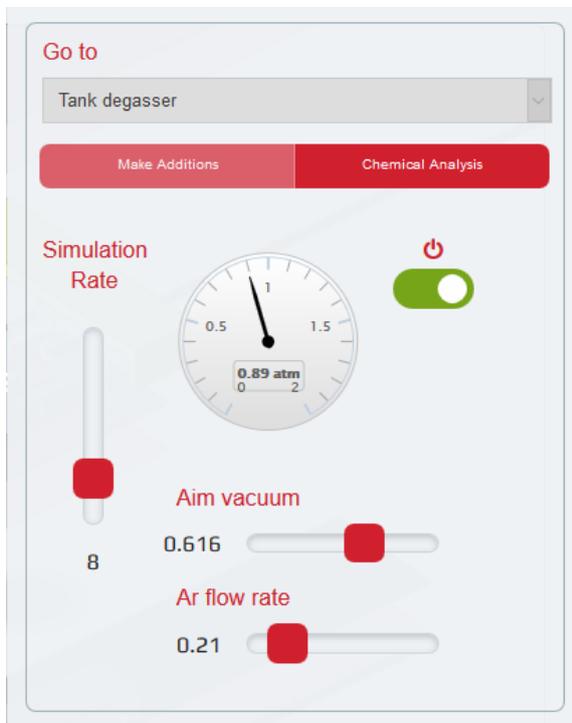


**Figure 8-10**. Screenshot of control panel of Tank Degasser.

### 8.2.7  Request Chemical Analysis

You can view the most recent chemical analysis at any time by pressing "Chemical analysis". There is no cost penalty for this.

Of course the steel chemistry may well have changed since the last analysis was made. To initiate a new analysis, press the **Take new sample** button. The analysis costs $40 and the results take approx 3 simulation minutes to arrive (e.g. about 22 real-world seconds if the simulation rate is set to ×8).

The time at which the sample was taken is displayed near the top of the dialog box. You must always remember that the composition may have changed since the sample was taken.

## 8.3  Simulation Results

As soon as you set down the ladle at any one of the casters, the simulation will end and the results of the run displayed, together with the total operating costs, expressed as $ per tonne.

An example of the summary of results is shown in the image below. The five criteria for success are displayed. Click on the Event Log button to help you analyze your results. Then, you can click on the Composition to see variation in time of composition.



**Figure 8-11**. Screenshot of Summary of results screen.

### 8.3.1   View Event Log

The event log keeps a chronological record of all the major processing steps, including alloy additions. This is useful for keeping track of what you have done so far during the simulation. It is also very useful in helping you analyze your results at the end of the simulation, as the log will often contain clues as to why you passed or failed the different criteria.

# 9   UNDERLYING SCIENTIFIC RELATIONSHIPS

This section presents the key underlying scientific theories and relationships that are required in order to successfully complete the simulation. In no way is it designed to be comprehensive treatments of steelmaking theory and practice – for this, the user is directed to other excellent publications.

## 9.1  Calculating Alloy Additions

Additives are added to the ladle for a variety of reasons

- To adjust the final steel composition;

- To deoxidize the steel by reacting with oxygen and forming oxides that will be absorbed into the slag;

- To modify inclusions present in the steel.

### 9.1.1 Calculating Additions to Achieve Aim Composition

#### 9.1.1.1 Elemental additions

In the simplest case where a pure element is added to the ladle, the amount of additive required, $m_{additive}$ is simply given by:

$$m_{additive} = \frac{\Delta\%X \times ladle\ mass}{100\%} \qquad 9\text{-}1$$

where $\Delta\%X$ is the required increase in $wt\%\ X$ (i.e. $\%X_{aim} - \%X_{current}$)

Example

Suppose a 250,000 kg ladle of steel currently contains 0.01% Ni. How much elemental Ni must be added to achieve an aim composition is 1.0% Ni?

$$m_{additive} = \frac{(1.0 - 0.01)\% \times 250,000\ kg}{100\%} = 2,475\ kg$$

#### 9.1.1.2 Master alloy additions

In many cases, it is more practical/economical to make additions through "**master alloys**" than by pure elements. (Master alloys are mixtures of 2 or more components).

