

**Application Example:**

# Using the Process Metallurgy Module to Calculate the Steel Deoxidation (Killing) on Tapping

Database(s):	TCOX11 or newer, OXDEMO	Module(s):	Process Metallurgy Module
Version required:	Thermo-Calc 2021b or newer	Calculator(s):	Equilibrium
Material/Application:	Steel deoxidation/killing		
Calculation name:	PMET_08_Steel_Deoxidation_on_Tapping		

## INTRODUCTION: DEOXIDATION OR “KILLING” OF STEEL

After primary steelmaking, for example in a basic oxygen furnace (BOF) or electric arc furnace (EAF), the liquid steel contains a large amount of dissolved oxygen [O] (400 to over 1000 ppm, [see example on kinetic simulation of BOF Process](#)). This oxygen must be removed from the liquid steel for several reasons, including:

- Desulphurization is not effective with high oxygen content in the steel ([see example on desulphurization](#))
- Continuous casting of un-killed steel is not possible and will result in “boiling” of the steel in the mould and massive porosity (Figure 1, right)

The two most widely applied methods of deoxidizing or killing the steel are by adding Al (Al-killed steel, Figure 1) or Si (Si-killed steel). These elements readily react with oxygen to form oxides that precipitate within the liquid steel. This does not reduce the total amount of oxygen in the liquid steel; it simply transforms the dissolved oxygen into an oxide precipitate. This oxide precipitate then needs to be removed from the steel by flotation during secondary metallurgy in the ladle furnace (LF). The oxides are lighter than steel and naturally float upwards. This upward motion is aided by purging the steel with Ar through porous plugs that are located in the bottom of the ladle.



*Figure 1 Schematic representation of deoxidation of steel by adding Al metal to the ladle (left). Blowholes formed during casting of a steel billet with insufficient deoxidation (right).*

Al is a very strong deoxidizing agent and very low values of dissolved oxygen can be achieved. The solid  $\text{Al}_2\text{O}_3$  that is formed has a plate-like morphology. The plates agglomerate to form large clusters that can be effectively removed by flotation. Even so, some of the solid  $\text{Al}_2\text{O}_3$  remains in the liquid and can cause problems later on in the process, for example, it can result in nozzle clogging during continuous casting. For this reason, Ca is sometimes added to the liquid steel in the ladle furnace. The Ca reacts with the solid  $\text{Al}_2\text{O}_3$  and transforms it into a liquid oxide that does not result in clogging.

Si forms discrete small and round  $\text{SiO}_2$  particles that do not agglomerate and are difficult to remove. Therefore, Si is mostly added in combination with Mn, as then an oxide liquid is formed which is far less detrimental to the downstream casting process. Also, the liquid precipitates tend to agglomerate to form large spherical oxide droplets that are more easily removed by flotation. As a rule of thumb, the Mn/Si ratio should be above 3:1 to assure liquid precipitate is formed. Often a combination of Si, Mn, and Al is used for deoxidation. This results in lower dissolved oxygen in the liquid steel, and, if the right amount of Al is used, it can result in predominantly liquid inclusions. Too much Al will, however, lead to the formation of solid  $\text{Al}_2\text{O}_3$  (corundum) or Mullite. In the following example we take a closer look at the deoxidation process using Thermo-Calc's Process Metallurgy Module.

## How to Run the Calculation

This example includes two calculation files. For one of them you'll need a license for Thermo-Calc 2021b or newer, the database TCOX11 or newer, and a license for the Process Metallurgy Module. The other calculation file is a simplified version that can be run with the free Educational Package and the OXDEMO database. You can also just read the PDF, which discusses the materials challenges and how Thermo-Calc can be used to solve them.

To run this example, open Thermo-Calc and navigate to the Help Menu → Example Files... → Process Metallurgy. This example includes two calculation files:

- **PMET\_08a\_Steel\_Deoxidation\_on\_Tapping.tcu**: a simplified version that can be run with the free Educational Package together with the OXDEMO database.

- **PMET\_08b\_Steel\_Deoxidation\_on\_Tapping.tcu**: requires a full license for Thermo-Calc 2021b or newer, the Metal Oxide Solutions Database TCOX11 or newer, and a license for the Process Metallurgy Module.

This document includes an in-depth description of both the examples, starting with PMET\_08a.



Read additional in-depth [Application Examples available for the Process Metallurgy Module](#), which discuss topics such as Desulphurization in a Ladle Furnace and the Basic Oxygen Furnace process.

