

Application Example:

## Using the Process Metallurgy Module to Calculate the Desulphurization in a Ladle Furnace (LF)

Database(s):	TCOX9, OXDEMO	Module(s):	Process Metallurgy Module (PMM)
Material/Application:	Ladle furnace / desulphurization	Calculator(s):	
Version required:	Thermo-Calc 2019b or newer		
Example file:	<a href="https://www.thermocalc.com/solutions/example-calculations/desulphurization-in-a-ladle-furnace/">https://www.thermocalc.com/solutions/example-calculations/desulphurization-in-a-ladle-furnace/</a>		

To run the calculation, download the example file, save it to your computer, then double click on it. The calculation will open in Thermo-Calc if you have Thermo-Calc installed on your computer and licenses for all databases<sup>1</sup> and modules listed above.

### INTRODUCTION: LADLE FURNACE, STEEL-SLAG REACTIONS, DESULPHURIZATION

The ladle furnace fulfils many purposes in the steelmaking process. Desulphurization, which we will focus on in this example, is merely one of them.

Desulphurization is usually performed by transferring S that is dissolved in the liquid metal to a CaO-rich slag phase. For this process to be successful, two conditions need to be fulfilled:

1. The slag must be fully liquid (liquid fraction > 0.9). This is required for kinetic reasons. The slag phase must be fluid so that it can emulsify with the liquid steel and form a large surface area where the reaction between steel and slag can take place.
2. The slag must take up a large amount of S from the liquid steel (have a “high sulphur capacity”) so that a significant amount of sulphur will move from the liquid steel to the slag phase.

It is difficult to decrease the S content in the liquid steel during steelmaking in a basic oxygen converter (BOF) or an electric arc furnace (EAF) because conditions are predominantly very oxidizing. Desulphurization is therefore usually performed in a subsequent step, during steel refining in a ladle furnace or a vacuum degasser after the steel has been fully killed by a suitable deoxidizing agent and the oxygen activity is low (Figure 1).

The following example explores these two conditions for an equilibrium between liquid steel and slag in a ladle furnace, trying to find good slag compositions.

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<sup>1</sup> You do not need the database version(s) that are listed, but results from other versions may vary slightly.

