

Non-Metallic Inclusion Changes in Si-Mn Killed Steels

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Abstract

Steel must be deoxidized during refining to avoid the formation of gas porosity during solidification, and many alloys. In the case of Si-Mn killed steels, Si and Mn are added to form low melting point inclusions that can prevent nozzle clogging and that are vitreous upon solidification, so they can deform upon mechanical processing. Depending on the activity of SiO_2 of the slags used during secondary refining, the steel-slag reactions can further deoxidize the steel and reduce oxides from the slag and refractories such as MgO , Al_2O_3 and CaO . These reduced elements can increase the melting point and hardness of the inclusions. Some of these impurities can enter the steelmaking process from the ferroalloys themselves because of their manufacturing process.

In this work, the process variables that influence the thermodynamics and kinetics of the non-metallic inclusion formation, transformation and removal are reviewed. It is found that the gas stirring rate is found to have a significant impact on the kinetics of steel-slag reactions and inclusion generation and removal. It is also found that basic slags will cause pick-up of Al, Mg and Ca and promote the formation of undesired inclusions in the steel melt. During solidification, inclusions can precipitate at different chemical compositions depending on the remaining dissolved oxygen content in the melt. Ferroalloys used for deoxidizing the steel such as FeSi typically contains Ca that will impact steel cleanliness and can be used to the advantage of the process, i.e. the treatment of alumina inclusions.

A one-parameter kinetic model for steel-slag-inclusion reactions is developed using FactSage. The potential effect of three different slag chemistries on the trajectory of inclusion modification are tested using the model for 1.25%Mn-0.25%Si steel. It is seen that Al, Mg and Ca pick-up are expected for all tested systems. The SiO_2 activity, directly influenced by slag binary basicity, controls the reduction of the oxides. For high basicity, alumina-containing slags, the inclusions will transform from liquid Mn-silicates to alumina to spinels to Ca, Mg-aluminates to liquid slag. For low basicity, low alumina slags, the inclusions will remain liquid. For $\text{CaO-SiO}_2\text{-MgO-CaF}_2$ slags, Mn-silicates are predicted to become $2\text{CaO}.\text{SiO}_2$ and MgO .

Inclusions in lollipop samples of degassed Si-killed steels with $\text{CaO-SiO}_2\text{-MgO-CaF}_2$ slags are analyzed using ASPEX automated feature analysis and inclusion extraction. The inclusions found

to be MgO and CaO-rich after degassing. After degassing, CaO-rich inclusions are found both containing and not containing fluorine, indicating Ca pick-up from slag and slag emulsification. After trimming, primary inclusions are mostly Ca-silicates and do not contain fluorine - their origin is discussed. It is observed that Mg content in steel increases during a heat while Ca content decreases.

Induction furnace experiments are done with MgO and CaO crucibles for different slag compositions. The one-parameter kinetic model predicts the inclusion composition over time. It is found that more basic slags in the $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2$ will drive more Al and Mg pick-up than less basic slags. The addition of 5%MnO and 10%CaF₂ to $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2$ slags did not significantly change the steel-slag reaction kinetics and non-metallic inclusion composition. It is found that $\text{CaO-SiO}_2\text{-MgO-CaF}_2$ are strongly desulfurizing and can modify Mn-silicate inclusions to forsterite and MgO. There is no observable CaO precipitation when the melt is reoxidized after equilibration. One experiment with $\text{CaO-SiO}_2\text{-CaF}_2$ slags in a $\text{CaO-3\%ZrO}_2$ crucible yielded CaO-containing inclusions, with estimated [Ca] before reoxidation of 0.3 ppm. It is found that Ca solubility in the steel is significantly lower than predicted by FactSage. Experiments using FeSi containing 2%Ca to deoxidize the steel and treat Al-killed and Si-killed steels showed that the Ca yield is higher than the typically observed for CaSi_2 powder addition in the same experimental setup. When [O] is higher (for Si-killed steels), the Ca yield is higher, and inclusions reach equilibrium faster than for Al-killed steels which have very low [O]. The inclusion-inclusion reactions in Ca-treated Al-killed steel took several minutes more than expected from kinetic models. It was found that the mass transfer coefficient for the configuration is controlled by convection in the melt, and there should not be significant differences when using 600g or 1000g melts for the experiments.

Confocal Laser Scanning Microscopy was used to observe the reoxidation behavior of a steel sample taken from a Si-killed degassed heat, where [Ca] and [Mg] was expected to be high. The steel sample was oxidized using ungettered argon. The gas phase mass transfer coefficient for a CSLM sample was measured by evaporation of Mn. The oxidation experiments could precipitate Mg-rich inclusions but there was no observable increase in the CaO content of these inclusions.

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1. Introduction

The cleanliness of steel and its control has been the subject of several studies in the last decades, maintaining and developing a close relationship between universities and the steel industry. The presence of non-metallic inclusions in steel, their quantity, chemical composition and morphology are closely related to both upstream and downstream processability and to the properties of the final product [1].

The amount of oxygen dissolved in steel is controlled by de-oxidation, in which an element with higher affinity for oxygen is placed in the steel bath, forming oxides as a result. Elements commonly applied for de-oxidizing steel, such as aluminum, silicon, calcium and magnesium, can yield oxides which are solid at steelmaking temperatures. Complex de-oxidation with multiple elements has been successfully employed as a method for generating lower melting temperature oxides. [2]

The addition of Si and Mn for deoxidation has been applied due to the general benefits of their reaction products to the steelmaking processes: formation of low-temperature melting manganese silicates (Figure 1), which can show high deformability at hot mechanical processing, reduction of nozzle clogging at continuous casting, and less expensive raw materials [3]. Thermodynamics for complex de-oxidation processes involving Al, Si and Mn and the mechanical behavior of the final product have been thoroughly studied [3][4][5]. Special steelmaking processes such as strip casting rely on the low melting temperature of manganese silicate inclusions present at the steel surface to act as a lubricant for the casting process, its ability to inhibit the appearance of MnS inclusions and act as a nucleant for acicular ferrite [6][7]. In Figure 2, a typical defect in tire cord caused by Ca, Mg, Al-containing oxide is shown. Figure 3 summarizes inclusion engineering selection for Si-killed bearing-grade steel – the lower their melting point and the lower their hardness compared to the steel matrix, the less harmful they are to the steelmaking process and the final product.

Secondary refining practices such as desulfurizing normally require lime-alumina top slags, due to the necessity of high sulfide capacity and compatibility of the liquidus temperature with the temperature of molten steel. Low activity of silica in the slag can shift the equilibrium between Si and Al at the steel-slag interface, promoting the reduction of Al_2O_3 from the slag [8]. The transport

of Al from steel-slag to steel-inclusion interface can cause the reoxidation of Al at inclusions. The presence of Al_2O_3 in Si-Mn killed steel inclusions can seriously affect their deformability and consequently the mechanical behavior of the steel [3]. Also, Al_2O_3 can affect the castability of the steel, due to its tendency of clustering at other alumina inclusions or refractory walls, such as stopper rods or continuous casting nozzles. Figure 4, it is seen that the typical phases at a nozzle clog are oxides that are solid at casting temperatures (melting temperature above 1550°C typically), such as Ca_2SiO_4 , Al_2O_3 , CaS , MgAl_2O_4 (spinel) and solid Ca-aluminates. Therefore, preventing the formation of such phases is fundamental for good secondary metallurgy practices.

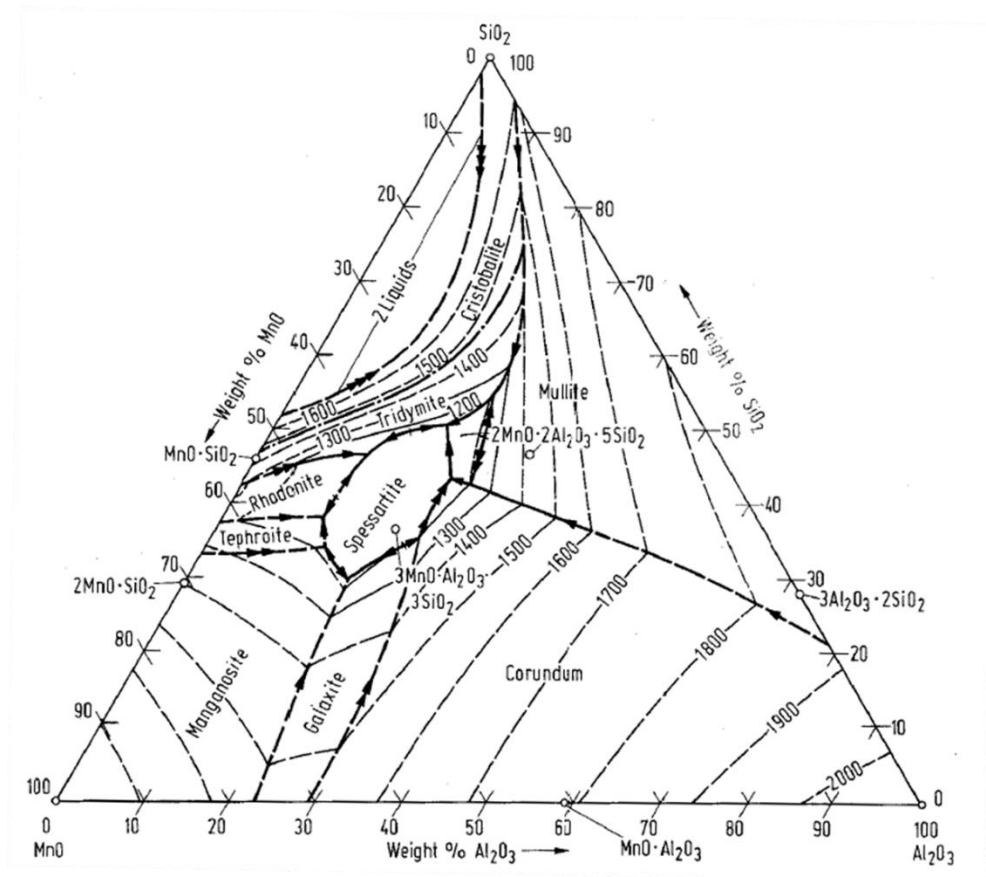


Figure 1 - $\text{MnO-SiO}_2\text{-AlO}_{1.5}$ ternary diagram with liquidus projections. Clogging is prevented if chemical composition of inclusions is inside the casting temperature isotherm. [9]

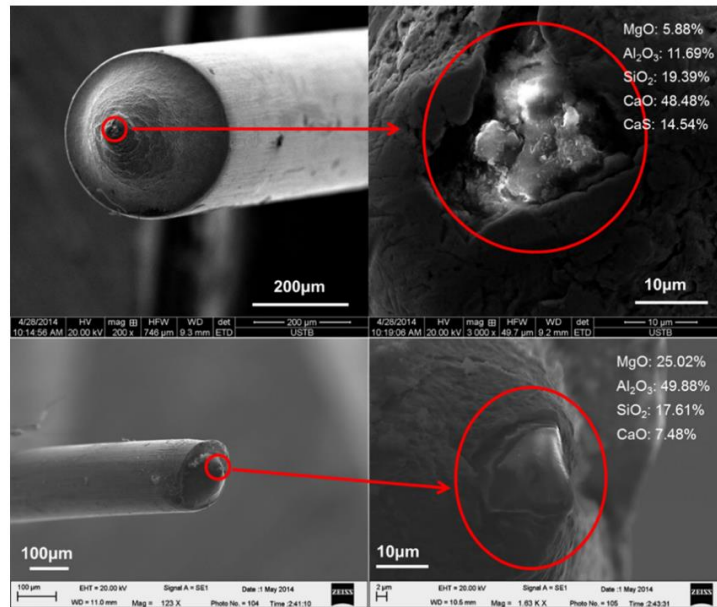


Figure 2 – Tire cord defect caused by a non-deformable oxide inclusion containing Al, Mg and Ca. [10]

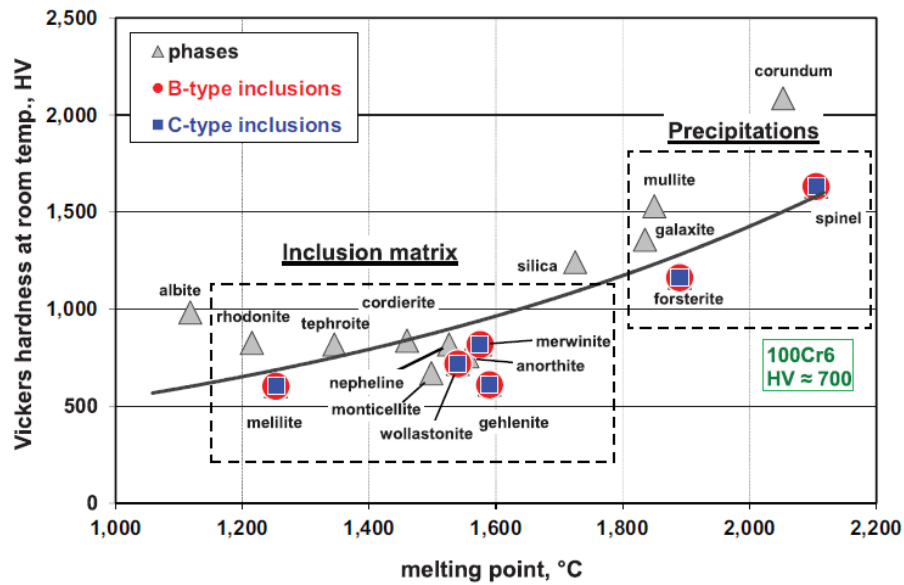


Figure 3 – Vickers hardness of inclusion matrix and precipitate phases in a bearing-grade steel versus their melting point. [11]

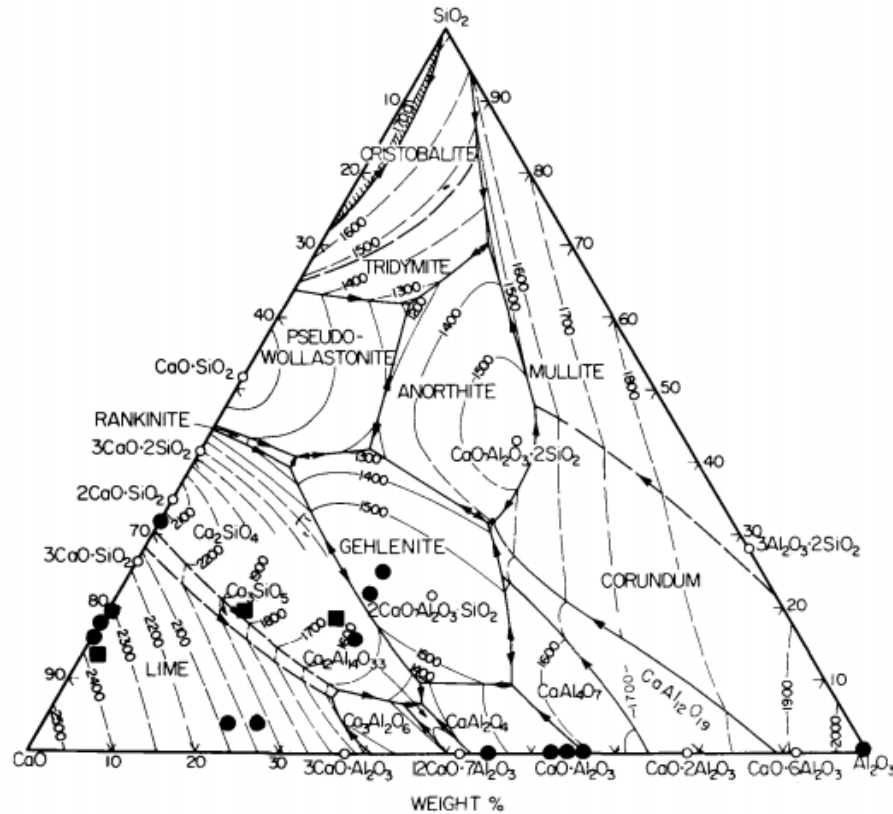


Figure 4 – Composition of non-metallics in plugged nozzles plotted in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ ternary phase diagram [12]

Recent efforts made by Van Ende et al. [13], Pistorius [14] and Harada et al. [15] explore computational thermodynamic software and its ability of executing iterative calculations to predict the kinetics of reactions in steelmaking reactors. These kinetic models can include rate-limiting steps such as mass transfer at the steel-slag and steel-inclusion interface. The application of these kinetic models can provide information on the influence of steel and slag chemistry on the ruling mechanisms for inclusion modification, the extent and timescale of these reactions.

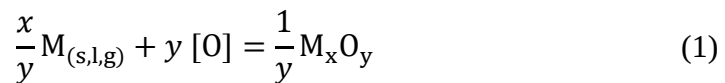
The objective of this work is to experimentally assess the rate-limiting steps of the inclusion modification phenomena in Si-Mn killed steels and the effects of slag and steel chemistry on the chemical composition and morphology evolution of the non-metallic inclusions.

2. Current State of Knowledge

2.1. Deoxidation equilibria of steels and thermodynamics of steel-slag systems

Non-metallic, oxide inclusions play a pivotal role in steelmaking. The solubility of oxygen in molten iron is in the order of 2160 ppm at 1600°C while it is in the order of parts per billion in solid steel. Therefore, the cast product would exhibit defects such as blowholes or internal oxides if dissolved oxygen were not removed before solidification. In modern steelmaking, elements with strong chemical affinity for oxygen are added to the molten steel for this purpose. These elements react with the oxygen present in the melt and precipitate in the form of oxides, which can be present in the process as either an overlying, lower-density slag phase or small, micron-sized particles distributed through the liquid metal phase. The thermodynamics of oxidation and dissolution reactions of elements used in steelmaking for deoxidation have been thoroughly studied and characterized and are summarized in this section.

In general, the oxidation of elements is written in the following form Eq. (1), while deoxidation equilibria can be written generally as given by Eq. (2).



$$K_{M_x O_y} = \frac{\left(a_{M_x O_y}^{\frac{1}{y}} \right)}{\left(a_M^{\frac{x}{y}} \right) a_O} \quad (2)$$

Since deoxidizers are mostly dilute in liquid iron, it has been proposed that a 1wt% reference state is generally used to evaluate the thermodynamics of dilution of alloys in steel [16]. According to Henry's law, the Henrian activity for 1wt% dilute alloys (whose dissolution reactions are given by Eq. (3)) can be given by Eq. (4).

$$M_{x(s,l,g)} = x[M] \quad (3)$$

$$h_M = K_M(a_{M_x})^{\frac{1}{x}} \quad (4)$$

The maximum solubility of oxygen in iron for a certain temperature and oxide composition is given by Eq. (4).



The thermodynamics of dilute oxygen in steel are particularly important to calculate the oxygen activities in steel. The dissolution thermodynamic equilibrium constant for oxygen in molten iron is given in the equation below and the Figure 5 shows its temperature dependency. With the knowledge of the system temperature and oxygen partial pressure, it is possible then to calculate what the oxygen activity is in that system with Eq. (6) and (7) [2]. The partial pressure of O_2 is given in atmospheres.

$$\ln\left(\frac{h_{\text{O}}}{\sqrt{p_{\text{O}_2}}}\right) = \frac{13922.3}{T} + 0.557 \quad (6)$$

$$\ln\left(\frac{a_{\text{FeO}}}{h_{\text{O}}}\right) = \frac{13195.8}{T} - 5.52 \quad (7)$$

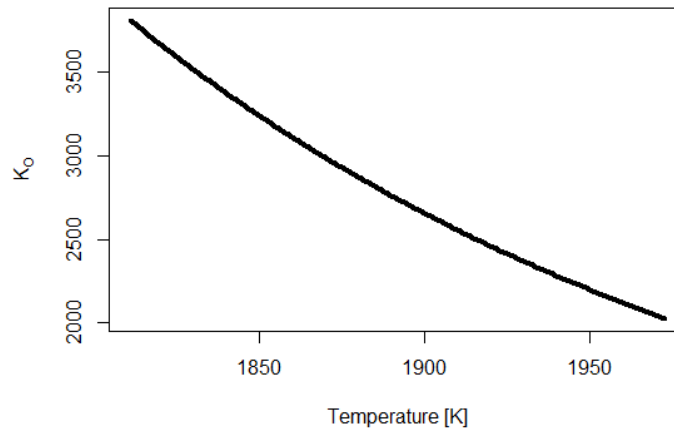
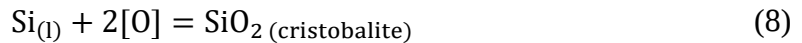


Figure 5 - Equilibrium constant for dissolution of gaseous oxygen in molten iron (as of Eq. 6a).