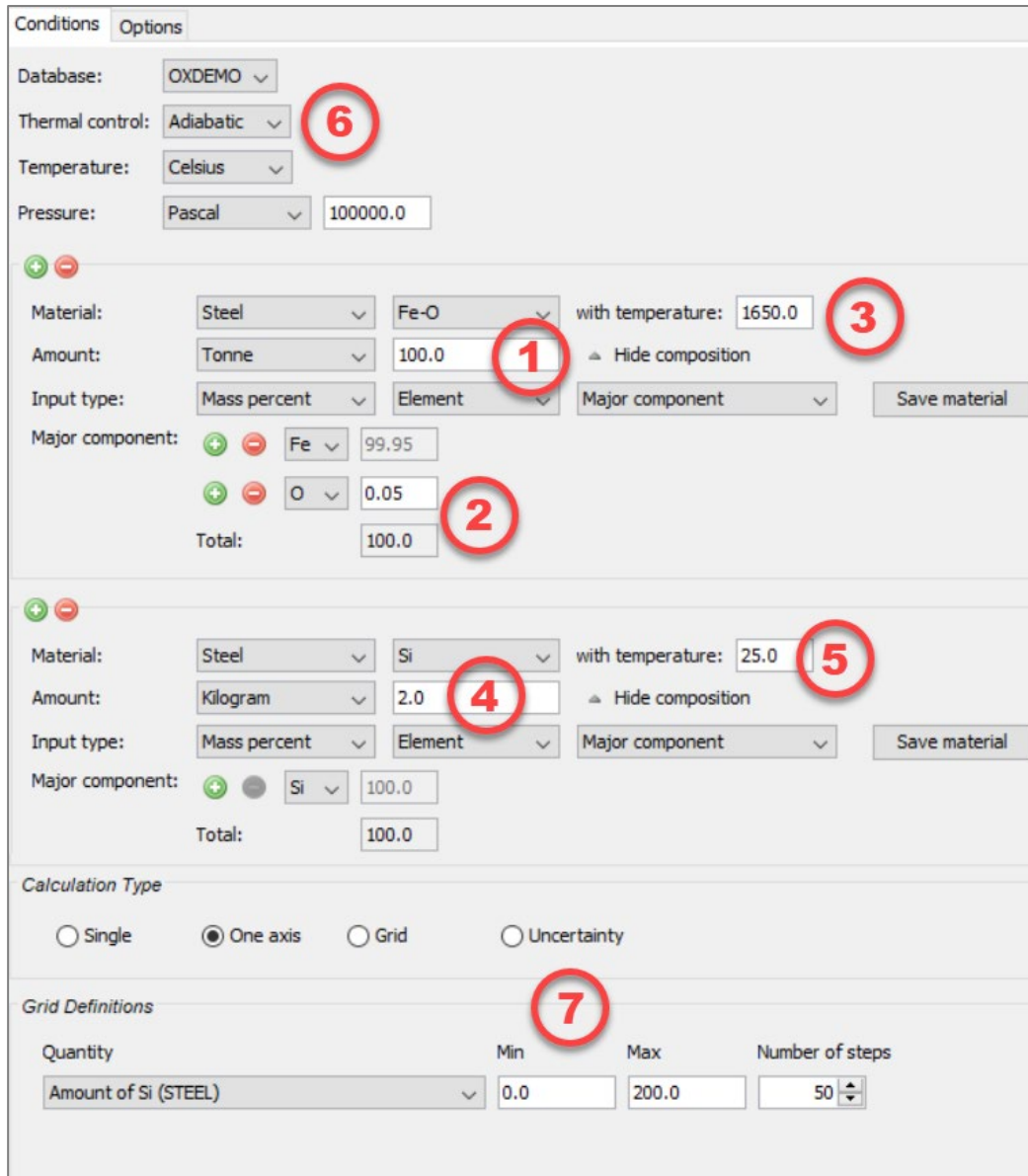
## EXAMPLE SETUP: AL-KILLING AND SI-KILLING

### ***Example file: PMET\_08a\_Steel\_Deoxidation\_on\_Tapping.tcu***

The Educational version of Thermo-Calc has full functionality, except that it is limited to 3 elements. In order for this example to be run with the free Educational version, we have simplified the chemical composition of the steel system so that it only contains Fe, O, and Al for Al-killing and Fe, O, and Si for Si killing.

A screenshot of how the calculation is set up in the Process Metallurgy Module is shown in [Figure 2](#). We assume we have 100 t of steel coming from an EAF (1). Its composition is pure iron with 500 ppm dissolved oxygen (2). The temperature of the steel is 1650 °C (3) and the killing agent we add (Si or Al, 4) has a temperature of 25 °C (5). We perform an adiabatic calculation (6). This means the temperature is free to adjust according to endothermic / exothermic reaction that might take place. Deoxidation is strongly exothermic, so the temperature is expected to increase.

