

Application Example:

Using the Process Metallurgy Module to Simulate the Vacuum Oxygen Decarburization (VOD) Process

Database(s):	TCOX10 or newer	Module(s):	Process Metallurgy Module
Version required:	Thermo-Calc 2021a or newer	Calculator(s):	Process simulation
Material/Application:	Stainless steel / Steel refining		
Calculation name:	PMET_07_Vacuum_Oxygen_Decarburization_Kinetics		

INTRODUCTION

This example is based on data of a real vacuum oxygen decarburization (VOD) process published by Ding *et al.* (2000) and shows how to set up the VOD process in Thermo-Calc's Process Metallurgy Module. Use of the following features in the Process Metallurgy Module are highlighted in this example:

- Change of pressure as a function of time during the process
- Change of reaction kinetics as a function of time during the process
- Selection of zone where degassing is allowed

How to Run this Calculation

If you have a license for Thermo-Calc 2021a or newer, as well as the databases and products listed below, you can follow along with this example in your software. Otherwise, you can 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 one calculation file:

- **PMET_07_Vacuum_Oxygen_Decarburization_Kinetics:** The example requires a license for Thermo-Calc, the Process Metallurgy Module, and the database TCOX10 or newer. The best results are obtained using the current database TCOX12.

Other software and database versions may work, but results may vary.

A similar example is included in our SDKs [TC-Python](#) and [TC-Toolbox for MATLAB®](#). The examples are installed locally in the SDK in the TC-Python or TC-Toolbox folders, and the full file path location is based on your OS. These examples are not directly accessible from the Thermo-Calc menu. See Thermo-Calc Installation Guides section "Installation Default Directory" for the path to the applicable folder location for your OS.

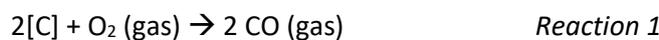
- In TC-Python: `pyx_PMET_05_VOD_process_simulation.py`
- In TC-Toolbox for MATLAB®: `matex_PMET_05_VOD_process_simulation.m`



Read additional in-depth [Application Examples available for the Process Metallurgy Module](#), which discuss topics such as Steel Deoxidation on Tapping and Kinetics of Steel Refining in a Ladle Furnace.

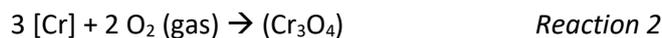
STEEL REFINING IN A VOD

One of the requirements of stainless-steel production is the ability to lower the carbon content without compromising on the Cr yield. Carbon is usually removed from steel by oxidation according to the following reaction:



Where square brackets [] indicate carbon dissolved in the liquid steel.

An unwanted side effect of this oxidation reaction is that Cr can simultaneously be oxidized according to the reaction:



Where the round brackets () indicate that the Cr-oxide is in the slag.

Note that it is not pure Cr_3O_4 that forms, but rather a Cr rich spinel phase that contains Cr+3 and also appreciable amounts of Cr+2, Mn+2, and Fe+2 in solid solution. This oxidation of Cr is unwanted as it reduces the Cr yield. One way to alleviate this problem is by running the whole process under a vacuum. This shifts *Reaction 1* to the right—the oxidation of carbon is thus favored compared to the oxidation of Cr, which is where the VOD process becomes relevant.

The VOD process can be split into the following three stages—oxygen blowing, degassing under a vacuum, and reducing. The stages are described below, followed by a graphic depicting the process.

Stage 1) Oxygen Blowing

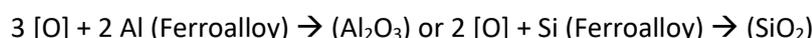
During the first stage, oxygen is blown into the VOD. Reaction kinetics are fast as the system is agitated. The main purpose during this stage is to reduce the C content of the liquid steel. Apart from C, several other elements that form stable oxides are at least partially oxidized and moved to the slag phase, such as Si, Cr, and Mn.

Stage 2) Degassing Under a Vacuum

During this stage, the pressure is reduced and no additions are made. The reduced pressure results in reduction of carbon content due to degassing by formation of CO gas according to *Reaction 1*.

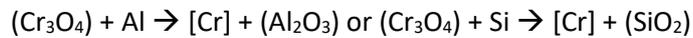
Stage 3) Reducing

The dissolved oxygen content in the liquid steel increases during oxygen blowing (stage 1). Adding alloys to the liquid steel that contain Al, Si, and Mn dramatically lowers the dissolved oxygen content according to reactions such as:



 This process and the involved reactions are identical to the well-known Al and Si “killing” practice on tapping steel from an electric arc furnace (EAF) or basic oxygen furnace (BOF) converter.

These reactions lower the oxygen activity in the whole system and can, to a certain degree, recover Cr that was lost to the slag phase during the oxygen blowing stage according to reactions similar to:



These additions result in the formation of non-metallic inclusions in the liquid steel that are gradually moved to the slag phase by flotation. This process is aided by Ar bubbling.

Also, during this stage slag formers such as lime, dolomite, and so forth, are added to control the slag composition and assure good sulfur removal ability. The topic of sulfur removal is not considered in this example but can be investigated using the Process Metallurgy Module and is discussed in [other examples](#).