Since steelmaking temperatures of steel are usually between 1773 K and 1973 K, the average temperature for steelmaking processes can be taken as 1873 K.

2.1.1 Thermodynamics of Si, Mn-Si and Mn-Si-Al deoxidation of steel

Silicon, when added to steel, will react with oxygen and form silicon dioxide, whose physical state at 1873 K is solid, and its allotropic form is cristobalite.



However, the dissolved oxygen content present in pure Si-deoxidized steel is still too high for practical applications. Therefore, manganese is added to react with SiO_2 to form liquid Mn-silicates in the form of $(\text{MnO})_x(\text{SiO}_2)$. These manganese silicates have very low liquidus temperatures and have the tendency to stay vitreous upon fast cooling; both characteristics are desirable for steelmaking and forming processes. The formation of a complex silicate will also decrease the activity of silica in the oxide phase, shifting equilibrium and maintaining an even lower oxygen solubility in steel (Figure 6).

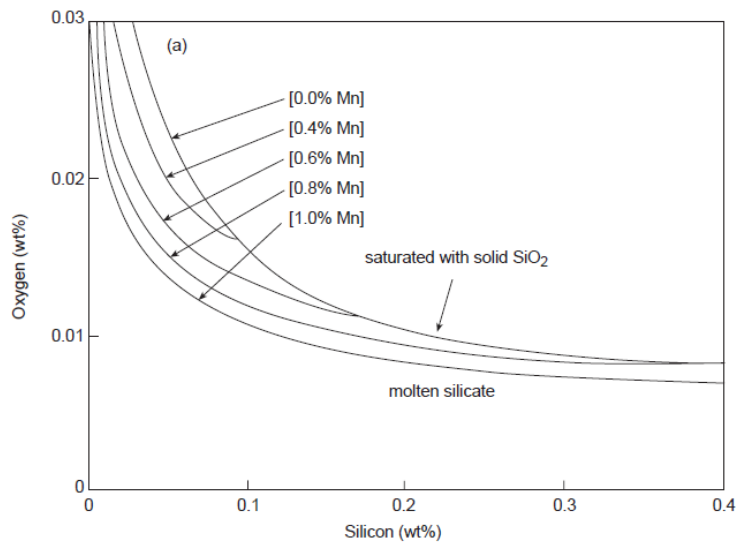


Figure 6 – Mn-Si deoxidation equilibria in steel at 1600°C [2]

Aluminum has a higher affinity for oxygen than both Si and Mn. Therefore, small amounts of Al present in solution will modify the inclusion chemical composition in Mn-Si killed steels. The solubility of oxygen in the molten iron will depend on the activities of Al and Si in steel and SiO_2

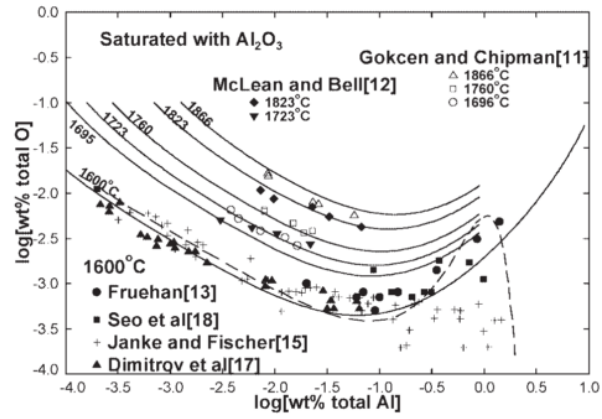
and Al_2O_3 in the non-metallic inclusions. Depending on the $a_{\text{Si}}/a_{\text{SiO}_2}$ and $a_{\text{Al}}/a_{\text{AlO}_{1.5}}$, either of the reaction pairs can control oxygen potential in steel. However, if Si-Mn deoxidation is performed with the intention of forming low melting point inclusions, Al pick-up must be prevented to avoid crystallization upon cooling or the formation of high-temperature solid phases such as corundum, which can also lead to nozzle clogging and thus reduced castability.

2.1.2 Thermodynamics of Al, Mg and Ca deoxidation of steel

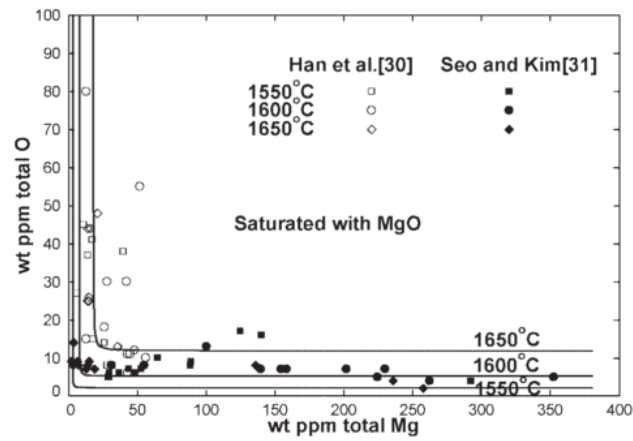
Aluminum is the most widely used deoxidant in steelmaking due to its high affinity with oxygen. As shown in Figure 7, when the amount of dissolved Al in the steel is around 300 to 500 ppm the oxygen solubility reaches a minimum of approximately 3 ppm. The product of reaction of Al and O is solid corundum (Al_2O_3) which is undesirable due to its very high melting point, high hardness and strong tendency to adhere and agglomerate to solid surfaces, generating large inclusion clusters and causing nozzle clogging.

In ladle steelmaking, lining refractories are usually MgO-C composites to prevent corrosion by slag. Usually, most steelmaking slags are saturated in MgO. Therefore, the presence of Mg in steel is expected (caused by the reduction of MgO) and can affect the chemical composition of the melt and present inclusions. Mg in steel can lead to the formation of Mg-bearing inclusions such as forsterite (Mg_2SiO_4), spinel (MgAl_2O_4) or periclase (MgO)-type inclusions.

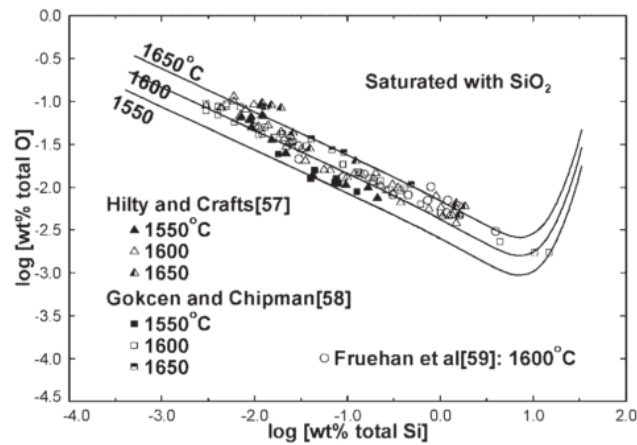
Calcium is widely used in steelmaking to modify the chemical composition and morphology of alumina and spinel inclusions by forming low melting temperature Ca-aluminates. Due to its very high affinity for oxygen and low solubility in steel, the solution thermodynamics of Ca in molten iron are a continuing challenge in steelmaking research, and several attempts have been made to assess the solubility coefficient and the interaction parameters between Ca and O through the Wagner formalism. The most widely accepted use of Ca in steelmaking is in its metallic form (as pure calcium, FeCa or CaSi_2 wires), however studies including the present work considered other modes of incorporation of Ca by non-metallic inclusions, such as Ca from ferroalloys (i.e. FeSi) and from slag reduction (by Al or Si).



(a)



(b)

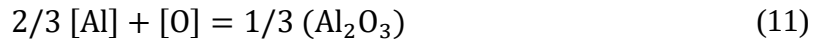


(c)

Figure 7 – Deoxidation equilibria for (a) Al, (b) Mg and (c) Si at steelmaking temperatures as compiled and modeled by In-Ho Jung et al. [17]

2.1.3 Deoxidation and steel-slag reactions

Non-metallic inclusions are particles entrapped in steel which may be products of chemical reactions occurring in liquid steel (e.g. deoxidation by Al, yielding Al_2O_3) or extraneous particles (e.g. MgO refractory grains, entrapped slag/mold flux). Controlling the chemical composition and morphology of non-metallic inclusions is fundamental to improve liquid steel processability and product performance. Inclusions that are liquid at casting temperatures (around 1550°C) will reduce clogging and allow longer casting sequences, while inclusions that remain liquid or deformable at lower temperatures will improve mechanical properties of steel products. This study focused on the modification of non-metallic inclusions present in Si-Mn killed steels. Deoxidation by Si-Mn is desirable for long products and strip casting due to the resulting low melting point manganese silicate inclusions, which will be deformable in later processing stages. In products such as cold drawn wires, stainless steels and strip-cast steels the presence of solid and non-deformable phases such as alumina (Al_2O_3), spinels (MgAl_2O_4) and Ca-bearing inclusions must be mitigated [2]. The typical deoxidation reactions are given by equations 9 to 11.



Several reports show Ca pick-up in inclusions under both laboratory and industrial conditions. The discussion on what is the dominating mechanism for Ca-pick up in Si-Mn killed steels is ongoing. There are four main proposed modes of Ca transport mechanism to the non-metallic inclusions, which will be further discussed along this thesis:

Endogenous inclusions:

- [Ca] originating from steel-slag reactions [18][19];
- ferroalloy impurities [20];

Exogenous inclusions:

- slag entrapment due to interface breakup [21][22];
- ladle glaze breakup [23].

2.1.4 Effect of slag and steel composition on inclusion modification of Si-Mn killed steels – chemical reactions and interfacial phenomena

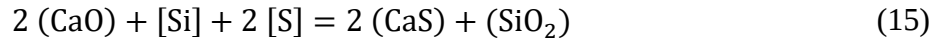
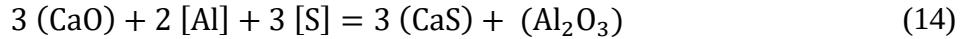
In secondary steelmaking, the process is often designed to provide reducing conditions to enable removal of S and O from the steel according to final product specification. Desulfurization is given by the following equation:



In practice, the most basic oxide capable of donating oxygen ions is CaO, and the desulfurization reaction can be written as:



Based on the chemistry of the desulfurization reaction, the lower the oxygen potential in steel, the higher the driving force for desulfurization. In the presence of a strong deoxidant such as Si, the reaction can be further rewritten as:



The equilibrium constant can be further written as the following:

$$K_{S-Al} = \frac{a_{CaS}^3 a_{Al_2O_3}}{a_{CaO}^3 h_{Al}^2 h_S^3} \quad (16)$$

$$K_{S-Si} = \frac{a_{CaS}^2 a_{SiO_2}}{a_{CaO}^2 h_{Si} h_S} \quad (17)$$

If the desulfurizing slag is saturated with S ($a_{CaS} = 1$), the driving force for desulfurization is capped. The solubility of CaS in slag is the inverse of the activity coefficient, as described below:

$$a_{CaS} = \gamma_{CaS} X_{CaS} \quad (18)$$

$$X_{CaS}(sat) = \frac{1}{\gamma_{CaS}} \quad (19)$$

The following literature show the currently reported values of CaS solubility for different slag systems.

The activities of (O^{2-}) and (S^{2-}) depend on the slag chemical composition. To summarize the effects, the sulfide capacity and the sulfur partition coefficient quantify the desulfurization capacity of a steel-slag system. Knowing the modified sulfide capacity C'_S (defined below) and the oxygen activity at the steel-slag interface, the sulfur partition ratio can be predicted. Sosinski and Sommerville developed an empirical correlation for sulfide capacity according to the slag chemical composition (in terms of optical basicity) and temperature [24].

$$K = \frac{a_{S^{2-}} h_O}{a_{O^{2-}} h_S} \quad (20)$$

$$K a_{O^{2-}} = a_{S^{2-}} \frac{h_O}{h_S} \quad (21)$$

$$C_S = (\%S) \sqrt{\frac{p_{O_2}}{p_{S_2}}} \quad (22)$$

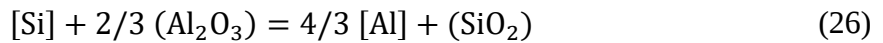
$$C'_S = (\%S) \frac{h_O}{h_S} \quad (23)$$

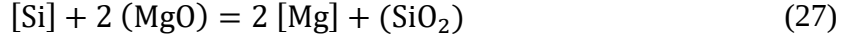
$$L_S = \frac{(\%S)}{[\%S]} \approx \frac{(\%S)}{h_S} \quad (24)$$

$$C'_S = L_S h_O \quad (25)$$

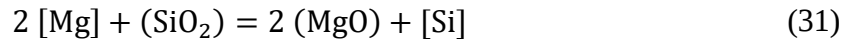
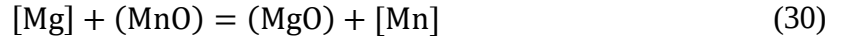
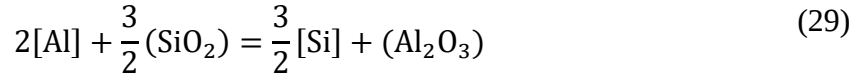
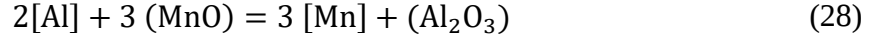
The very low oxygen potentials required for desulfurization can partially reduce oxides that are more stable than the main initial deoxidation product. For example, if the activity of Si is high enough and the activity of SiO_2 is low enough, the solubility of elements such as Al, Mg and Ca can increase at the interface and then reoxidize in the bulk steel, becoming part of the non-metallic inclusion population.

MgO and alumina-containing slags tend to react with Si-killed steels, with the following reactions taking place at the steel-slag interface (eq. 26-27):





The picked-up aluminum (and magnesium) would then be transferred to the steel bulk, where it would react at the steel-inclusion interface (eq. 28-31):



To achieve equilibrium, the chemical potential of each species must be the same in all phases. Therefore, inclusions and slag would in general tend to the same chemical composition at equilibrium. Due to the low solubility of elements like Ca and Mg in steel, transfer of these elements from steel-slag interface to the bulk of steel are potentially rate-limiting for approach to equilibrium.

In cases where there is a deoxidized steel in contact with a desulfurizing basic, MgO saturated, Al_2O_3 containing top slag, the oxygen partial pressure at the steel-slag interface is expected to be much smaller than in bulk steel (or steel-inclusion interface). A non-zero concentration of Ca and Mg in solution in the steel is expected; the concentrations would be controlled by the activity of oxygen in the steel. Even though the thermodynamic data on solubility products of CaO and MgO in steel are subject to debate, their evidently low solubility is expected to be rate-limiting for the transfer of Ca and Mg to the steel-inclusion interface.

Inclusion analysis during secondary refining of Al-killed steels indicates Ca pick-up for very long processing times and strong stirring conditions [20]. It appears that the extent of inclusion modification by Ca is increased for Si-bearing steels (Figure 8). It is not clear whether Si acts to reduce the oxygen partial pressure at steel-slag interface, further reducing Ca and Mg, or if there is an interaction parameter effect of Si which increases the solubility of Ca in steel.

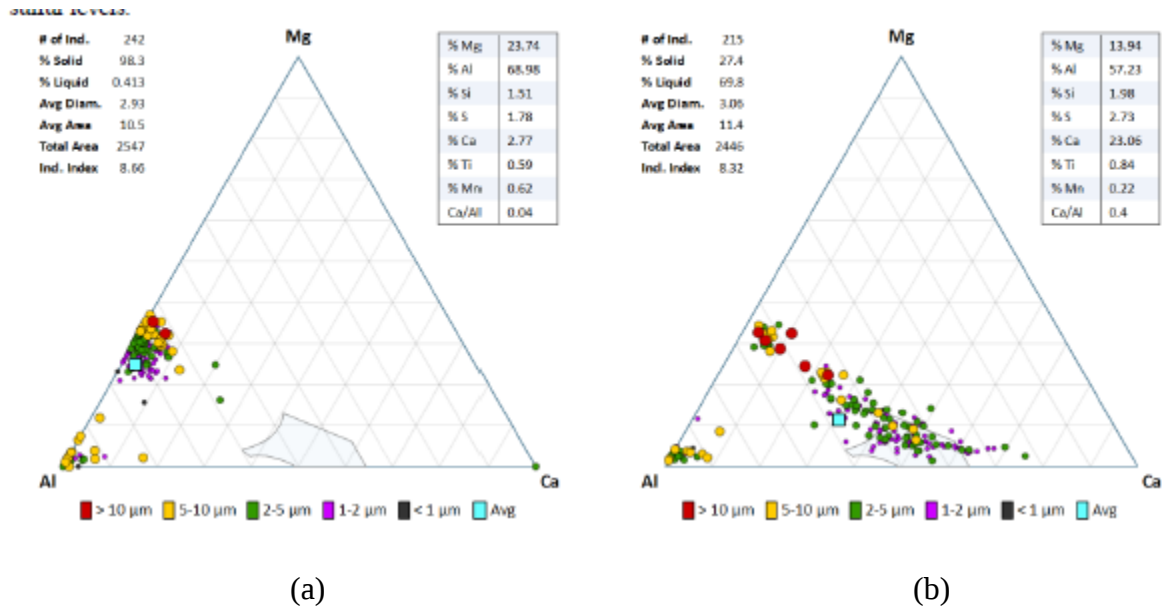


Figure 8 - (a) Inclusions after desulfurization for a Si-restricted grade (%Si < 0.03). (b) Inclusions after desulfurization for a Si-bearing grade (%Si = 0.23) where SiMn was added. The Si-bearing grade shows Ca pick-up in inclusions. [20]

Several reports [19,21,25–27] demonstrate that Ca-pick up occurs in Si-killed steels, which can increase inclusion melting temperature, promote formation of crystalline phases and reduce inclusion deformability. However, the actual mechanism by which Ca is transported to inclusions is not clear. Reports in literature showing Ca-containing inclusions do not match the expected kinetic trajectory for steel-slag reactions. For example, findings of Wang et. al [21] used MgO contents in a inclusion as a tracer for entrained slag. The CaO content in those inclusions vary around 20wt%CaO, although similar levels of MnO (20wt%) are found in the same types of inclusions. If the conditions are reducing enough so Ca is reduced from the slag, no MnO would be expected in the inclusions. However, the population of Mn-silicates decrease over time with the formation of Mn, Al-silicates, meaning that Si is indeed reducing Al_2O_3 from the slag. The elevated oxygen activity for Si-Mn killed steels in comparison to Al-killed steels would slow down Ca and Mg pick-up from refractories and top slag, however basic slags containing Al_2O_3 will promote the reduction of Al_2O_3 . Increasing [%Al] will eventually transform liquid, deformable manganese silicates into hard, solid alumina or spinel inclusions over time. FactSage macro-based kinetic simulations predict Ca-pick up as the system reaches equilibrium and composition of non-metallic inclusions approach top slag composition. However, laboratory simulation results fail to exhibit

Ca pick-up for extended reaction times [28]. There is an abrupt increase in Ca content in inclusions if strong ladle stirring is employed, especially during desulfurization and degassing. Chen et al. [19] showed Ca silicoaluminate formation for very low Al steel, so Ca and Mg solubility in these steels would be limited by the increased oxygen activity. Pires et al. [25,26] reported inclusions containing simultaneously CaO and MnO. The presence of MnO in inclusions is another indication of increased oxygen activity in steel and appears to will rule out the possibility of increased Ca and Mg reduction from slag, unless MnO precipitation upon solidification is predicted. MnO precipitation with solidification required significant dissolved oxygen, which is also incompatible with CaO reduction.