We are interested in what happens to the steel if we increase the amount of deoxidation agent, so we perform a one axis calculation with the amount of Si or Al ranging from 0 to 200 kg (7).



Conditions Options

Database: OXDEMO

Thermal control: Adiabatic

Temperature: Celsius

Pressure: Pascal 100000.0

Material: Steel Fe-O with temperature: 1650.0

Amount: Tonne 100.0

Input type: Mass percent Element

Major component: Fe 99.95 O 0.05 Total: 100.0

Material: Steel Si with temperature: 25.0

Amount: Kilogram 2.0

Input type: Mass percent Element

Major component: Si 100.0 Total: 100.0

Calculation Type

Single One axis Grid Uncertainty

Grid Definitions

Quantity	Min	Max	Number of steps
Amount of Si (STEEL)	0.0	200.0	50

Figure 2. Screenshot of the Process Metallurgy Module in Thermo-Calc showing how to set up the example on steel deoxidation.

## EXAMPLE RESULTS

The calculations in Figure 3 show that Al (left) is a far stronger deoxidation agent than Si (right). After adding about 60 kg of Al, the dissolved oxygen in the liquid steel [O] drops to below 10 ppm and the Al dissolved in the liquid steel, [Al], sharply increases. Adding more Al does not significantly lower the dissolved oxygen. Si is a much weaker deoxidation agent and can only lower the dissolved oxygen to about 120 ppm. However, adding Si in combination with other elements can reduce the dissolved oxygen further, as will be shown in the second part of this example.

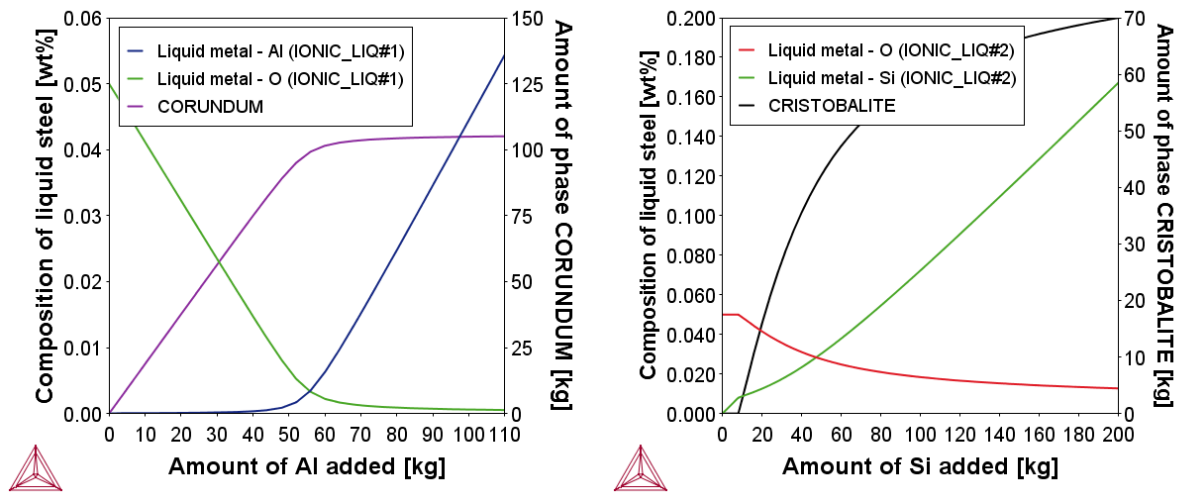


Figure 3. Reduction of the dissolved oxygen in the liquid steel [O] as a function of the amount of Al (left plot) or Si (right plot) added.

As mentioned, this calculation is performed under adiabatic conditions. The initial temperature of the liquid steel is set at 1650°C, but it is free to change due to exothermal or endothermal reactions that take place. The deoxidation reactions



are strongly exothermic, which means that even the small additions of Al and Si result in a marked increase in the temperature, see Figure 4.