In such cases the amount of the desired element in the master alloy must be taken into account.

The "recovery rate" – i.e. the amount of the element that actually increases the liquid steel composition rather than being lost to the slag, etc. – also needs to be included in the calculation.

$$m_{additive} = \frac{100 \times \Delta\%X \times ladle\ mass}{\%X\ in\ master\ alloy \times recovery\ rate\ of\ X} \qquad 9\text{-}2$$

Example

A 250 tonne ladle of steel contains 0.12%Mn at tap. Calculate how much high carbon ferromanganese (HCFeMn) must be added to achieve a composition of 1.4%Mn.

From Table 7-2 we see that HCFeMn contains 76.5%Mn. The typical recovery rate for Mn is 95% (from Table 7-3). Substituting these values gives:

$$m_{HCFeMn} = \frac{100\% \times (1.4 - 0.12)\% \times 250,000 \; kg}{76.5\% \times 95\%} = 4,403 \; kg$$

### 9.1.1.3 Pickup of Other Elements

When adding master alloys it is also important to be aware of, and if necessary calculate, the effect of other components on the overall steel composition. The amount of **pickup** (i.e. increase) of a given element is given by re-arranging equation 9-2 to give:

$$\Delta\%X = \frac{m_{additive} \times \%X \; in \; master \; alloy \times recovery \; rate \; of \; X}{100 \times ladle \; mass} \qquad 9\text{-}3$$

Example

In the previous example, calculate the amount of carbon pickup.

HCFeMn contains 6.7%C (Table 7-2) with a 95% recovery rate (Table 7-3).

$$\Delta\%C = \frac{4,403 \; kg \times 6.7\% \times 95\%}{100\% \times 250,000 \; kg} = 0.112 \; \%C$$

Clearly such an increase in carbon could be critical in certain low carbon and ultra-low carbon steel grades. In such cases, it would be necessary to use the more expensive low carbon or high purity ferromanganese master alloys.

### 9.1.1.4 Mixing Times

It is important to be aware that alloy additions made to the ladle **do not** result in instantaneous changes to the steel composition, but take a finite time to dissolve.

In the simulation, be sure to allow sufficient time for alloy additions to dissolve by observing the following trends:

- Powders, wires and fine particle additions dissolve faster than coarse particles or bars;
- Stirring the ladle (i.e. by argon bubbling) accelerates the dissolution process and is also essential for homogenizing the liquid steel composition;
- Mixing times will increase as the temperature decreases.

You can expect well-stirred powder additions made at higher temperatures to dissolve fastest. Bars added at lower temperatures without stirring will take many minutes to dissolve and the ladle steel may not be homogenized by the time it arrives at the casting unit.

### 9.1.1.5  When to Make Additions

Ladle additions can be made at tap, and at each of the secondary steelmaking units (flushing station, degassers, CAS-OB and ladle furnace).

In general **bulk additions** are normally made at tap, with **'trimming' additions** being made at subsequent stages.

Of vital importance is whether additions are made before or after the steel is deoxidized.

### 9.1.1.6  Chilling Effect of Additions

Most ladle additions result in a decrease in steel temperature. For this simulation, assume that each 1000 kg results in a 6°C reduction in bath temperature. (In reality the exact amount depends upon the heat capacity and heat of solution of the various solutes.)

The one important exception is aluminum, which will react exothermically with any oxygen present (either dissolved in the steel, or injected through a lance) to heat the steel. See section 7.2 "Temperature".

## 9.2  De-oxidation

Aluminum is a very powerful deoxidizing agent and controls the oxygen activity in the liquid steel by the chemical reaction:

$$2[Al] + 3[O] \rightarrow (Al_2O_3) + \text{heat energy} \qquad\qquad \text{9-4}$$
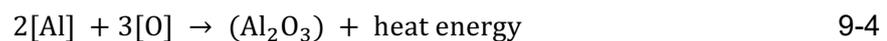
for which the equilibrium constant is given by:

$$K_{Al-O} = \frac{a_{Al_2O_3}}{a_o^3 . a_{Al}^2} \qquad\qquad \text{9-5}$$

where

$$\log K_{Al-O} = \frac{62,780}{T[K]} - 20.5 \qquad\qquad \text{9-6}$$

Re-arranging equation 9-5 in terms of oxygen activity gives:

$$a_o = \sqrt[3]{\frac{a_{Al_2O_3}}{K_{Al-O} \cdot a_{Al}^2}}$$

9-7

The relationship between $a_o$ and $a_{Al}$ is plotted for three different temperatures in Figure 9-1. From this, we see that **de-oxidation with aluminum is more efficient at lower temperatures**.
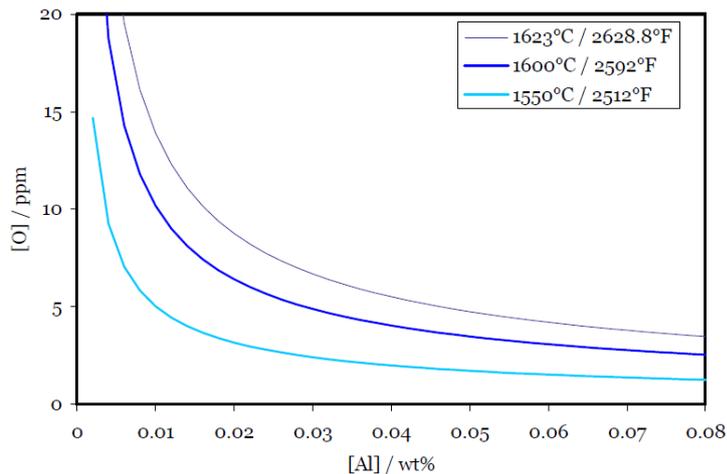


**Figure 9-1**. Al-O equilibrium curves at three different temperatures.

### 9.2.1 Calculating AL Additions
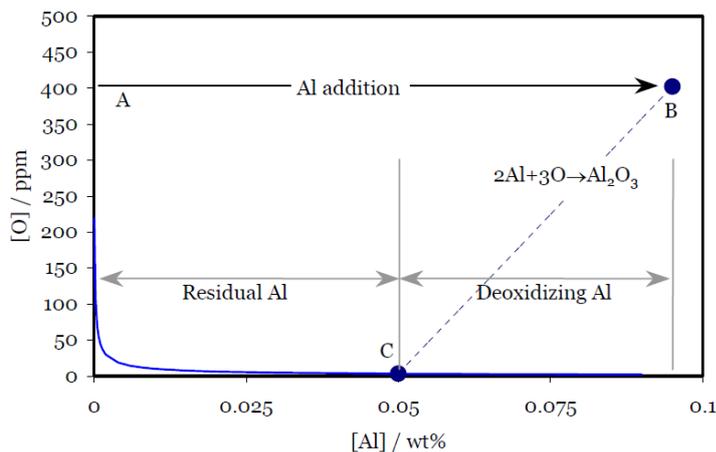


**Figure 9-2**. Calculating the required Al addition from the starting O activity.

Let's assume a starting composition of 400 ppm oxygen and no aluminum, represented by point A on the diagram.

An addition of about 0.095% aluminum is represented by point B. As this is well above the equilibrium Al-O curve, aluminum and oxygen will react to form $Al_2O_3$. Assuming stoichiometry,

2 atoms of Al (=54 mass units) react with 3 of oxygen (=48 mass units), thereby following the line down to point C - the equilibrium composition at this temperature. The weight percentage of aluminum required for de-oxidation is therefore:

$$\%Al_{deox} \approx \frac{54}{48}[\%O]_{initial}$$  9-8

When calculating the total aluminum addition required, this value must be added to the aim (or residual) Al composition of steel.

Example

A 250 tonne ladle of steel having an oxygen content of 450ppm (0.045%) is to be Aldeoxidized at tap. Assuming an Al recovery rate of 60% and an aim Al composition of 0.04%, calculate the amount of 98% Al alloy addition that is required.