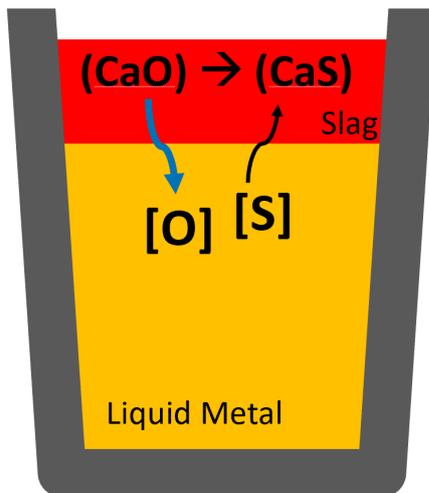


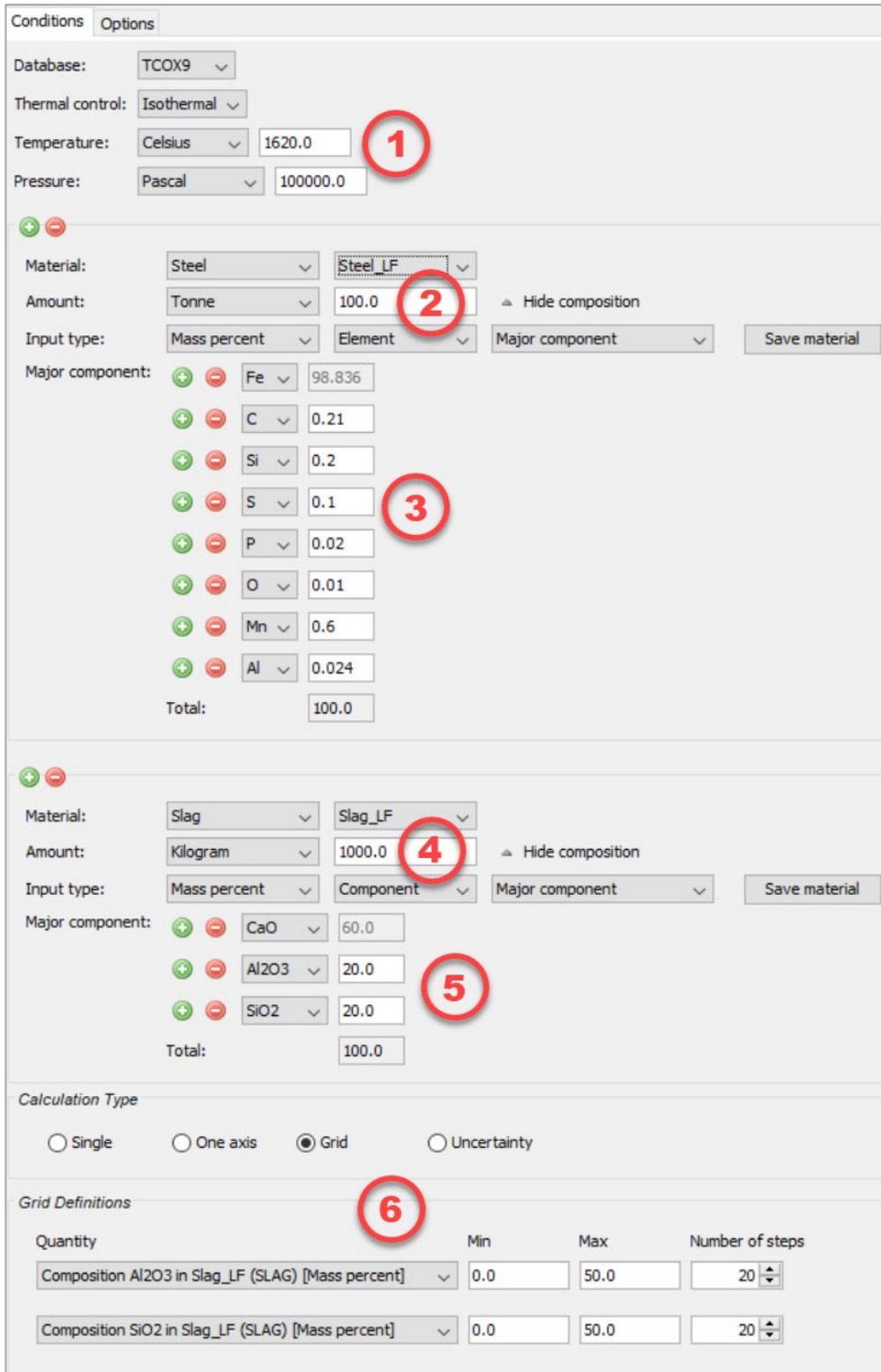
Figure 1. The principle of desulphurization is to transfer the sulphur dissolved in the liquid steel to a CaO-rich slag phase. This process is typically carried out in a ladle furnace (LF). Image of the ladle furnace at Swiss Steel ([www.swiss-steel.com](http://www.swiss-steel.com)).

## EXAMPLE: DESULPHURIZATION IN A LADLE FURNACE

### Example file: *Ex-7\_Ladle-Furnace\_TCOX.tcu*

This example is based on the example PMET\_02\_Ladle\_furnace.tcu that is packaged with Thermo-Calc 2019b and newer (Help → Example Files... → Process Metallurgy → PMET\_02\_Ladle\_furnace.tcu). There is also a video demonstrating the setup of the example: <https://www.youtube.com/playlist?list=PLfv6McToaTGS4g5LC9tjijqCo9OX2-YOa>

In this document, we expand on the original calculation and add complexity so that it corresponds better to a real situation. Figure 2 is a screenshot of the Process Metallurgy module which shows how to set up the calculation. We perform an isothermal calculation at 1620°C (1), which is a typical temperature in a ladle furnace. The amount of steel in the ladle furnace is 100 t (2) and it contains a rather high S content of 0.1 wt% (3). We then add 1000 kg of a slag phase (4) containing CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> (5). We are interested in finding out how the composition of the slag phase influences the Sulphur content in the steel. For this we perform a grid calculation, changing the SiO<sub>2</sub> and the Al<sub>2</sub>O<sub>3</sub> content of the slag (6).