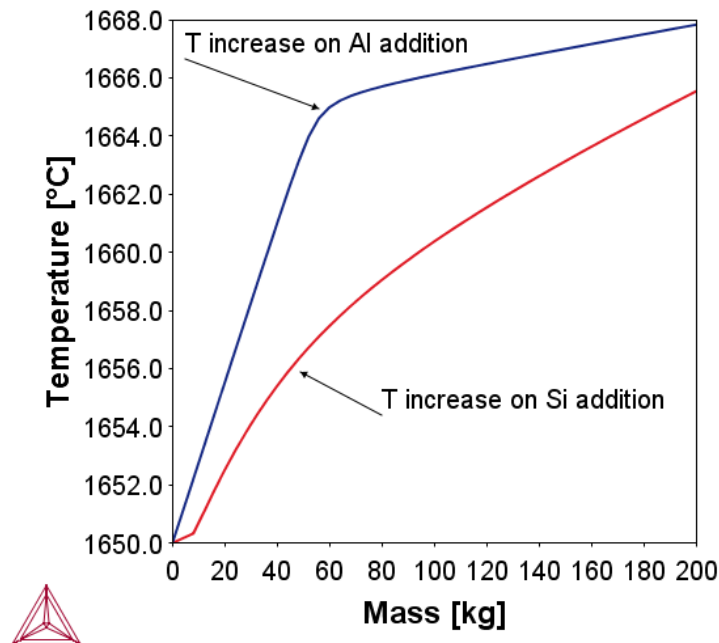


Figure 4. Temperature increase on adding Al or Si (both with a temperature of 25 °C) to liquid steel at 1650 °C that contains 500 ppm of dissolved oxygen.

## EXAMPLE SETUP: AL- AND SI-KILLING AND INCLUSION MODIFICATION

**Example file: *PMET\_08b\_Steel\_Deoxidation\_on\_Tapping.tcu***

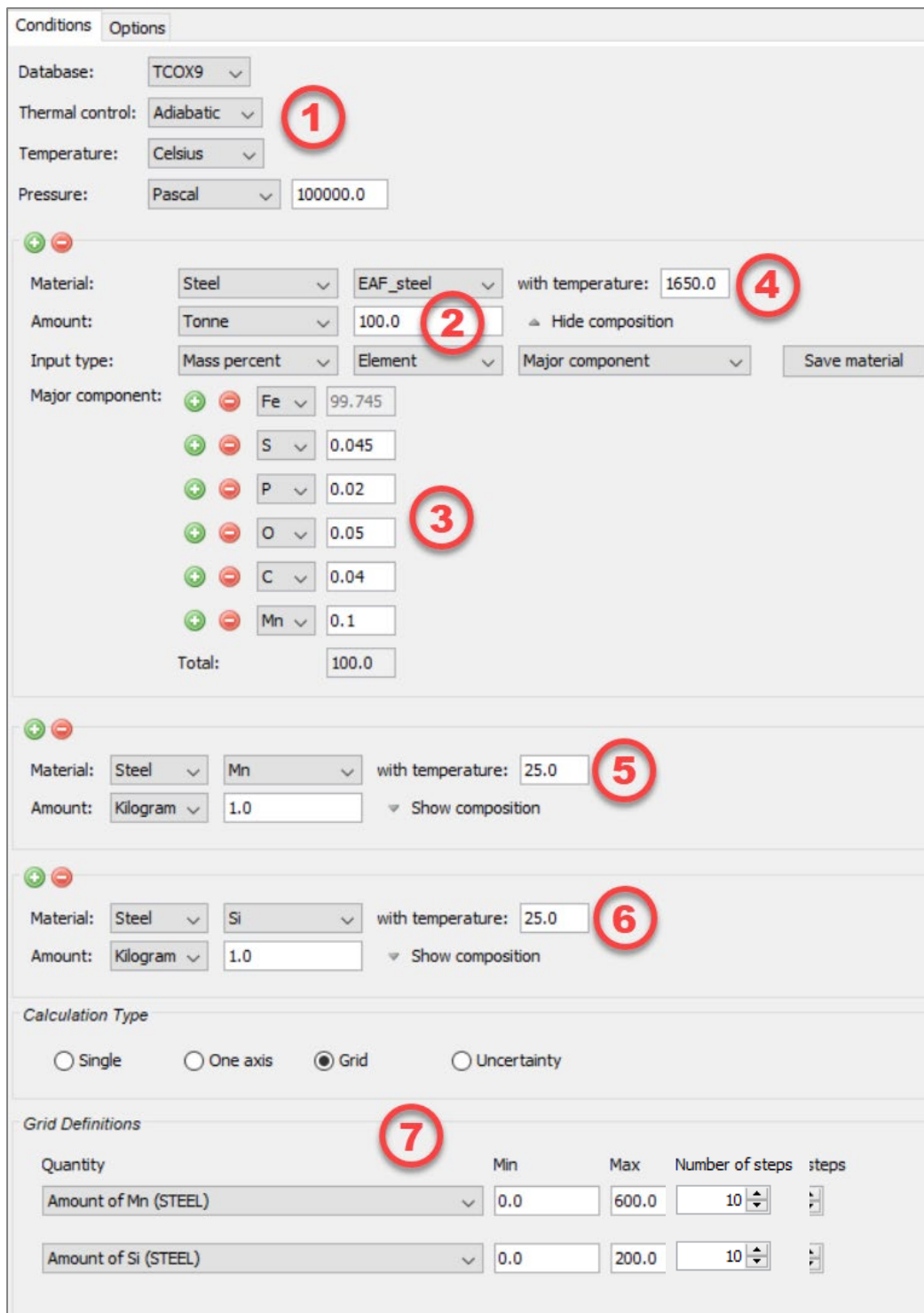
As mentioned in part 1 of this example, both solid cristobalite ( $\text{SiO}_2$ ) and solid corundum ( $\text{Al}_2\text{O}_3$ ) are not desirable in the liquid steel as they cause problems during further processing of the steel. Many processes have been developed to transform these inclusions into less damaging ones by inclusion modification or inclusion engineering. This is a large and complex topic and many interesting calculations on inclusion engineering can be performed using the Process Metallurgy Module. Here we show two simple and common processes that are used to transform the solid  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  inclusions into liquid oxides. As more than 3 elements are required for these calculations, the full version of Thermo-Calc and the TCOX11 or newer database are required. Different databases might result in slightly different results, but the differences are negligible.