Aluminum for de-oxidation (from equ. 9-8) (54/48) × 0.045% = 0.051%

+ Aim aluminum                                     0.040%

= Total aluminum required                          0.091%

Now use equation. 9-2 to compute the mass of alloy addition.

$$m_{Al} = \frac{100\% \times 0.091\% \times 250,000\ kg}{98\% \times 60\%} = 386\ kg$$

TIP: Remember that as the steel cools after de-oxidation, the Al-O 'solubility product' (i.e. the curve in Figure 9-1) also becomes lower. This means that Al and O continue to react, with the possibility of very fine $Al_2O_3$ particles forming. Unless these have time to float out, these will be trapped in the final product.

For more information on $Al_2O_3$ inclusion formation and removal, see Section 9.8 "Steel Cleanness".

## 9.3  Decarburization

### 9.3.1  Thermodynamics of Decarburization

The removal of dissolved carbon from the steel during vacuum degassing arises from the following reaction:

$$[C]\ +\ [O] \rightarrow CO\ (g)$$  9-9
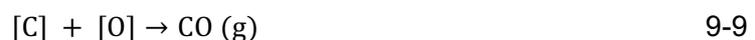
for which the equilibrium constant is given by:

$$K_{C-O} = \frac{p_{CO}}{a_C a_O}$$

9-10

For low concentrations, the C and O activities are equivalent to their concentrations, such that:

$$K_{C-O} = \frac{p_{CO}}{[\%C].[\%O]}$$

9-11

$$\log K_{C-O} = \frac{1,168}{T[K]} + 2.07$$

9-12
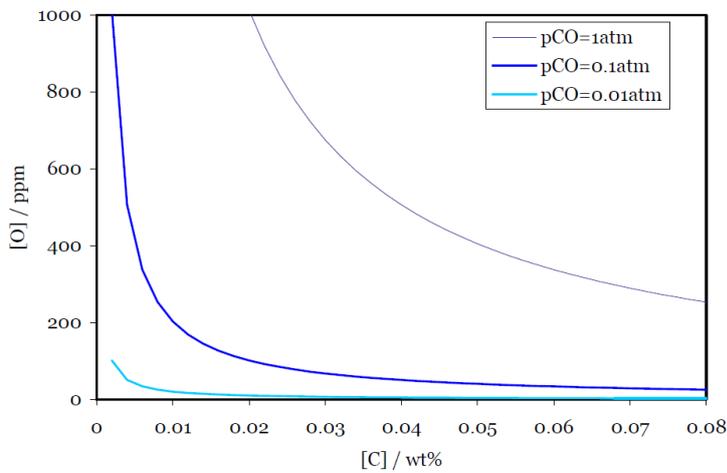


**Figure 9-3**. Equilibrium [C] and [O] concentrations at different pressures.

### 9.3.2  Decarburization Kinetics

The rate of decarburization is given by the following relationship:

$$\ln\left\{\frac{[\%C]_f - [\%C]_{equ}}{[\%C]_i - [\%C]_{equ}}\right\} = -k_c t$$

9-13

where

$[\%C]_f$ = the carbon concentration after time $t$

$[\%C]_i$ = the initial carbon concentration

$[\%C]_{equ}$ = the equilibrium carbon concentration

$k_c$ = the rate constant for decarburization, min$^{-1}$

Re-arranging equation 9-13 in terms of the final carbon concentration gives:

$$[\%C]_f = [\%C]_{equ} + \left([\%C]_i - [\%C]_{equ}\right) \exp(-k_c t)$$

9-14

where $[\%C]_i$ and $[\%C]_f$ are the carbon contents before and after decarburization, respectively, $[\%C]_{equ}$ is the equilibrium carbon content, and $k_c$ is the rate constant for decarburization. For RH degassers the rate constant is given by the following relationship.

$$k_c = \frac{Q}{V_b \rho} \frac{q}{\frac{Q}{\rho} + q}$$

9-15

where

$Q$ = circulation rate of liquid steel, in kg min$^{-1}$

$V_b$ = volume of the steel bath in the ladle, in m$^3$

$\rho$ = density of liquid steel ~ 7,200 kg m$^{-3}$

$q$ = volumetric mass transfer coefficient of decarburization, in m$^3$ min$^{-1}$

