Application Example:

Using the Process Metallurgy Module to Simulate Kinetics of Steel Refining in a Ladle Furnace (LF)

Database(s):	**TCOX10 or newer**	Module(s):	**Process Metallurgy Module**
Version required:	**Thermo-Calc 2020b or newer**	Calculator(s):	**Process simulation**
Materials/Application:	**Ladle furnace / Desulphurization**		
Calculation name:	**PMET_06_Ladle_Furnace_Kinetics**		

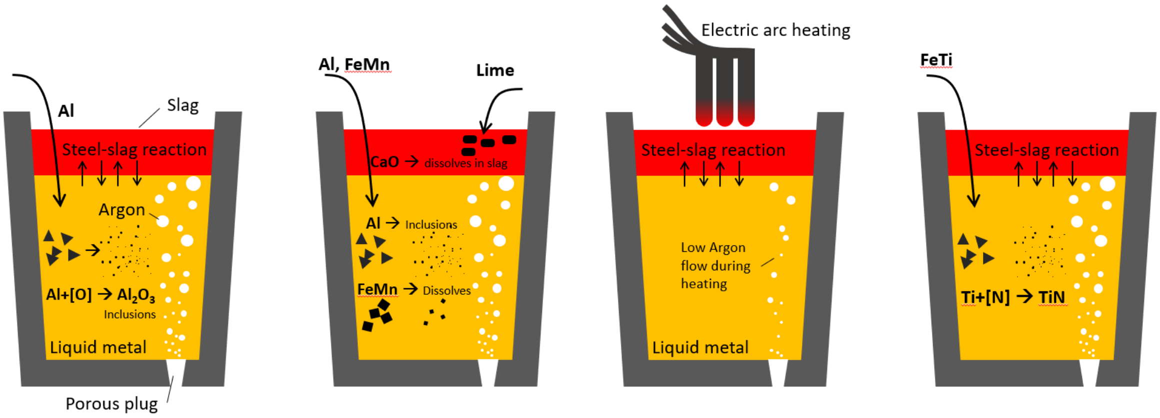
INTRODUCTION

After steelmaking, which is mostly performed in a basic oxygen furnace (BOF) or electric arc furnace (EAF), the steel is usually tapped into a ladle where certain additions are made (deoxidation agents, slag formers, certain alloying elements) and then transferred to the ladle furnace (LF). The LF fulfils many purposes in the steel refining process, the most important being:

- Temperature control / heating by an electrical arc.
- Mixing by Ar or N_2 bubbling through porous plugs in the bottom of the ladle to achieve homogeneous temperature and composition throughout the ladle.
- Removal of unwanted non-metallic phases / inclusions such as corundum (Al_2O_3), liquid oxide inclusions, spinel, on so on, by flotation, aided by Ar or N_2 bubbling.
- Modification / engineering of non-metallic inclusions so that they are not detrimental for the downstream processing and/or the final product.
- Removal of unwanted volatile elements such as Pb, Zn, Sn, and so on. Due to their high vapor pressure, these elements are enriched in the rising Ar or N_2 bubbles. After the gas escapes out of the ladle and cools, they condense, forming copious amounts of dust.
- Removal of unwanted elements such as sulphur by liquid steel / slag reactions.
- Lowering of the dissolved gas content. In the LF this is mainly achieved through chemical reactions. For direct removal of dissolved gas, vacuum degassing (VD) is usually required.
- Alloying and trimming of the steel to achieve the exact alloy composition required by the specification of the steel that is to be produced.

The reactions taking place in a LF are a complex interplay between equilibrium thermodynamics that define the direction of chemical reactions, and kinetics that define how fast the equilibrium state is approached.

In this example, a full kinetic simulation of the LF refining process schematically shown in Figure 1 is set up using Thermo-Calc's Process Metallurgy Module. The simulation is based on an LF process described in a publication by Graham and Irons [1], and the results of the simulation are compared to their experimentally determined steel, slag and inclusion composition as a function of processing time.



Time = 1 min	**Time = 20 min**	**Time = 27 min**	**Time = 39 min**
105 kg Al added to	140 kg Al added	Heating by electric arc	46 kg of FeTi added
165 t liquid steel	50 kg FeMn added		
4.95 t slag	100 kg Lime added		
Ar bubbling	Ar bubbling	Ar bubbling	Ar bubbling

Figure 1. Overview of the LF process to be simulated in this example.

How to Run the Calculation

If you have a license for Thermo-Calc 2020b 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 access the calculation, open Thermo-Calc and navigate to the Help menu → Examples Files… → Process Metallurgy. This example includes one calculation file:

- **PMET_06_Ladle_Furnace_Kinetics.tcu**: requires the database TCOX10 or newer, a full license of Thermo-Calc 2020b or newer, and a license for the Process Metallurgy Module. The best results are obtained using the current TCOX12 database.

There is also a Video demonstrating the setup of this example.

Read additional in-depth Application Examples available for the Process Metallurgy Module, which discuss topics such as Steel Deoxidation on Tapping and the Basic Oxygen Furnace process.

DESCRIPTION OF THE KINETIC MODEL OF THE LADLE FURNACE

In this example, the thermodynamic equilibria of the various reactions taking place are calculated using the CALPHAD database TCOX10, and the reaction kinetics are simulated using the Effective Equilibrium Reaction Zone (EERZ) model. This kinetic model assumes that local equilibrium at the liquid steel slag interface is reached, but that the kinetics of the reaction is limited by the mass and heat transfer along compositional and thermal gradients to and from this reaction interface. This means that only a fraction of the liquid steel and the slag phase reach thermodynamic equilibrium during a certain time-step.

In the following, a detailed description is given on how the EERZ model is implemented in Thermo-Calc's Process Metallurgy Module using the LF process as an example. More details and background information can also be found in the publication by Mason *et al.* [2].

Kinetics of the Reaction between Liquid Steel and Slag, Reaction Zone

Considering only the reaction between the slag phase and the steel liquid phase, one time-step can be subdivided as follows (sketches 1-6 in Figure 2):

1) The initial situation with a liquid steel (steel zone) and slag phase (slag zone) next to each other but *not* in equilibrium.
2) An EERZ is defined encompassing a fraction of the liquid steel phase and a fraction of the slag phase. The size of the zone is determined by the mass transfer coefficients in the steel and the slag zone. A fast mass transfer results in a large EERZ and results in fast kinetics and vice versa. Empirical relations between mass transport and parameters such as viscosity of the liquid steel and slag, stirring intensity, number and positioning of porous plugs, surface area, and so on can be found in the literature.
3) The bulk chemical composition within the EERZ is calculated.
4) The equilibrium phase fractions and phase compositions within the EERZ are calculated.
5) The oxide phases in the EERZ are mixed with the rest of the slag phase and the metallic phases in the EERZ are mixed with the rest of the liquid steel.
6) A new liquid steel and slag composition is achieved that is closer to equilibrium. In the next time-step, the cycle restarts at 1.

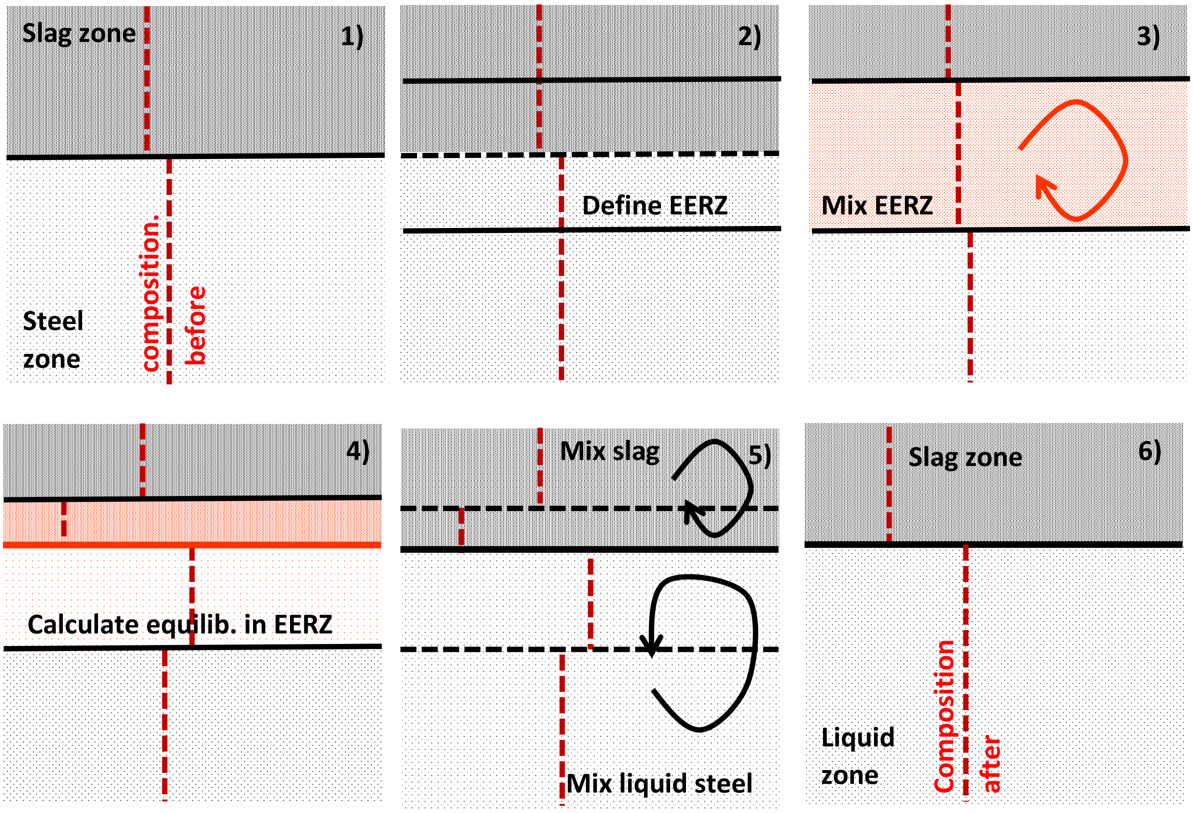


Figure 2. Schematic of the kinetic model assuming only the reaction between the liquid steel and the slag phase.