Conditions Options

Database: TCOX9

Thermal control: Isothermal

Temperature: Celsius 1620.0

Pressure: Pascal 100000.0

Material: Steel Steel\_LF

Amount: Tonne 100.0

Input type: Mass percent Element

Major component:

+	-	Fe	98.836
+	-	C	0.21
+	-	Si	0.2
+	-	S	0.1
+	-	P	0.02
+	-	O	0.01
+	-	Mn	0.6
+	-	Al	0.024
Total:			100.0

Material: Slag Slag\_LF

Amount: Kilogram 1000.0

Input type: Mass percent Component

Major component:

+	-	CaO	60.0
+	-	Al <sub>2</sub> O <sub>3</sub>	20.0
+	-	SiO <sub>2</sub>	20.0
Total:			100.0

Calculation Type

Single  One axis  Grid  Uncertainty

Grid Definitions

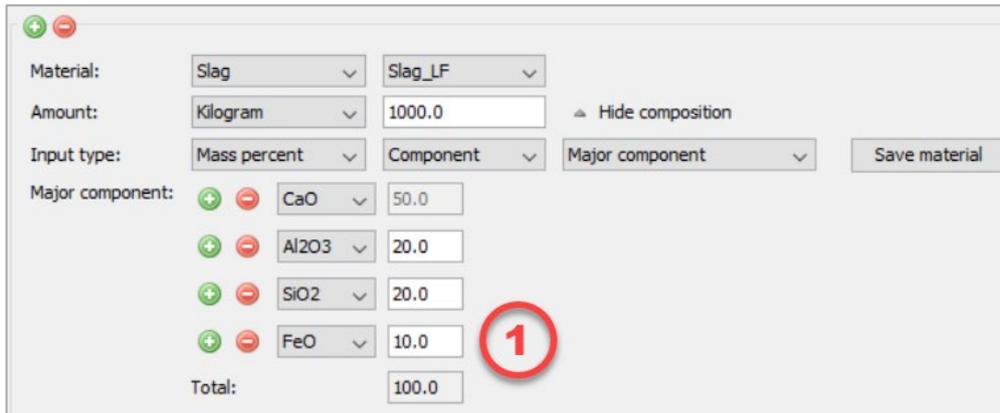
Quantity	Min	Max	Number of steps
Composition Al <sub>2</sub> O <sub>3</sub> in Slag_LF (SLAG) [Mass percent]	0.0	50.0	20
Composition SiO <sub>2</sub> in Slag_LF (SLAG) [Mass percent]	0.0	50.0	20

Figure 2. Screenshot of the Process Metallurgy Module showing how to set up the example on steel desulphurization as a function of the slag composition.

## Quantifying Furnace Slag Tapped into the Ladle

A very common problem during steelmaking is that some of the furnace slag, which is oxidized and rich in FeO, is tapped into the ladle. It is known that this reduces the desulphurizing ability of the slag

in the ladle furnace. To quantify this effect, we perform the same calculation as above, except that we add 10 wt% FeO to the slag phase (1) (Figure 3).



Material:	Slag	Slag_LF
Amount:	Kilogram	1000.0
Input type:	Mass percent	Component
Major component:	CaO	50.0
	Al2O3	20.0
	SiO2	20.0
	FeO	10.0
Total:		100.0

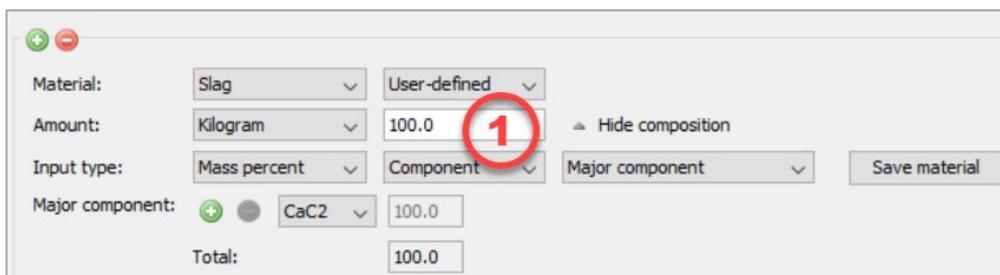
Figure 3. Same calculation as outlined in Figure 2 except that the slag composition now contains 10 wt% FeO (1).