For this simulation, we can take typical values of $Q$ = 80,000 kg min$^{-1}$, $V_b$ = mass of steel / density = 250,000 / 7,200 = 34.7 m$^3$, and $q$ = 18 min$^{-1}$. Substituting these values into the previous equation gives:

$$k_C = \frac{80,000}{34.7 \times 7,200} \frac{18}{\frac{80,000}{7,200} + 18} = 0.164\ min^{-1}$$

Example

How long does it take to decarburize a 0.045%C steel down to 0.002%C, assuming an equilibrium carbon content f [%C] of 0.0015?

$$t = -\frac{1}{k_C} \ln\left\{ \frac{[\%C]_f - [\%C]_{equ}}{[\%C]_i - [\%C]_{equ}} \right\} = -\frac{1}{0.164} \ln\left\{ \frac{0.002 - 0.0015}{0.045 - 0.0015} \right\} \approx 27min$$
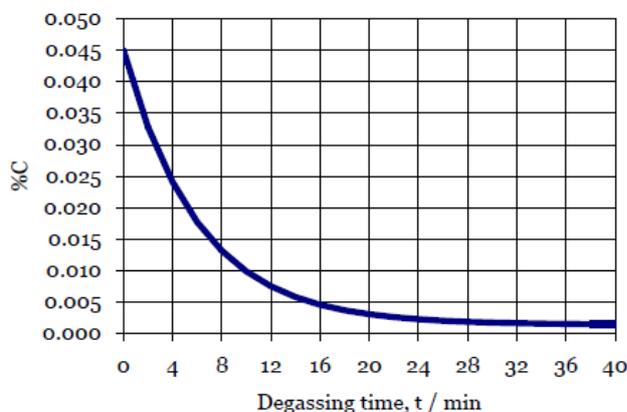


## 9.4 Desulfurization

Certain grades of steel, such as those used for gas and oil pipelines require very low levels of sulfur. Desulfurization in the ladle is driven by the chemical reaction:

$$3(\text{CaO}) \ 2[\text{Al}] \ + \ 3[\text{S}] \ \rightarrow 3(\text{CaS}) \ + \ (\text{Al}_2\text{O}_3) \qquad\qquad \text{9-16}$$

In practice, this is achieved by:

- Adding a synthetic CaO based desulfurizing slag at vessel tapping;

- **Aluminum deoxidizing** the steel to very low oxygen activity (otherwise the Al will react preferentially with O);
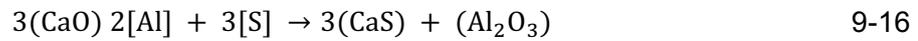
- **Vigorously stirring the steel** in the tank degasser to thoroughly mix the metal and slag.

The process control for each of these steps is now described.

### 9.4.1 Desulfurizing Slag Addition

You will have the option of adding a synthetic CaO based slag at the beginning of the simulation, prior to tapping. Use the sliders to:

- Specify the **mass of slag** to be added. The more slag you add, the more sulfur you can remove, but this must be set against the cost of the slag.

- Specify the **slag composition** in terms of the ratio between CaO and $\text{Al}_2\text{O}_3$. Slags with higher CaO concentrations tend to have higher sulfur distribution ratio, $L_\text{S}$, and are thus more effective at removing sulfur. However, there is a risk of the slag solidifying at higher these higher CaO levels unless a sufficiently high temperature is maintained.

In theory, the 'equilibrium' sulfur concentration $[\%S]_{equ}$ for a given slag is given by:

$$[\%S]_{equ} = [\%S]_0 \frac{\left(\dfrac{1}{L_S}\dfrac{W_m}{W_S}\right)}{1 + \left(\dfrac{1}{L_S}\dfrac{W_m}{W_S}\right)} \qquad\qquad \text{9-17}$$

where

$[\%S]_0$ = the initial sulfur concentration, in wt%

$L_\text{S}$ = the sulfur distribution ratio, given by $(\%S)/[\%S]$

$W_\text{S}$ = the weight of the slag, in kg

$W_\text{m}$ = the weight of the metal, in kg

Equation 9-17 can be re-arranged in terms of the amount of slag required to achieve a specified sulfur concentration, i.e. by setting $[\%S]_{aim} = [\%S]_{equ}$:

$$W_S = \left(\frac{W_m}{L_S}\right)\left(\frac{[\%S]_0 - [\%S]_{aim}}{[\%S]_{aim}}\right)$$

The value of $L_S$ is a complex function of slag composition, the dissolved aluminum content of the steel, temperature, etc. Clearly, to minimize the amount and cost of desulfurizing slag to be used, a high value of $L_S$ is required. By selecting a CaO: $Al_2O_3$ ratio of about 1.2, fully deoxidizing the steel with Al, and by desulfurizing at a temperature well above 1600°C, you should be able to achieve $L_S$ values of 500 and above.