A screenshot of how the calculation is set up in the Process Metallurgy Module is shown in Figure 5. We select an adiabatic calculation (1) and we input 100 t of liquid steel (2) with a composition that might be typical of a steel from an EAF (3) and give it a temperature of 1650 °C (4). We kill the steel by adding a combination of Mn and Si, both having a temperature of 25 °C when added (5,6). We make a grid calculation, adding from 0 to 600 kg of Mn and from 0 to 200 kg of Si (7).

As a comparison, we set up a corresponding calculation for Al killing. For this calculation, (5) and (6) are changed to Al and Ca respectively, and the grid calculation has 0 to 80 kg of Al added and 0 to 30 kg of metallic Ca added.

Here we choose 10 steps for each of the two axes of the grid resulting in a total of 100 equilibrium calculations. This results in a calculation time of about 30 min. Choosing fewer steps shortens the

calculation time but results in lower resolution of the calculation results. Note that the plots in this document are calculated with more steps in order to have a better resolution.



The screenshot shows the 'Conditions' tab of the Thermo-Calc Process Metallurgy Module. The interface is divided into several sections with numbered annotations:

- 1**: Thermal control: Adiabatic
- 2**: Amount: 100.0
- 3**: Major component: Fe 99.745, S 0.045, P 0.02, O 0.05, C 0.04, Mn 0.1
- 4**: with temperature: 1650.0
- 5**: Material: Steel, Mn, with temperature: 25.0
- 6**: Material: Steel, Si, with temperature: 25.0
- 7**: Grid Definitions section, showing a table with columns: Quantity, Min, Max, Number of steps, steps.

Quantity	Min	Max	Number of steps	steps
Amount of Mn (STEEL)	0.0	600.0	10	
Amount of Si (STEEL)	0.0	200.0	10	

Figure 5. Screenshot of the Process Metallurgy Module showing how to set up the example on steel deoxidation using a combination of Si and Mn to kill the steel. Using a combination of Al and Ca can be set-up in an analogous way.



## EXAMPLE RESULTS

Figure 6 shows a contour plot of the dissolved oxygen in the liquid steel (blue lines) after adding varying amounts of Si and Mn (Si-killed steel, left plot) or Al and Ca (Al-killed steel, right plot). Al is a much more powerful deoxidizing agent that allows the dissolved oxygen to be reduced to below 10 ppm. Deoxidizing with Si can reduce the dissolved oxygen to about 100 ppm.

The red contour lines show whether the formed oxides are solid or a liquid oxide. Adding Mn to Si-killed steel converts the solid cristobalite into a Si-Mn-oxide. This is termed *SiMn killing*. Typically, the Mn is added together with the Si during tapping. Adding Ca to Al-killed steel transforms the solid corundum into a Ca-Al-oxide. This process is termed *Ca-treatment*. The Ca is added to the steel at a later stage during ladle refining when the steel is largely desulphurized. If the Ca is added before desulphurization, it reacts with the sulphur, forming CaS, and does not react with the  $\text{Al}_2\text{O}_3$ . As Ca treatment is performed later during the ladle refinement, a large fraction of the solid  $\text{Al}_2\text{O}_3$  will already have floated out of the liquid steel, therefore much lower amounts of Ca are required to transform the remaining  $\text{Al}_2\text{O}_3$  than indicated in Figure 6. Also note that a lot of Ca is lost due to evaporation and oxidation before it is able to react with the oxygen dissolved in the liquid steel. Therefore, if theory says 10 kg of Ca are required to transform the solid  $\text{Al}_2\text{O}_3$  into liquid oxides, in reality, significantly more might have to be added as the rest is lost.

