Case 2: Desulphurization

Desulphurization of Hot Metal in the De-S station,
Desulphurization of steel during Ladle treatment
and calculating Sulphide Capacity
The hot metal tapped out of the blast furnace typically contains 0.04-0.07% S.

The oxygen converter must be charged with metal having 0.01-0.001% S.

To reduce the amount of sulphur in the hot metal between the blast furnace and the oxygen converter, desulphurization is usually performed at a De-S station.

Blast Furnace (BF)  Torpedo Car  Basic Oxygen Furnace (BOF)

0.04-0.07% S  0.01-0.001% S
The following reactions have been proposed to reduce the sulphur content in hot metal:

\[
\begin{align*}
\text{Mg(s)} + \text{S} & \rightarrow \text{MgS(s)} \\
\text{CaC}_2 + \text{S} & \rightarrow \text{CaS(s)} + 2\text{C} \\
\text{CaO} + \text{S} + \text{C} & \rightarrow \text{CaS(s)} + \text{CO(g)} \\
\text{Mg} + \text{CaO} + \text{S} & \rightarrow \text{CaS(s)} + \text{MgO(s)} \\
\text{CaO} + 2\text{Al} + \text{S} + 3\text{O} & \rightarrow (\text{CaO} \cdot \text{Al}_2\text{O}_3) (S) \\
(\text{CaO} \cdot \text{Al}_2\text{O}_3)(s) + \text{S} & \rightarrow (\text{CaO} \cdot \text{Al}_2\text{O}_3)(S)
\end{align*}
\]

In the following pages, it will be shown how FactSage could be used to calculate the efficiency of each desulphurizing agent.

It will then be shown how the exact amount of desulphurizing agent can be selected to achieve the desired sulphur content.
Desulphurization of Hot Metal using Mg

1. Double-click on units...

2. ... to select the desired units

3. Enter the hot metal composition and put <A> for the desulphurizing agent amount

4. Click on “Data Search”...

5. ... and select the FTmisc database

6. Click “Next”
Desulphurization of Hot Metal using Mg

1. Right-click on “pure solids”

2. The selection contains data from both FTmisc and FactPS. Some of the data is overlapping (highlighted in red as “Duplicates”)

3. We need to select each phase only once, so we will have to “suppress duplicates”
Desulphurization of Hot Metal using Mg

1. Left-click on “suppress duplicates”

2. Then enter the database names in the order they should be prioritized. Here, FTmisc was given advantage over FactPS

3. Press “OK”

4. Press “apply” – now the number of solids selected should be inferior to that selected in the beginning.
Desulphurization of Hot Metal using Mg

1. Left-click to select the liquid steel solution phase

2. If you don’t see the available solution phase, click “show all”

3. Enter the desired equilibrium temperature.

4. We will vary the amount of desulphurizing agent from 0 to 1 g in steps of 0.01 g

5. Press “Calculate”
Desulphurization of Hot Metal using Mg

Now we want to see how the amount of sulphur in the hot metal decreased with the addition of magnesium.

1. Press “Output” → “Plot” → “Plot Results…”
2. Press “Axes”
3. This window will pop-up
1. Press “Y-variable”

2. Select “weight %” in “log10(Y)” scale

3. Select the maximum, minimum and increment value for the graph

4. In the same way, select Alpha as the X-variable
Desulphurization of Hot Metal using Mg

Now we can see that the axes have been selected. We just need to choose sulphur as the species.

1. Press “Select” species

2. Select S(FeLQ) – sulphur in the liquid steel solution.

3. Press “OK”
1. Now we can see that both the axes and the species have been selected.

2. The “Plot” button is now activated. Click it!
Desulphurization of Hot Metal using Mg

1. It can be seen that after the addition of 0.1g Mg, the desulphurization is not so effective.

2. If our target was 0.001% S, we can read off the graph that this sulphur level will be achieved after adding approximately 0.05g Mg.