Example

Assuming a tap sulfur concentration of 0.008 wt % and a sulfur distribution ratio, $L_S$ of 500, what is the very minimum amount of desulfurizing slag that must be added to a 250 tonne ladle of steel in order to achieve a S level of 0.002wt%?

Using equation 9-18:

$$W_S = \left(\frac{250}{500}\right)\left(\frac{0.008\% - 0.002\%}{0.002\%}\right) = 1.5 \; tonnes$$

Note: The kinetics of desulfurization are such that the 'equilibrium' level of 0.002wt% sulfur would in practice only be reached after an infinite stirring time.

### 9.4.2   De-oxidation
Before stirring in the tank degasser, the steel must be fully deoxidized with aluminum. See §9.2 (De-oxidation).

### 9.4.3   Stirring In the Tank Degasser
Desulfurization is controlled by liquid phase mass transfer. To achieve rapid desulfurization, good mixing between the metal and slag is essential. This is achieved by vigorous Ar gas stirring at high levels of vacuum in the **tank degasser**.

The stirring power density, $\varepsilon$ is given as a function of Ar gas flow rate and tank pressure in equation 9-26.

The desulfurization rate constant, $k_S$ appears to increase quite slowly with $\varepsilon$ at lower values, but increases rapidly above $\varepsilon \sim 70$ W tonne$^{-1}$. This is perhaps explained by the fact that a

critical stirring power density is required to emulsify the slag with the metal. In this simulation, you can assume:

$$k_S = 0.031\varepsilon^{0.25} \text{ for } \varepsilon < \sim 70 \text{ W tonne}^{-1}$$

9-19

and

$$k_S = 8\times10^{-6}\varepsilon^{2.1} \text{ for } \varepsilon > \sim 70 \text{ W tonne}^{-1}$$

9-20

$$t = \frac{\ln\left[\frac{[\%S]_t}{[\%S]_o}\left\{1 + \frac{1}{L_S}\left(\frac{W_m}{W_S}\right)\right\} - \frac{1}{L_S}\left(\frac{W_m}{W_S}\right)\right]}{-k_S\left[1 + \frac{1}{L_S}\left(\frac{W_m}{W_S}\right)\right]}$$

9-21

Example

A 250 tonne ladle of steel with initially containing 0.01%S is covered with 2 tonnes of a desulfurizing slag with an $L_S$ value of 500. After de-oxidation, it is then injected with Ar with a stirring power density, $\varepsilon$ equivalent to 100 W tonne$^{-1}$. Calculate the time required to achieve 0.003%S.

Firstly, calculate $k_S$ for $\varepsilon$ = 100 W tonne$^{-1}$ using equation 9-20.

$$k_S = 8\times10^{-6}\times100^{2.1} = 0.127 \text{ min}^{-1}$$

Now insert this value into equation 9-21:

$$t = \frac{\ln\left[\frac{0.003\%}{0.010\%}\left\{1 + \frac{1}{500}\left(\frac{250}{2}\right)\right\} - \frac{1}{500}\left(\frac{250}{2}\right)\right]}{-0.127\left[1 + \frac{1}{500}\left(\frac{250}{2}\right)\right]} \sim 13 \text{ mins}$$

Note: The combination of vigorous Ar gas bubbling at very low pressures in the tank degasser can result in excessive slag foaming and the risk of slag 'overflowing' the ladle. In practice, the vacuum level and Ar gas flow rate in the tank degasser have to be finely controlled throughout the stirring process to prevent this from happening. This implies therefore that the stirring power density $\varepsilon$, and hence rate constant $k_S$ fluctuate throughout the duration of the desulfurization treatment, and that the equation 9-21 would no longer be steady state.