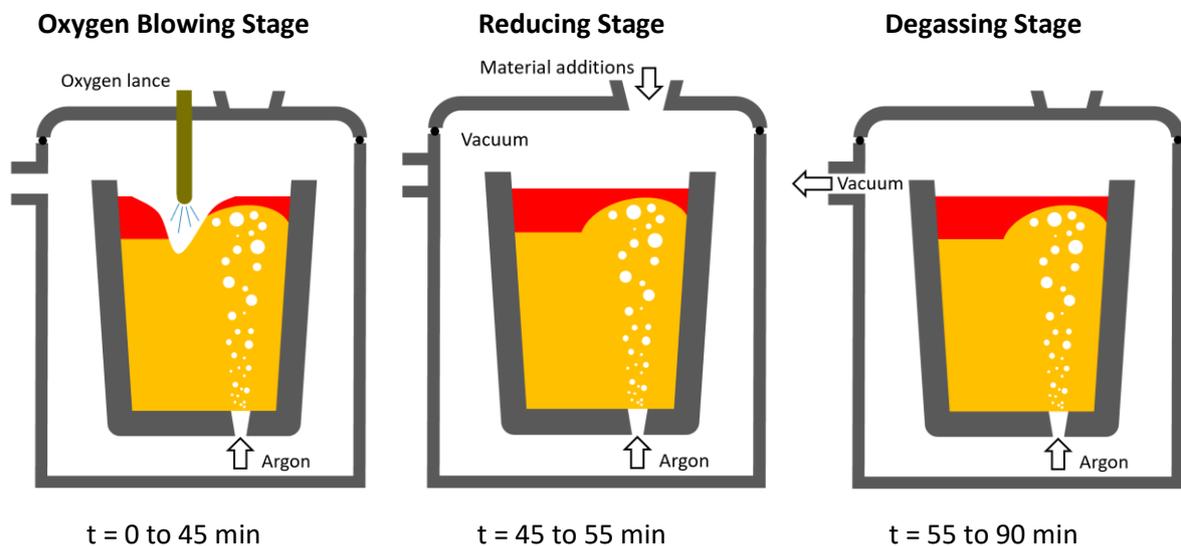


Figure 1. Schematic of the three stages of the VOD process.

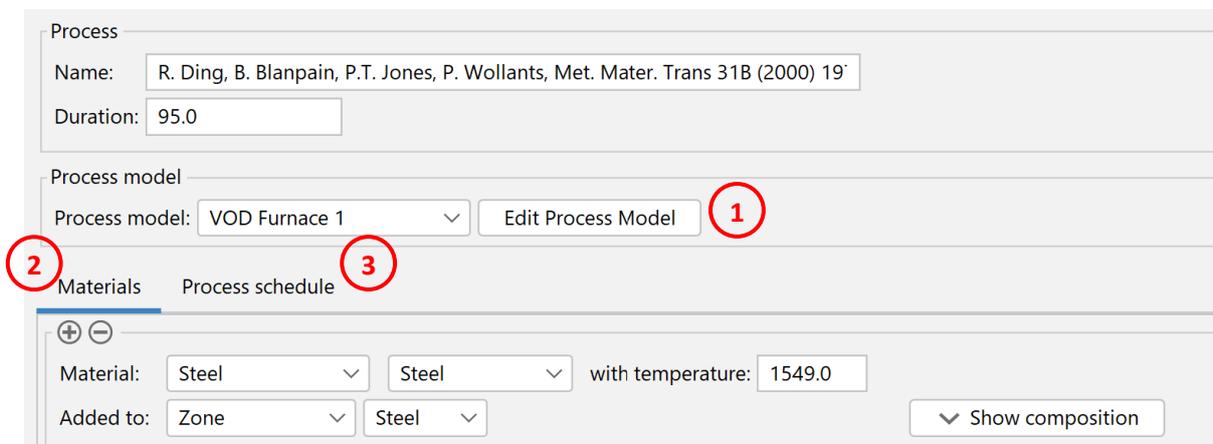
Reference

R. Ding, B. Blanpain, P.T. Jones, P. Wollants, “Modeling of the vacuum oxygen decarburization refining process,” *Met. Mater. Trans* 31B (2000) 197-206.

EXAMPLE SETUP

This example is based on data of a real VOD process published by Ding *et al.* (2000). As with all kinetic simulations in the Process Metallurgy Module, three steps are required to set up the simulation in the Process Metallurgy Module's Configuration window:

- 1) **Edit Process Model** where equipment and general process dependent kinetic parameters are defined.
- 2) **Materials** where all materials added during the process are defined.
- 3) **Process Schedule** where the timeline of the process is defined, stating what happens at which time.



The screenshot shows the configuration window for a kinetic process simulation. It is divided into three main sections:

- Process:** Name: R. Ding, B. Blanpain, P.T. Jones, P. Wollants, Met. Mater. Trans 31B (2000) 19; Duration: 95.0
- Process model:** Process model: VOD Furnace 1; Edit Process Model button (circled 1)
- Materials / Process schedule:** Materials tab (circled 2) and Process schedule tab (circled 3). The Materials section shows: Material: Steel (dropdown), Steel (dropdown), with temperature: 1549.0; Added to: Zone (dropdown), Steel (dropdown); Show composition button.

Figure 2. The three sections on the Process Metallurgy Module Configuration window where you set up a kinetic process simulation.

Step 1: Edit Process Model

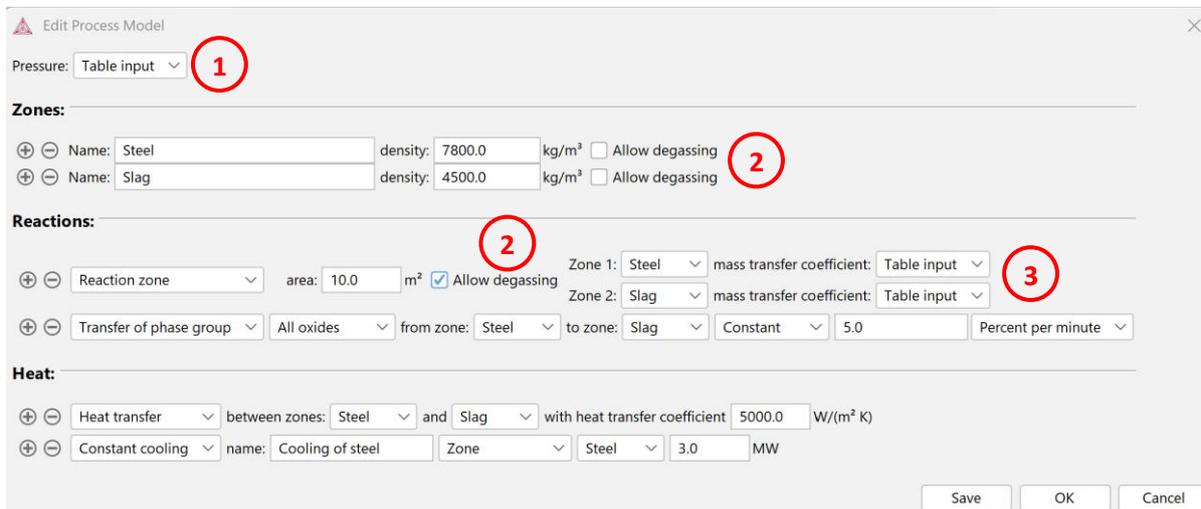
Click **Edit Process Model** to open the window where the following is defined. The numbers correspond to those in Figure 3.