Effect of CaF_2 addition to top slag on steel-slag chemical reactions

In Al-killed steels, Al_2O_3 is generally used as a flux to lower the melting temperature of slag. However, in Si-killed steels Al pick-up must be avoided, so the utilization of Al_2O_3 must be minimized. As an alternative to alumina, fluorite (CaF_2) is a common conditioner used to decrease slag melting temperature and viscosity, without major changes in the refining properties as shown in Figure 9 for sulfur and aluminum partition [29]. CaF_2 allows an increased binary basicity (higher lime solubility), improving sulfide capacity of slag. There is no direct indication that fluorite addition will promote slag breakup, since the addition of CaF_2 is expected to increase steel-slag interfacial tension [30] although lowering viscosity can decrease the critical velocity for the establishment of Kelvin-Helmholtz instability [31]. CFD simulations presented by Irons et al. [32] also corroborate this hypothesis. However, the increased basicity range will permit lower SiO_2 activities, which lower drop O and S interfacial concentrations which may lead to Marangoni-related emulsification [30]. Decreased slag viscosity will also improve mass transfer in the slag phase for reactions which involve elements with low equilibrium partition coefficients and mixed mass transfer control, such as sulfur [29].

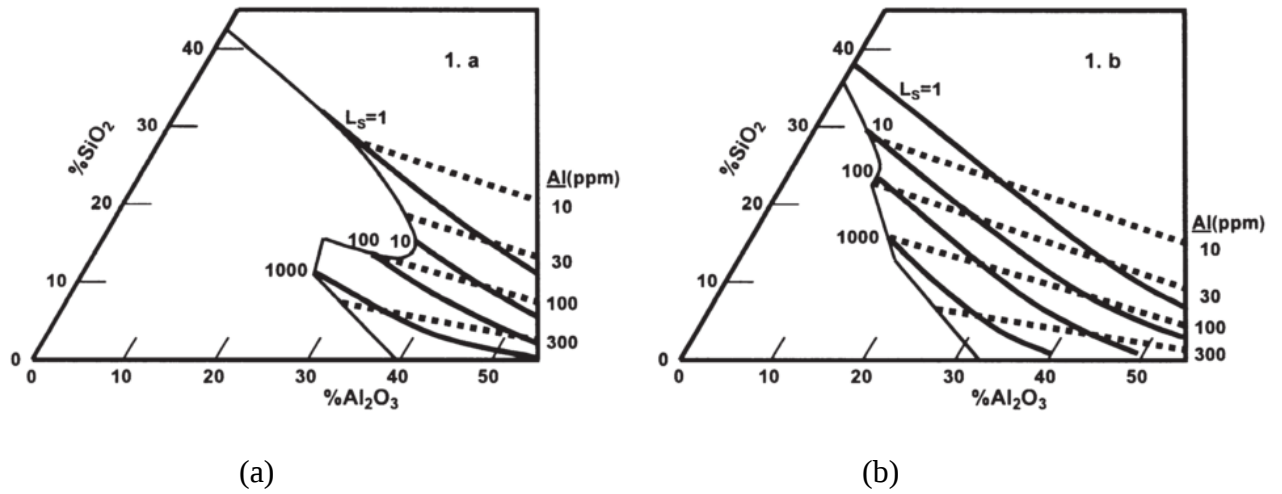


Figure 9– Equilibrium sulfur partition ratio (L_S) and aluminum activity in steel with $h_{Si} = 0.2$ at 1600°C for two slag systems – (a) CaO-Al₂O₃-SiO₂; (b) CaO-Al₂O₃-SiO₂-5%MgO-10%CaF₂.

[29]

Modeling non-metallic inclusion composition changes using FactSage macros incorporating CaF₂ as a slag component is more challenging because of limitations of the available thermodynamic databases. FactSage 7.0 has two main slag solution models which incorporate fluoride – SLAGH (includes F/Cl + several oxides including Fe²⁺, Fe³⁺, Mn²⁺, Mn³⁺, no S) and OXFL (Ca, Mg, Na, Al, Si-containing oxyfluorides) [33]. Therefore, modeling secondary metallurgy processes where CaF₂ is present is a challenge, since sulfur equilibrium calculations would need to be done in a parallel calculation using the resulting oxide activities from each iteration, which can lead to errors due to possible effects of S on slag structure when close to CaS saturation. As an alternative, one can assume that the oxide activities are not significantly changed with the addition of CaF₂ in slag. Laboratory experiments and FactSage macro modeling of steel and inclusion composition changes for a system containing CaF₂ agreed, as reported by Shin et al. [18].

2.2 Kinetics of steel-slag-inclusion-refractory reactions

2.2.1. Kinetics of steel-slag reactions

2.2.1.1. Steel-slag reaction kinetic modeling

The current literature does not contain experimental assessment of the possible rate-determining steps for *Al*, *Ca* and *Mg* pick-up in *Si-Mn* killed steels. The work presented here tests the possibility of steel and slag mass transfer to their common interface as the rate-determining steps for inclusion modification.

When a steel-slag reaction occurs, the possible rate limiting steps are the transfer from the reacting species from their respective bulk phases to the interface, the chemical reaction itself, the transfer of the resulting species to the respective bulk phases and finally bulk mixing of each of the phases. Due to the high temperatures, chemical reaction is not expected to limit the kinetics. The kinetic model used to predict the effect of basic slags in Si-Mn killed steels inclusion modification is based on the surface renewal theory [34], shown in Figure 10, with modeling similar to that proposed by Guthrie [35]. The amount of mass of phase transferred to the interface is given by equation (32), where ΔW_i is the transferred mass phase per timestep, m_i is the steel mass transfer coefficient, $A_{interface}$ is the projected interface area between the two liquid phases and ρ_i is the density of the phase.

$$\frac{dW_i}{dt} = m_i A_{interface} \rho_i \quad (32)$$

Diffusivities of elements or ions can be estimated using the Stokes-Einstein equation, where k_B is the Boltzmann constant, T is the temperature of the medium, η is the kinematic viscosity of the medium and r is the effective radius of the diffusing species.

$$D = \frac{k_B T}{6\pi\eta r} \quad (33)$$

The relative mass transfer coefficients in steel and slag can be estimated by equation (34) [34], where D_i is the molecular diffusivity in medium i , v is the surface velocity at the interface and r is the crucible (or ladle) radius.

$$m_{steel} = 2 \left(\frac{D_i v}{\pi r} \right)^{\frac{1}{2}} \quad (34)$$

The viscosity of steelmaking slags is expected to be around two orders of magnitude larger than the viscosity of steel at 1600°C [35], therefore, molecular diffusivity is expected to be two orders of magnitude smaller in slags than in steels. Thus, slag mass transfer coefficient is expected to be approximately 10 times smaller than mass transfer coefficient in steel.

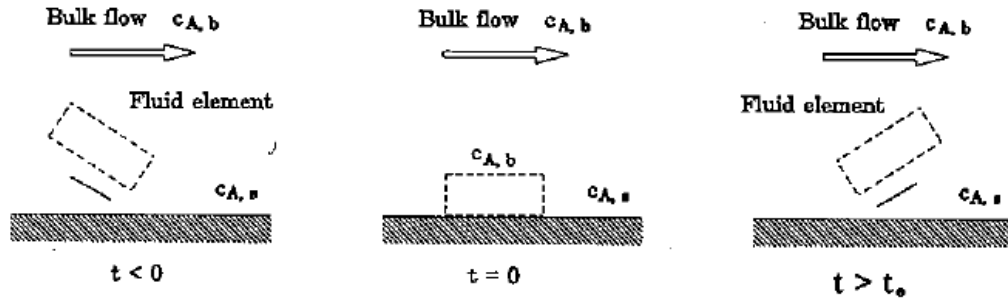


Figure 10 - Surface renewal theory schematics (Higbie model) [34]

The interfacial concentration of species in steel and slag were calculated as the equilibrium between the transferred masses of steel and slag, with the masses transferred in each time step calculated by Eq. 35 and 36. The bulk phases are assumed to be well-mixed, so the reaction products are mixed back to the bulk phases at each calculated timestep.

$$\Delta W_{steel} = m_{steel} A \rho_{steel} \Delta t \quad (35)$$

$$\Delta W_{slag} = m_{slag} A \rho_{slag} \Delta t \quad (36)$$

Mass transfer coefficients for these reactions can be obtained in the literature for ladles, taking in account the stirring power. The mass transfer coefficient could also be back-calculated from the observed aluminum pick-up in the steel bath:

$$\frac{d[i]}{dt} = -m_i \frac{A_{interface}}{V_{steel}} ([\%i] - [\%i]_{eq}) \quad (37)$$

For mixed control of slag and steel mass transfer, the overall mass transfer coefficient can be written as the following [36]:

$$m_{eff} = \frac{1}{\frac{1}{m_{steel}} + \frac{1}{m_{slag}} \frac{\rho_{slag}}{\rho_{steel} L_i}} \quad (38)$$

If the partition coefficient does not change during reaction, the effective rate constant k' and the change in concentration of a reacting element i can be calculated as it follows, assuming the masses in the system, the mass transfer coefficients and the partition coefficient do not change over time.

$$k' = \frac{m_{eff} \rho_{steel} A}{W_{steel}} \left(1 + \frac{W_{steel}}{W_{slag} L_i} \right) \quad (39)$$

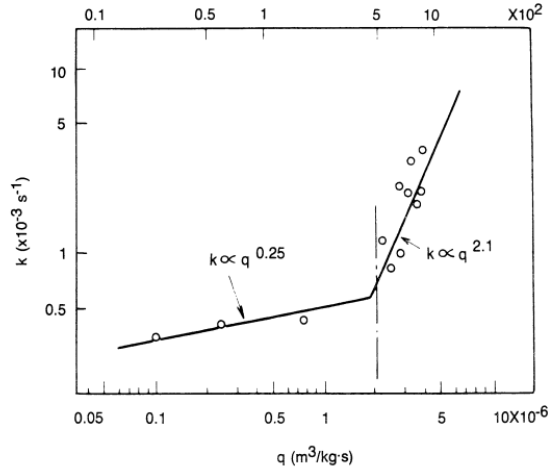
$$\ln \left(\frac{([\%i] - [\%i]_{\infty})}{([\%i]_0 - [\%i]_{\infty})} \right) = -k' t \quad (40)$$

Nucleation and growth of inclusions will not be considered as rate-determining steps for slag-based chemical composition modification, so it is assumed that the inclusion population will be in equilibrium with the composition of liquid steel. This assumption will be verified in Section 2.3, on the kinetics of steel-inclusion reactions.

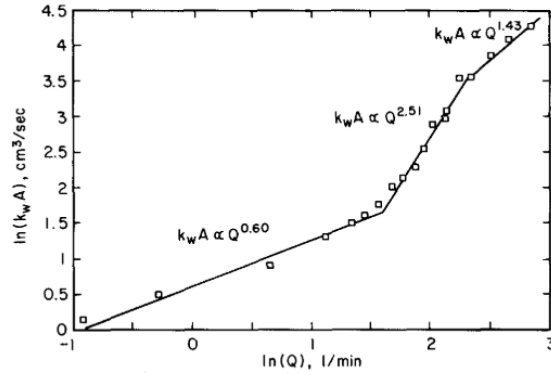
During ladle refining, the steel-slag interface can be disturbed by strong stirring, arcing and chemical reactions involving surface-active elements such as O and S [37][38][39][40,41]. In practice, there are different mass transfer regimes according to the intensity of bulk agitation i.e. bottom-blown Ar gas or electromagnetic stirring. From Figure 11, it is seen that generally there is an inflection point in the increase of the rate constant for steel-slag reactions with increasing Ar flowrate. This is an indication of a different mass transfer regime at the steel-slag interface – the researchers attribute this effect to the breaking up of slag into small droplets that will significantly increase its surface area. In the figure, it is seen that for both steel-slag systems (Figure 11a) and water-oil modeling (Figure 11b) there are critical Ar flowrates will shift the mass transfer regime to a stable liquid-liquid surface to an emulsion around the slag “open eye”, the spout caused by the column of bubbles rising to the surface (gas plume). This emulsification will also be responsible for a new population of inclusions in the steel by ejection of small droplets of slag. The stronger the stirring, the smaller the equilibrium droplet size at the ejection site [42]. Abel [43] calculates the mass transfer rate (cm^3/s) for steel-slag reactions as it follows, in function of the stirring power input ϵ (dyne.cm/s), liquid density ρ_L (g/dm^3), volume of upper phase V_u (dm^3), ladle height H_L (cm), mass diffusivity D (cm^2/s), gas flowrate at temperature and pressure (dm^3/s), density

difference between upper and lower phase $\Delta\rho_{L-u}$ (g/dm³), liquid-upper phase surface tension σ_{L-L} (erg/cm²), maximum stable bubble diameter d_B (cm) and gas holdup coefficient α (typically 0.22).

$$mA = 3.21 \frac{\epsilon^{1.07} \rho_L^{1.06} V_u^{0.63} H_L^{0.3} D}{Q_{g,T,P}^{0.19} \Delta\rho_{L-u}^{0.8} \sigma_{L-L}^{1.32} d_b^{1.95} (1 - \alpha)^{0.05}} \quad (41)$$



(a)



(b)

Figure 11 – Experimental observation of mass transfer for liquid-liquid reactions due to bottom-blown stirring gas. (a) Rate constant for desulfurization in a 2.5 ton pilot-scale ladle as a function of specific Ar flowrate [44], (b) Relationship between $k_w A$ (water mass transfer rate) of thymol removal as a function of gas flowrate for a water-light paraffin oil 1:7.2-scale ladle model with a single center tuyère in terms of the order of dependence n [40].

Both cases in Figure 11 demonstrate a different mass transfer regime for higher flowrates, which is explained to the formation of slag droplets that are entrained in the steel and increases the surface area available for steel-slag reactions.

2.2.1.2. Steel-slag emulsification behavior

As discussed in the previous section, strong stirring can introduce a new population of inclusions in the steel due to detachment by strong eddies around the gas plume. The detachment process is a balance between the inertial forces at the plume due to recirculation of steel, the buoyancy force of the detached particle and the surface force at the point of detachment. The equilibrium size of these ejected droplets and their stability will depend on the slag speed (which depends on the Ar flowrate), take-off angle and thermophysical properties of the slag such as surface tension, viscosity and density difference between slag and steel [40,45,46]. The schematics of this process is shown in Figure 12.

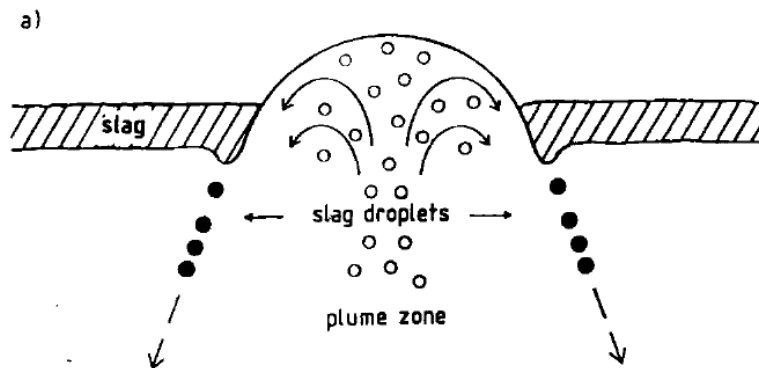


Figure 12 – Schematics of slag detachment process at the steel-slag interface around the gas plume [45]

Plant trials for 60-ton heats of Si-killed carbon steel using an acid slag (around 20-30%CaO, 50-60%SiO₂, 8-12%Al₂O₃, 5%MgO), with strong stirring around 35-45 STP m³/h (9.7-12.5 STP l/min.t) showed that many inclusions smaller than 20 microns are generated from emulsification (in this case, steel-slag reaction must be ruled out because of the high oxygen potential of the slag, enough to oxidize carbon) [42,46], as seen on the pseudo-ternary diagram of Figure 13. The inclusions containing CaO had slag-like composition. The report also shows that the content of CaO-containing inclusions increases for higher Ar blowing pressure and smaller stirring times, therefore these CaO inclusions will appear when you vigorously stir the melt and do not give

enough time for these inclusions to coagulate and float. The report is not clear in what is the Si-containing ferroalloy added in the steel (both the dissolution of SiMn and FeSi are discussed earlier), therefore an alternative conclusion could be that the shorter processing times prevent the floatation of Ca-silicates formed upon ferroalloy (FeSi) addition.

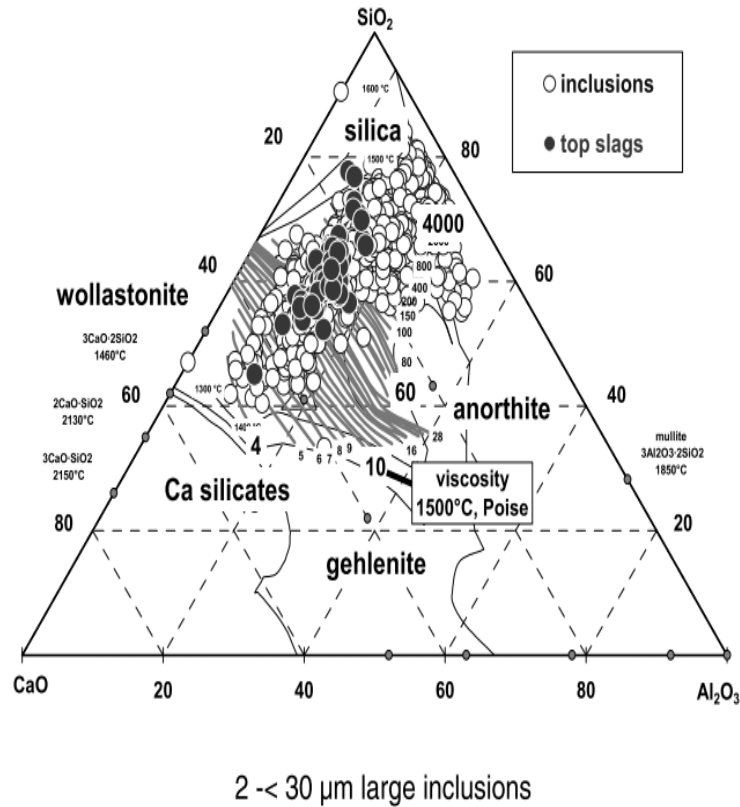


Figure 13 – Pseudo-ternary diagram for a CaO-Al₂O₃-SiO₂-5%MgO system comparing non-metallic inclusions and slag chemical composition for a Si-killed steel stirred with an acid slag (%CaO/%SiO₂ = 0.5). Less viscous compositions are broken down into smaller inclusions [42,46]

Other than the physical entrainment of slag in the steel, chemical reactions might also play a role in emulsification due to their effect on changes in surface energy. The measured values for contact angle and surface energy are strongly dependent on the solute content of surface-active elements such as oxygen and sulfur in steel. Increasing amounts of O and S can drop surface energy values

from the order of 1.5 J/m^2 to 0.2 J/m^2 , as seen on Figure 14. The increase in oxygen activity in steel is also shown to decrease the interfacial energy of steel-slag interfaces in contact with $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$. [30] Inhomogeneity in O and S contents along the steel-slag interface will promote flow due to the solutal Marangoni effect, which can lead to shape instability of the phases. Changes in surface energy over time between a reacting droplet-substrate-gas system have been reported (dynamic wetting phenomena), and has been proposed as a means to measure reaction kinetics of different systems [30][47]. Self-emulsification phenomena involving oxygen and sulfur transfer across the interface have been reported (Figure 15). In the steelmaking practice, steel and slag will be constantly exchanging O and S, so both Marangoni and Kelvin-Helmholtz instabilities are expected to influence steel-slag reaction kinetics and the introduction of small particles of slag in steel, which could be small enough to become non-metallic inclusions. Reports show that steel-slag interface in a ladle furnace at the end of desulfurization is expected to be more stable [48], however laboratory trials for silicon-slag reactions in the presence of an impeller show that mechanical stirring will drive surface disintegration while the reaction is taking place [49]. Swartz et al. [22] summarized the possible slag entrapment phenomena and the steel-slag properties which will influence the critical velocity for interface break-up.