These six steps outline the general principle of the EERZ model without addition of alloys or other materials and without considering heat input or heat loss.

Material Additions and Process Schedule

Various materials are added to the ladle at different points in time during steel refining in an LF: Ferroalloys are added to the steel as bulk addition or by wire feeding, slag formers are added to the slag, and so on, gas (typically Ar or N_2) is bubbled through the steel to mix it, thereby promoting inclusion flotation, dissolution of alloys and temperature homogenization.

The method by which the material is added determines the predominant way it dissolves and reacts. Heavy ferroalloys such as ferromanganese sink through the slag phase then melt and dissolve in the liquid steel. They should, therefore, be added to the steel zone. Lighter metals such as Al can be added to the stirring eye (the point where the rising Ar bubbles displace the slag on the surface) where they react partially with the slag phase and partially with the liquid steel. Adding Al away from the stirring eye results in it reacting mainly with the slag phase. Al could also be added by wire feeding. Careful control of the feeding speed and angle based on the speed at which the wire melts result in the Al being added deep into the liquid steel. This means Al could be added to the slag zone, steel zone, reaction zone, or a split between the three, depending on the actual method of addition.

Slag formers such as lime (CaO) are mostly added to the stirring eye so they are well mixed and quickly dissolved in the slag phase. Adding them away from the stirring eye results in them being very slowly dissolved into the slag phase. They are best added to the slag zone, as part of the addition might be assumed to be added to the reaction zone.

Figure 3 illustrates how one-time material additions are handled. Additions to the steel or slag zone are dissolved and mixed in the respective zone before the EERZ is defined, and additions to the EERZ are dissolved after the zone is defined.

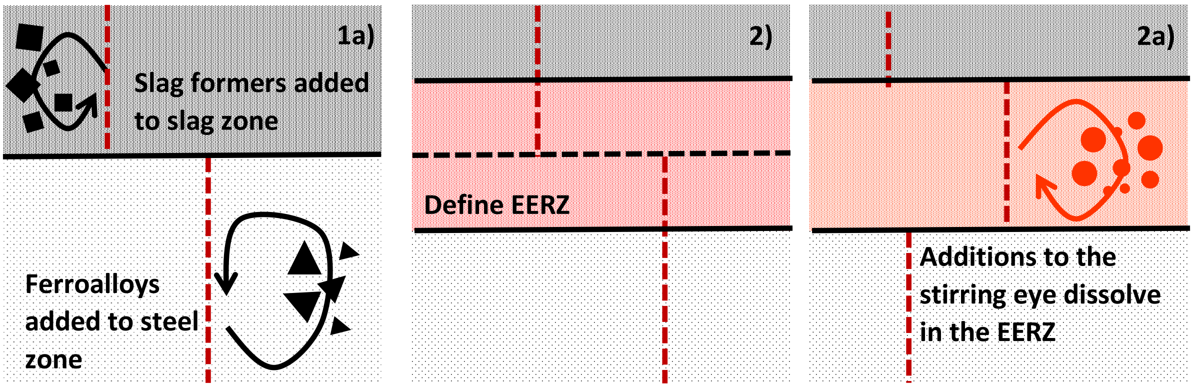


Figure 3 Schematic of the kinetic model for material additions.

Material Additions with Formation of New Phases: Transfer of Phase Group

The assumption made above is that the added material melts and dissolves in the zone to which it is added. This assumption is mostly true if a ferroalloy addition is made to the liquid steel zone or a slag former is added to the slag phase. However, certain additions result in the formation of a “foreign” phase, in other words, non-metallic phases in the liquid steel zone and metallic phases in the slag zone. The most typical example for this is the addition of a deoxidizing agent such as Al or Si to the liquid steel coming from the converter or EAF, that contains a large amount of dissolved oxygen. Such an addition results in the formation of Al_2O_3 (corundum), SiO_2, or other more complex solid oxides or even liquid oxide droplets. These phases (often referred to as inclusions) have a lower density than the liquid steel and gradually float upwards aided by rising gas bubbles from purging gas that is fed through porous plugs at the bottom of the ladle. At every time-step, a certain fraction of these inclusions combine with the slag phase and are removed from the liquid steel. The rate at which this happens is governed by the phase transfer per time-step given in percent per minute.

The same approach is used to model the transfer of metallic phases formed in the slag zone. If, for example, due to slag carryover from the furnace, the slag contains high amounts of FeO and MnO, then strongly reducing slag conditioners (metallic Al or CaC_2) can be added to the top of the slag where they melt and reduce the FeO and MnO, possibly even SiO_2 and other slag components to metallic Fe, Mn, and Si. The resulting liquid metal droplets sink through the slag and combine with the liquid steel. This process of phase transfer is outlined in Figure 4.

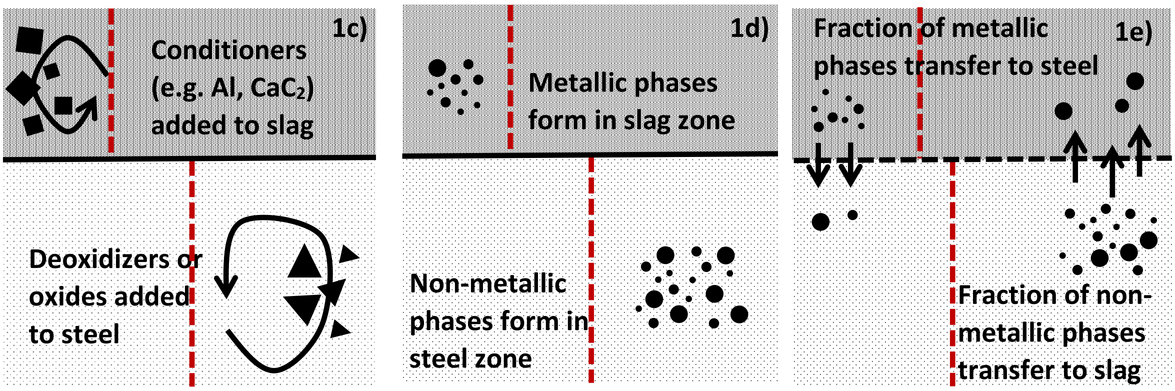


Figure 4. Schematic of the kinetic model for material additions resulting in the formation of new phases and the transfer of these newly formed phases from one zone to another.

In this example, the addition of Al at times 1 minute and 20 minutes results in the formation of solid Al_2O_3 in the steel zone that is transferred to the slag zone by phase transfer.

Isothermal versus Isenthalpic or Adiabatic Equilibrium Calculations

There are two ways to define thermal conditions when calculating thermodynamic equilibrium. The first is to fix the temperature (isothermal condition). This requires that heat evolving from exothermal reactions, for example, the heat evolved by the oxidation of [C] dissolved in hot metal to CO / CO_2 gas by oxygen blowing in a converter, is dissipated out of the system and the enthalpy of the system gets lower. The heat required for endothermic reactions must flow into the system, thereby increasing the enthalpy. In most cases, this is not a good approximation of real systems.

The second possibility is to fix the enthalpy of the system (adiabatic conditions). This allows work to be exchanged with the surroundings, but not heat. The work that is exchanged is volume change against the external pressure ($P \cdot dV$). This term becomes important for calculations involving the gas phase, and significant differences are obtained for calculations under vacuum conditions or ambient conditions. Fixing the enthalpy means that heat evolving from an exothermic reaction stays in the system and results in a temperature increase and vice versa for an endothermic reaction. Process simulations in Thermo-Calc’s Process Metallurgy Module use such adiabatic conditions.

Heat Addition and Heat Loss at Each Time-step

For adiabatic calculations, heat can also be added or removed from the system. For example, heat can be lost through the ladle walls or heat can be input by electric arc heating. The increase or decrease of enthalpy in the system results in an increase or decrease of the temperature. The heat added to or removed from the system must be attributed to a certain zone. Heat lost by conduction through the ladle walls could be removed from the steel zone, and heat loss by radiation off the top of the ladle from the slag zone. Heat added by electric arc heating is probably best accounted for by adding enthalpy to the EERZ. It is important to note that heat is also added when materials are added. The added heat corresponds to the enthalpy of the added materials at the temperature they have on addition.

Heat Exchange between the Various Zones

When implementing adiabatic conditions, different amounts of heat are generated in, added to or removed from the different zones. This results in the zones having different temperatures. The temperatures equalize by the flow of heat from the hotter to the cooler zones. The heat flow is controlled by heat transfer coefficients between the zones.