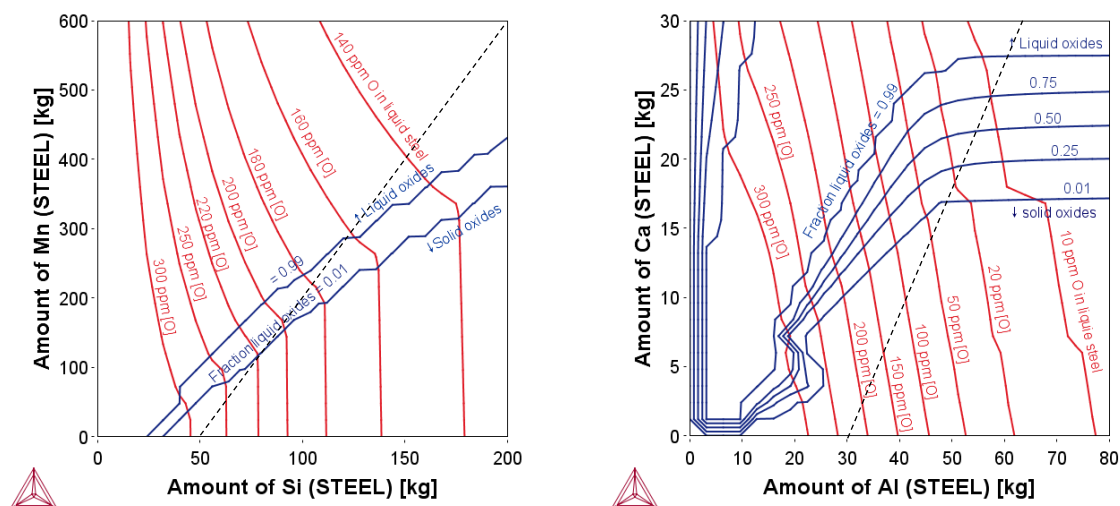


Figure 6. Contour plots showing oxygen dissolved in liquid steel (blue contour lines) and fraction of the formed oxide inclusions that are liquid (red contour lines). The left plot is for Si-Mn killing, the right plot for Al killing with subsequent Ca treatment. Later we will calculate sections through these plots along the dotted lines.

As the calculation is performed under adiabatic conditions, we can also plot how the temperature of the liquid steel changes due to the additions. The addition of Mn alone cools the steel as it simply dissolves without releasing notable amounts of heat. Addition of Si, Al, and Ca on the other hand, result in a marked increase in temperature due to the exothermal oxidation reactions incurring, but only if there is dissolved oxygen in the steel that can react.



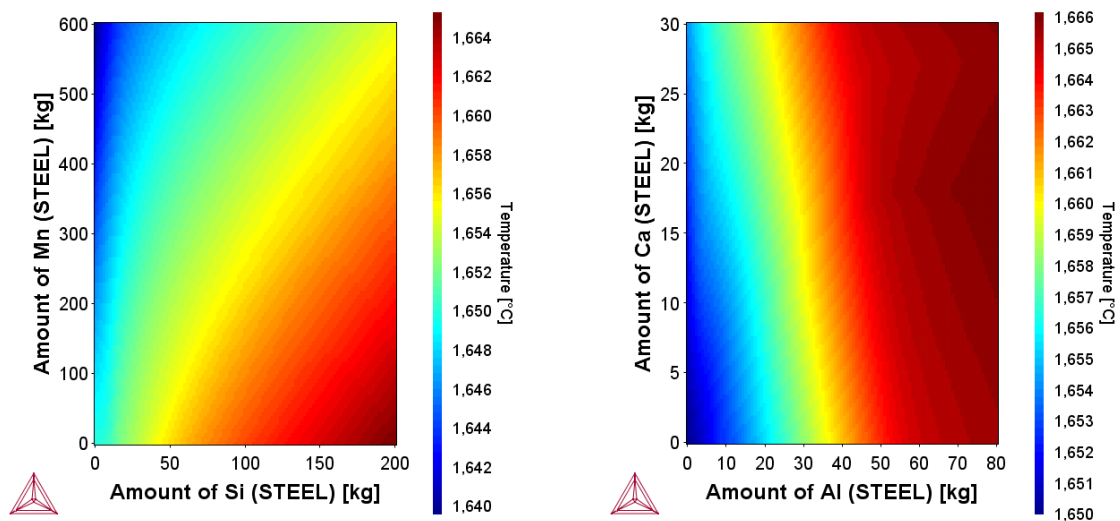


Figure 7. Heat maps showing the temperature of the liquid steel after adding the deoxidizing agents.