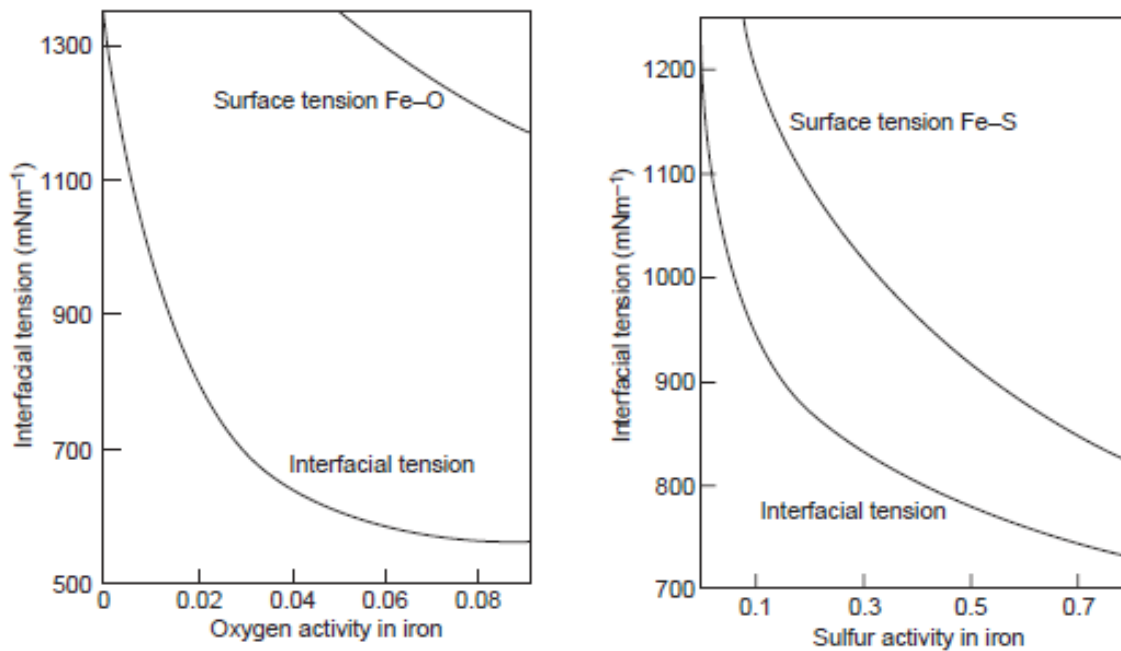


Figure 14 - Dependence of interfacial tension on the oxygen and sulfur Henrian activities in molten iron [50]

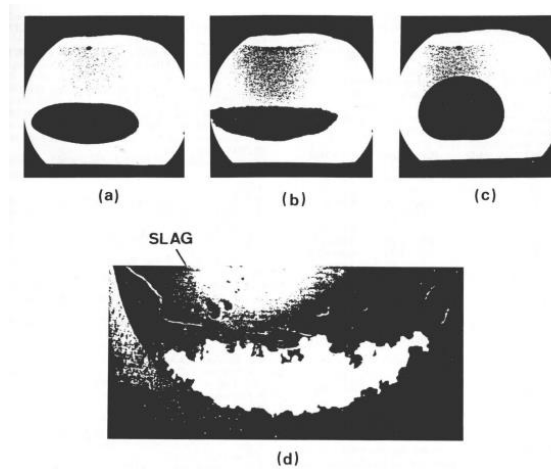


Figure 15 – Illustration of dynamic wetting phenomena – Al-containing metal droplet reacting with SiO₂-containing slag [30]. (a) 7 min; (b) 18 min; (c) 40min after immersion. (d) Polished section, after quenching, of a droplet corresponding to configuration (b).

Looking back to the practical observations on steel-slag behavior, the combination of physical slag entrainment and chemical reactions involving O and S might break the slag into very small particles and generate a new population of Ca-containing inclusions in the steel.

2.2.2. Kinetics of steel-inclusion reactions

2.2.2.1. Steel-inclusion reaction kinetics

The fluid flow behavior of a non-metallic inclusion in the steel melt, either solid or liquid, can be approximated as a free-falling body in a medium. The steel-inclusion reaction can be limited by transfer of reacting species from the steel across the boundary layer to the inclusion interface, transfer of reactants and products across the product layer if product layer or inclusion is solid, and chemical reaction at the interface. In the case of liquid inclusions, it can be assumed that the inclusion chemical composition is fully mixed from the Hadamard-Rybczynski solution [51], which predicts strong convection currents inside a droplet due to drag and surface tension effects. However, this is expected only for larger particles in which the buildup of surface-active elements at the interface prevents the formation of convection patterns inside the droplet. The very same effect predicts an increase of 50% in the terminal velocity of a liquid particle as compared to the Stokes' law for solid spherical particles of the same volume [51]. Since the inclusions are several orders of magnitude smaller than steel melt depth, it can be assumed that the inclusions are in terminal velocity due to buoyancy. The Stokes terminal velocity of a free-falling sphere in a fluid is given by:

$$v = \frac{2}{9} \frac{(\rho_{inclusion} - \rho_{steel})gR^2}{\mu} \quad (42)$$

The Reynolds number for a free-falling inclusion, then, is given by:

$$Re_{particle} = \frac{\rho_{steel}vd_{inclusion}}{\mu} \quad (43)$$

The mass transfer coefficient for steel-inclusion reactions then can be calculated from the Sherwood number:

$$Sh = \frac{k_{steel}d_{inclusion}}{D_{steel}} \quad (44)$$

$$Sc = \frac{\mu}{\rho_{steel}D_{steel}} \quad (45)$$

The mass transfer correlation for free-falling spheres in a fluid then can be written as:

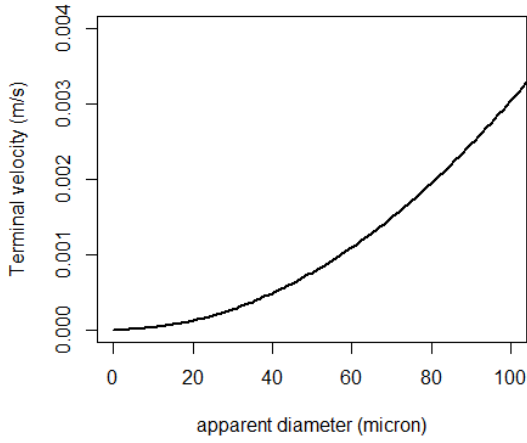
$$Sh = 2 + 0.552Re_{particle}^{0.5}Sc^{0.3333} \quad (46)$$

Therefore, the mass transfer of steel around the free-falling particle can be calculated. Therefore, the volume of steel reacting with inclusions in a certain time can be calculated as:

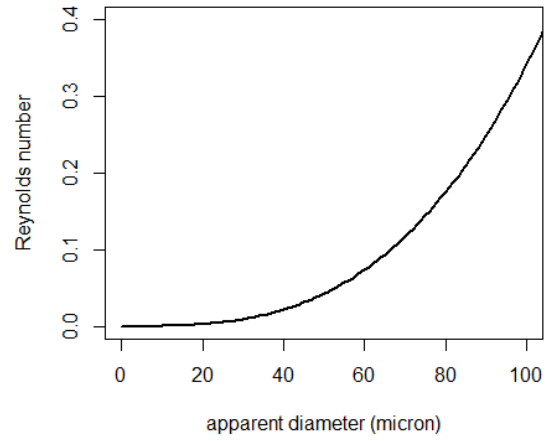
$$m_{steel}A_{inclusions} = m_{steel} \frac{V_{inclusion}^{total}}{V_{inclusion}} A_{inclusion} \quad (47)$$

The Stokes velocity, Reynolds and Sherwood numbers and mass transfer coefficient are plotted in Figure 16. This number must be compared to the obtained for the steel-slag reaction interface, so the rate limiting step can be decided. There are several correlations for the mass transfer coefficient of steel to the slag for argon-stirred ladle. The chosen equation to estimate mass transfer coefficient in ladle was developed by Ishii et al. [52]. It is seen that, for most of the time, the rate limiting step will be the steel-slag reaction rather than the steel-inclusion reaction, unless most of the inclusions are unusually large (Figure 17).

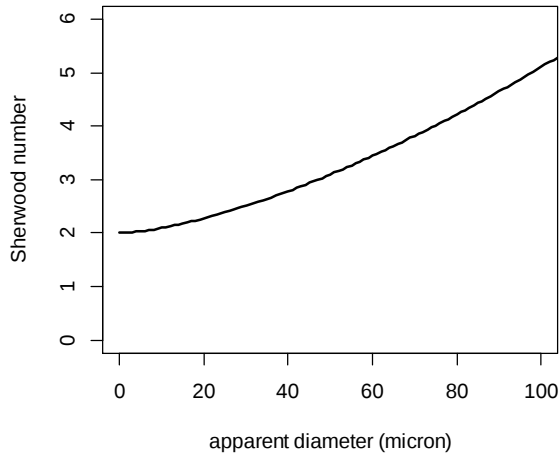
It is very unlikely that solid-solid reaction kinetics are rate-controlling. Since steel-inclusion kinetics are expected to be fast, the main rate-controlling mechanism for inclusion-inclusion reactions might be the transport of reacting species through the steel layer (diffusivity of species at solid-solid interfaces might be 2 to 3 orders of magnitude lower than the diffusivity of species in the liquid) [53]. Therefore, the chemical potential gradient between two inclusions will be resolved by transportation of these species until the equilibrium is reached. In the case of severe oxygen potential differences in steel, such as the simultaneous presence of CaS and Al₂O₃ inclusions in the steel, the formation of Ca-aluminates will be mediated by the transfer of dissolved [Ca], [Al] and [O] through the liquid steel to the reacting interfaces. Since the solubility of Ca is much smaller than the solubility of O [16], [O] will most likely control the mass-transfer limited inclusion-inclusion reactions [54]. Schematics of this process can be found on Figure 18.



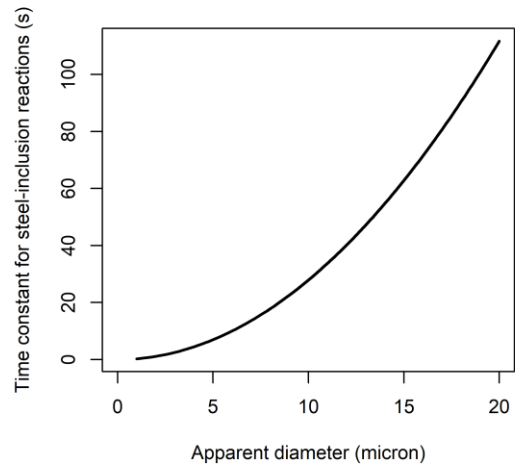
(a)



(b)



(c)



(d)

Figure 16 – Calculated values for (a) Stokes terminal velocity, (b) Reynolds number at free fall, (c) Sherwood number and (d) mass transfer coefficient in function of the particle diameter. The reference values for the calculations are: $\rho_{steel} = 6962 \text{ kg/m}^3$, $\rho_{particle} = 3500 \text{ kg/m}^3$, $\mu_{steel} = 6.2 \times 10^{-3} \text{ Pa.s}$, $D_{steel} = 10^{-9} \text{ m}^2/\text{s}$, $g = 9.81 \text{ m/s}^2$, 50 ppm of inclusion concentration (approx. 20 ppm [O] total).

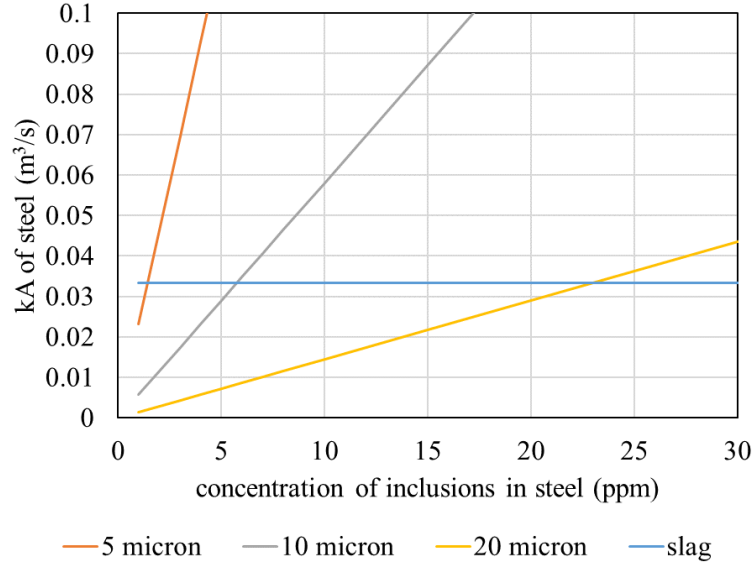


Figure 17 – Comparison between steel-slag mass transfer and steel-inclusion mass transfer for different sizes of inclusions and inclusion concentrations in steel at ladle furnace conditions (150t, 3m diameter, $m_{steel} = 4.7 \times 10^{-3} \text{ m/s}$). The steel-inclusion reactions will be slower only when a low concentration of large inclusions is present in steel.

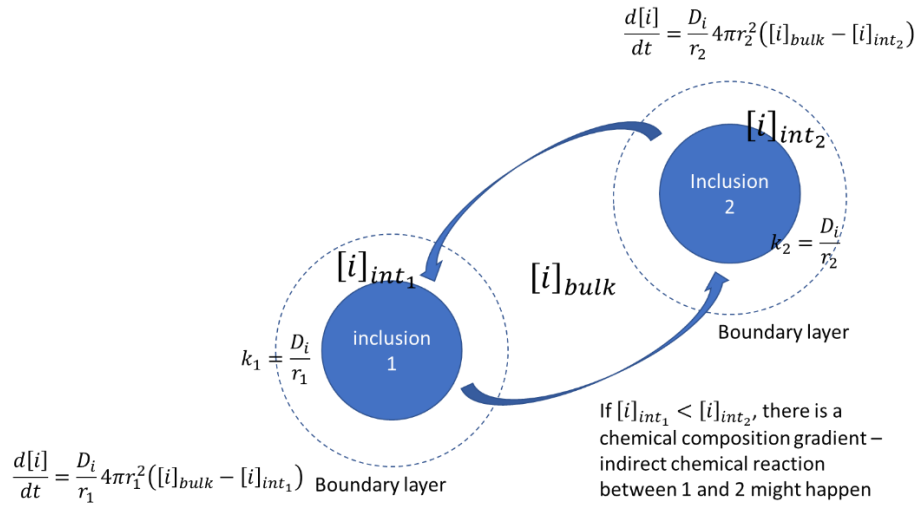
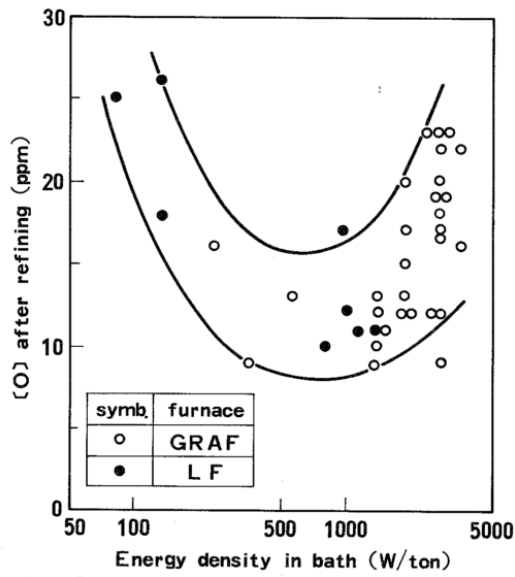


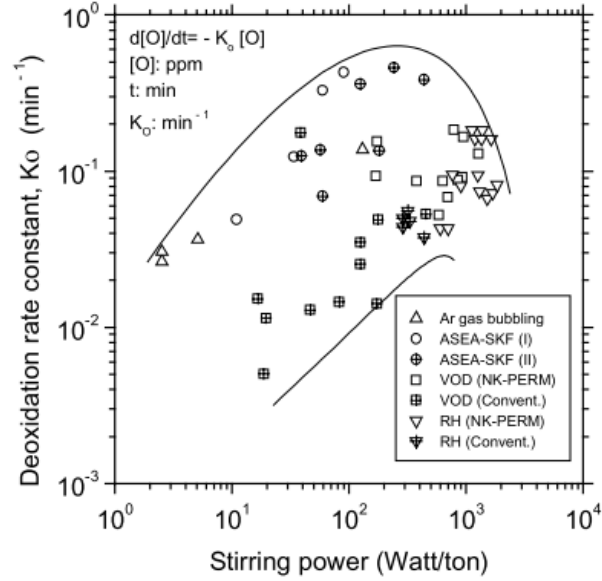
Figure 18 – Schematics for “ripening mechanism” of inclusion-inclusion reactions – collision and chemical ripening. [34,55]

2.2.2.2. Inclusion removal kinetics

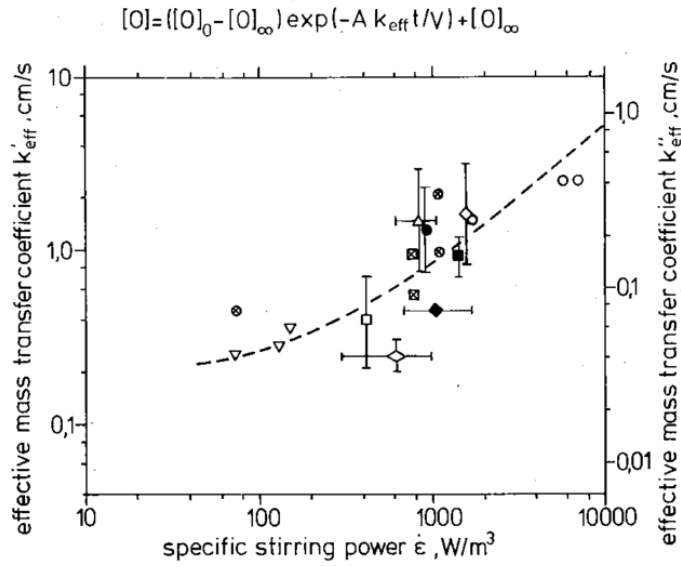
Understanding the inclusion removal kinetics for ladle processing is fundamental for process and quality control to obtain the desired $[O]_{\text{total}}$ in the cast product and prevent clogging. The initial amount of inclusions in the steel will depend on the total $[O]$, temperature and amount of deoxidizer added at EAF/BOF tapping. Upon deoxidation, the amount of inclusions formed in the steel will be proportional to the difference between the initial dissolved oxygen and the dissolved oxygen after alloying. The subsequent decrease in inclusion concentration by flotation afterwards is expected to follow first-order reaction kinetics, and the mass transfer coefficient for oxygen removal depends on the stirring power in the melt [56–58] (as seen on Figure 19b and Figure 19c). The steady-state $[O]_{\text{total}}$ depends on the stirring power as well. A stir that is too strong might expose a significant area of the steel to air and cause reoxidation, as well as slag entrainment (Figure 19a). Size of inclusions will depend on the supersaturation levels of $[O]$ and the deoxidant, as well as the temperature of the melt [59]. As discussed in Section 2.2.2.1, the terminal velocity of an inclusion is proportional to the square of its radius, so larger inclusions will be more easily removed by floatation.