## Recovering the Desulphurizing Ability with Deoxidation Agents

There are various methods of recovering the desulphurizing ability of the ladle slag phase after accidentally contaminating it with furnace slag. For example, the slag can be conditioned with deoxidation agents such as CaC<sub>2</sub> or Al pellets. These react with the FeO in the slag according to the following reactions:



Round brackets () indicate compounds that dissolve in the slag phase and square brackets [] indicate elements that dissolve in the liquid steel. These slag conditioners essentially deoxidize the slag and return the iron that is bound up as FeO in the slag phase back to the steel. One way of calculating the conditioning of the slag with CaC<sub>2</sub> is shown in Figure 4.

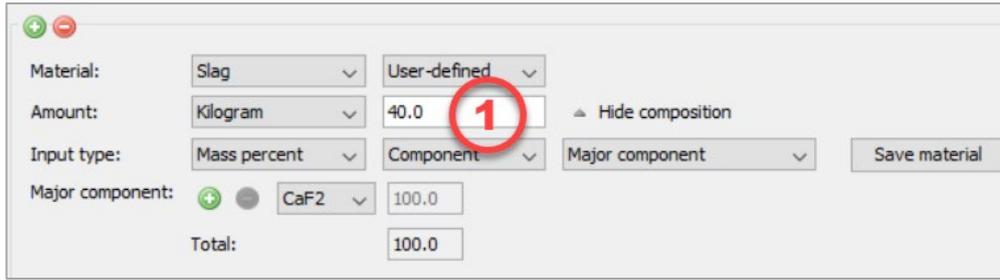


Material:	Slag	User-defined
Amount:	Kilogram	100.0
Input type:	Mass percent	Component
Major component:	CaC2	100.0
Total:		100.0

Figure 4. Same calculation as shown in Figure 3 except that 100 kg of CaC<sub>2</sub> is added as slag conditioner (1).

## Adding a Fluxing Agent to Improve Desulphurizing Ability

Alternatively, the melting point of the slag can be reduced by adding the fluxing agent CaF<sub>2</sub>. This allows the CaO content of the slag to be increased without the slag turning hard (solidifying). The higher CaO content improves the desulphurizing ability of the slag, even if it is contaminated (oxidized) by FeO. One way of calculating this is shown in Figure 5.



Material:	Slag	User-defined	
Amount:	Kilogram	40.0	Hide composition
Input type:	Mass percent	Component	Major component
Major component:	CaF2	100.0	Save material
Total:		100.0	

Figure 5. Same calculation as shown in Figure 3 except that 40 kg of CaF2 is added as slag fluxing agent (1).

## EXAMPLE RESULTS

Figure 6, top left plot shows that a slag composition of CaO - 10wt% SiO<sub>2</sub> - 15 wt% Al<sub>2</sub>O<sub>3</sub> (area shaded blue) is ideal for this particular process, as the slag is over 90% liquid and is able to reduce the S content in the liquid steel to below 0.01 wt%. If the slag is contaminated by 10 wt% FeO (for example from slag carry-over from the furnace, plot top right) its desulphurizing ability is markedly reduced (blue lines showing the S content in the liquid steel move towards CaO corner) and it is not possible to find a slag composition that is both liquid and reduces the S content of the steel to below 0.01 wt%.

This situation can be somewhat recovered by de-oxidizing the slag by a slag conditioner, such as Al or in this case CaC<sub>2</sub>. The bottom left plot is calculated for a slag contaminated by 10 wt% FeO, but 100 kg of CaC<sub>2</sub> is added to condition the slag. It can be seen that this de-oxidation of the slag recovers its desulphurizing ability.

The plot in the bottom right finally shows the situation when 40 kg of CaF<sub>2</sub> are added to the slag phase, again assuming it is contaminated by 10 wt% FeO. While the addition of CaF<sub>2</sub> does not deoxidize the slag and the slag's desulphurizing ability is not improved for a given composition, it does allow the use of a slag that is richer in CaO without risking the formation of a hard, partially solidified slag. When adding CaF<sub>2</sub> as a fluxing agent, an ideal operation window for the slag composition opens up at about 7 wt% SiO<sub>2</sub> and 10 wt% Al<sub>2</sub>O<sub>3</sub>.