3. However, there is a better way.
Desulphurization of Hot Metal using Mg: Composition target

1. Right-click on the Ftmisc-FeLQ selection

2. Click on "composition target"

3. This window will pop-up

Ferrous Processing 13
Desulphurization of Hot Metal using Mg: Composition target

1. Select “element composition”
2. Choose element S
3. Enter the desired value (here – 0.001%)
4. Press “OK”
Desulphurization of Hot Metal using Mg: Composition target

1. Now “C” indicates that we have selected a composition target for this calculation.

2. We must leave the <A> field blank, because <A> is what we want to calculate.

3. Press “Calculate”. Note that only one calculation will be performed.
Desulphurization of Hot Metal using Mg: Composition target

1. The value for reducing sulphur content to 0.001% is 0.0494g.

2. The mass fraction of S is exactly what we want it to be.

### Results - Equilib 1400 C, A=0.0494

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>Mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.80721</td>
<td>0.94395</td>
</tr>
<tr>
<td>Mn</td>
<td>5.2188E-03</td>
<td>6.0038E-03</td>
</tr>
<tr>
<td>S</td>
<td>1.4893E-05</td>
<td>1.0000E-05</td>
</tr>
<tr>
<td>Si</td>
<td>8.5071E-03</td>
<td>5.0032E-03</td>
</tr>
<tr>
<td>Mg</td>
<td>1.7562E-05</td>
<td>6.9384E-06</td>
</tr>
<tr>
<td>C</td>
<td>0.17904</td>
<td>4.5028E-02</td>
</tr>
<tr>
<td>MgS</td>
<td>0.11251</td>
<td></td>
</tr>
</tbody>
</table>

(0.11251 gram, 1.9960E-03 mol)

(1400 C, 1 atm, S1, a=1.0000)
Desulphurization of Hot Metal using CaC$_2$

In the same manner, we can calculate the desulphurization ability of CaC$_2$

$$\text{CaC}_2 + \text{S} \rightarrow \text{CaS(s)} + 2\text{C}$$

We will keep the same hot metal composition, the only thing we will change is the desulphurizing agent.

This example can be found in EquiCase2-2.dat
Desulphurization of Hot Metal using CaC$_2$

The same conditions are selected
Desulphurization of Hot Metal using CaC₂

After addition of 0.14g of CaC₂, the amount of S in the hot metal becomes so small, that the reaction does not proceed and CaC₂ is precipitated as a solid phase.
Desulphurization of Hot Metal using CaC₂

This can also be seen on the graph – after $<A> = 0.14$, the sulphur level remains constant.

1. In order to compare this graph with the graph for Mg desulphurization, we should save this figure.

2. But first, to differentiate this curve from the others, we will change the labels.
Desulphurization of Hot Metal using CaC$_2$

1. Double-click on one of the labels

2. Edit the text (curvy brackets are for subscript)

3. Can increase the text size to see better and make it bold

4. All other labels were deleted for clarity by selecting the label and pressing "delete".
Desulphurization of Hot Metal using CaC₂

1. Press “File” → “Save as…”

2. The graph will be saved as a .fig file.
Desulphurization of Hot Metal using CaC$_2$: Composition target

With CaC$_2$, the amount needed to bring the sulphur level down to 0.001% is 0.1279g.
With CaO, CO gas is evolved during the reaction, so we must select the gas species as possible products.

This example can be found in EquiCase2-3.dat
The following curve is obtained with CaO.

Using Composition Target, it is found that 0.2238g of CaO is needed to bring the sulphur level down to 0.001%.
For the CaO+Mg mixture, no gas was selected and all solids were selected.

The value \(<A>\) was given for CaO and for Mg.

This example can be found in EquiCase2-4.dat
The drop at $<A>=0.11$ is due to CaC$_2$ precipitating instead of MgS.
With CaO+Mg, the amount needed to bring the sulphur level down to 0.001% is 0.0494g CaO + 0.0494g Mg.
Desulphurization of Hot Metal using CaO+Al

For the CaO+Al mixture, no gas was selected and all solids were selected.

The value $<A>$ was given for CaO and $<2A>$ for Al.

Since there is no CaO-Al$_2$O$_3$ solid solution incorporating S, we must choose the pure solids where a combination of CaO-Al$_2$O$_3$ compounds and CaS will simulate this solution.

This example can be found in EquiCase2-5.dat
The change of stable phase between different CaO-Al2O3 compounds creates the steps in this graph.
With CaO+Al, the amount needed to bring the sulphur level down to 0.001% is 0.1305g CaO + 0.2610g Al.
Desulphurization of Hot Metal using CaO+Al₂O₃

The species selection for this reaction is the same as for the previous example.

This example can be found in EquiCase2-6.dat
The change of stable phase between different CaO-Al₂O₃ compounds creates the steps in this graph.
With CaO+Al₂O₃, the amount needed to bring the sulphur level down to 0.001% is 0.3874g CaO + 0.3874g Al₂O₃.
1. To compare the different desulphurization methods, it is convenient to plot all the obtained curves on one graph.