1) The system **Pressure** can either be kept constant or change as a function of time. The pressure vs. time curve is defined in the **Process Schedule** table (select **Pressure>Table input**) and is valid for bulk and reaction zones of the system. The pressure of the input material (only relevant for gas phase inputs) and exhaust zone is atmospheric. The gas undergoes adiabatic expansion / compression when moving to or from the zones. The pressure only affects reactions involving the gas phase; there is no effect of pressure on the condensed phases.

2) You can define which zone the gas can escape from in both the **Zones** and the **Reactions** sections. If the **Allow degassing** check box is selected, all the gas phase formed is removed from the zone in each timestep and moved to the exhaust gas zone. This functionality gives some control over degassing kinetics. Allowing degassing in all zones results in very fast removal due to degassing, which is probably not realistic in most cases.

3) The reaction kinetics between the zones can change as a function of time by using the **Table input** option and then entering this information in the **Process Schedule**. In almost all steelmaking processes, large changes in reaction kinetics are introduced as a function of time by, for example, changing the stirring rate.

Details of the meanings of all other parameters can be found in the [Thermo-Calc documentation \(when in Thermo-Calc press F1\)](#). It is important to note that, as of Thermo-Calc 2021a, it is still only possible to define two reaction zones. Defining a third will cause an error during calculation. The possibility to define a third reaction zone will hopefully be implemented in the near future.



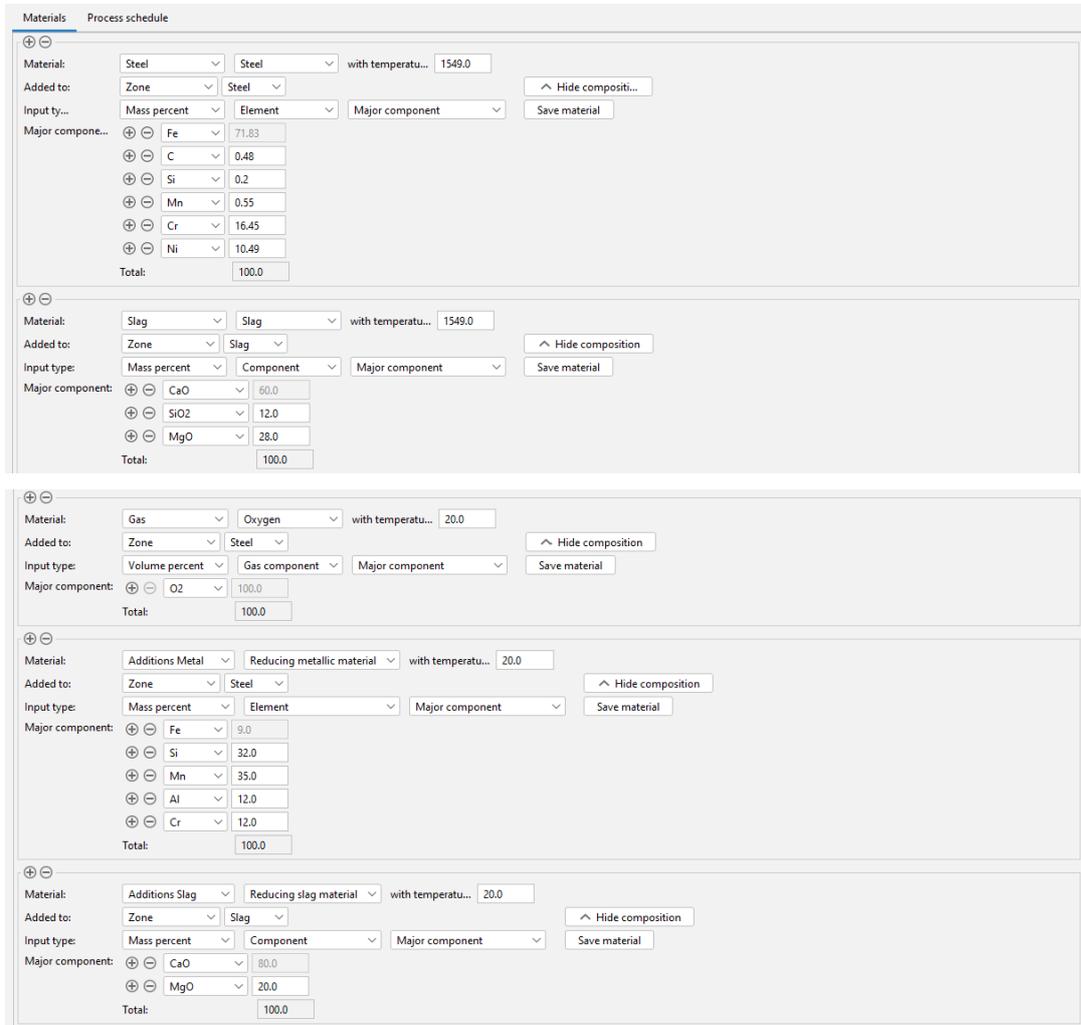
The screenshot shows the 'Edit Process Model' window with the following settings:

- Pressure:** Table input (highlighted with a red circle 1)
- Zones:**
 - Steel: density: 7800.0 kg/m³, Allow degassing (checked) (highlighted with a red circle 2)
 - Slag: density: 4500.0 kg/m³, Allow degassing (checked) (highlighted with a red circle 2)
- Reactions:**
 - Reaction zone: area: 10.0 m², Allow degassing (checked) (highlighted with a red circle 2)
 - Zone 1: Steel, mass transfer coefficient: Table input (highlighted with a red circle 3)
 - Zone 2: Slag, mass transfer coefficient: Table input (highlighted with a red circle 3)
 - Transfer of phase group: All oxides, from zone: Steel, to zone: Slag, Constant, 5.0, Percent per minute
- Heat:**
 - Heat transfer: between zones: Steel and Slag, with heat transfer coefficient: 5000.0 W/(m² K)
 - Constant cooling: name: Cooling of steel, Zone: Steel, 3.0 MW

Figure 3. Defining the process model in the various sections of the **Edit Process Model** window. Highlighted features in this example are described in the text.