## 9.5  Hydrogen Removal

### 9.5.1  Thermodynamics

Dissolved hydrogen is removed from liquid steel by the formation of diatomic gaseous hydrogen:

$$[H] \rightarrow \frac{1}{2}\text{H}_2(g) \qquad\qquad 9\text{-}22$$

Where

$$\log \frac{[ppm\ H]}{(p_{H_2})^{1/2}} = -\frac{1,900}{T} + 2.423 \qquad\qquad 9\text{-}23$$

Table 9-1 Relationship between the equilibrium dissolved hydrogen concentration and pressure at 1600°C.

| $p\text{H}_2$ | ppm H |
|---|---|
| 1.0 | 25.6 |
| 0.1 | 8.10 |
| 0.01 | 2.56 |
| 0.001 | 0.81 |

In practice, modern degassers can attain pressures down to about 0.001 atm. so that under optimum operating conditions, steels with hydrogen levels below 1ppm can be produced.

### 9.5.2 Kinetics of Hydrogen Removal

Clearly, the ultra-low pressures discussed above are only achieved at the top surface of the steel when it is exposed to vacuum. At the bottom of the ladle, the ferrostatic pressure is ~5 atmospheres, which from equation 9-23 is equivalent to an equilibrium hydrogen level of 57 ppm at 1600°C. Therefore a high metal circulation rate coupled with vigorous stirring is required to fully degas the metal.

The kinetics of hydrogen removal are therefore dominated by mass transfer in the liquid steel, for which the rate equation is given by:

$$\ln\left\{\frac{[H]_f - [H]_{equ}}{[H]_i - [H]_{equ}}\right\} = -k_H t \qquad\qquad 9\text{-}24$$

where

$[H]_f$ = the hydrogen concentration in mass ppm after time $t$

$[H]_i$ = the initial hydrogen concentration, in mass ppm

$[H]_{equ}$ = the equilibrium hydrogen concentration, in mass ppm

$k_H$ = the rate constant for hydrogen removal, min$^{-1}$

Re-arranging equation 9-24 in terms of the final hydrogen concentration gives:

$$[H]_f = [H]_{equ} + \left([H]_i - [H]_{equ}\right)\exp(-k_H t)$$ 9-25

In **tank degassers**, the rate constant $k_H$ is determined largely by the argon stirring gas flow rate. For the current simulation, you can assume the following relationship:

| Plant | $k_H$ / min$^{-1}$ |
|---|---|
| Tank degasser | $0.0576\dot{V}$ + 0.02 <br> where $\dot{V}$ is the argon gas flow rate, in N m$^3$ min$^{-1}$. |
| Recirculating degasser | 0.13 |

## 9.6  Ladle Stirring

Homogenization of bath temperature and composition by argon bubbling is primarily caused by the dissipation of the buoyant energy of the injected gas. The following equation is used to calculate the stirring power.

$$\varepsilon = 14.23 \left(\frac{VT}{M}\right)\log\left(\frac{1+H}{1.48P_o}\right)$$ 9-26

where:

$\varepsilon$ = stirring power, W tonne$^{-1}$

$V$ = gas flow rate, N m$^3$ min$^{-1}$

$T$ = bath temperature, K

$M$ = bath mass, tonnes

$H$ = depth of gas injection, m

$P_o$ = gas pressure at the bath surface, atm (i.e. =1 atm when the steel is exposed to air)

## 9.7  Electrical Reheating

The energy $E$ required to raise the bath temperature by $\Delta T$, assuming 100% efficiency is given by

$$E = mC_p\Delta T \tag{9-27}$$

where $m$ is the mass of the bath, and $C_p$ the specific heat capacity at constant pressure. Alternatively we can re-arrange to give the theoretical temperature increase:

$$\Delta T_{th} = \frac{E}{mC_p} \tag{9-28}$$

The theoretical **rate** of heating, can therefore be written:

$$\left(\frac{dT}{dt}\right)_{th} = \frac{dE}{dT}\frac{1}{mC_p} = \frac{P}{mC_p} \tag{9-29}$$