(a)



(b)



(c)

Figure 19 – Effect of stirring in oxygen removal kinetics for Al-killed steels. (a) Effect of stirring energy in the total oxygen by the end of refining treatment [60]. Effect of stirring power on deoxidation rate in various refining processes (Ar gas bubbling, ASEA-SKF, VOD and RH) [58]. (c) Effect of stirring power in the mass transfer coefficient of oxygen (inclusion) removal [57].

There is a non-zero time for an inclusion to dissolve in the slag; arguably, if the eddies are too strong, it can carry over the inclusion back to steel before it has the chance to completely dissolve. If slag is too viscous or the concentration gradient between the slag and the inclusion is small, the time for an inclusion to dissolve can vary by orders of magnitude [61–65]. The calculation shown in Figure 20 takes in account the mass-transfer limited dissolution of a free-falling spherical particle in a liquid oxide medium as given by Yan et al. [63]. For the typical size range of an inclusion, especially for Si-Mn killed steels that are very soluble in steelmaking slags, the dissolution time can be much smaller than one second. Therefore, it can be assumed that incorporation of inclusion by the slags should not be rate-limiting. In Figure 21, all the mechanisms for inclusion nucleation, growth, coalescence and removal are listed, and the ultimate inclusion size will depend on this balance between the reaction rates. This figure represents a Ca-treated Al-killed steel, so diffusion (or mass transfer) growth and coalescence is expected to take a much longer time than for higher [O] Si-Mn killed steels.

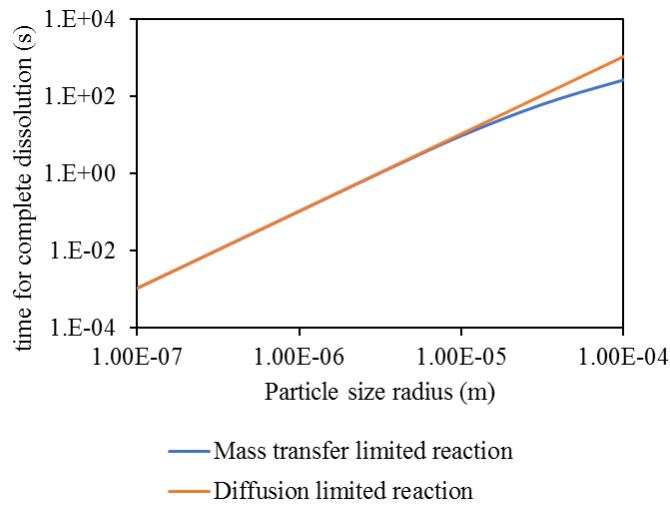


Figure 20 – Expected dissolution time of a spherical Al_2O_3 inclusion in a 30wt% Al_2O_3 CaO- Al_2O_3 -MgO slag [63]

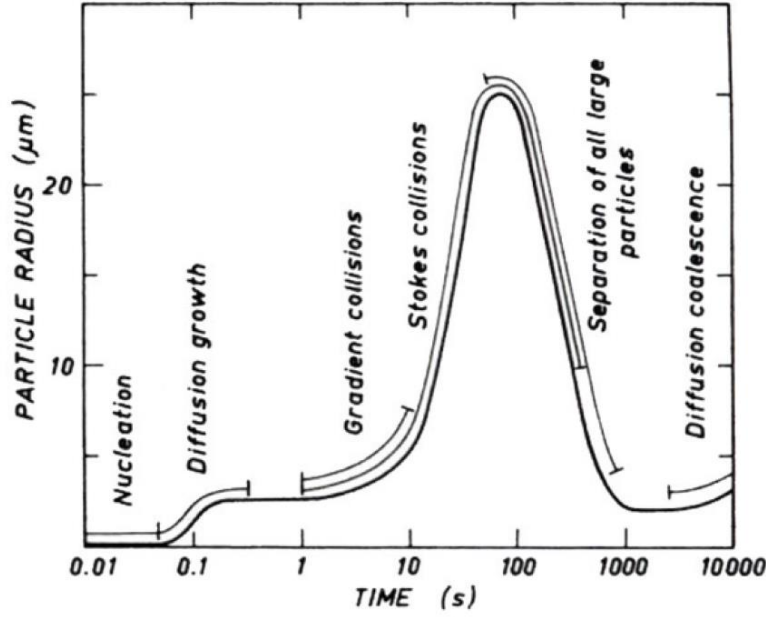


Figure 21 – Summary of phenomena controlling the size of non-metallic inclusions in steel and their timescales. [66]

2.3. Precipitation of inclusions during solidification

The assessment of the inclusion population at steelmaking temperatures can be a challenge, since the high dissolved oxygen content for Si-Mn killed steels will precipitate during solidification as secondary inclusions. The resulting inclusion size can be estimated as follows. Zener [67] described the diffusion-limited growth of spherical particles in a matrix using the following equation, in which i is the expected limiting species for growth (for example, [O], [Ca], [Mg] in Ca-treated Al-killed steel) and $D_{i,bulk}$ is its mass diffusivity (m^2/s) in the bulk matrix (liquid steel in the case of a precipitating inclusion). C_{bulk} is the concentration of the limiting species in the bulk matrix, $C_{particle}$ is the concentration of the limiting species in the precipitating particle and $C_{interface}$ is the particle-matrix interfacial concentration.

$$\frac{dr}{dt} = \frac{D_{i,bulk}}{r} \frac{(C_{bulk} - C_{interface})}{(C_{particle} - C_{interface})} \quad (48)$$

The effect of local chemical composition changes and the kinetics of this precipitation for different cooling rates in Al-Ti deoxidized steel has been studied by Goto et al. [68] (Figure 22). Won and Thomas [69] analyzed microsegregation during solidification of steels analytically. Lehmann et al. [70] modeled the kinetics of nucleation and growth of inclusions during steel solidification, using classical nucleation theory for homogeneous nucleation, assuming that growth is controlled by the diffusion of oxide monomers to the nuclei. The modeling results show the effect of undercooling on the size distribution of inclusions during solidification, as shown in Figure 23.

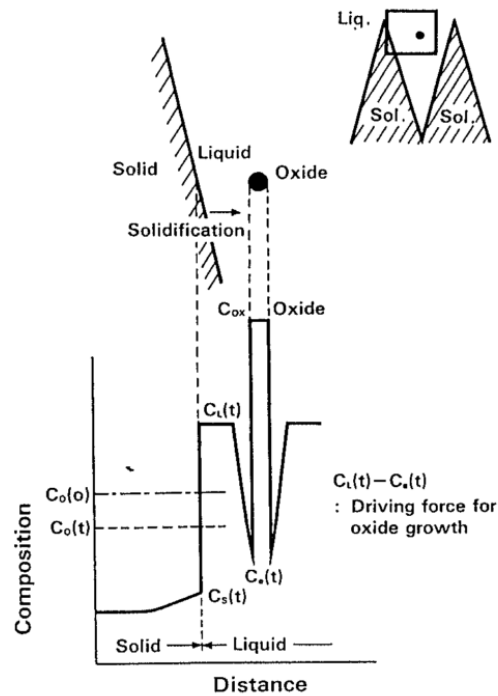


Figure 22 – Effect of microsegregation during solidification into oxide inclusion stability [68].

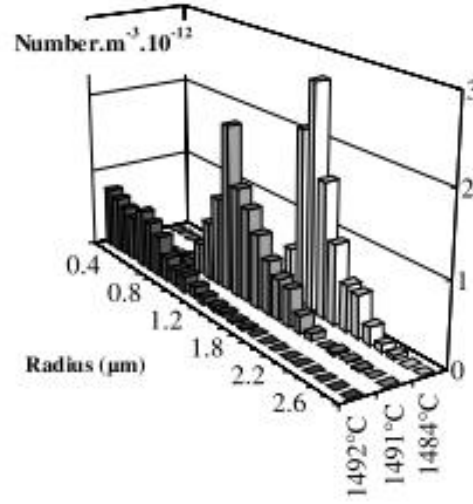


Figure 23 - Influence of undercooling on the nucleation of non-metallic inclusions (Mn-Si-Al-Ti-O) in steel [70]. The histograms show the modeled size distribution of inclusions in undercooled liquid at three different temperatures. With lower temperature, nucleation ceases and mass transfer-controlled growth continues until full solidification.

The maximum size of second-phase microsegregation products are generally limited by the volume of the remaining liquid steel upon solidification, which is in the length scale of the secondary dendritic arm spacing. Empirical correlations are given by equations (48) and (49), where λ_{SDAS} is the secondary dendrite arm spacing, $[\%C]$ is the weight percent of carbon in liquid steel and $\dot{T}$ is the cooling rate in K/s . Secondary dendrite arm spacing is expected to decrease with increasing cooling rate and carbon content for $[\%C] \leq 0.15\%$, but it is expected to increase with carbon content for $[\%C] > 0.15\%$ due to the increasing gap between solidus and liquidus temperature.

$$\lambda_{SDAS} (\mu m) = (169.1 - 720.9 * [\%C]) * \dot{T}^{-0.4935} \text{ for } [\%C] \leq 0.15\% \quad (49)$$

$$\lambda_{SDAS} (\mu m) = 143.9 * \dot{T}^{-0.3616} * [\%C]^{(0.5501 - 1.996[\%C])} \text{ for } [\%C] > 0.15\% \quad (50)$$

Wilde and Perepezko [71] studied the incorporation of particles by a dendritic solidification front. For a planar solidification front, comparisons between thermal conductivity [72] and heat capacity [73] of the liquid and the particle are used to predict the incorporation behavior. For both criteria, alumina inclusions should be pushed by steel with a planar solidification front. However, for dendritic solidification fronts, incorporation of inclusions will depend on the local fluid flow

conditions. Figure 24a and Figure 25b illustrates the different incorporation behavior that can happen in the solidification front. Empirical correlations for the primary dendrite arm spacing in low-alloyed steels [74] can be described by eq. (50). Primary dendrite arm spacing is expected to decrease with increasing cooling rates, however the dendrite tip radius is expected to be much larger than the inclusions for the observed cooling rates in near-net shape castings [6].

$$\lambda_{PDAS} = 278.748 * (\dot{T}^{-0.2063}) * ([\%C])^n \quad (51)$$

$$\begin{cases} n = -0.3162 + 2.033[\%C] & \text{if } [\%C] \leq 0.15\% \\ n = -0.019 + 0.492[\%C] & \text{if } 0.15\% < [\%C] < 1.0\% \end{cases}$$

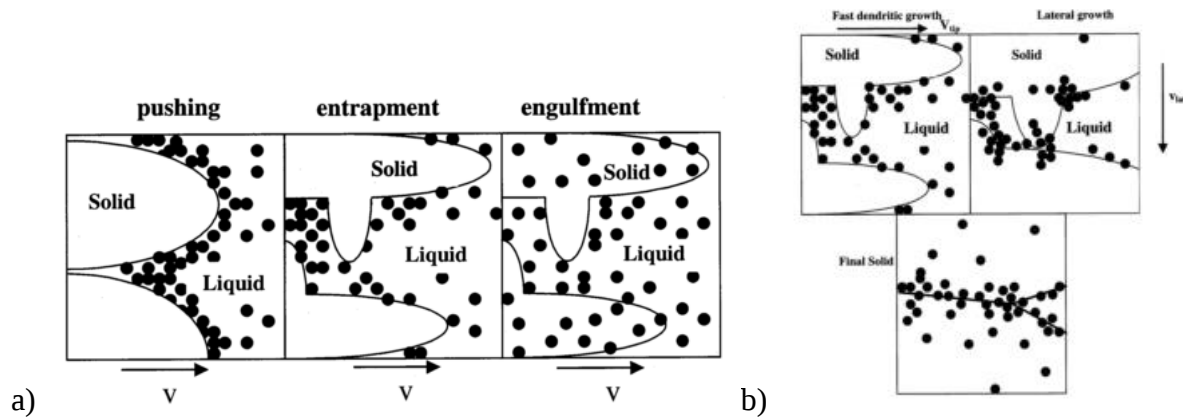


Figure 24 - Schematic illustration of: a) the possible interaction modes of a dendritic solid/liquid interface with dispersed foreign particles; b) incorporation process via lateral growth of dendrites [71]

The work by Haug et al. [75] on Al-4.5%Cu alloys shows that fast solidification rates can promote intergranular flow of enriched solute to the surface, showing a minimum solute concentration at a certain distance from the casting surface. The secondary manganese silicate inclusions (that form during solidification) also have a much lower melting temperature than steel, therefore macrosegregation and exudation due to intergranular flow of liquid inclusions can be expected.

2.4. Experimental observation of Ca, Mg and Al pick-up in industrial practice and laboratory experiments

2.4.1. Effect of steel-slag reactions

There are many accounts in the literature where the formation of Ca, Mg and Al-containing inclusions are attributed to steel-slag reactions in steelmaking practice. Garlick et al. [76] demonstrated that Al and Ca pick-up in Si-Mn killed steels can be disruptive to casting by forming high melting point materials. Several other authors correlated steel-slag thermodynamics to the formation of high melting point oxide inclusions [21,27,77–80] and observed that reducing the activity of the main steel deoxidation product (SiO_2 for Si-killed steels, Al_2O_3 for Al-killed steels) by increasing binary slag basicity would enhance the pick-up of minor elements such as Al and Mg. These elements would encounter a more oxidized melt in the bulk steel than at the steel-slag interface and reprecipitate as an inclusion. These Al, Mg and Ca-containing inclusions are harder and have a higher melting point than typical Mn-silicates. This effect of slag composition on enhanced pick-up is explained by the deoxidation reaction – if the oxide activity is lower, the deoxidation equilibrium is shifted to the right and the local oxygen partial pressure is decreased. The account on Ca pick-up is more confusing. Ferroalloys, especially FeSi75, will contain metallic calcium. In literature, there are not many accounts of observed inclusion Ca pick-up while strictly controlling the Ca content in ferroalloys, ensuring the observed Ca is from reduction from slag. Pretorius [20] reported Ca pick-up with SiMn trimming (Ca pick-up from ferroalloys are not expected), which could be from steel-slag reactions. For laboratory experiments, documented and statistically relevant Ca pick-up measurements were done by Mu et al. [81] for high Al steels ($[\text{Al}] > 0.5\text{wt}\%$) and Kumar et al. [54] for high Al and high Si steels ($[\text{Al}] > 0.3\text{wt}\%$, $[\text{Si}] > 1\text{wt}\%$). The observations from their accounts and this thesis' results estimates that the Ca solubility in steel is significantly smaller (3 to 4 orders of magnitude) than the prediction by commercial thermodynamic simulation packages. The expected Ca pick-up from slag can be estimated from the following equation:

$$\frac{d[\text{Ca}]}{dt} = \frac{k_{\text{steel}} A_{\text{steel}} \rho_{\text{steel}}}{W_{\text{steel,bulk}} * 100} ([\text{Ca}]_{\text{bulk}} - [\text{Ca}]_{\text{eq}}) \quad (52)$$

The bulk calcium concentration can be assumed to be zero since the oxide inclusions are efficient Ca getters. For a strong stirred (10 NL/(min.t) Ar flowrate), 1600°C, 100-ton ladle with 2.63 m diameter, the mass transfer coefficient for steel-slag reactions is around $m_{steel} = 3 \times 10^{-3}$ m/s [52,82] and the cross-sectional ladle area is 5.45 m². FactSage predicts Ca solubility of 11 ppm for a 0.2%Si and CaO, MgO-saturated 56%CaO-24%SiO₂-5%MgO-15%CaF₂. If the solubility of Ca in the steel is an arbitrary number of 11 ppm, the expected Ca pick-up per hour in inclusions is 50 ppm Ca/hour. For strongly desulfurized, deoxidized and stirred steels, the steel-slag reaction can cause inclusion modification, but for most systems this number is too small for steel-slag reactions to the source of the several ppm of Ca in early stages of ladle processing.

2.4.2. Effect of ferroalloy additions

Ferroalloys such as FeSi, FeTi, FeMn and Al are typically added to the oxidized steel bath as deoxidants and to alloy the steel. Guthrie [83] and Argyropoulos [84] described the mechanism of dissolution of ferroalloys in molten iron, shown in Figure 25. It is expected that the mechanism of ferroalloy dissolution will determine the thermal and solutal profiles at the dissolution front. Larger inclusions are expected to nucleate on the surface of higher melting point, lower thermal diffusivity alloys. Different ferroalloy compositions should also lead to different supersaturation and inclusion composition and morphology. Ferrosilicon containing 75wt%Si has a significantly higher melting point and is expected to yield solid silica inclusions (SiO₂), whereas silicomanganese (7:2:1 Mn:Si:Fe ratio) yields manganese silicate inclusions. Ferroalloys such as FeSi, FeTi, FeMn and Al are typically added to the oxidized steel bath as deoxidant agents. Guthrie [83] and Argyropoulos [84] described the mechanism of dissolution of ferroalloys in molten iron, shown in Figure 25. It is expected that the mechanism of ferroalloy dissolution will determine the thermal and solutal profiles at the dissolution front. Larger inclusions are expected to nucleate on the surface of higher melting point, lower thermal diffusivity alloys. Different ferroalloy compositions should also lead to different supersaturation and inclusion composition and morphology. Ferrosilicon containing 75wt%Si has a significantly higher melting point and is

expected to yield solid silica inclusions (SiO_2), whereas silicomanganese (20wt%Si, 70wt%Mn, 10wt%Fe, sat. C) is expected to yield modified liquid complex manganese silicates.[85]

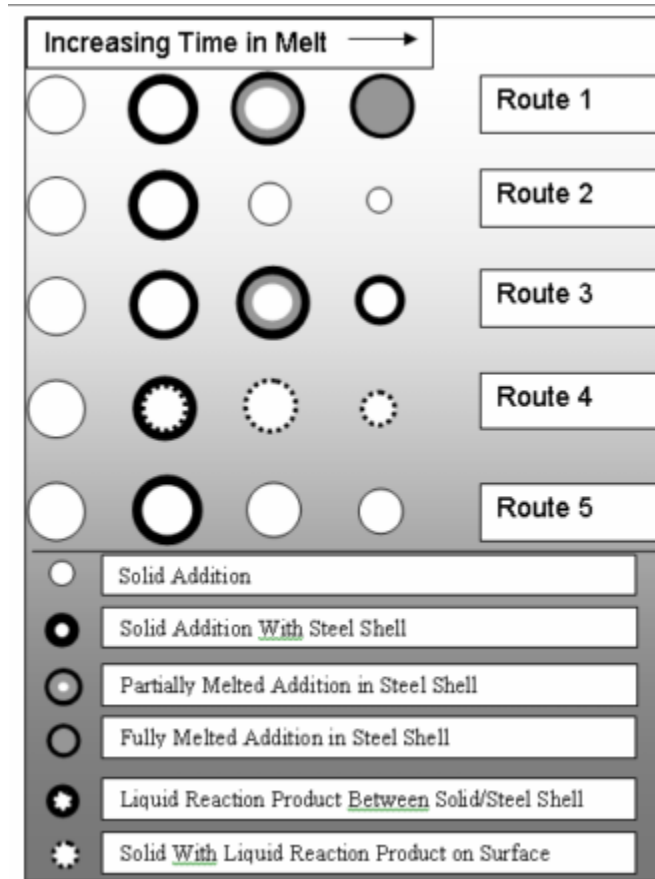


Figure 25 - Proposed mechanisms for ferroalloy dissolution in molten steel [83]

The mechanism of ferroalloy dissolution depends on the particle size distribution of the added material, melting point of the alloy, density of the particle, its thermal properties such as conductivity, heat capacity, melting point and enthalpy of mixing. The concentration of the desired element throughout the steel bath will also take a finite time to become homogeneous [86]. A solid steel shell can form on the ferroalloy surface due to local conditions of heat transfer, and its growth and remelting are possible rate-determining steps for incorporation of the element into the steel bath. The mechanism of dissolution of ferroalloys in liquid steel was modeled by Argyropoulos [84].