Step 2: Define Materials

As in most publications dealing with real industrial steelmaking processes, only very rough process parameters and material compositions are given in the publication, usually to protect proprietary information. In the publication by Ding *et al.* (2000), at least the actual measured initial and final steel composition is given. In the example, the amounts and compositions of all other alloys and additions entered (see Figure 4) are best-guess estimates.



The screenshot displays the 'Materials' configuration window for a VOD process, showing five distinct material input sections. Each section includes a material name, zone, input type, and a list of major components with their respective percentages.

Material	Zone	Input Type	Component	Percentage (%)
Steel	Steel	Mass percent	Fe	71.83
			C	0.48
			Si	0.2
			Mn	0.55
			Cr	16.45
			Ni	10.49
			Total	100.0
Slag	Slag	Mass percent	CaO	60.0
			SiO ₂	12.0
			MgO	28.0
			Total	100.0
Gas	Steel	Volume percent	O ₂	100.0
			Total	100.0
Additions Metal	Steel	Mass percent	Fe	9.0
			Si	32.0
			Mn	35.0
			Al	12.0
			Cr	12.0
			Total	100.0
Additions Slag	Slag	Mass percent	CaO	80.0
			MgO	20.0
			Total	100.0

Figure 4. Defining the materials to be used in the VOD process. The information is entered on the **Materials** tab section of the Process Metallurgy Module's **Configuration** window.

Step 3: Process Schedule

On the Process Metallurgy Module's **Process schedule** tab, the additions and process parameters are defined as a function of time. The possibility to define the pressure of the system and also the reaction kinetics between the zones as a function of time is shown in Figure 5. As part of Step 1, the **Pressure** and the **mass transfer coefficient** settings both have **Table input** selected, and it is here in the Process Schedule where this information is entered. In this case, the reaction kinetics are significantly faster than the O₂ blowing process.

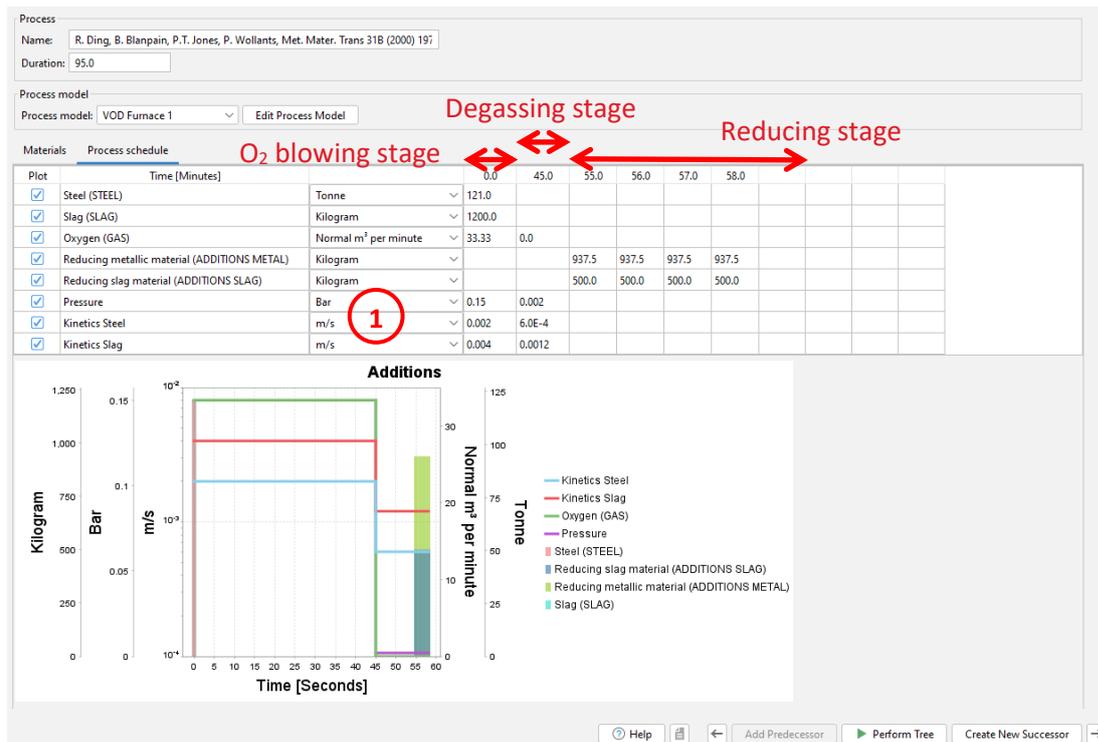


Figure 5. On the **Process schedule** tab, material additions, changes in process parameters, and so forth are entered as a function of time. As part of the set up, you can consider changes in reaction kinetics and system pressure as a function of time by adding these in the Process schedule table.

EXAMPLE RESULTS

In the following, the simulation of the VOD process using the Process Metallurgy Module is compared to the results published by Ding *et al.* (2000).

 The results from Ding *et al.* (2000) are also simulation results, based on a simple model using essentially mass balance and reaction equilibrium constants. The only experimental points available are initial and final measured temperature and initial and final measured steel composition.