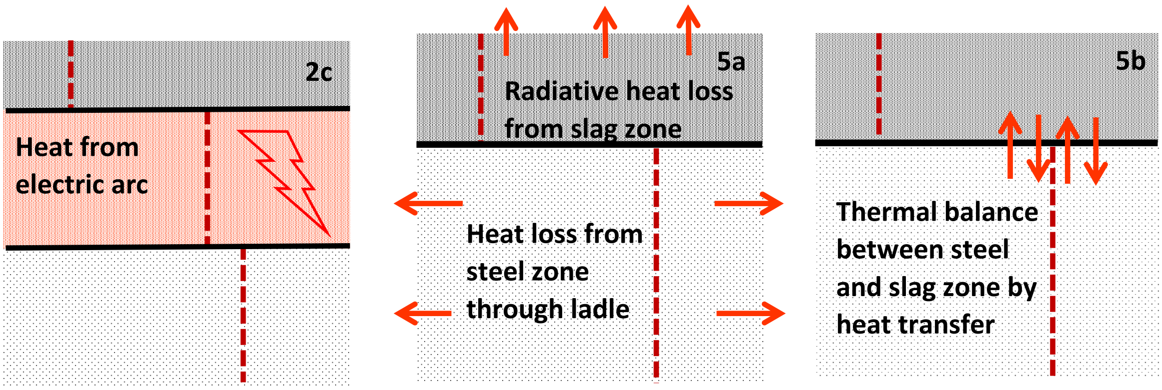


Figure 5. Heat added to and removed from the system and heat exchange between different zones.

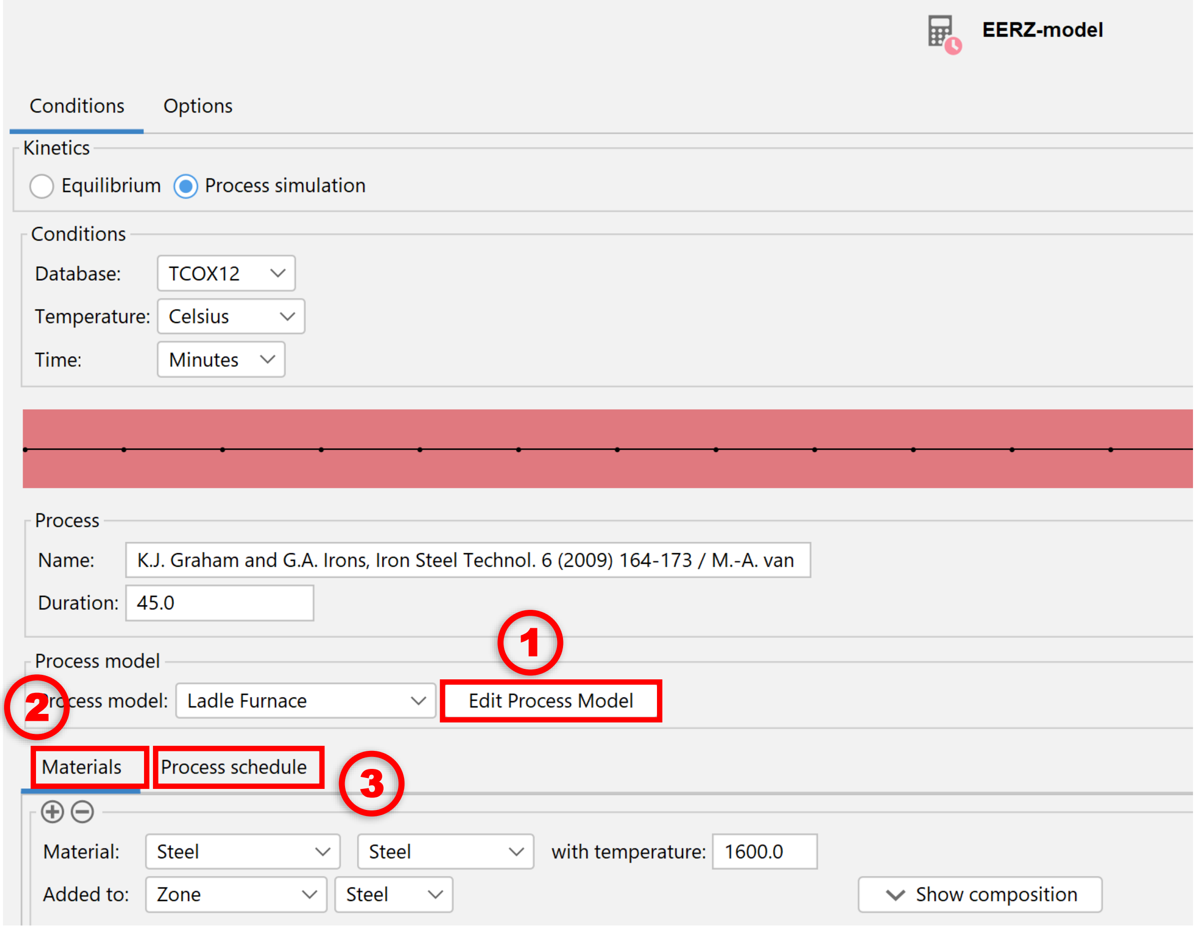
EXAMPLE: KINETIC SIMULATION OF THE LADLE FURNACE PROCESS

The example sets up a kinetic simulation of the LF process shown in Figure 1 applying the EERZ model as outlined in the previous section. All kinetic simulations in the Process Metallurgy Module require setting up the following three steps:

Edit Process Model (1)
Here general kinetic parameters are defined. It is assumed that they are specific for the general process and the equipment size and shape that is used in the experiment and must only be defined once.

Define Materials (2)
In this tab, all the material compositions that are to be used during the process are defined.

Define the Process Schedule (3)
In this tab, the steelmaking recipe is entered, which defines at what times how much of which materials are added.



Kinetics: ○ Equilibrium ● Process simulation

Conditions

Database: TCOX12

Temperature: Celsius

Time: Minutes

Process

Name: K.J. Graham and G.A. Irons, Iron Steel Technol. 6 (2009) 164-173 / M.-A. van

Duration: 45.0

Process model

Process model: Ladle Furnace

Material: Steel Steel with temperature: 1600.0

Added to: Zone Steel

Figure 6. The three steps for settings up a kinetic simulation in the Process Metallurgy Module.

Step 1: Edit the Process Model

The first step in setting up a kinetic simulation in the Process Metallurgy Module is to edit the Process Model. Here, various kinetic parameters are defined that are assumed to be related only to the type of process and geometry of the equipment used. The idea is that there is one set of parameters for this specific ladle furnace, a different set of parameters are required for a basic oxygen furnace (BOF), then different parameters for the vacuum degasser, and so forth. The parameters should, however, be independent of chemical compositions and process parameters, so the same values should be able to be used for different heats and recipes being processes in one and the same furnace.

The parameters to be defined are:

1) Pressure
Pressure can be either assumed to be constant or it can be changed in function of time. If it should change in function of time, then select **Table input** and enter the pressure in the process schedule table. Changing pressure is used mainly for processes that involve vacuum, like Vacuum Degassing (VD), Vacuum Oxygen Decarburization (VOD), Ruhrstahl-Heraeus Process (RH-Degassing), etc. Note that the pressure only influences reactions involving the gas phase.

2) Zones

Here the zones are defined and can be given meaningful names. Note that in the current release, only two zones can be used. The zones must be assigned a fixed density[1]. When the checkbox **Allow degassing** is selected, any gas phase that forms during the process is removed at each calculation step and is not allowed to react with the zone. This type of calculation could be termed “open calculation”. It should be noted that the expansion work ($P \cdot dV$) is always accounted for in the energy balance.

3) Reactions

This is where the kinetics of the reaction between the two zones is defined. The kinetics are a function of the area where reactions can take place (in this case the area of the steel-slag interface) and how fast the mass transport is to and away from this reacting interface.

The reaction kinetics are defined by mass transfer coefficients in the steel and the slag. Many suggestions for numerical values can be found in the literature coming from experiments and CFD simulations.

Transfer of phase group is primarily used to calculate inclusion flotation. In this example, adding Al to the steel zone containing 100 ppm of dissolved oxygen at time = 1 min results in the formation of solid Al_2O_3 oxides (Corundum). These gradually float up, out of the liquid steel and combine with the slag phase on top. The settings shown in Figure 7 (4) mean that 3 % of oxides are removed from the steel zone and transferred to the slag zone per minute.

4) Heat

Here addition and removal of heat and heat transfer between zones is defined. The heat lost by convection and radiation is given as a constant value. A zone must be defined where the heat is lost from. Here we assume 3.2 MW of heat is lost from the steel zone. For the heat that is added by active heating, for example using an electric arc, only the heating efficiency is given here[2]. The electrical power (in MW) and power-on, power-off times are given in the process schedule. However, the zone to which the heat is added must be defined. Here we assume that the heat from the electric arc is added to the reaction zone.

As heat can be added to (or generated by exothermal reactions in) different zones, the temperatures of the steel zone, slag zone and reaction zone can be very different. The parameter for the heat transfer coefficient controls how much heat flows from one zone to the other. A large value results in a quick equalization of the temperature.