2. Press “Open”

3. Select one of the previously saved figures
Desulphurization of Hot Metal

1. Press “superimposed figure”

2. Select all the other saved figures.
It can now readily be seen that Mg and CaO+Mg are the most effective hot metal desulphurizing agents.
It is also convenient to compare the amounts obtained using “Composition Target”
We will now apply the same calculations for the desulphurization of steel in the ladle.

The starting steel contains 0.01% S and it needs to be reduced down to 0.001% S.

We will also assume that a slag is present in the ladle. It consists of 40% CaO, 40% Al₂O₃, 10% MgO and 10% SiO₂. The ratio of slag to metal is 1/10.
Desulphurization of Steel using Mg

1. Enter the metal and slag composition

This example can be found in EquiCase2-7.dat

2. In “Data Search” select FTmisc and FToxid
Desulphurization of Steel using Mg

1. Enter the <A> and Temperature

2. Select liquid steel and SlagA as the solutions

3. Note that the slag phase is selected with possible immiscibility

4. Press “Calculate”
Desulphurization of Steel using Mg

Results show a slag phase and a metal phase

Solid periclase (MgO) appears as \(<A>\) is increased

We can plot the results in the same way as was done for the hot metal desulphurization in the previous slides
A constant decrease in metal sulphur content is observed.
Desulphurization of Steel using Mg

Another useful way to visualize these results, is the sulphur partition coefficient:

\[ L_s = \frac{[S_{\text{in slag}}]}{[S_{\text{in metal}}]} \]

1. Press “Output” → “Save or Print” → “Save or Print As …”

2. Select “Open Text Spreadsheet”

3. Press “Spreadsheet Setup”
Desulphurization of Steel using Mg

1. Select “Alpha” as the property column

2. Select “wt%” as the Species properties

3. Select the desired species
Desulphurization of Steel using Mg

1. Select sulphur from liquid steel and all elements from the slag

2. Press “OK”
Desulphurization of Steel using Mg

1. Press “OK” on this window and the next one
Desulphurization of Steel using Mg

1. A spreadsheet with the composition of slag and metal at each <Alpha> value will appear.

2. It is convenient to copy the whole table and paste it in Excel.

<table>
<thead>
<tr>
<th>Alpha</th>
<th>Wt% S(FeLQ)</th>
<th>Wt% Fe_FToxid-SLAGA#1</th>
<th>Wt% Mn_FToxid-SLAGA#1</th>
<th>Wt% Ca_FToxid-SLAGA#1</th>
<th>Wt% S_FToxid-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000000E+00</td>
<td>5.9035700E-03</td>
<td>2.0963060E-01</td>
<td>1.0012288E-01</td>
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<td>4.0877252E</td>
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<tr>
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<td>1.6878202E-02</td>
<td>2.9131459E+01</td>
<td>8.5982755E</td>
</tr>
</tbody>
</table>
1. All unnecessary columns were deleted keeping only the sulphur content in the steel and the slag.

2. The last column was used to calculate the sulphur partition coefficient \( L_s \).

3. Plotting Alpha against \( \log(L_s) \)

<table>
<thead>
<tr>
<th>Alpha</th>
<th>Wt% S(FeLQ)</th>
<th>Wt% S_FToxid-SLAGA#1</th>
<th>( \log(L_s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00E+00</td>
<td>5.90E-03</td>
<td>4.09E-02</td>
<td>0.840367</td>
</tr>
<tr>
<td>1.00E-02</td>
<td>5.33E-03</td>
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<td>2.00E-02</td>
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<tr>
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<td>6.24E-02</td>
<td>1.222706</td>
</tr>
</tbody>
</table>
Desulphurization of Steel using Mg: Composition target

As before, it is possible to calculate the composition target for liquid steel at 0.001% S.

Here, we see that 0.3558g Mg is needed to attain the desired sulphur composition.
Performing the same operations using CaC$_2$, the following graph is obtained.

Using “composition target” it was found that 0.5446g of CaC$_2$ is needed to obtain the desired sulphur composition.

Performing only one “composition target” calculation is a lot faster than the 101 calculations needed to construct this graph.

This example can be found in EquiCase2-8.dat
1. Performing the same operations using CaO, the following graph is obtained.

2. It can be seen from this graph, that there is no value of Alpha for which \( \log(\text{wt}\% S) = -3 \).

3. “Composition target” scans Alpha values from 0 to 1 only. So no solution is found for the composition target calculation.