Temperature

The increase in temperature during the oxygen blowing stage is due to exothermal oxidation of C, Si, Mn, and Cr (Figure 6). The heat loss from the converter due to radiation and convection, set as 3.7 MW in the **Edit Process Model** window, results in a natural cooling of about 2°C / min when there is limited contribution from reactions taking place in the converter. This is the case during the degassing stage and also toward the end of the VOD process.

The added slag formers result in a strong cooling effect of the **Slag** zone (see the temperature drop at 55 min). The reason is that these are solid and close to room temperature when added. A lot of heat is required to heat these up and melt them. The heat transfer between the **Steel** zone and the **Slag** zone (set at 5000 W/m² K in the **Edit Process Model** window) results in the evening out of the temperature difference between the slag and steel zone.

Interestingly the ferroalloys that are added to the steel zone result in an **increase** of the temperature of the steel zone, even if they are also added at room temperature and must be heated up and melted. The reason for this is that the exothermal effects due to the deoxidation of the liquid steel (the main reaction being Al in the ferroalloys reacting with dissolved oxygen in the steel to form Al₂O₃) outweighs the cooling effect of the alloy addition. This result is in strong contrast to the simulation by Ding *et al.* (2000) who probably did not account for the exothermal deoxidation reactions correctly, resulting in an overestimation of the cooling effect by the alloy addition and also resulting in a poor reproduction of the measured temperature at the end of the process.

Other interesting effects are the bumps in the slag temperature at ~10 min and again at ~80 min. These are not calculation errors or numerical uncertainties but are due to phase transformations taking place in the slag phase, most notably the formation and disappearance of the Cr-spinel phase and the change in fraction of liquid slag.

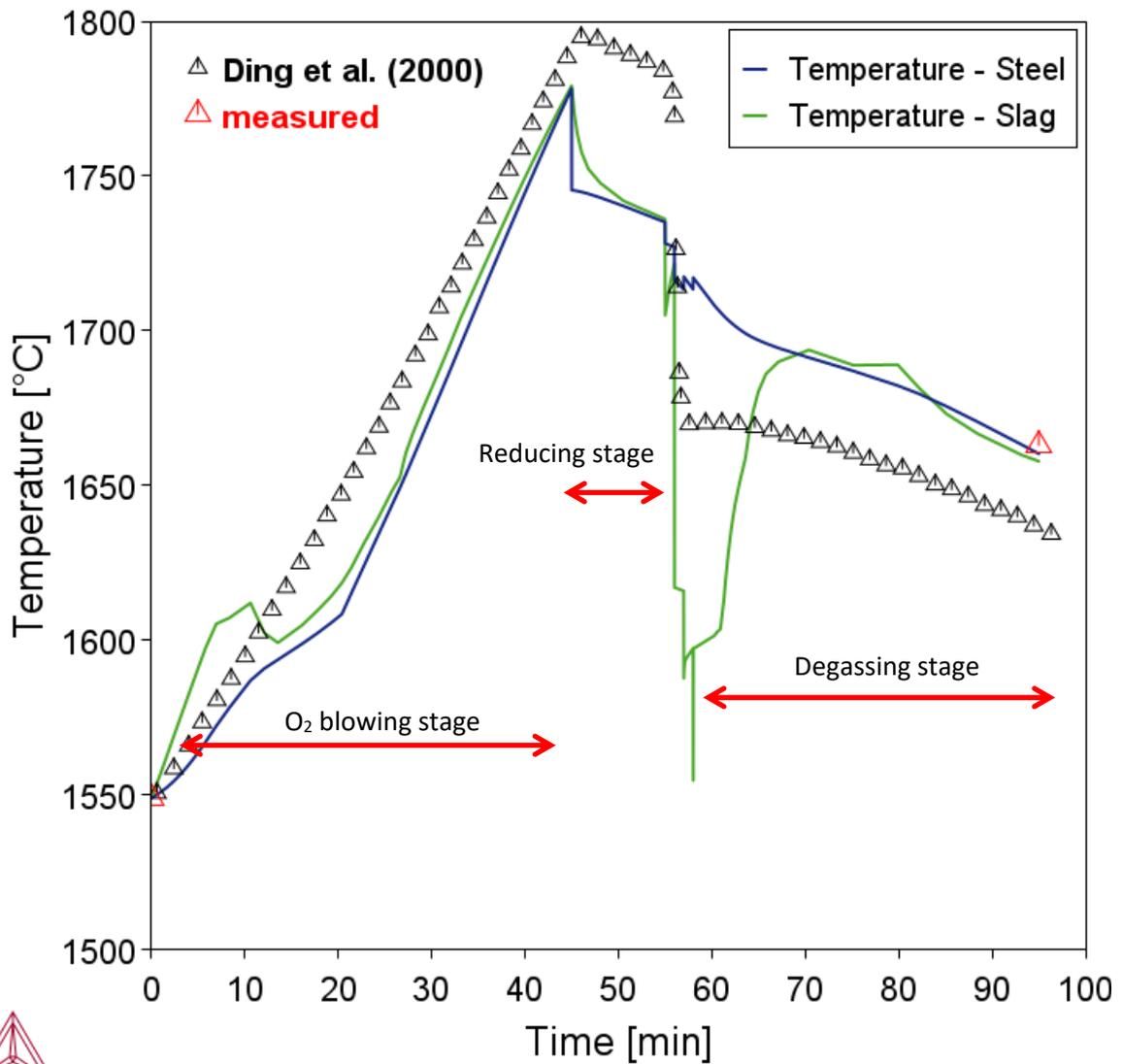


Figure 6. Calculated temperature in the steel and slag zones as a function of processing time in the VOD compared to the simulation results from the publication by Ding et al (2000). Note that the only experimental data available is the initial and final temperature (red triangles). The black triangles are simulation results by Ding et al.

Steel Composition

Many aspects of the change in steel chemistry important for the VOD process are very well reproduced by this simple model.