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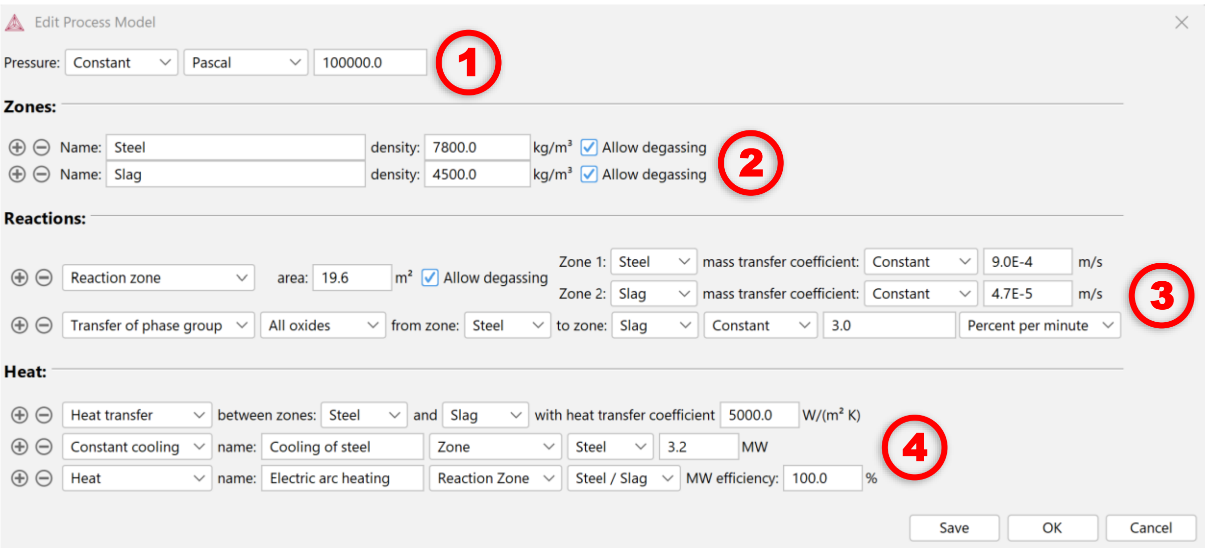
[1] Note that the density could be accurately calculated by Thermo-Calc as a function of composition and temperature. But in the Process Metallurgy Module, the density is only used to calculate approximate volumes that are in turn used to calculation the kinetic parameters, so an accurate value is not required. Calculating the density only unnecessarily increases calculation times.

[2] The reason for this is that usually the electric power is known. In this case the LF has 20 MVA rated power, we find that a heat input of 11.7 MW results in the correct heating rate. If the furnace is being operated at full power this would indicate a 60 % overall heating efficiency.


Edit Process Model

Pressure: Constant | Pascal | 100000.0

Zones:

Name: Steel density: 7800.0 kg/m³ ☑ Allow degassing
Name: Slag density: 4500.0 kg/m³ ☑ Allow degassing

Reactions:

Reaction zone area: 19.6 m² ☑ Allow degassing | Zone 1: Steel mass transfer coefficient: Constant 9.0E-4 m/s | Zone 2: Slag mass transfer coefficient: Constant 4.7E-5 m/s
Transfer of phase group | All oxides | from zone: Steel | to zone: Slag | Constant | 3.0 | Percent per minute

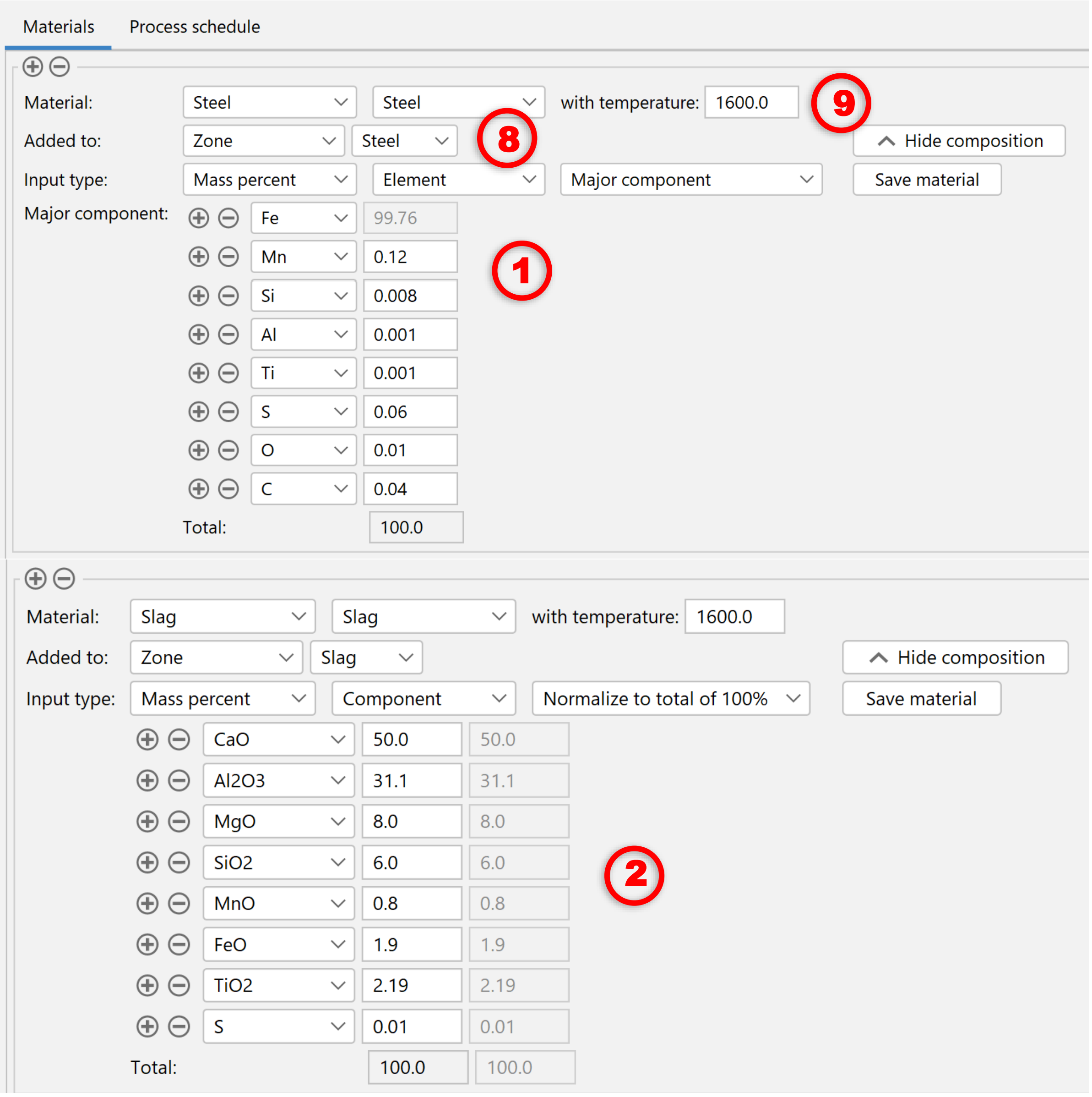
Heat:

Heat transfer between zones: Steel and Slag with heat transfer coefficient 5000.0 W/(m² K)
Constant cooling name: Cooling of steel | Zone | Steel | 3.2 MW
Heat name: Electric arc heating | Reaction Zone | Steel / Slag | MW efficiency: 100.0 %

Figure 7. Basic settings for kinetic simulations in the Process Metallurgy Module. These settings should only have to be defined once for a given type of process and given size and geometry of equipment being used.

Step 2: Define Materials / Chemical Composition

The next step in setting up a kinetic simulation in the Process Metallurgy Module is to define the materials and chemical composition. All the chemical compositions of the raw materials that are going to be used can be defined and stored in the program, the idea being that users can compile a library of materials that are regularly used in their own steel plant or research facility. This allows one to pick and choose materials instead of having to re-enter them for each calculation. The compositions of all materials used in this simulation need to be given, these are shown in Figure 8 (numbers 1-7), also the zone to which each material is to be added needs to be given (8) and the temperature on addition of each material (9).



Material: Steel | Steel | with temperature: 1600.0

Added to: Zone | Steel

Input type: Mass percent | Element | Major component

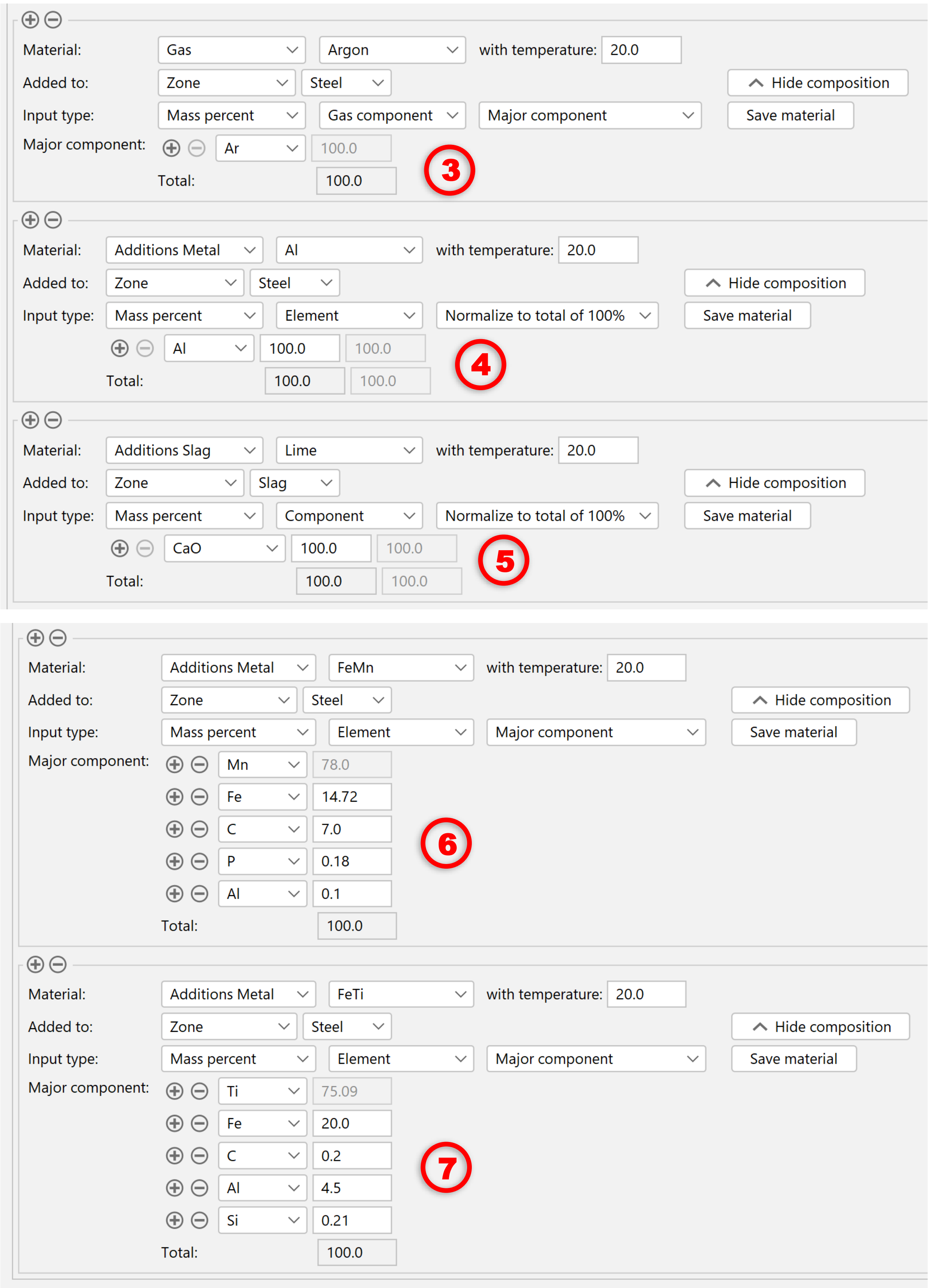
Major component:	
Fe	99.76
Mn	0.12
Si	0.008
Al	0.001
Ti	0.001
S	0.06
O	0.01
C	0.04
Total:	100.0