where $P$ is the heating power. Thus the temperature rise in time $\Delta T$ is given by:

$$\Delta T_{th} = \frac{P\Delta T}{mC_p} \tag{9-30}$$

Of course heating is not 100% efficient, as heat is lost to the electrodes, atmosphere, ladle refractories, etc. The electrode efficiency $\eta$ is defined as the ratio of actual to theoretical heating

$$\eta = \frac{\Delta T_{act}}{\Delta T_{th}} \tag{9-31}$$

$$\Delta T_{act} = \frac{\eta P\Delta T}{mC_p} \tag{9-32}$$

or, expressed in terms of the heating time for a required temperature increase, $\Delta T_{req}$:

$$\Delta t = \frac{mC_p\Delta T_{req}}{\eta P} \tag{9-33}$$

Example

The heat capacity of liquid steel, $C_p$ is approximately 0.22 kW h tonne$^{-1}$ °C$^{-1}$. If the power of the ladle arc furnace, P is 20 MW, calculate the time required to heat a 250 tonne bath by 15°C, assuming an electrode efficiency of 55%.

$$\Delta t = \frac{250 \text{ tonne} \times 0.22 \text{kW h tonne}^{-1}\,{}^{\circ}\text{C}^{-1} \times 15\,{}^{\circ}\text{C}}{0.55 \times 20{,}000 \text{ kW}} = 0.075 \text{ h} = 4.5 \text{ min}$$

## 9.8  Steel Cleanness

Section 9.2 showed how aluminum de-oxidation results in the formation of $Al_2O_3$ particles in the liquid steel. If these are not able to float out into the slag before casting, these particles are trapped in the final product as inclusions. For many applications, a certain amount of $Al_2O_3$ inclusions does not significantly affect the properties. However, certain applications, such as linepipes for oil and gas distribution require very 'clean' steels – i.e. with very low levels of oxide and sulfide inclusions, since these can act as crack initiation sites.

The chemistry of oxide and sulfide formation and subsequent removal during secondary steelmaking is extremely complex and the subject of ongoing research. A comprehensive treatment of inclusions is therefore beyond the scope of this simulation. However, you will be required to consider the broad effects of de-oxidation on $Al_2O_3$ formation, and ensure that you allow sufficient time for $Al_2O_3$ particles to float out. This process can be accelerated by the gentle stirring of the ladle.

During aluminum de-oxidation, $Al_2O_3$ particles are formed according to equation 9-4. The mean particle diameter (and hence rate of flotation) is found to be dependent on the initial dissolved oxygen content.

- For higher initial dissolved oxygen contents (above about 200ppm, or 0.02%), larger $Al_2O_3$ particles are formed, which according to Stokes' law (see below) float to the slag layer relatively quickly.

- Lower initial dissolved oxygen contents result in smaller $Al_2O_3$ particles that take considerably longer to float out.

Stokes law states that the terminal velocity of flotation, $u$ for spherical particles (or bubbles) is proportional to the square of the diameter, $d$, as given by:

$$u = \frac{gd^2\Delta\rho}{18\eta} \qquad\qquad 9\text{-}34$$

where

$g$ = 9.81 m s$^{-1}$,

$\Delta\rho$ = the difference in densities between the particle and liquid steel,

$\eta$ = the viscosity of the liquid steel (~6.1×10$^{-3}$ N s m$^{-2}$ at 1600°C)

In the simulation, you are 'rewarded' for accurately calculating the amount of aluminum for de-oxidation in one go. If you have to make subsequent 'trimming' Al additions, the lower dissolved oxygen content will result in the formation of very small Al$_2$O$_3$ particles, which will be difficult to remove from the steel.

You will aim to achieve 'moderate', 'low' or 'very low' levels of inclusion depending on the chosen grade.

Table 9-2 Effect of initial dissolved oxygen and stirring on the time required to achieve 'very low' level of inclusions. For 'low' levels, the times can be reduced by about 20%; for 'moderate' levels by about 40%.

| Initial dissolved O / ppm | No stirring | Stirring |
|---|---|---|
| 600 | 14 min | 5 min |
| 100 | 47 min | 15 min |
| 30 | 108 min | 36 min |

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