- Chromium:** Cr content in the liquid steel is reduced during the O₂ blowing stage due to oxidation and movement of Cr-spinel to the slag phase. During the reduction stage a lot of the Cr is recovered by reversal from the slag phase back into the liquid steel.
- Carbon:** The removal of C by oxidation to CO gas as a function of processing time—one of the main purposes for applying the VOD process—is also well reproduced.
- Oxygen and Aluminum:** Oxygen can be present in the steel zone either in dissolved form [O] or as a “foreign” phase. During the O₂ blowing stage the O content is increased partially due to the increased amount of dissolved oxygen [O] and partially due to the formation of CO gas bubbles and Cr-spinel inclusions. During the degassing stage, the O content decreases due to the removal of CO gas bubbles and flotation of Cr-spinel. On the addition of Al rich ferroalloys, the dissolved oxygen drops dramatically. The Cr-spinel is quickly replaced by Al₂O₃. Flotation of these Al₂O₃ inclusions during the reduction stage results in gradual lowering of the total O and Al content.
- Silicon:** The Si content is initially lowered by oxidation and uptake in the slag phase. Significant amounts of Si are added to the steel on addition of the ferroalloys. However, no Si-rich inclusions are formed, as the Al that is also added to the liquid steel has a significantly higher affinity for O. The dissolved Si does, however, react with the slag and plays an important role in the reversal of Cr from the slag back into the liquid steel according to the following reaction:



It should be noted that the Process Metallurgy Module is significantly better at reproducing the measured final Si content in the liquid steel compared to the original model of Ding *et al.* (2000).

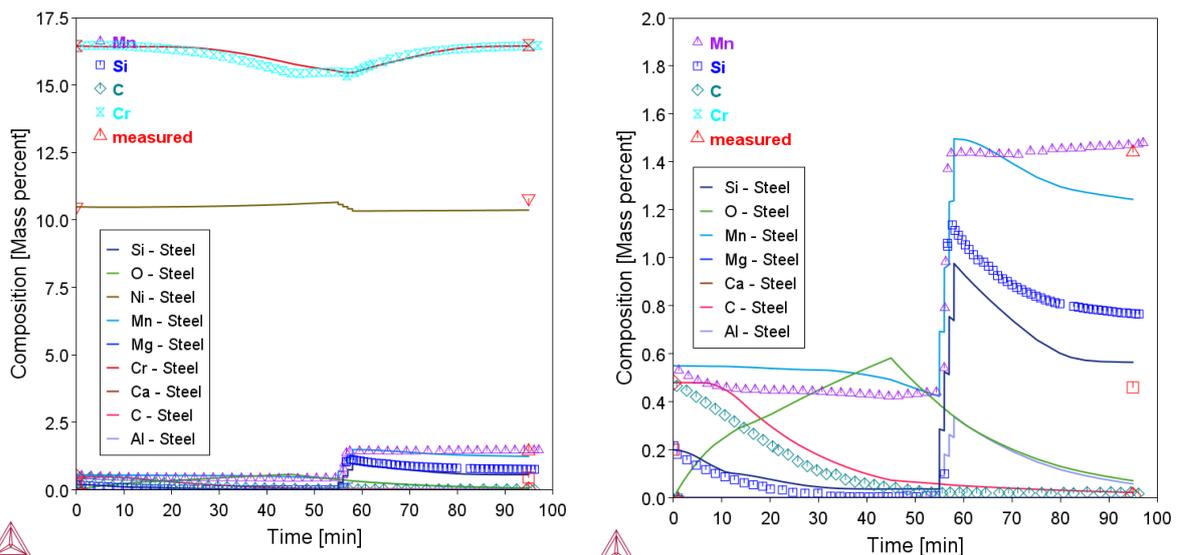


Figure 7. Comparison of the evolution of the chemical composition of the steel zone as a function of processing time with the simulation results of Ding *et al.* (2000). Note that the only experimental data available is the initial and final composition (open red symbols). All other symbols are simulation results by Ding *et al.* (2000). The right figure is a zoomed in version of the left figure.

Slag Composition

The evolution of the slag composition in the VOD process is highly complex. It can basically be divided into two parts.

- 1) During the O₂ blowing stage, the amount of slag strongly increases due to the oxidation of Si, Mn, and very importantly, Cr, from in the liquid steel. The formed slag is only partially liquid and unreactive, meaning it cannot, for example, aid in the steel desulfurization.
- 2) During the reduction stage, alloy additions are made to reduce the active oxygen in the steel zone. This results in the “killing” of the steel and the formation of Al₂O₃ inclusions. These float out of the steel zone, resulting in a gradual reduction of the total O and Al content in the steel zone (see discussion above and dotted line for O and Al content in Figure 7). As these inclusions are moved to the slag zone, they result in a pronounced increase in Al₂O₃ content of the slag (see dotted red line in Figure 8).

The slag composition is, of course, closely related to the steel composition due to the constraint of mass balance. The same processes as described above can be observed on the addition of the ferroalloys to the steel zone—the contrast in oxygen activity between the steel and the slag zone resulting from Al rich ferroalloys drives the dissolved Si in the steel zone to the slag zone. The Si entering the slag zone reduces the Cr-oxide to metallic Cr and enables the reversal of the Cr back out of the slag zone and into the steel zone according to a reaction similar to the following:



 The additions of slag formers to the slag phase during the reduction phase are made to obtain a liquid slag with high basicity and sulfur capacity. This is done to further lower the sulfur content in the liquid steel. This important topic is not discussed in Ding *et al.* (2000) and, therefore, is also not included in this example. The example can easily be modified to investigate desulfurization.