Material: Slag | Slag | with temperature: 1600.0

Added to: Zone | Slag

Input type: Mass percent | Component | Normalize to total of 100%

CaO	50.0	50.0
Al2O3	31.1	31.1
MgO	8.0	8.0
SiO2	6.0	6.0
MnO	0.8	0.8
FeO	1.9	1.9
TiO2	2.19	2.19
S	0.01	0.01
Total:	100.0	100.0



Material: Gas, Argon, with temperature: 20.0
Added to: Zone, Steel
Input type: Mass percent, Gas component, Major component
Major component: Ar 100.0
Total: 100.0

Material: Additions Metal, Al, with temperature: 20.0
Added to: Zone, Steel
Input type: Mass percent, Element, Normalize to total of 100%
Al 100.0 100.0
Total: 100.0 100.0

Material: Additions Slag, Lime, with temperature: 20.0
Added to: Zone, Slag
Input type: Mass percent, Component, Normalize to total of 100%
CaO 100.0 100.0
Total: 100.0 100.0

Material: Additions Metal, FeMn, with temperature: 20.0
Added to: Zone, Steel
Input type: Mass percent, Element, Major component
Major component: Mn 78.0
Fe 14.72
C 7.0
P 0.18
Al 0.1
Total: 100.0

Material: Additions Metal, FeTi, with temperature: 20.0
Added to: Zone, Steel
Input type: Mass percent, Element, Major component
Major component: Ti 75.09
Fe 20.0
C 0.2
Al 4.5
Si 0.21
Total: 100.0

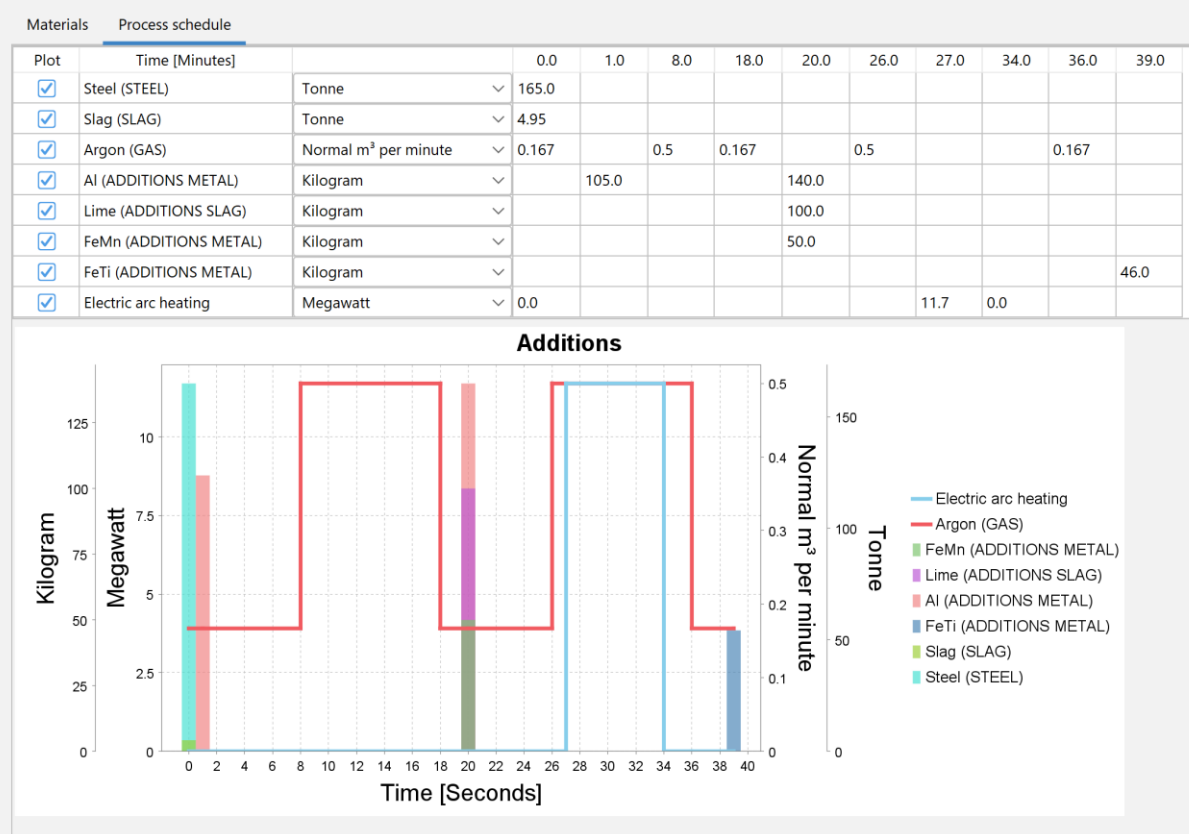
Figure 8. A screen shot of the Process Metallurgy Module defining the compositions and input temperatures of the materials that are to be used in the process and defining which zone they are to be added to.

Process Schedule

The third and last step in setting up a kinetic simulation is to set-up the process schedule. This is the actual steelmaking recipe that defines at which time how much of which material is added to the LF.

The process schedule for this example should correspond to the one reported by Graham and Irons [1]. Gaps in the reported process parameters in the original publication are filled following the assumptions made by van Ende and Jung [3], who set up a similar simulation of this LF process using the EERZ model.

The process schedule is entered in a table form. A graph visualizing all additions is automatically generated below the table, see Figure 9. The ladle furnace steel refining process schedule as published by Graham and Irons [1]Figure 9.



Materials | Process schedule

Plot	Time [Minutes]		0.0	1.0	8.0	18.0	20.0	26.0	27.0	34.0	36.0	39.0
☑	Steel (STEEL)	Tonne	165.0									
☑	Slag (SLAG)	Tonne	4.95									
☑	Argon (GAS)	Normal m³ per minute	0.167		0.5	0.167		0.5			0.167	
☑	Al (ADDITIONS METAL)	Kilogram		105.0			140.0					
☑	Lime (ADDITIONS SLAG)	Kilogram					100.0					
☑	FeMn (ADDITIONS METAL)	Kilogram					50.0					
☑	FeTi (ADDITIONS METAL)	Kilogram										46.0
☑	Electric arc heating	Megawatt	0.0						11.7	0.0		

Figure 9. The ladle furnace steel refining process schedule as published by Graham and Irons [1] entered into the Process Metallurgy Module in Thermo-Calc.

Comments on the Selected Compositions of Input Materials and Process Schedule

1) Liquid steel

The composition given is more or less typical for steel coming from an EAF. The paper by Graham and Irons suggests a somewhat higher dissolved oxygen content before deoxidation, but here we have followed the value given in the later paper by van Ende and Jung [2].

2) Slag

The slag composition is also more or less typical. About 30 wt% Al_2O_3 is required to make sure the slag is liquid at the temperatures maintained in the LF, and the 8 wt% MgO assures the slag is "saturated" in MgO, thereby reducing the dissolution and erosion of the MgO-rich refractory cladding of the ladle. The slag also contains 2 wt% FeO which is most certainly unwanted and a result of slag carryover from the EAF. FeO in the slag increases its oxygen activity, thereby decreasing the ability of the slag to desulphurize the steel.

3) Argon

In most cases Argon is used as a stirring gas in the LF. The effects of O_2 or N_2 impurities could be investigated if this is of interest by changing the gas composition. Sometimes N_2 is used as stirring gas for cost reasons, however, only if dissolution of N in the liquid steel is of no concern. In this case the final grade to be produced is probably a deep-drawing grade, where dissolved N is most definitively unwelcomed. In fact, the late addition of FeTi is very probably to scavenge dissolved N from the liquid steel.