This example can be found in EquiCase2-9.dat
1. Because we need to go outside the 0 to 1 range, the amount of CaO was selected to be <10A>

2. It was then found that 2.368g of CaO is necessary to obtain 0.001% S
Performing the same operations using CaO+Mg, the following graph is obtained.

Using "composition target" it was found that 0.2746g of CaO and 0.2746g Mg is needed to obtain the desired sulphur composition.
Performing the same operations using CaO+Al, the following graph is obtained.

Using “composition target” it was found that 0.1699g of CaO and 0.3398g Al is needed to obtain the desired sulphur composition.
Performing the same operations using CaO+Al$_2$O$_3$, the following graph is obtained.

Using “composition target” it was found that 15.49g of CaO and 15.49g Al$_2$O$_3$ is needed to obtain the desired sulphur composition.
Comparing the different desulphurization agents.
Calculating Slag Sulphide Capacity

A good way of comparing the ability of a slag to absorb sulphur is the sulphide capacity calculated in the following manner:

$$C_S = (S_{\text{in slag}})^*\left(\frac{P_{O_2}}{P_{S_2}}\right)^{1/2}$$

In the following slides, the sulphide capacity of four different slags will be calculated.
Calculating Slag Sulphide Capacity

1. Enter the amount and species for the first slag

2. Select FactPS and Ftoxid databases

This example can be found in EquiCase2-13.dat
Calculating Slag Sulphide Capacity

1. Select gas and SlagA as possible products

2. We will calculate the sulphide capacity at three temperatures: 1580, 1600 and 1620°C

3. Press “Calculate”
Calculating Slag Sulphide Capacity

It is now possible to calculate the sulphide capacity using these results.

In the next slides, two ways of calculating sulphide capacity will be demonstrated.
Calculating Slag Sulphide Capacity

The first way is to use Excel

1. Save the results in a spreadsheet

2. Press “Spreadsheet setup”
Calculating Slag Sulphide Capacity

1. Set T(C) as the system property

2. We need wt%S and the activity of O_2 and S_2 in the gas, so select “wt%” and “a” as the species properties.

3. Select the species
Calculating Slag Sulphide Capacity

1. Select O2(g), S2(g) and All Elements in SlagA

2. Press “OK” on all three screens
Calculating Slag Sulphide Capacity

1. All the needed results (and even more) appear in the spreadsheet.

2. Copy the results in Excel and delete the unnecessary columns.

3. Calculate the sulphide capacity in a separate column.

4. Plot log(Cs) versus temperature.
Calculating Slag Sulphide Capacity

Another way to plot the sulphide capacity is to use the function builder tool coupled with Fact-XML.

1. Press “Edit/Create functions” under the Fact-Function-Builder Menu.
Calculating Slag Sulphide Capacity

1. We need to select wt%S as one variable

2. Select “Amount/Composition” under “Variable selection”

3. Select “wt%”

4. Right-click on S(total) in slag and add it to variables list
Calculating Slag Sulphide Capacity

1. The amount of S now appears in the variables list.

2. Right-click on the variable and rename it to “wtS”

3. Partial pressure and activity of a gas is the same thing, so we need to select activity of O₂ and S₂ in the gas as the two other variables.
Calculating Slag Sulphide Capacity

1. Select “Activity” under “Variable Selection”

2. Right-click on the O2 and S2 and add them to the variable list

3. Rename the variables to aO2 and aS2 accordingly
Calculating Slag Sulphide Capacity

1. Enter the function for log(Cs)

2. Press “preview results”

3. Note that the results are the same as for the Excel calculation
Calculating Slag Sulphide Capacity

1. Save the function as “Sulphide_Capacity”

2. Close the window
Calculating Slag Sulphide Capacity

1. Go back to the “Results” window, and select the “Sulphide_Capacity” function group

2. Check “Always calculate function groups”

3. Click “Refresh Results …”
Calculating Slag Sulphide Capacity

1. A separate “Functions” tab will appear with the results of the calculations.

2. Each tab will have the information on the function along with the calculated equilibrium.
Calculating Slag Sulphide Capacity

1. In order to plot the sulphide capacity as a function of temperature, press the XML button

2. Then select “Graph” → “Setup”

3. Import the “Sulphide_Capacity” function
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1. Select “Functions” as the Y-Axis
2. Select “Temperature” as the X-axis
3. Adjust the min and max values, the step, etc.
4. Press “Draw”
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The figure is then obtained.
Repeating the same procedure for the other slag compositions, it is possible to compare the sulphide capacity of the different slags.