It is also known that impurities in ferroalloys can yield transient inclusions that will persist in the steelmaking process. Standard high-grade ferrosilicon can have up to 1.5%Al and 0.5%Ca [87].

Wijk and Brabie [88] showed the presence of Ca-containing intermetallics (Figure 26) in standard FeSi75 grades containing up to 1000 ppm Ca such as Si_2Ca , $\text{Si}_2\text{Al}_2\text{Ca}$ and $\text{Fe}_4\text{Si}_8\text{Al}_6\text{Ca}$ due to CaO reduction by Si. It is shown that these intermetallics can directly affect steel cleanliness especially for Si-deoxidized steels where there are restrictions to Al, Mg and Ca concentrations in liquid steel. Work by Story et al. [89] correlated the formation of Ca-aluminates prior to Ca-treatment for Si-bearing grades as compared to Si-restricted grades. In Figure 27 (left), it is seen that Si-bearing steels have more Ca-containing inclusions although the mechanism is not well understood – they might be formed by ferroalloy Ca pick-up, slag entrainment or steel-slag reactions. The increase in spinel inclusions (Figure 27 – right) is likely because Si in steel can prevent a significant increase in the oxygen partial pressure at the steel-slag interface by Al consumption from FeO/MnO/SiO_2 reduction or desulfurization [8]. Pretorius [90] patented a process showing Ca-containing ferrosilicon is effective in modifying Al_2O_3 inclusions to Ca-aluminates, substituting use of Ca wire. Ferroalloys can also have large amounts of impurities present in form of non-metallic inclusions, which can significantly change the initial inclusion population for high-alloyed steels, such as advanced high strength (AHSS) and stainless steels. Pande [91] and Bi [92] did extensive characterization of several grades of ferroalloys to quantify impurities such as oxygen, sulfur, nitrogen and tramp elements, as well as impurities that are insoluble in the ferroalloy matrix, which will have an impact on the steel inclusion population. Inclusion characterization involved 3D observation by inclusion extraction, size distribution measurement and average chemical composition [92].

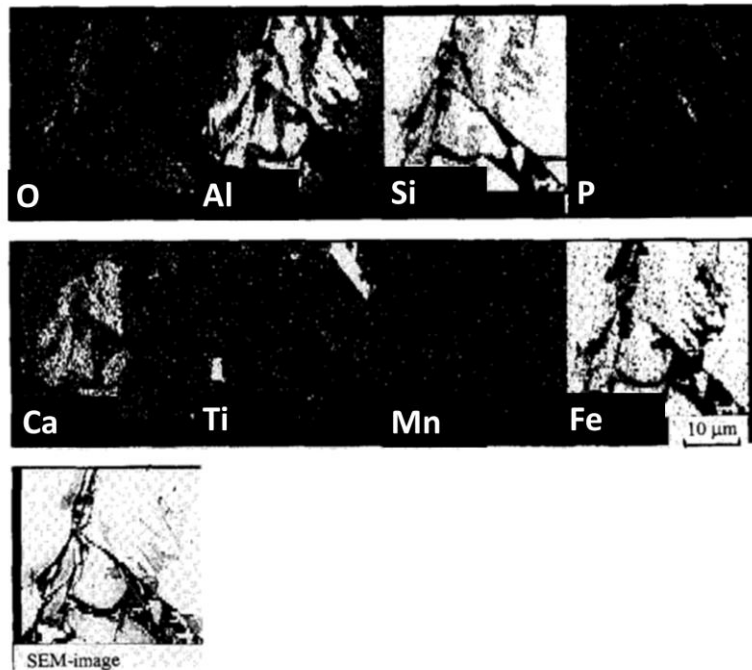


Figure 26 – SEM/EDS map of intermetallic phase in standard grade FeSi75 [88]

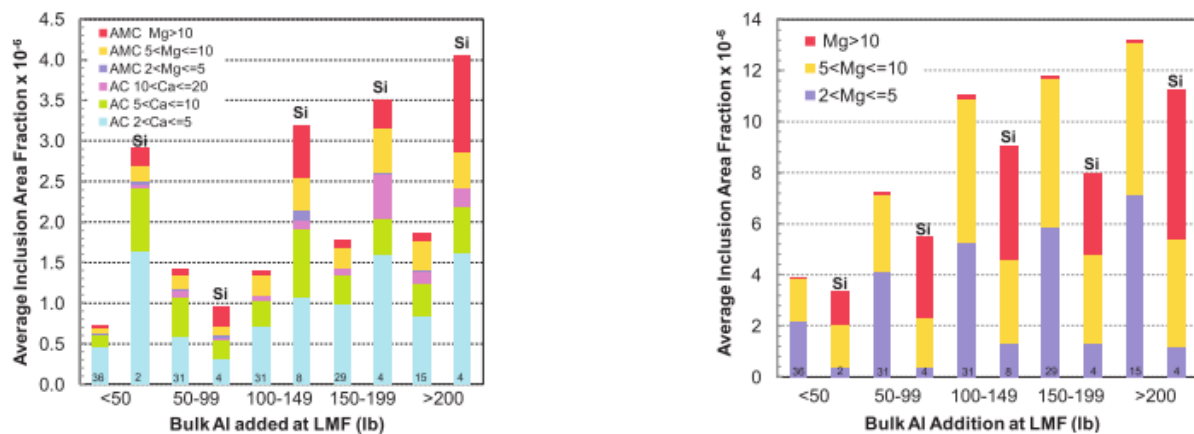


Figure 27 – On the left – effect of bulk Al additions on the concentration of CaO-containing alumina (AC) and spinel (AMC) inclusions. On the right – effect of bulk Al additions on the concentration of spinel inclusions. “Si” above a bar denotes grades containing Si, numbers inside bars are number of heats in average. [89]

Yan et al. [93][94] and Van Ende et al. [95] developed different experimental setups to observe reactions occurring at steel-ferroalloy interface, where for different stages of alloy dissolution the composition, morphology, spatial distribution and size distribution of inclusions can be assessed. The experiment of Van Ende [95], depicted in Figure 28, showed different zones along the reaction and diffusion front where morphology and size distribution of inclusions varied greatly.

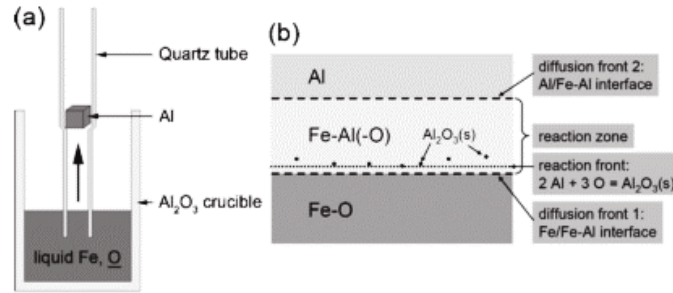


Figure 28 - Schematics of the experimental setup for Fe-Al-O interfacial reactions observation [95]

In Figure 29a, it is shown that the Al_2O_3 inclusions are present through the initial Al-Fe interface until the diffusion front, which is the maximum length reached by aluminum in the experiment timescale. Large angular inclusions in Zone 3, probably the initial Fe-Al interface, developed through heterogeneous nucleation, and the presence of trace Si and Fe show that initial oxides could have acted as nucleants for the first formed inclusions. Nucleation and growth of the inclusions happened in a region of maximum supersaturation, as depicted by Figure 29b. The low availability of O and Al between the diffusion front and the original interface limited the growth of inclusions, explaining the observation of small inclusions in this area. The growth of larger, dendrite-like inclusions requires more intense transport of O to the aluminum diffusion front.

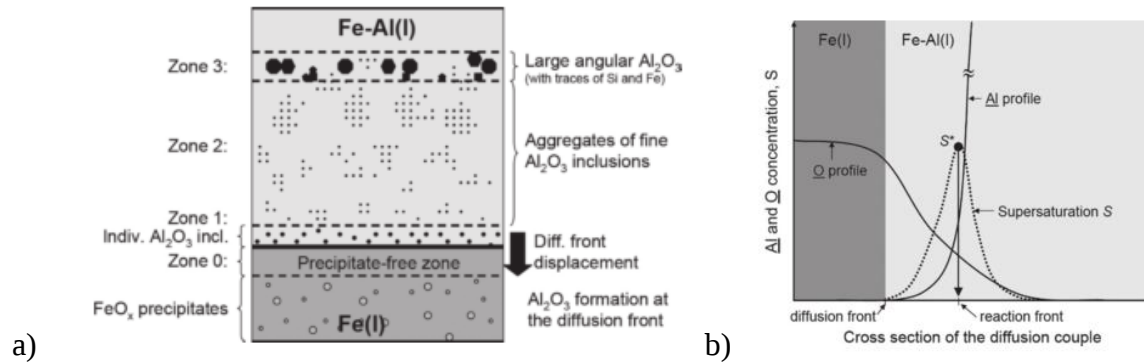


Figure 29 - a) Observed differences in inclusion size, morphology and composition along the sample; b) proposed mechanism for inclusion modification at the reaction and diffusion front [95]

Impact of ladle age on steel cleanliness

Work by Tripathi et al. [23] shows that ladle age can affect steel cleanliness, through development of ladle glaze. However, the presented data does not show substantial inclusion concentration increase for the analyzed heats (Figure 30). The presence of glaze can protect the steel from reacting with the refractory or can penetrate the refractory and create exogenous inclusions from the detachment of refractory grains.

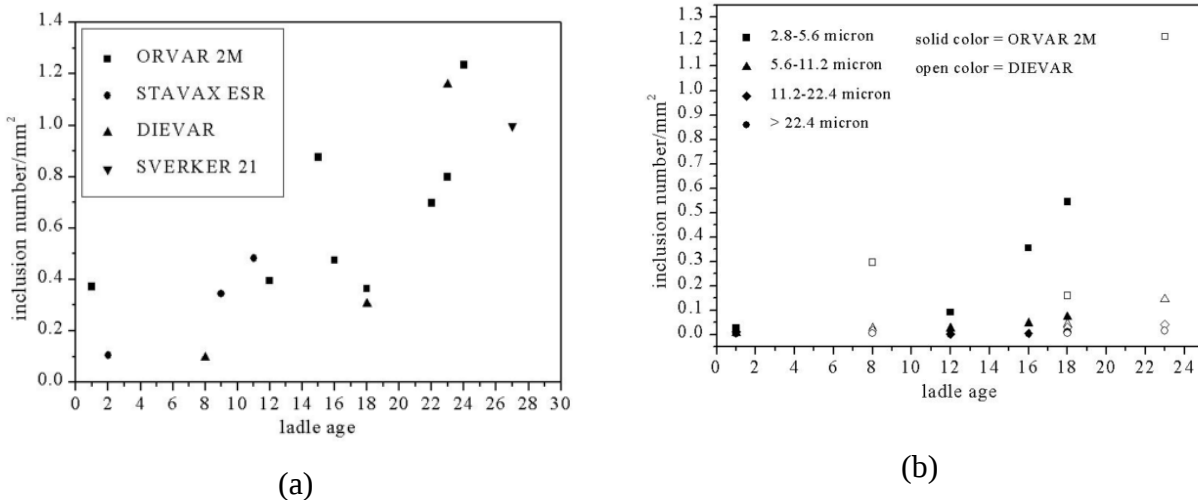


Figure 30 - Non-metallic inclusion concentration in Al-killed steel grades in function of ladle age. (a) Inclusions before Al deoxidation. (b) Inclusions after desulfurization [23]

3. Motivation

In industrial steelmaking practices for Si-Mn killed steels, the appearance of Al, Mg and Ca in non-metallic inclusions has been reported [19,21,76,80,96–99]. These non-metallic inclusions are detrimental to the castability and mechanical properties of the product since they are solid or non-deformable [3,76,100]. There are not enough studies to quantify separately the effects of the following phenomena in the Ca, Mg or Al pick-up in steel during processes in which very low interfacial oxygen activities must be achieved:

- 1) chemical reduction of oxides from slag;
- 2) ferroalloy cleanliness;
- 3) refractory wear or slag entrapment.

So far, the quantification of Ca, Mg and Al pick-up in these steels has been analyzed in terms of complete steel-slag equilibration (which is at best an incomplete description) [27] or using general qualitative arguments [21,76,97]. When in equilibrium, the slag and inclusions must have equal oxide activities, therefore their composition must be similar. Whenever the species in inclusions differ in activity from the slag, thus not in equilibrium, the kinetics of the steel-slag system must be understood. There is also the necessity to find ways of separating non-metallic inclusions and understand their origin, and the quantifying the rate phenomena governing their modification. The goal is to understand what process parameters can be changed in secondary metallurgy to enhance processability of these steels.

4. Hypotheses

1. A one-parameter liquid-liquid kinetic model using FactSage can successfully predict final inclusion composition in Si-Mn killed steel processing. The Si-SiO₂ reaction pair controls p_{O_2} at the steel-slag interface and thus the reduction of more stable oxides such as MgO and Al₂O₃ to steel.
2. Slag emulsification and ferroalloy impurities are more likely to be responsible for Ca pick-up in inclusions in typical ladle treatment situations than from reduction of CaO from steel-slag reactions. When the steel is vigorously stirred with a very deoxidizing slag (i.e. very low SiO₂ activity), there is significant Mg and moderate Ca pick-up.
3. Pressure does not influence the desulfurization of Si-Mn killed steels.
4. Calcium pick-up from ferroalloys is more efficient than via Ca-alloy wires. The mechanism of Ca pick-up involves the local reduction of excess dissolved oxygen, creating a new population of inclusions that will grow to be the definitive population of inclusions for that steel.
5. The chemical composition for secondary (solidification) inclusions in Si-Mn killed steels is significantly different than the primary population due to the consumption of Ca, Mg and Al as the liquid locally cools, precipitating more oxidized, Mn and Si-rich phases. Local cooling rate will affect their size, making the inclusions otherwise invisible appear to the SEM/EDS-based automated feature analysis.
6. Evaporation effects influence liquid metal observations in CSLM.

5. Experimental and Modeling Evaluation of Transient Inclusion Kinetics

This chapter the methodology and results used to study the influences of steel, slag, ferroalloy composition and process parameters on the thermodynamics and kinetics of oxide inclusions in Si-Mn-killed steels.

Initially, a kinetic model using FactSage macros for steel-slag-inclusion reactions is developed to study the effects of different slag compositions on the chemical composition of the steel, the chemical composition and morphology of inclusions, the possible transient inclusions and the kinetics of oxygen removal. Three different slags are studied – a high basicity, high alumina $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2$ slag, a low basicity, low alumina slag $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2$ slag, and a high basicity $\text{CaO-SiO}_2\text{-CaF}_2\text{-MgO}$ slag. It is seen that the main driver for Al, Mg and Ca pick-up is the SiO_2 activity in the slag. The possible transient inclusions depend on the extent of Al, Mg and Ca transfer from slag to steel.

The FactSage model predicts extensive Ca transfer from slag to steel. In the next section, steel samples from industrial trials are analyzed. These samples were taken for Si-killed steels degassed in the presence of $\text{CaO-SiO}_2\text{-CaF}_2\text{-MgO}$ slag and are thoroughly desulfurized. The resulting steel is very clean, with < 20 ppm total O. However, there are many CaO-containing inclusions, whose source is not very clear. There are inclusions that contain fluorine, which is an indication of slag entrainment, and some inclusions have large MgO and CaO contents without fluorine with a large spread in chemical composition. This spread appears to be caused by precipitation of inclusions during solidification. This section studies the evolution of the inclusions for these heats through SEM and automated feature analysis, inclusion dissolution and thermodynamic calculations, showing that Al and Mg pick-up is very efficient for these steel-slag systems, but more work is needed to understand the source of Ca, which can be also from ferroalloys.

The ladle refining process was simulated using an induction furnace, where electrolytic iron was molten, deoxidized using laboratory-made SiMn to avoid contaminations by Al, Mg and Ca and then added slag of different compositions. The experiments aimed to test the effect of slag basicity, Al_2O_3 , MnO content in the slag and the absence of MgO in the system (using a CaO crucible) in

the transient inclusion kinetics and to test whether [Si] can reduce Al_2O_3 , MgO and CaO from the slag. It was experimentally confirmed that those changes are mostly limited by steel-slag reactions, and the lower the SiO_2 in the slag, more Al and Mg pick-up from slag can happen. The kinetics of inclusion transformation due to Mg pick-up are significantly faster than for Ca pick-up, even for the CaO crucible experiment. For the current experimental setup, adding 1% and 5%MnO or 10%CaF₂ did not change the steel-slag reaction kinetics. It is also seen that the inclusion removal kinetics are limited by mass transfer, with similar mass transfer coefficients for the steel for steel-slag reactions. The mass of steel does not change the mass transfer coefficient significantly.

Since the reduction of CaO from slag by Si was not verified to be an efficient way to transport Ca to inclusions in our experiments, the effect of Ca as a ferroalloy impurity was tested using laboratory made FeSi75-2%Ca for deoxidation and for treatment of both Al-killed steels and Si-Mn-killed steels. The treatment is very effective, with Ca yield ranging from 20% in Al-killed steels to 50% in Si-Mn-killed steels. The dissolved oxygen content plays a role in both the Ca yield and in the inclusion-inclusion reaction kinetics. A FactSage model was developed to understand the mechanism for inclusion-inclusion reactions limited by steel mass transfer. The results are very dependent on what are the estimated solubilities of Ca and O in steel.

Finally, another approach was used to test the solubility of Ca in the steel. A piece of a lollipop sample after degassing was molten in an MgO crucible in the Confocal Laser Scanning Microscope under gettered Ar gas (p_{O_2} in the order of 10^{-20} atm). The gas was switched to ungettered Ar (p_{O_2} in the order of 10^{-5} atm) for finite times, and then the final inclusion composition was analyzed using SEM/EDS. The reoxidation experiment was successful in reoxidizing Mg, but not Ca. The high vapor pressure of Mn and the formation of a Mn-oxide plume at the gas phase helps to control oxygen transfer to the melt. Since Mg also has a high vapor pressure, Mg loss also impacts the non-metallic inclusion composition leading to reoxidation of the steel. The gas-phase mass transfer kinetics for a CSLM droplet was studied in detail.

5.1. Experimental methods

5.1.1. Induction furnace experiments

Furnace setup

The experiments were performed in an induction furnace (shown in Figure 31) with 15kW Ameritherm power supply operating around 130 to 140 kHz of frequency. A graphite crucible measuring 7.1 cm outer diameter, 6.8 cm inner diameter and 14.4 cm deep is used as a susceptor.

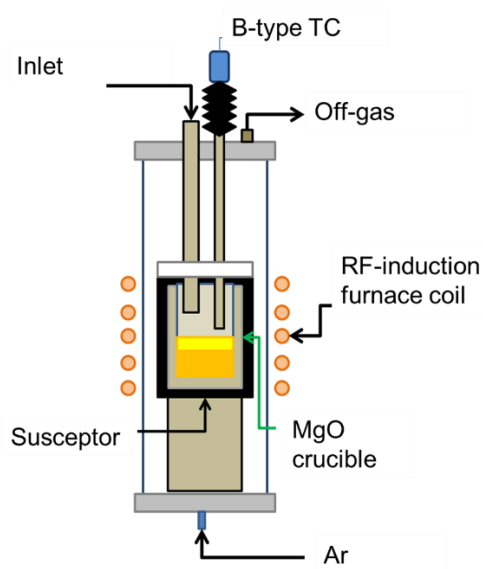


Figure 31 – Schematics of induction furnace system used to perform liquid steel studies.