Adding a combination of Si and Mn or Al and Ca results in many more reactions in the liquid steel. For example, one might want to know how the concentration of all elements changes along the sections marked with dotted lines in Figure 6.

There are probably several ways to do this. A simple way is shown in Figure 8. First, the amount of Si (or Al) where the section starts on the x-axis is entered (1), then we define a material that corresponds to the slope of the section (2). Performing a one axis calculation, stepping with this material, will result in the section of interest.

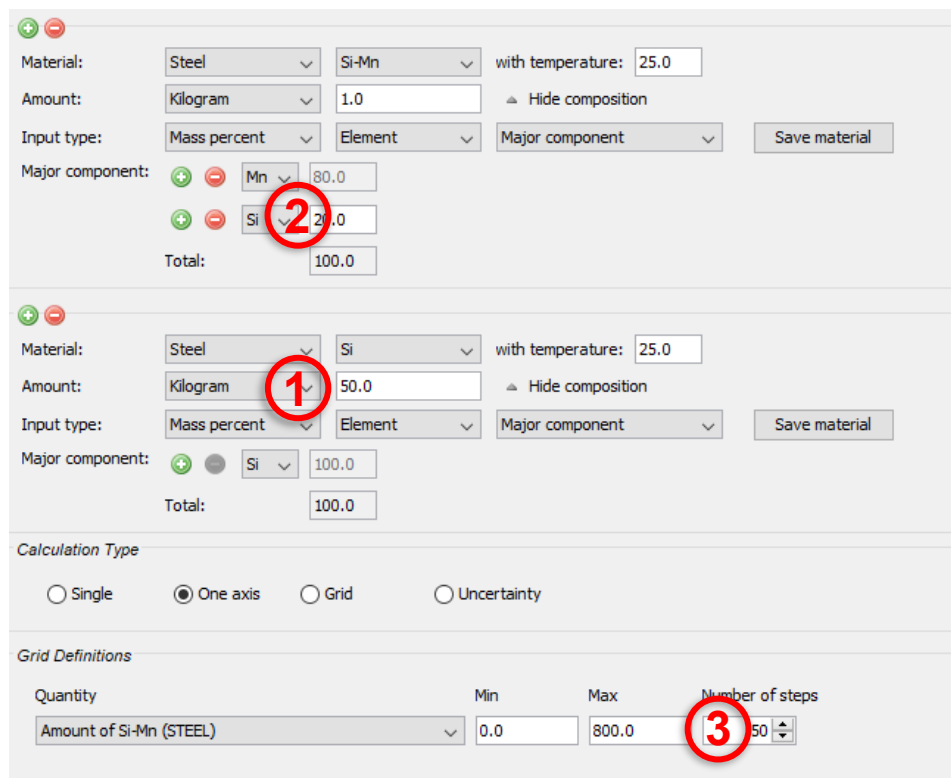


Figure 8. Screenshot of the Process Metallurgy Module showing how to calculate sections along the dotted lines of the grid-plots shown in Figure 6.

Many more properties of the liquid metal and the formed inclusions can now be plotted in these sections. The top two plots in Figure 9 show how the type and amount of inclusions change. In the case of Si-Mn killing (left), the relation is quite simple: solid cristobalite is transformed into an oxide liquid. For Al killing and subsequent Ca treatment (right), there is a succession of inclusions according to the  $\text{Al}_2\text{O}_3 - \text{CaO}$  phase diagram:  $\text{Al}_2\text{O}_3 \rightarrow \text{C1A6} (6\text{Al}_2\text{O}_3 \cdot \text{CaO}) \rightarrow \text{C1A2} (2\text{Al}_2\text{O}_3 \cdot \text{CaO}) \rightarrow$  complex oxide liquid.

The other plots in Figure 9 show how the composition of the liquid metal and the composition of the liquid inclusions that are formed changes in function of amount of SiMn or CaAl that is added.

## KINETICS OF THE DEOXIDATION PROCESS

These calculations only examine the equilibrium conditions for deoxidation. While many important predictions can be made, important kinetic information is missing, most importantly how the inclusions float up and are removed from the liquid steel and transferred to the slag phase as a function of time. Also, it should again be noted that Ca treatment of Al killed steel is performed towards the end of ladle refining, while the Al killing itself is performed right at the start during tapping. Therefore, for this process, the time axis is very important to simulate the whole process in a realistic way.