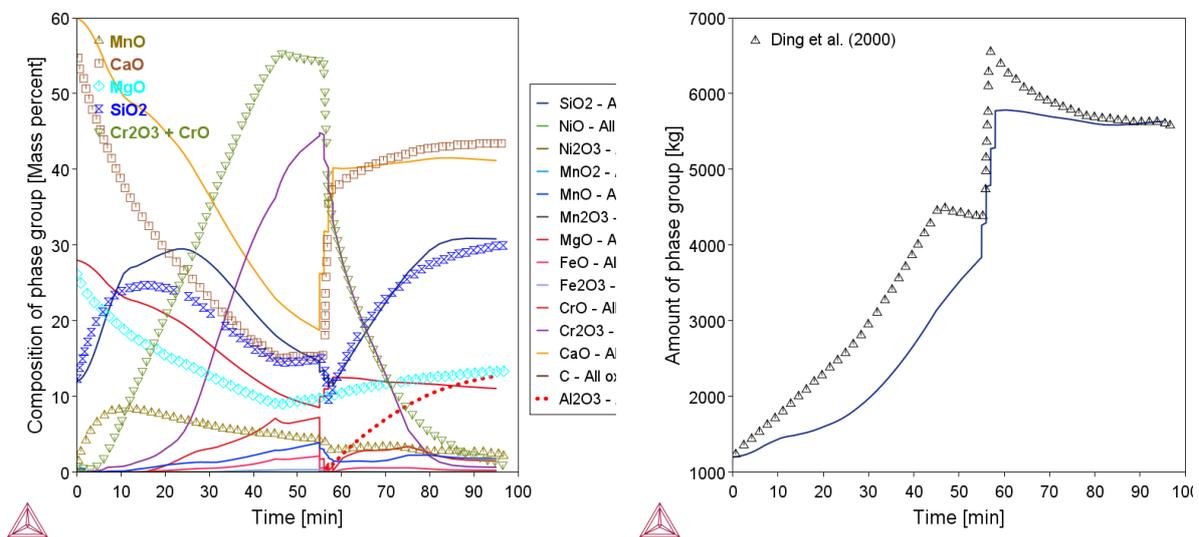


Figure 8. Evolution of the slag chemistry (left) and slag amount (right) as a function of time. The comparison is made to the simulation results by Ding *et al.* (2000) (open symbols) only, as no experimental data is available.

ADDITIONAL RESULTS AND EXTENTIONS TO THE EXAMPLE

As is the case for all examples included with Thermo-Calc, this example is intended to provide a starting point for users to adapt and expand upon the concepts and features available in our software. In particular for the Process Metallurgy Module, these examples are also to help users gain a deeper understanding of a given process.

Below is a selection of further plots that are presented to highlight additional information that can be obtained using the Process Metallurgy Module, and which show more advanced ways to set up a model based on equilibrium constants, similar to that by Ding *et al.* (2000).

The section numbers below correspond to the same numbers for each plot as part of Figure 9.

1) Liquid fraction of slag phase. Slag compositions are usually carefully tailored in order to have a high fraction of liquid phase. Only if this is the case can adequate reaction kinetics be expected between the slag and the liquid steel. Slags with a high fraction of solid phases (“hard slag”) tend to remain passively on top of the liquid steel and are essentially useless for processes such as desulfurization.

2) Slag and steel viscosity. The viscosity of the slag (and to a lesser extent the liquid steel) is important to understand the reaction kinetics between liquid steel and slag. The TCS Metal Oxide Solutions Database (TCOX) contains viscosity of both slag and liquid steel as a function of temperature and composition, which can conveniently be plotted as a function of time during the process.

3) Slag basicity. An important function of slags is to remove unwanted dissolved impurities from the steel phase, most importantly sulfur. Traditionally certain characteristic numbers have been defined based on the slag chemistry that gives an indication of how well-suited the slag is to absorb sulfur (“sulfur capacity”). A selection of these values (various definitions of slag basicity, Bells ratio, and so forth) are implemented in the Process Metallurgy Module for plotting.

4) Slag constitution / phase make up. The phase-by-phase constitution of the slag as a function of processing time is available for plotting. For the VOD process described in this example, it can be seen that the slag initially contains a low liquid fraction. As temperature increases during O₂ blowing, the liquid fraction starts increasing. After about 20 minutes, the oxygen potential is high enough for the oxidation of Cr, which results in the formation of Cr-rich spinel in the slag phase. During the reduction stage, the Cr-spinel is gradually decomposed (reduced) and the Cr is reversed to the liquid steel. As a side note: these phase changes are what cause the blips in the slag temperature curve shown in Figure 6.