4) Aluminum

The first addition of Al is very early in the processing. Probably this Al is added during tapping to kill (or deoxidize) the steel coming from the EAF. The second Al addition is probably to "condition" the slag, the aim being to keep the oxygen potential low and promote the reduction of the FeO and also MnO in the slag phase to metallic Fe and Mn and to return these elements to the liquid steel. At the same time the decreased oxygen potential will improve the desulphurizing ability of the slag (increase its sulphur capacity).

5) Lime

The late addition of lime (CaO) might be an attempt to increase the slag basicity and thereby improve its sulphur removal ability.

6) FeMn

Ferromanganese might be added to trim the alloy to the Mn content required by the specification of the steel to be produced. It might also be added to make sure any solid SiO_2 inclusion is turned into a liquid Si-Mn-oxide.

7) FeTi

Even though this is not mentioned anywhere in the publication by Graham and Irons [1] or van Ende and Jung [2], the late addition of FeTi suggests that an attempt is being made to produce a deep drawing grade without vacuum treatment. High dissolved N contents in the steel are detrimental to the drawing ability. Usually, low N contents are assured by vacuum degassing (VD) treatment. If no VD is available at the steel plant, Ti can be alloyed to the steel, the aim being that the Ti reacts with the dissolved N forming stable solid Ti-nitrides (TiN), thereby scavenging the N dissolved in the liquid steel. This strategy is not entirely unproblematic, as the TiN inclusions can result in clogging issues during continuous casting, ductility dip cracking (DDC) during solidification and also to cracking during the drawing process. It should be noted here that TCOX10 does contain the element N and also the TiN phase (that is actually an FCC MC carbide), so the formation of TiN precipitates could be simulated. However, they are not stable at these high temperatures and only precipitate shortly before solidification. The proper way of simulating the precipitation of nitrides on solidification would be to take the liquid steel composition as calculated using the Process Metallurgy Module at the last time-step of the LF refining process and perform a solidification simulation using the steel database TCFE that contains a far more comprehensive collection of solid carbide and nitride phases compared to the TCOX database.

EXAMPLE RESULTS

Many different aspects of the reactions taking place in the LF can be plotted and analyzed. Here, only some are presented, discussed and compared to the experimental data from Graham and Irons [1].

Temperature

The heat loss by radiation and convection is assumed to be removed from the steel zone (see number 4 in Figure 7). This is the reason why -in general- the temperature of the steel zone is lowest. The heat input by electric arc heating, on the other hand, is assumed to go into the reaction zone. This is the reason why the reaction zone is so much hotter than both the steel and the slag zone during arcing. The heat added to the reaction zone then flows into both the steel zone and the slag zone by the mixing at the end of each time-step (see step 3 in Figure 2). In general, the reaction zone is hotter than both the steel and slag zone. The reason for this is that the reaction occurring between the steel and the slag phase is exothermic. At each time when additions are made, the resulting temperature changes in the zones to which the additions are made can be observed and interpreted. At t = 20 min, for example, it is seen that the addition of 100 kg of CaO to the slag zone results in a significant lowering of the temperature of the slag zone. This makes sense as a large amount of energy is needed to heat up the solid CaO and melt and dissolve it in the slag zone. The Al and FeMn additions, on the other hand, result in a temperature increases of the steel zone. The reason for this is that the energy required to heat up and melt the FeMn and Al is offset by the strongly exothermal reaction of the Al with the dissolved oxygen [O], resulting in the observed net temperature increase.

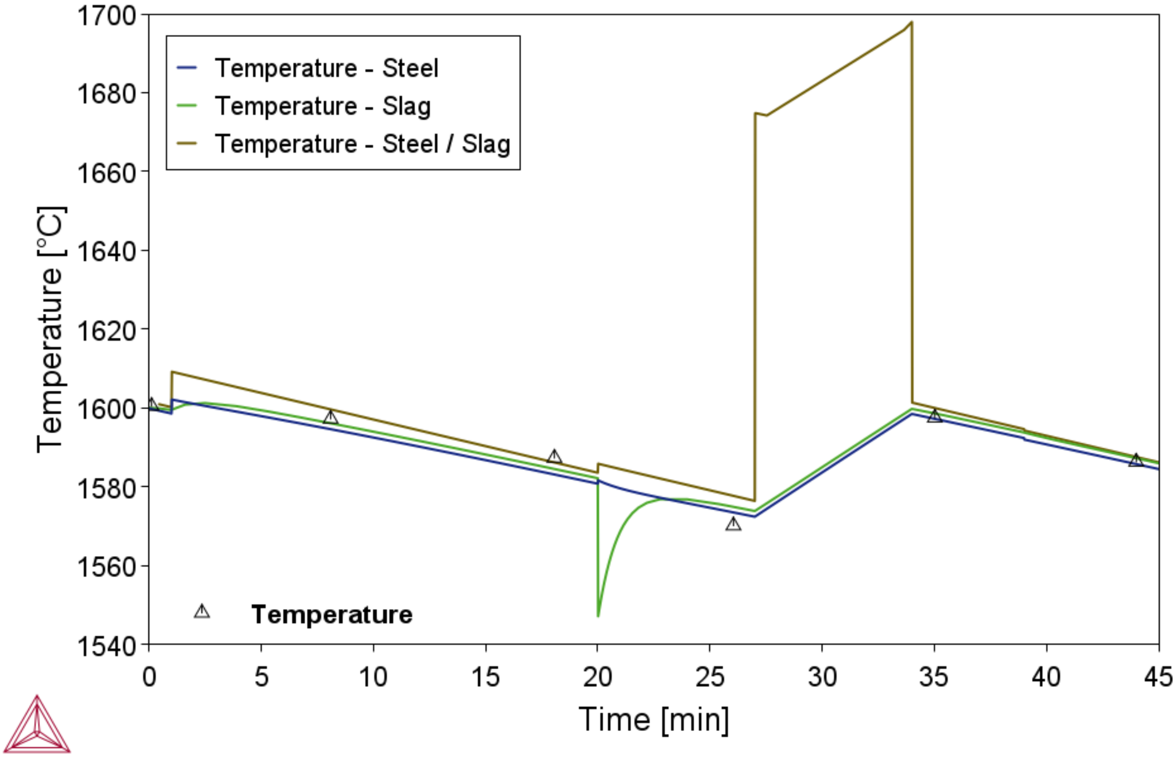


Figure 10. Temperature evolution of the steel zone, slag zone and reaction zone during the LF treatment.

Liquid Metal Composition and Amount

It is reassuring to see that already this simple model captures all the relevant chemistry changes in the liquid steel. The experimentally determined S, Mn, and Ti contents are reproduced to within experimental accuracy. The Al and Si content in the liquid steel are satisfactorily reproduced. However, the Al content seems slightly on the high side, whereas Si is on the low side. We discuss these deviations in more detail later on.

(Note: the values plotted here are so-called total Al and total Si contents. This means the Al and Si can be present in the liquid steel either in the dissolved state or as a solid non-metallic inclusion. This is also what is measured by the spark spectrometer, by which the analysis was made).