The main furnace enclosure is an 85 mm OD, 80 mm ID and 50 cm long fused silica tube. An insulation layer is provided between the enclosure and the susceptor using alumina felt. The two water-cooled caps are made of stainless steel. A half-inch thick disk, with 7 cm of diameter is used as a lid for the graphite crucible, insulating its contents from radiation. A 0.75in OD alumina tube with open ends, around 30 cm long, is used as a port for taking samples and adding material, placed in the center of the stainless-steel furnace cap. A 0.375in OD alumina tube, closed in one end, is used as a shield to protect the thermocouple assembly from slag attack. The bottom of the shield is positioned inside the graphite crucible, usually more than 5 centimeters away from the top surface to correctly measure the temperature inside the crucible enclosure. Inside the shield, a B-type thermocouple is inserted for temperature measurement. There is a gas inlet in the bottom furnace cap that is used to purge and fill the furnace with argon, and the gas outlet is placed at the

top furnace cap. High-temperature fire bricks are used to keep the graphite crucible at the same level of the induction coil.

In this work, ceramic slip-cast crucibles (i.e. MgO, CaO) are filled with electrolytic iron chips. The chips are molten and brought to the desired temperature (typically 1600°C). The iron is then deoxidized, and slag is added (see Section 5.3 for more details). Through the experiment, samples are pipetted using 6 mm OD x 4 mm ID silica tubes then water-quenched.

Slag preparation

To prepare the slags used in the IF experiments, CaCO_3 is calcinated at 1000°C in a box furnace overnight. After cooled, the resulting CaO is mixed with the desired amount of other oxide powders such as SiO_2 , MgO, Al_2O_3 and CaF_2 , pressed as pellets and added to a graphite crucible. The pressed powder mixture is brought to the induction furnace and molten to 1600°C. After the slag is cooled down to room temperature, it is crushed using a mortar and pestle then powdered to a very fine grain size using a carbide puck mill. The resulting powder is then decarburized in a box furnace for at least 12 hours. The final slag powder is then added to the steel during steel-slag reaction experiments as described in Section 5.3.

5.1.2. Non-metallic inclusion analysis

Automated feature analysis

Most of the non-metallic inclusion analyses performed for this work were done in the ASPEX Explorer. Typically, a full cross-section of an induction furnace sample or a lollipop sample are analyzed. The sample is cut, mounted in conductive resin, ground and polished to 1 μm using diamond suspension. The scanning areas can range from 3 to 20 mm^2 depending on the availability in each sample and the inclusion concentration. A mesh of 1300x magnification fields is generated by the microscope software. The full cross-sections are analyzed to detect possible inhomogeneity caused by solidification in the samples. The voltage used was 10 kV and average spot size of 40% to reduce the electron beam interaction volume while maintaining sufficient overvoltage for EDX analysis and contrast for particle detection and measurement. The estimated spatial resolution for an oxide embedded in a steel matrix for this configuration is 0.35 micron [106]. The vector files used to convert the peak counts in EDX analysis to actual compositional values are optimized for 20 kV in ASPEX, not having an effective correction for low voltages. Since Mn has a significantly

higher atomic number than the other typical elements present in inclusions such as Al, Mg, Si and O, at 10 kV, the element would be under-analyzed if the 20 kV vector files were used. Therefore, the Merlet algorithm [116,117], implemented in an Excel spreadsheet, was used to transform the element peak ratios into inclusion elemental analysis.

5.2. FactSage kinetic modeling of steel-slag-inclusion reactions

5.2.1. Kinetic modeling: macro calculations

As it is described in the next sections on steel-slag experiments, liquid steel containing 400 ppm (by mass) oxygen was deoxidized by adding Si-Mn. These experiments were conducted in MgO or CaO-ZrO₂ crucibles with different starting slag compositions, usually CaO, MgO-saturated CaO-SiO₂-Al₂O₃-MgO-CaF₂ systems. It was found that many elements such as Al, Mg and Zr were reduced from slag and crucibles that eventually reprecipitated in the bulk steel as oxide inclusions. and the purpose of the experiments and modeling was to quantify the actual and predicted rate and extent of the change in the composition of the oxide inclusions.

The choice of experimental conditions and observed changes in oxide inclusion compositions guided the choice of reaction steps which were modeled: Since the slag was MgO saturated, crucible-slag reaction was not considered in the model. Experimental results (presented later, in section 5.3) showed that MgO pick-up by oxide inclusions was quite limited; model calculations indicate the reason for this is the low concentration of magnesium (in steel) produced by steel-slag reactions, much lower than the concentration of dissolved aluminum. The small extent of MgO pick-up by the oxide inclusions was adequately modeled by considering magnesium pick-up from slag during steel-slag reaction. Hence, steel-crucible reaction was not considered in the model. (Some formation of magnesiowüstite by steel-crucible reaction before deoxidation would be expected, but if this did occur it did not appear to affect the change in inclusion composition and was not modeled.)

Thus, of the reactions and processes shown in Figure 32, the kinetics of steel-slag reaction and oxide inclusion flotation (discussed below) were explicitly modeled with FactSage macro calculations. The steel-slag reaction was assumed to be under mass transfer control, and steel-inclusion reactions at equilibrium. FactSage 6.4/7.2 was used for the calculations, using the FToxid database for slag and oxide inclusions and the liquid iron model from the FTmisc database [101].

The species considered in the liquid slag and oxide phases were Al, Ca, Fe(II), Fe(III), Mg, Mn(II), Mn(III) and Si oxides and dissolved sulfur; the species considered in the liquid steel were Fe, Mn, Si, Al, Mg, Ca, S and O.

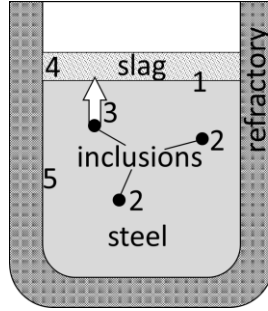


Figure 32 - Reactions which can contribute to changes in nonmetallic inclusion composition:

1. Steel-slag reactions; 2. Steel-inclusion reactions; 3. Flotation of inclusions and incorporation into slag; 4. Slag-refractory reactions; 5. Steel-refractory reactions

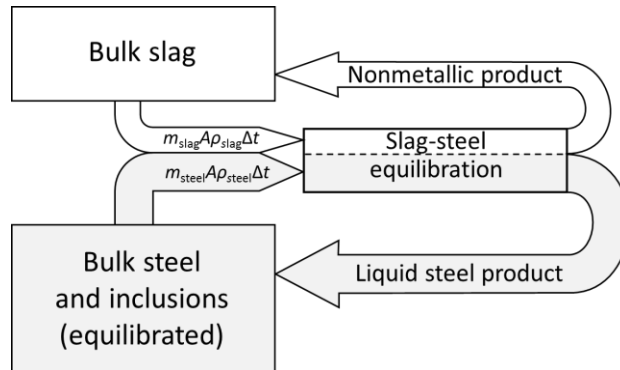


Figure 33 - Schematic of one iteration of the FactSage macro calculation procedure for steel-slag-inclusion reactions

Figure 33 illustrates the calculation steps of the model. Mass transfer in steel and slag – to the steel-slag interface – was explicitly considered, by allowing masses of slag and steel equal to $m_i A \rho_i \Delta t$ to react to equilibrium for each time step Δt (where m_i is the mass transfer coefficient in phase i , ρ_i the density of phase i , A the projected interfacial area between slag and steel, and Δt the length of the time step). This calculation method is exactly equivalent to flux equations of the form shown in Equation 1 (where $[\%M]$ is the mass percentage of element M in the steel, $[\%M]_{\text{int}}$ its concentration at the steel-slag interface, and W_{steel} is the total steel mass).

$$\frac{d[\%M]}{dt} = -\frac{mA\rho\Delta t}{W_{steel}}\{[\%M] - [\%M]_{int}\} \quad (53)$$

After each reaction step, all steel and dissolved elements in the steel (including dissolved oxygen) were returned to the bulk steel. All non-metallic reaction products of the interfacial steel-slag reaction (for each time step) were transferred to the bulk slag. The non-metallic products which were transferred to the slag included oxide inclusions which had been carried to the slag-steel reaction zone by the flow of steel. This implies that all oxide inclusions in the reacting steel volume were assumed to float to the slag; this is in line with the observation that the mass transfer coefficient for oxide inclusion flotation is similar to that for steel-slag reaction [57]. Another implication of this approach is that the way in which steel-slag reactions change the composition of oxide inclusions in the bulk steel is by the dissolution of elements (aluminum and magnesium, in the case considered here) into the steel at the steel-slag interface; these elements subsequently mix into the bulk steel and react with the oxide inclusions and with dissolved oxygen to change the chemical composition of the oxide inclusions.

After each time step, the liquid steel remaining after slag-steel equilibration (containing the dissolved elements from that reaction) was mixed back into the bulk steel, homogenized and re-equilibrated. The results of the equilibrium calculation were the new oxide inclusion composition and concentration, and new bulk steel composition (including dissolved oxygen), at the end of each time step. The resulting oxide inclusion compositions (changing with reaction time) were compared with the results of laboratory experiments, described in the next section.

Initial steel and slag compositions and relevant mass transfer coefficients are given in Table 1 and 2. Both steel and slag mass transfer were considered as possible rate-determining steps. As in previous work, it was assumed that the slag mass transfer coefficient is one-tenth the steel mass transfer coefficient [102]. The steel mass transfer coefficient was estimated by fitting experimentally observed aluminum pick-up and desulfurization from steel and slag (by steel-slag chemical reaction) with the kinetic model. Because the aluminum concentration in the steel was low (tens of parts per million by mass), the accuracy of aluminum analyses would affect the accuracy with which steel mass transfer can be fitted.

5.2.2. Application of modeling to predict non-metallic inclusion composition changes in a ladle furnace

The utilization of high alumina, basic slags is expected to promote aluminum pick-up in steel for the conditions simulated. The simulation results are shown in Figure 34 and Figure 35. It is expected from the simulations that increasing aluminum concentrations in the steel will reduce manganese silicate inclusions, forming solid phases such as corundum and magnesium spinel. It is predicted that at longer times, a lower rate of consumption of dissolved silicon by aluminum pick-up results in pick-up of magnesium and calcium from slag, causing the formation of Ca and Mg-containing higher melting temperature phases such as CM_2A_8 and CA_2 . The oxide activities during the steel-slag reactions are plotted in Figure 36 – the oxide activities, especially MgO and Al_2O_3 will control the amount of solute that will go into solution. Therefore, changes in the stabilities of oxides will change the increase rate of reducing solutes transported from the slag. The overall composition shown in Figure 35 shows the rapid reduction of Mn and Si from inclusions and the increase in Al, Mg and Ca concentrations in the inclusions. As the steel composition approaches equilibrium with slag, the activities of oxides in inclusions will approach the activities in the slag, so inclusion compositions are expected to asymptotically approach the equilibrium slag composition.

In contrast to the utilization of high alumina slags, it is shown that less basic, low alumina slags maintain the inclusions liquid for the whole simulated processing time as seen in Figure 37 and Figure 38. Aluminum, calcium, and magnesium pick-up is much less than for high alumina slags, reflecting the higher silica activity (hence giving less-reducing conditions for a given silicon concentration in the steel). The presence of silicon and manganese in the inclusion is predicted to persist throughout most of the process, and it is expected that the inclusions will retain low melting points. In contrast, in the absence of alumina when modeling CaF_2 -based slags, the interfacial oxygen potential is low enough to drive significant Mg and Ca to form dicalcium silicate and MgO inclusions by the end of ladle treatment, according to the FactSage databases. These can be seen in Figure 39 and Figure 40.

The decrease in inclusion content follows the same exponential decay as the total oxygen, which is attributed to flotation. Therefore, the oxygen decay is expected to follow similar kinetics to aluminum pick-up or desulfurization. The kinetics of oxygen removal is similar for the different cases. The time constant (62.8% of equilibrium oxygen removal) is approximately 500 s. Although

the total oxygen is predicted to be similar after ladle processing for all three cases, the higher silica activity in the less basic (high-alumina) slag contributes to both less aluminum pickup and less pick-up of Mg and Ca by the steel. The alumina content in the silicates will depend on the extent of aluminum pick-up during processing. Figure 41 shows the effect of different slags in contact with Si-killed steels on the dissolved oxygen and inclusion content evolution.

Table 1 - Main parameters used in kinetic model: initial metal composition, contact area and mass transfer coefficients

T (K)	[%Mn]	[%Si]	[O]_{total} (ppm)	[S] (ppm)	Interfacial area [m²]	Steel mass transfer coefficient [m/s]	Slag mass transfer coefficient [m/s]
1873	1.25	0.25	100	20	7.07	5.61×10^{-3} [52]	5.61×10^{-4}

Table 2 - Ladle processing conditions considered in the simulations

Mass of steel (t)	Mass of slag (t)	Argon flowrate (Nl min⁻¹ t⁻¹)	Ladle diameter (m)	Processing time (s)
150	1.7	14	3	3600

Table 3 - Initial slag composition (mass percentages)

Slag	(%CaO)	(%SiO₂)	(%Al₂O₃)	(%MgO)	(%CaF₂)
High alumina	47	8	35	10	-
Low alumina	47	35	8	10	-
No alumina	56	24	0	5	15

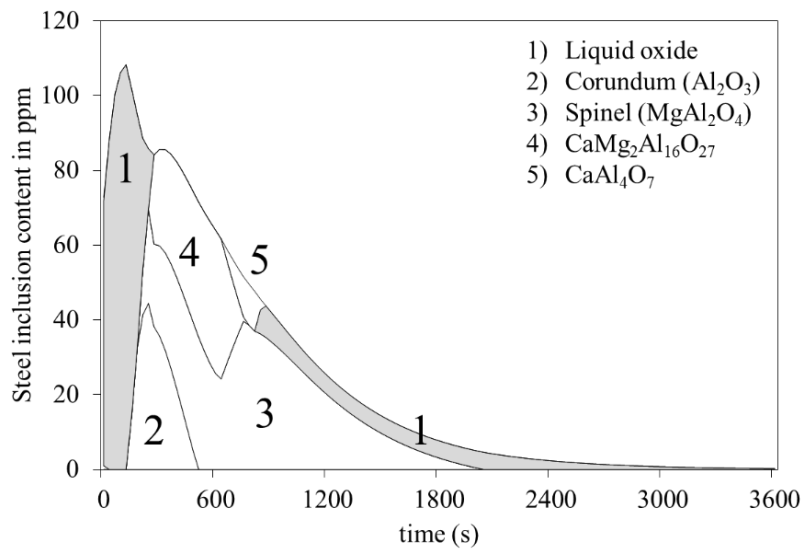


Figure 34 – FactSage macro simulation results showing transient inclusion phases for Si-Mn killed steels with basic, high alumina slags

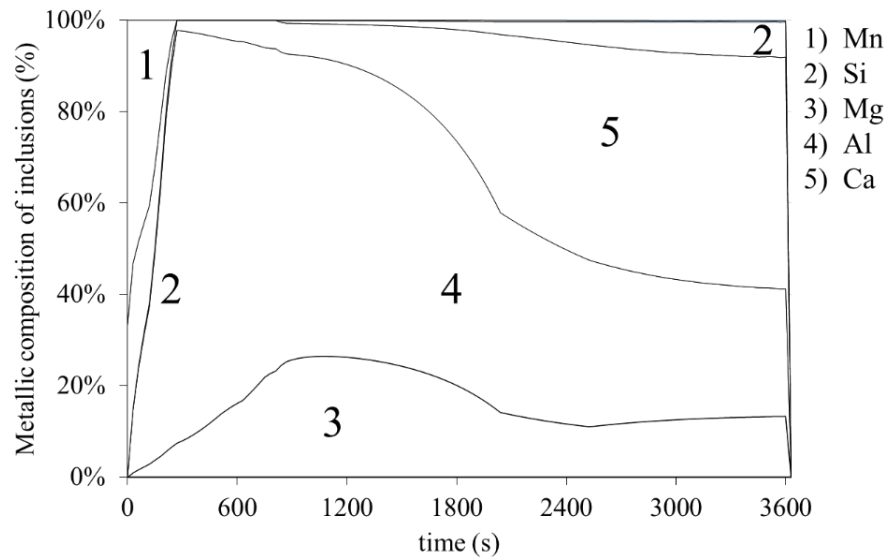


Figure 35 – Overall normalized cation composition of transient inclusions shown in Figure 34

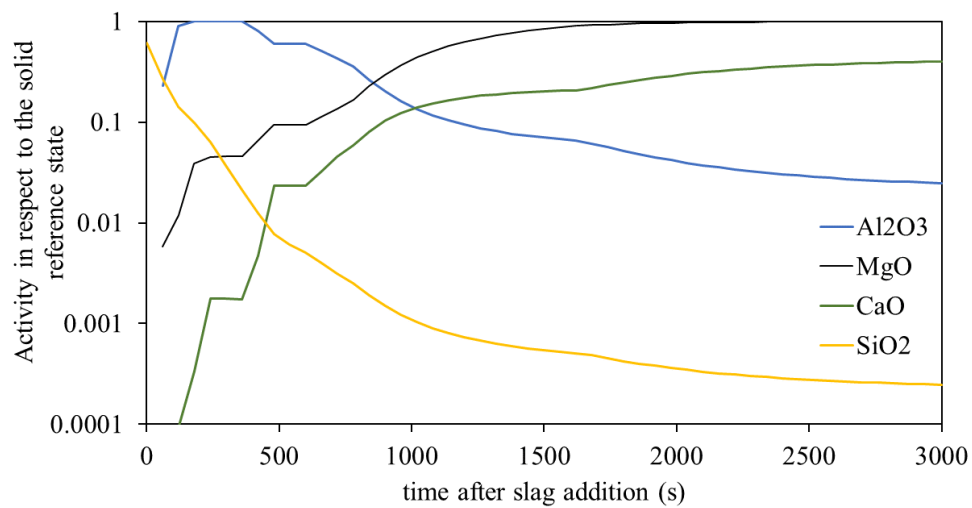


Figure 36 – Calculated oxide activities in the non-metallic inclusions for the simulation with high basicity, high Al_2O_3 slag.