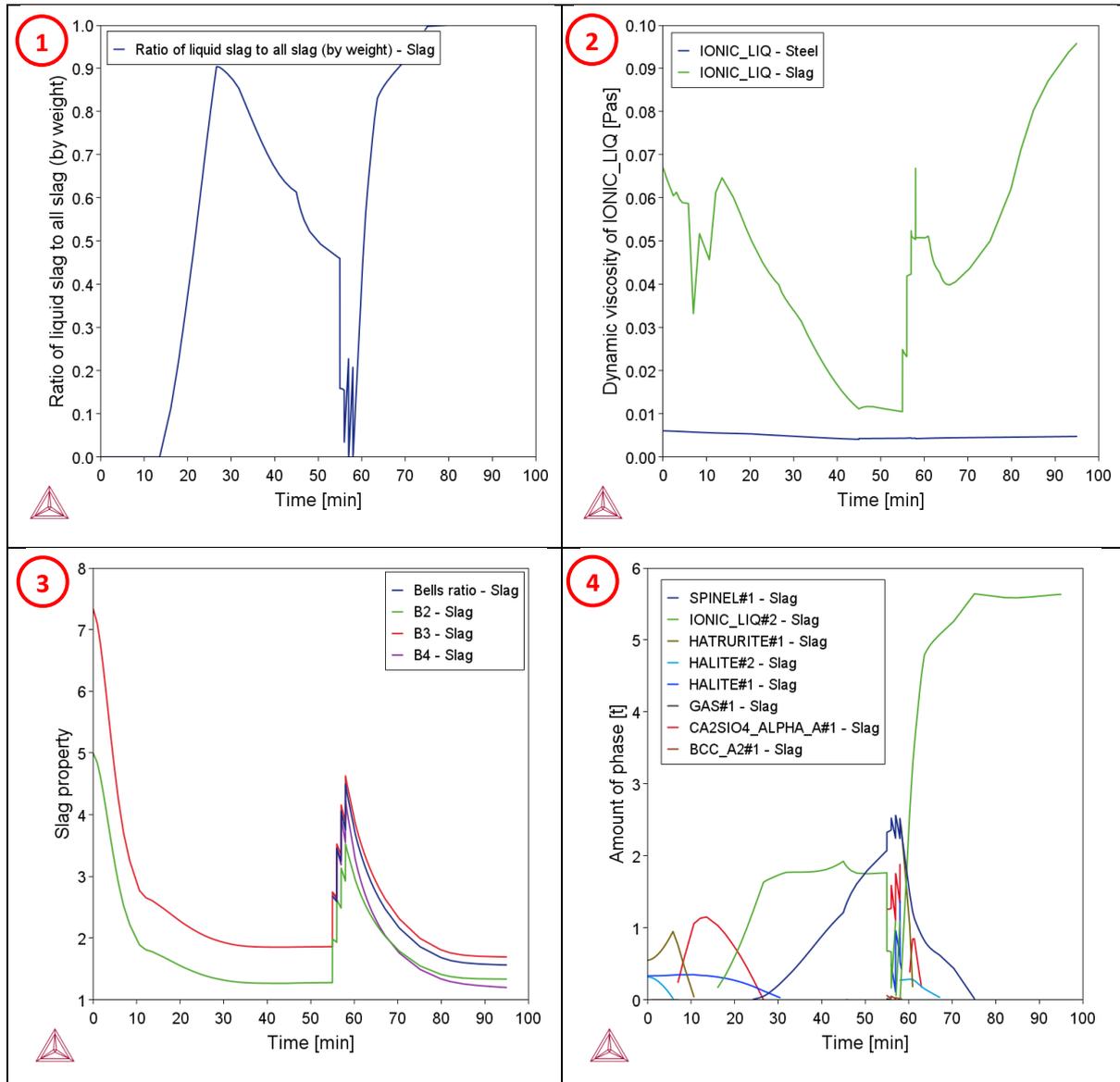
5) Inclusions in liquid steel. Non-metallic “foreign” phases can form in the liquid steel zone by the reaction of oxygen with elements that have a high affinity for oxygen. Such phases are typically called inclusions and are gradually removed from the liquid steel by flotation due to their lower density and also by the general upward motion induced by Ar stirring. For this VOD process, it can be seen that the O₂ blowing first forms CO gas inclusions that are gradually removed from the liquid steel zone.

Note that selecting the **Allow degassing** check box for the **Steel** zone in the **Edit Process Model** window in *Step 1: Edit Process Model*, would result in these gas bubbles immediately being removed from the steel zone.

After about 20 minutes the oxygen activity is high enough for the formation of Cr-spinel inclusions that are gradually moved to the slag zone. On the addition of the Al containing ferroalloys at 55 min,

the oxygen activity in the liquid steel drops dramatically and the Cr-spinel inclusions are quickly transformed into Al_2O_3 corundum.

6) Oxygen activity in steel and slag zone. This is an interesting plot showing how the oxygen activities change as a function of time in the steel zone and the slag zone. During the O_2 blowing stage, the activity in the steel zone is increased as it is assumed that the O_2 is added mainly to this zone. The oxygen activity in the slag phase gradually follows suit due to steel-slag reaction kinetics. On the addition of Al rich ferroalloys at the start of the reduction stage, the oxygen activity in the steel zone drops dramatically. This difference in oxygen activity between the two zones is what drives the reversal of Cr out of slag back into the liquid steel (see also discussion above and Figure 8).



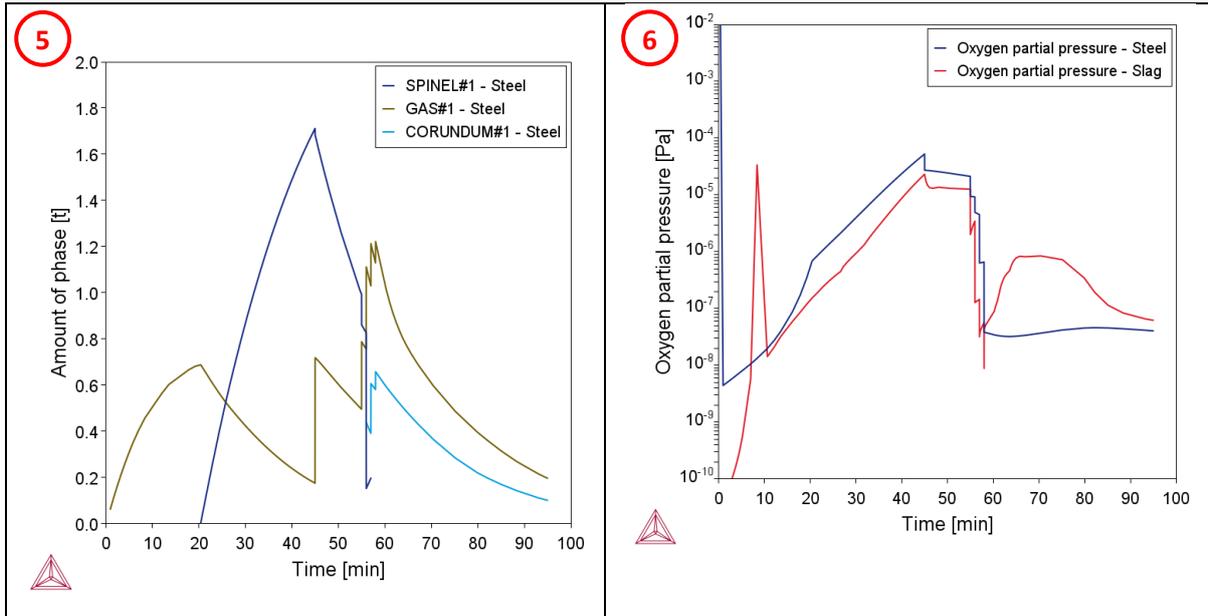


Figure 9. Additional plots and data that can be extracted from the kinetic simulation of the VOD using the Process Metallurgy Module in Thermo-Calc.