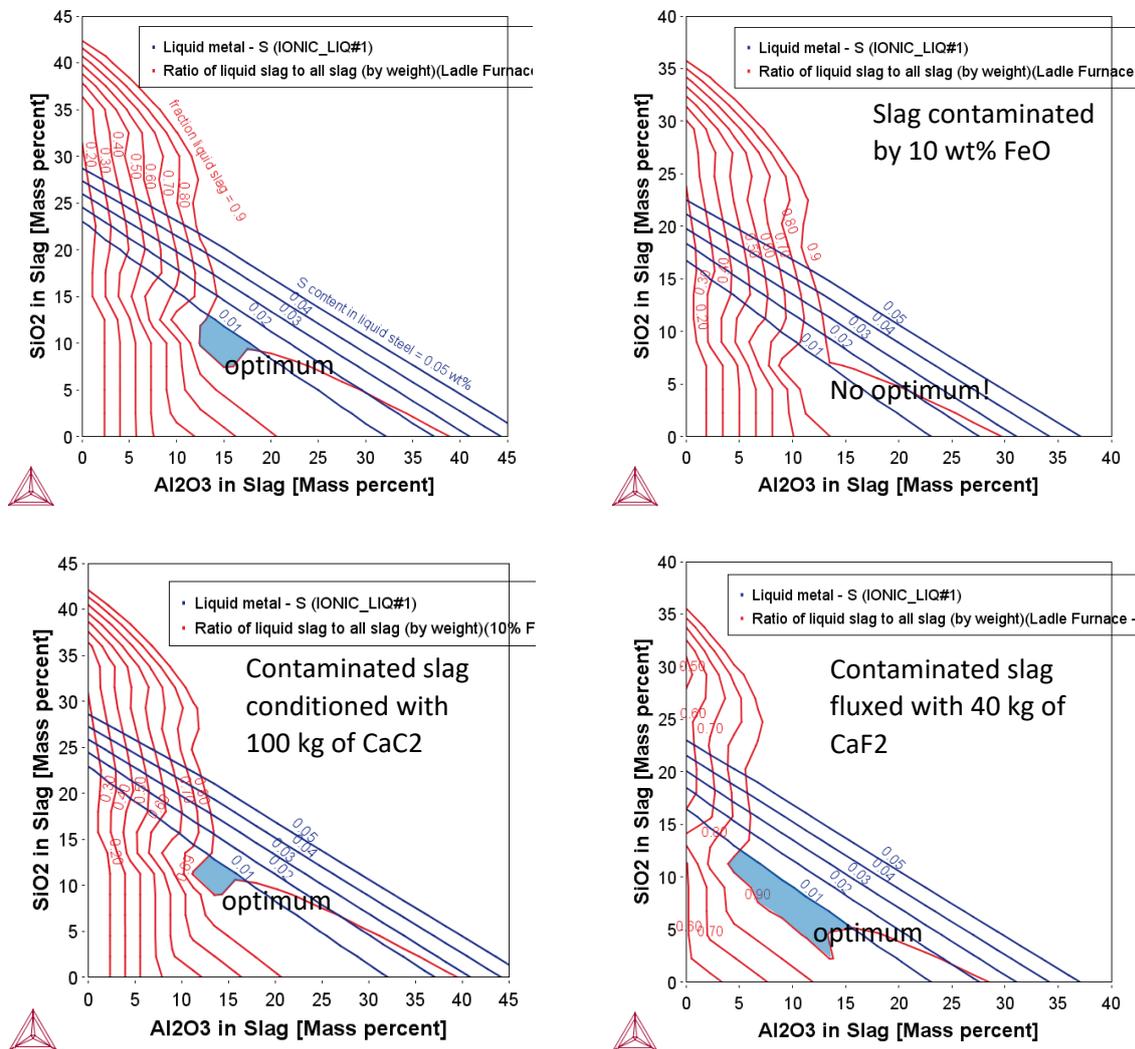


Figure 6. Plots showing the fraction of liquid slag as a function of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> content (red contour lines) and amount of S in the liquid steel phase in equilibrium with the slag (blue contour lines). The optimum slag composition is where the slag is at the same time liquid and the S content in the steel is low. No optimum is found when the slag is contaminated with FeO (top right), but the slag desulphurizing ability can be recovered by either conditioning it with CaC<sub>2</sub> (bottom left) or fluxing it with CaF<sub>2</sub> (bottom right).

## KINETICS OF THE DESULPHURIZATION PROCESS

Steel desulphurization is strongly limited by reaction kinetics and never reaches equilibrium. While the calculations shown are useful and interesting as they show where the reactions are heading and if -in principle- sound process parameters are chosen, they will not predict the final composition of the liquid steel. A better understanding of the process can be obtained by introducing kinetic models.