Beginning in Thermo-Calc 2020b, the Process Metallurgy Module allows for such kinetic simulations. This example, [Kinetics of Steel Refining in a Ladle Furnace](#), shows how to set up a kinetic simulation using the Process Metallurgy Module.

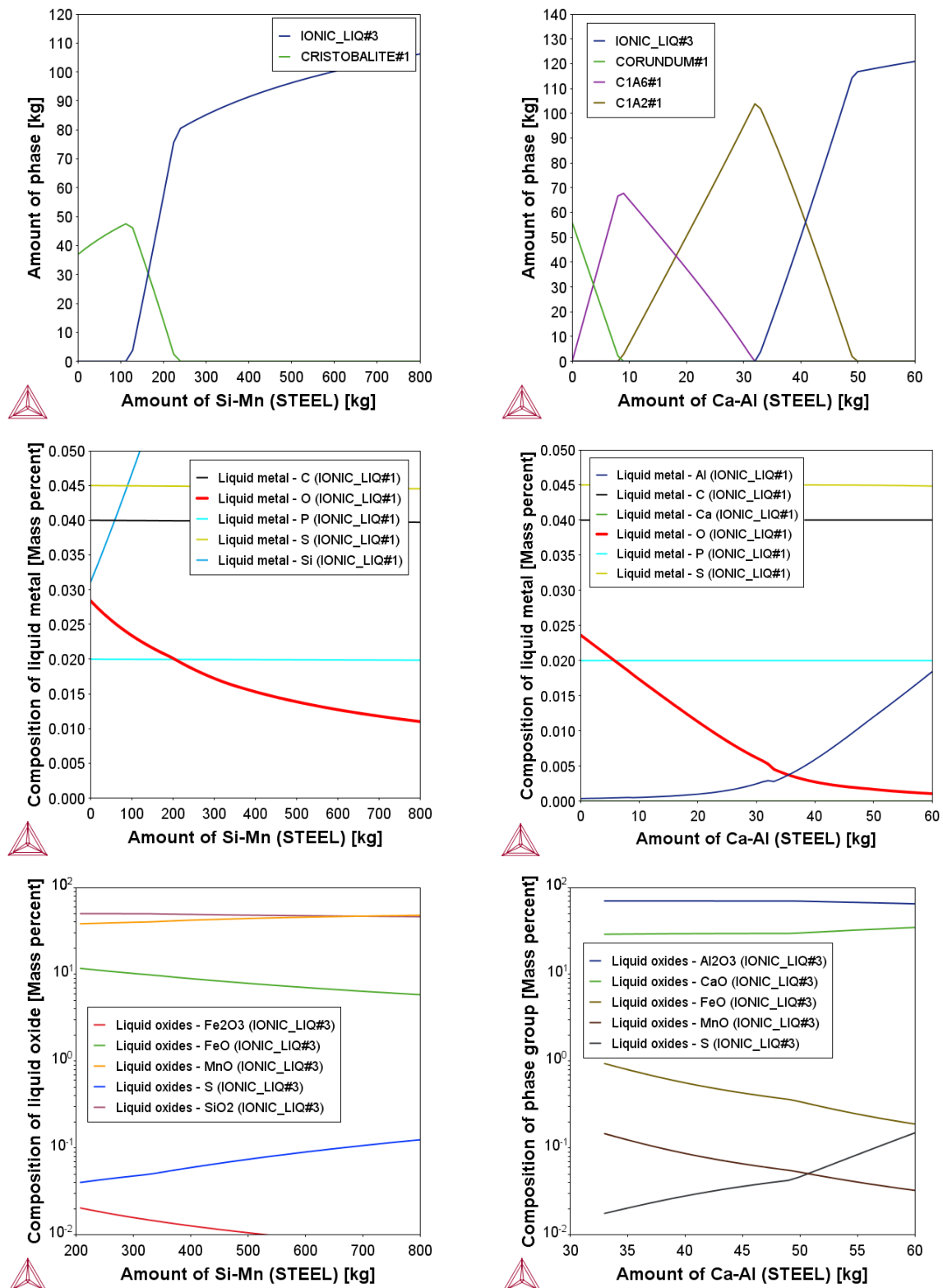


Figure 9. Plots showing some of the properties that can be calculated using the Process Metallurgy Module. The plots are sections along the dotted lines of the grid-plots showing in Figure 6. The plots on the left are for Si-Mn killing, and the plots on the right for Al killing with subsequent Ca treatment. The plots show evolution of inclusion type (top), composition of the liquid steel (middle), and composition of the liquid inclusions formed (bottom).