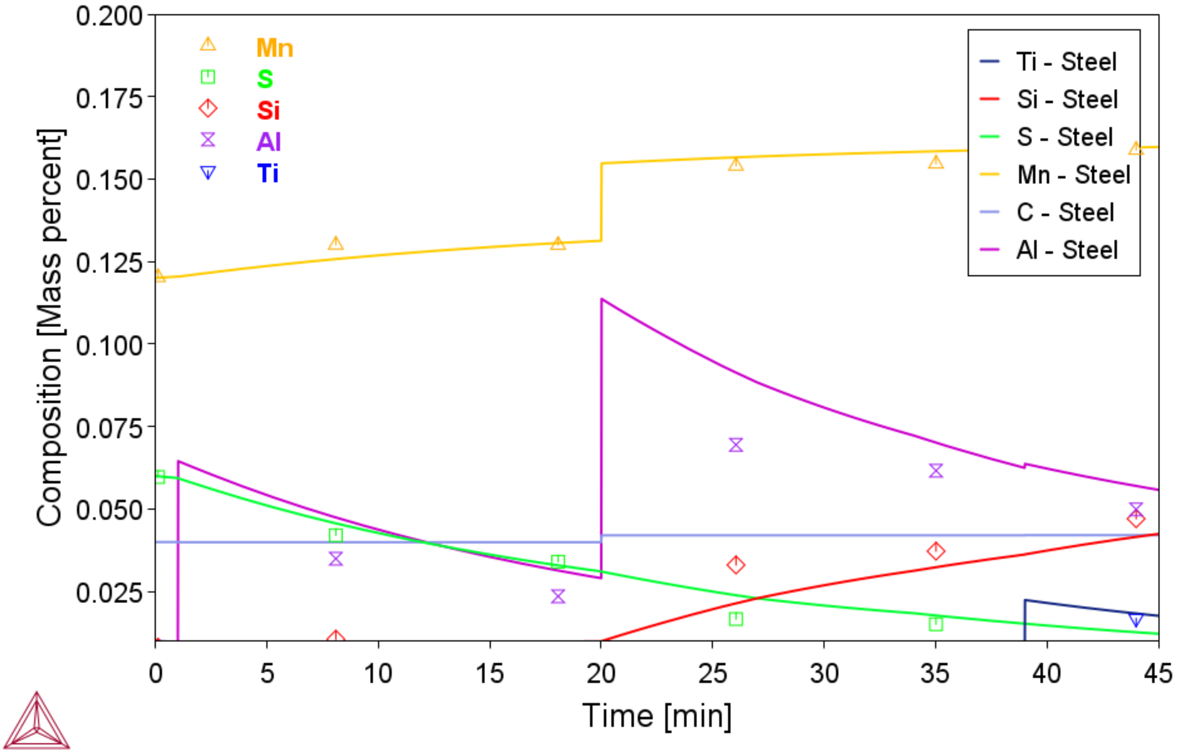
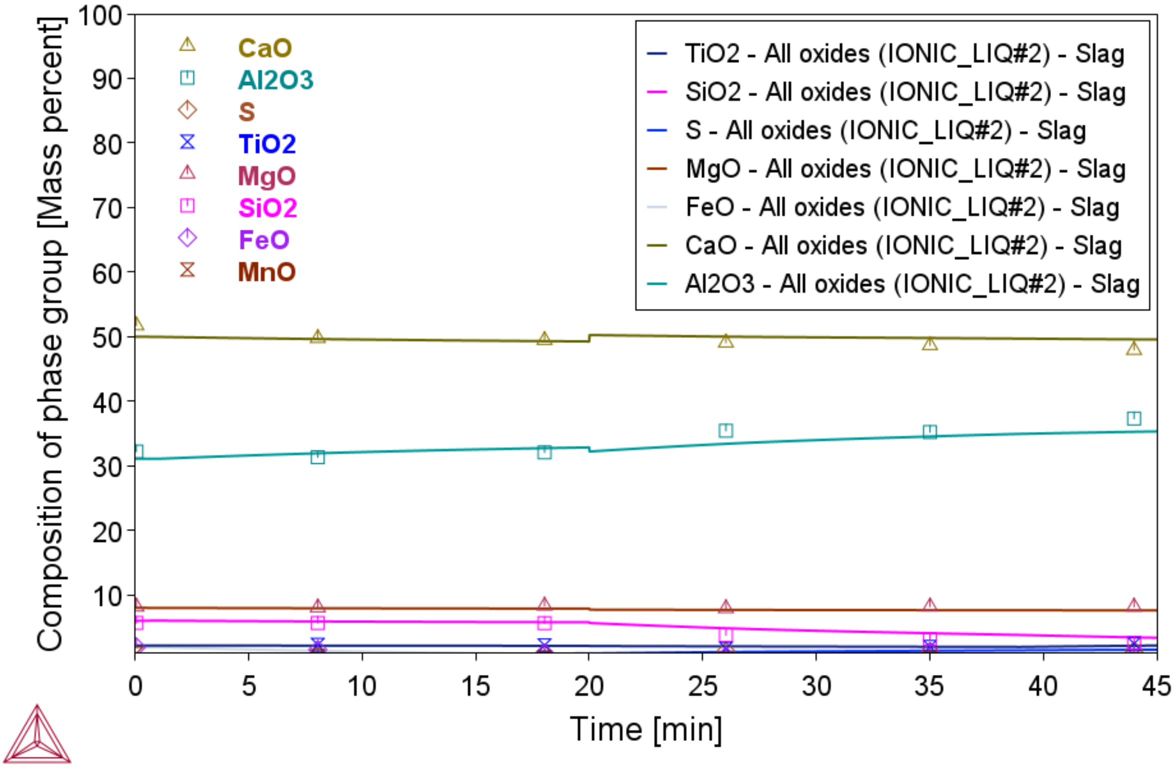


Figure 11. Evolution of the steel chemistry during ladle furnace treatment. Most of the experimentally measured datapoints are well reproduced by this simple model set-up, demonstrating that the underlying processes are well captured.

Slag Composition and Amount

The general trend of the experimentally determined slag composition is also well reproduced. While the composition of the main slag constituents CaO, Al_2O_3, and MgO (top plot in 12) do not change much, excellent agreement is achieved for the prediction of the decrease of MnO and FeO contents in the slag phase by reduction reactions. Additionally, the increase in S content due to desulphurization of the liquid steel by the slag phase is very well reproduced (bottom plot in 12).



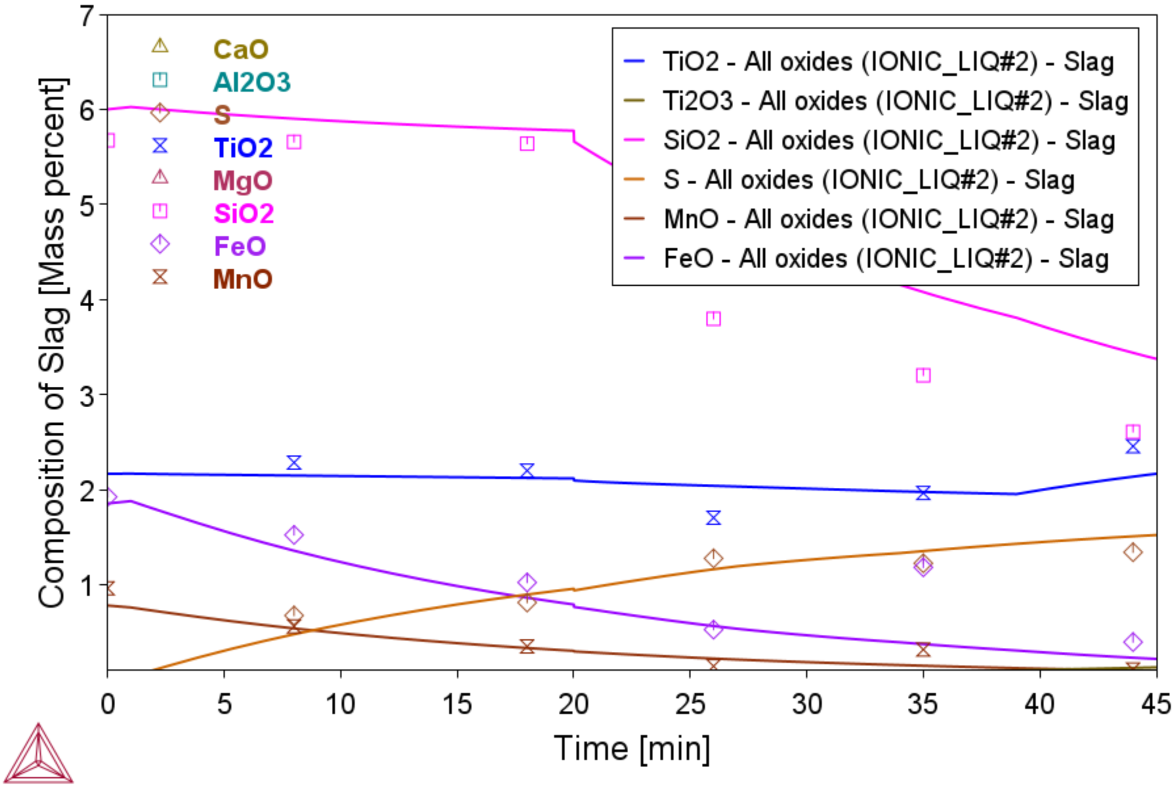
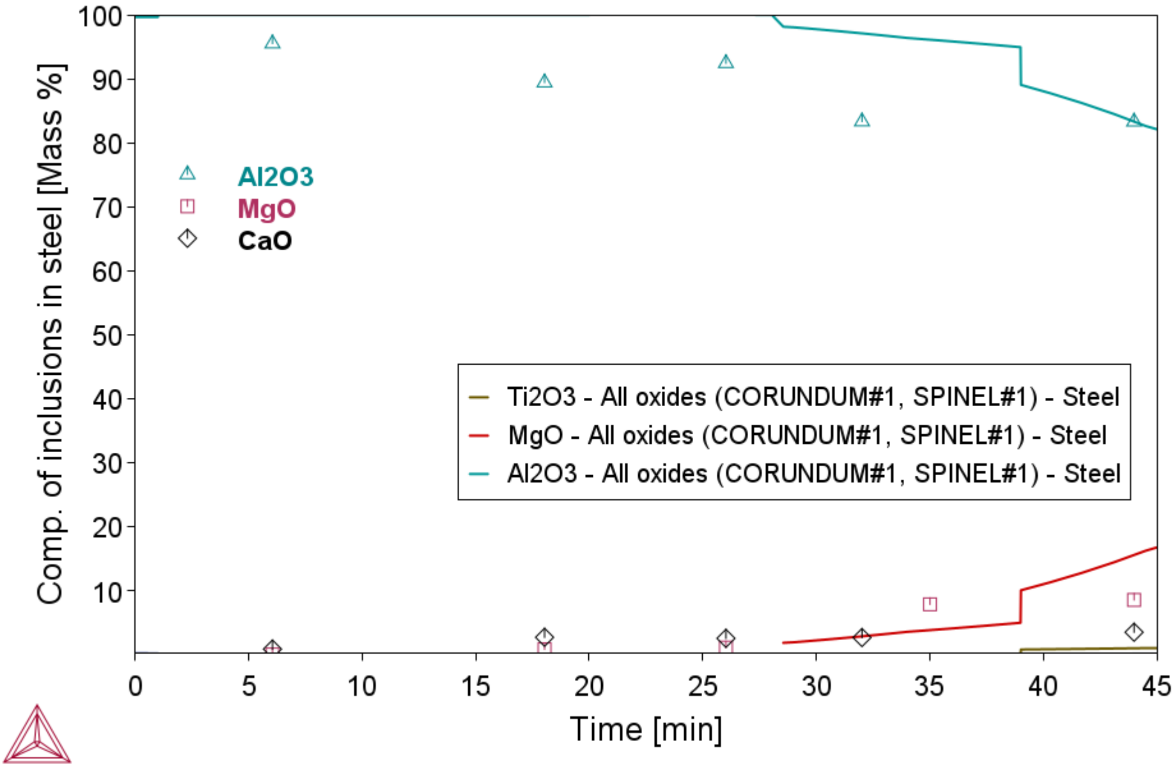


Figure 12. Evolution of the slag composition as a function of processing time. The bottom plot is an enlargement showing the evolution of the minor components.

The calculated decrease of the SiO_2 content, on the other hand, is somewhat underestimated. This matches the underestimation of the Si pickup in the liquid steel shown in Figure 11 and suggests that the model underestimates the reversal of Si from the slag to the steel during processing.

Inclusion Composition

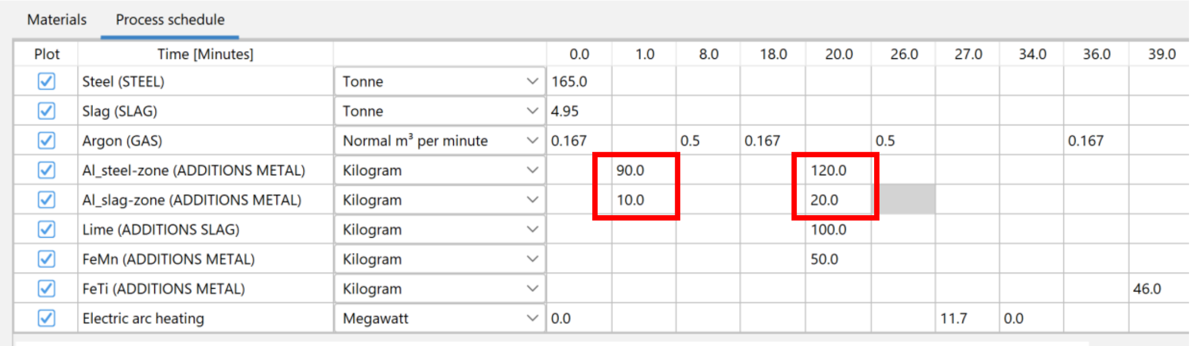
Finally, the calculated and measured inclusion compositions are compared. Up to about 25 minutes into processing, the inclusions are almost pure solid corundum (Al_2O_3), then a second population of MgO rich spinel inclusions start forming. This result captures the essence of what is experimentally observed.



9Figure 13. Evolution of the inclusion composition as a function of processing time.

Further Tuning of the Parameters Used for the Simulation

As noted above, some discrepancies are observed between the simulated and experimentally observed steel and slag chemistries. It is an interesting exercise to reflect on what is causing this discrepancy and think of ways of improving the model parameters. For example, it can be seen in Figure 11 that the Al content in the liquid steel is somewhat too high whereas the Si content is somewhat too low. The high Al content might be explained by assuming that not all of the added Al is dissolved in the steel; maybe part of it melts in the slag zone. This can be easily implemented by defining two Al materials and adding one to the steel zone (the fraction of the added Al that is assumed to dissolve in the liquid steel) and the other to the slag zone (the fraction of the Al that is assumed to react with the slag phase). The split chosen is shown in Figure 14.



Plot	Time [Minutes]		0.0	1.0	8.0	18.0	20.0	26.0	27.0	34.0	36.0	39.0
☑	Steel (STEEL)	Tonne	165.0									
☑	Slag (SLAG)	Tonne	4.95									
☑	Argon (GAS)	Normal m³ per minute	0.167		0.5	0.167		0.5			0.167	
☑	Al_steel-zone (ADDITIONS METAL)	Kilogram		90.0			120.0					
☑	Al_slag-zone (ADDITIONS METAL)	Kilogram		10.0			20.0					
☑	Lime (ADDITIONS SLAG)	Kilogram					100.0					
☑	FeMn (ADDITIONS METAL)	Kilogram					50.0					
☑	FeTi (ADDITIONS METAL)	Kilogram										46.0
☑	Electric arc heating	Megawatt	0.0						11.7	0.0		

Figure 14. Part of the added Al is assumed to dissolve in the liquid steel, the rest in the slag phase.

As seen in Figure 15, this simple expansion of the model results in a much-improved fit of the experimentally measured Al content. It also results in a very slight increase of the Si content in the liquid steel as more Si is reversed out of the slag phase back into the liquid steel due to the more reducing conditions in the slag phase.

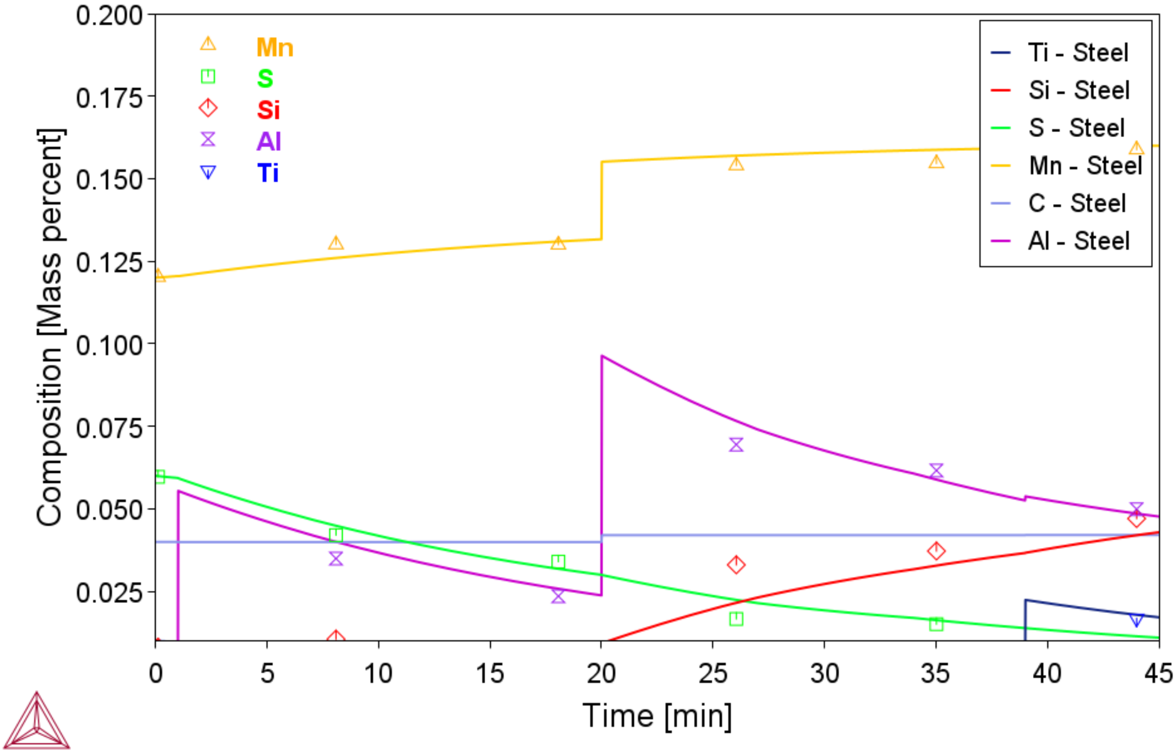


Figure 15. Calculated liquid steel chemistry compared to experimental data under the assumption that not all the added Al dissolves in the liquid steel.

There are other ways by which the simulation can be improved, but as very little information is available from the publication of this particular LF process, not even the exact compositions of the input materials are known, thus tuning or tweaking of parameters is purely speculative.

Outlook

Kinetic process simulations as a function of time became available in Thermo-Calc as of 2020b. However, the flexibility of the model is still limited and users are advised to familiarize themselves with the following details that may help guide the necessary settings required for a specific process simulation:

- The Process Metallurgy Module is available with the databases OXDEMO or TCOX, version 10 or newer.
- It is only possible to perform simulations at a constant total pressure throughout the simulation time.
- It is only possible to define two zones. In most cases these will be a metallic liquid and a non-metallic liquid (slag). It is also possible to define other pairs of zones, to study the reaction of two metallic liquid zones, or the reaction of a solid with a liquid, for example the reaction of solid inclusions with liquid metal, or the erosion of solid refractory material by a slag phase.
- The densities of the zones are constant and do not change as a function of composition or temperature.

- It is only possible to define one transfer of phase group. In most cases this is the transfer of oxides from the steel zone to the slag zone by flotation, but other choices are also possible, for example the transfer of liquid metal from the slag zone to the steel zone, and so on.
- It is only possible to define the transfer of a phase *group* from one zone to the other. It is not possible to define the transfer of one specific phase, such as corundum, for example.
- The transfer of phase group can only be constant as a function of time.
- The mass transfer coefficients that determine the reaction kinetics are constant and cannot change as a function of time. The same is true for the cooling and the heat transfer between the zones.
- Consequently, it is also not possible to allow these parameters to change as a function of other parameters, for example the flow rate of Ar.
- There is no melting model implemented. This means that if a certain amount of a solid is added at a given time, it is assumed that the whole addition is completely equilibrated within the zone in one timestep. For example, if FeMn is added to liquid steel, then it is assumed that the FeMn is completely melted and no temperature gradients are present in the steel zone after one time-step.
- The Process Metallurgy Module is not currently available with TC-Python.

Depending on how the process simulation tool is received by our user base and the feedback from the Thermo-Calc community all over the world, we will start removing these limitations step-by-step and continue to develop and improve the Process Metallurgy Module. We will also continue to test it, apply it to different types of (maybe even non-ferrous) metallurgical processes and explore further possible applications.

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