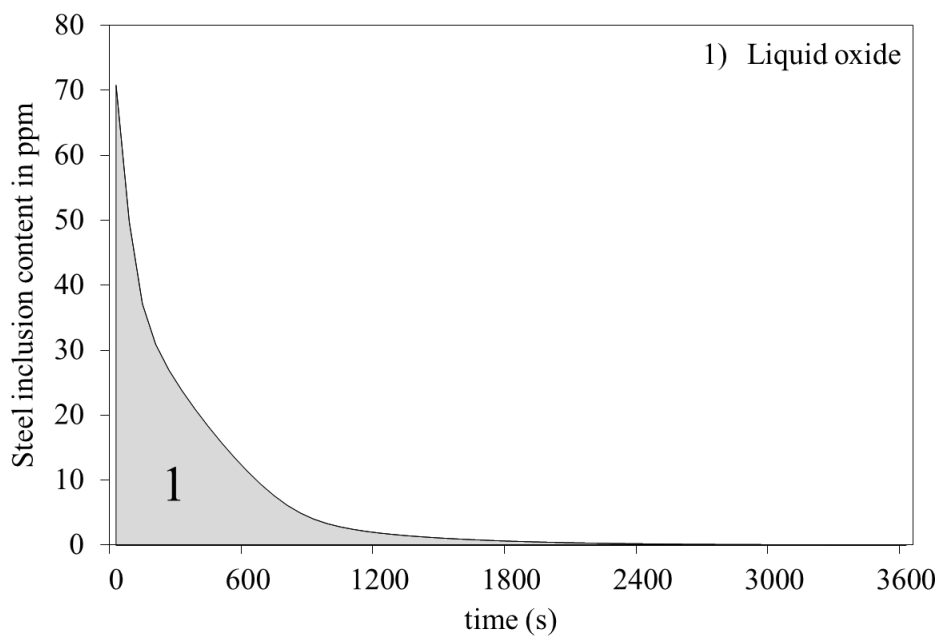


Figure 37 – FactSage macro simulation results showing transient inclusion phases for Si-Mn killed steels with less basic, low alumina slags

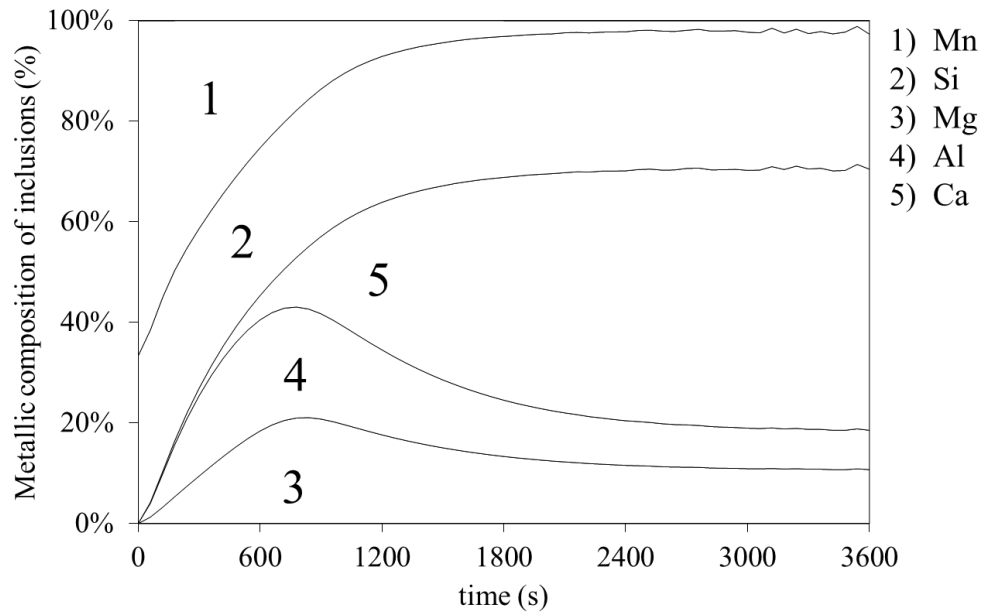


Figure 38 - Overall normalized cation composition of transient inclusions shown in Figure 37

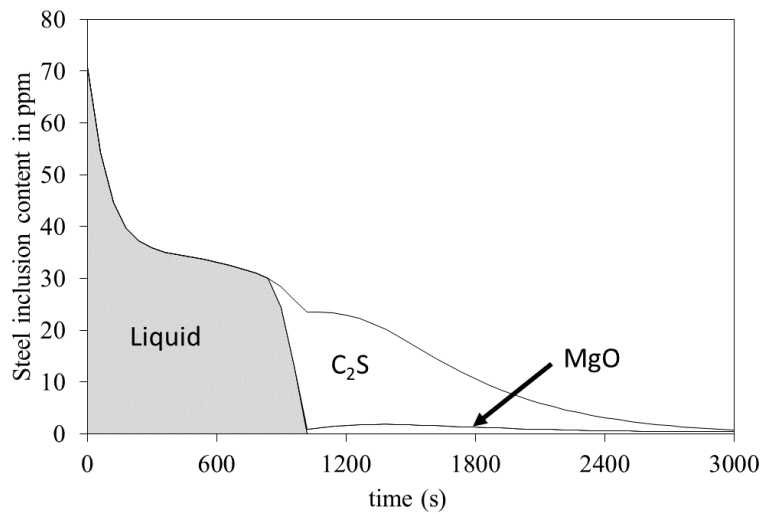


Figure 39 - FactSage macro simulation results showing transient inclusion phases for Si-Mn killed steels with CaF_2 -based, CaO, MgO-saturated slag

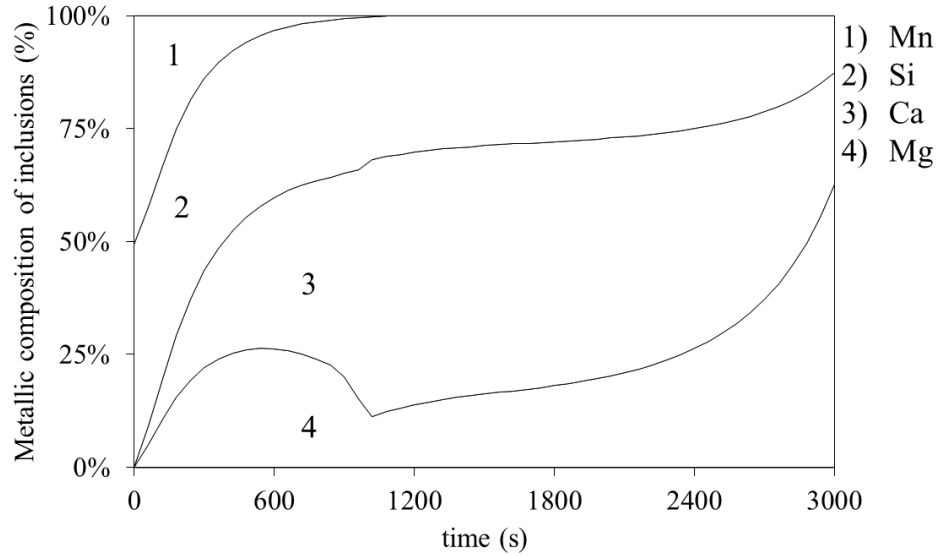


Figure 40 - Overall normalized cation composition of transient inclusions shown in Figure 39.

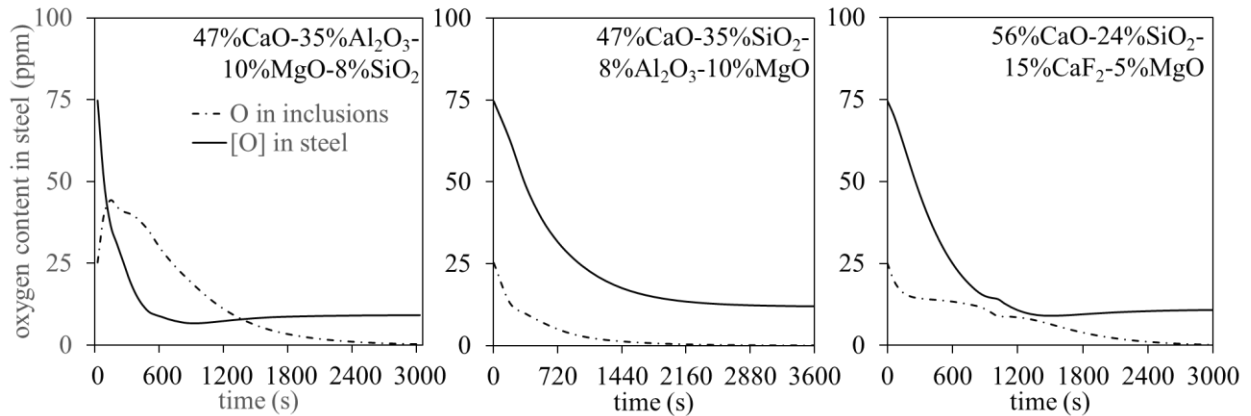


Figure 41 – Predicted evolution of dissolved and bound oxygen contents in steel for different slag compositions in contact with 1.25%Mn-0.25%Mn steel.

5.3. Observation of non-metallic inclusions of industrial samples

Certain industrial practices such the one filed as a patent by Panda et al. [103] using a vacuum degasser to improve stirring can lower the sulfur content of steel from 300-400 ppm to 10-20 ppm S when using 15-25 kg/t of CaO, MgO-saturated CaO-SiO₂-MgO-CaF₂ slag. The most recent experimental assessments for the sulfide capacity of CaO-SiO₂-MgO-CaF₂ system [104] does not predict such a deep desulfurization for these systems, while assessments for this system at lower

temperatures predict CaS solubility up to 10% at CaO saturation and 1300°C (1573 K) [105]. However, the silica activity for this system is very low, so the expected oxygen potential at a Si-killed steel and fluoride-based slag interface is very low due to the observed extent of desulfurization and the high solubility of CaO in this slag. The inclusion evolution during the desulfurization treatment of these steels represent an ideal condition to study the transfer of Ca and Mg to the inclusions while minimizing the influence of Al pick-up. Therefore, this section aims to investigate inclusion modification during desulfurization of Si-Mn killed steels in the presence of an Al₂O₃-free slag through experiments and inclusion analysis of industrial trials, focusing on Mg, Al and Ca pick-up.

5.3.1 Setup

Three lollipop samples taken from different heats at the end of degassing process were cut, prepared and analyzed for non-metallic inclusions as described in Section 5.1.2 and Figure 42. One of the samples was analyzed with FEG-SEM Quanta 600 using Aztec Feature analysis at 10 kV, in which the cutoff size for the inclusion analysis is expected to be at least 0.2 micron smaller than that of the ASPEX Explorer [106].

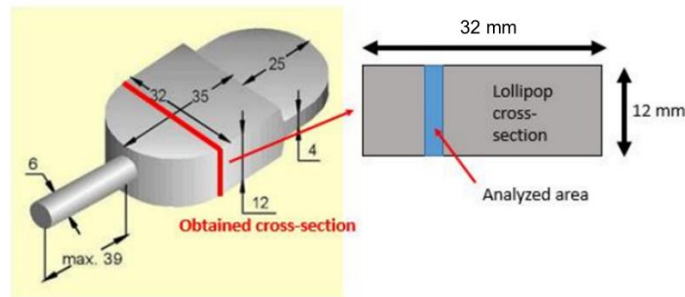


Figure 42 - Schematics of lollipop sample (obtained from Heraeus-Electronite). The measurements shown in the figure are in millimeters; the dotted line indicates the cross-section used for metallography and non-metallic inclusion analysis.

5.3.2 Results and Discussion

5.3.2.1. Inclusions after degassing

Figure 43 show the typical non-metallic inclusion composition of a Si-Mn killed steel sample taken at the end of vacuum degassing (dividing the inclusions into three size ranges: less than 1 micron, between 1 and 3 micron and larger than 3 micron). Due to the strongly reducing process conditions and strong stirring, the steel is very clean (7 inclusions per square millimeter and 9 parts per million in area of inclusions analyzed). The plots were separated in two projections of chemical composition – Ca-Si-Mg and Mn-Si-Al. Overall, the chemical composition distribution of the inclusions shown here are similar in some aspects; the smaller, micron-sized inclusions range from Mg-Si-O (Mg_2SiO_4 , forsterite) to a slag-like $\text{CaO-SiO}_2\text{-MgO}$ composition. The first sample (Figure 43) exhibit a distinct population of MnO-SiO_2 inclusions, an indication that there was reoxidation during the process or sampling. The reoxidation effect is consistent with the increase in area fraction of inclusions. [104]

There is a significant population of Ca-containing inclusions (considering this is a non-Ca treated steel) ranging from small sizes (around 1 micron) to tens of microns. Many smaller than 1 micron inclusions are MnO-SiO_2 inclusions and Mg-silicates. The amount of Mn-rich inclusions vary from sample to sample. For inclusions between 1 and 3 micron in size, in the three samples compositions ranging from Ca-silicate to MgO are found. For inclusions larger than 3 micron, the chemical composition is consistently similar to slag.

The presence of small Ca and Mg-bearing inclusions suggest that such inclusions were formed during reoxidation or cooling/solidification. Due to the reducing conditions of the steel-slag system, significant Mg and Al transfer from slag and refractory to steel is expected. These elements, once mixed with the bulk steel, will recombine with oxygen forming small inclusion nuclei containing Ca, Si and Mg.

However, it is very difficult to confirm that there was Ca pick-up from slag to steel which modified the inclusions that were present at that stage. The larger particles contain several phases upon solidification such as pure MgO, CaS, cuspidine and Ca-silicates. The method of ASPEX energy-dispersive X-ray analysis is chord raster mode, which means the inclusion composition will be

analyzed along a chord (or diameter) of the detected particle. When a steel sample is prepared for SEM observations, different sections of an inclusion might be exposed for observation. Since large inclusions might have radially distributed inhomogeneity due to solidification (as is the case for the inclusion shown in Figure 44), the apparent chemical composition of the inclusion taken from the EDS analysis might be different than its original average composition. Figure 44 shows a picture of a slag-like particle in steel and its correspondent EDS mapping, showing MgO as a primary solidification phase, in a Ca_2SiO_4 matrix, with regions showing F peaks (cuspidine) and S (CaS). The presence of fluorine and sulfur indicates that the particle is indeed an entrapped slag inclusion. Figure 45 shows a smaller inclusion (around 10 micron) exhibiting a similar slag-like composition, although F cannot be analyzed since its $\text{K}\alpha$ peak overlaps with Fe- $\text{L}\alpha$ peak in the EDS spectrum. The inclusion shown in Figure 44 is large enough so beam interaction with the matrix is minimized and few Fe peaks are collected (from the observed Fe $\text{K}\alpha$ peak count).

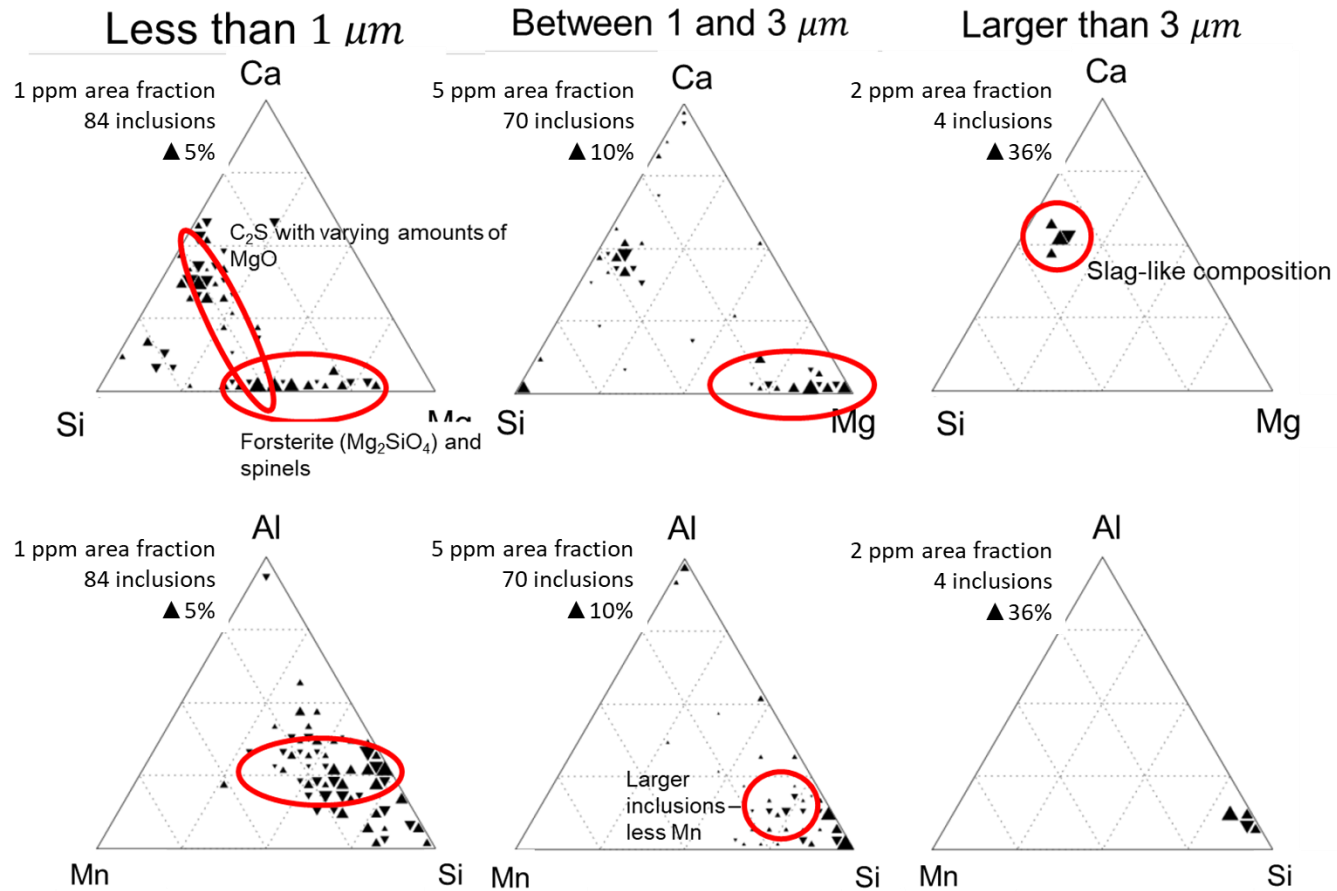
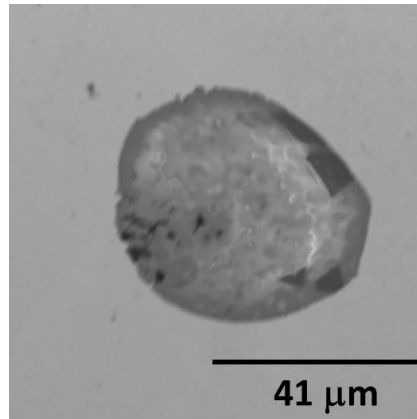
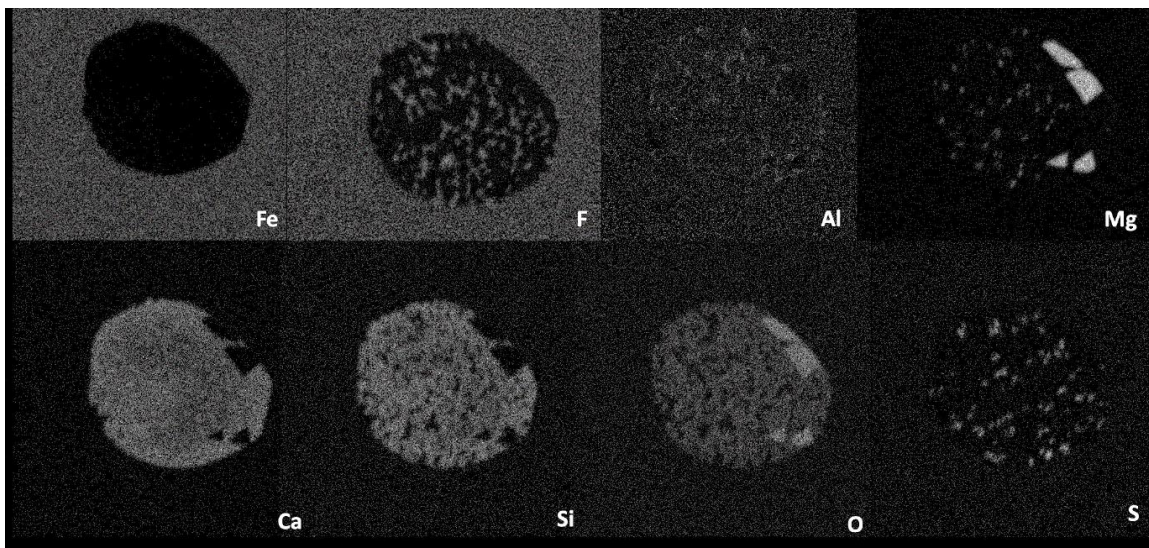


Figure 43 – Chemical composition of non-metallic inclusions after degassing of Si-Mn killed steel with $\text{CaO-SiO}_2\text{-CaF}_2\text{-MgO}$ for different sizes.



(a)

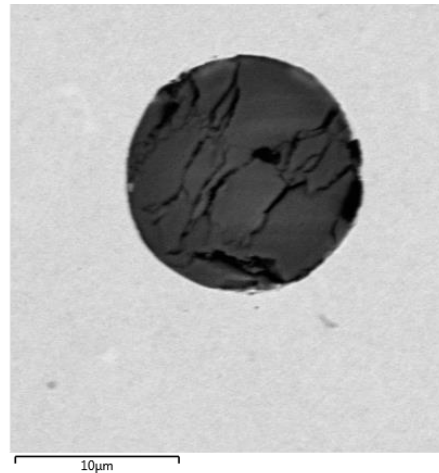


(b)

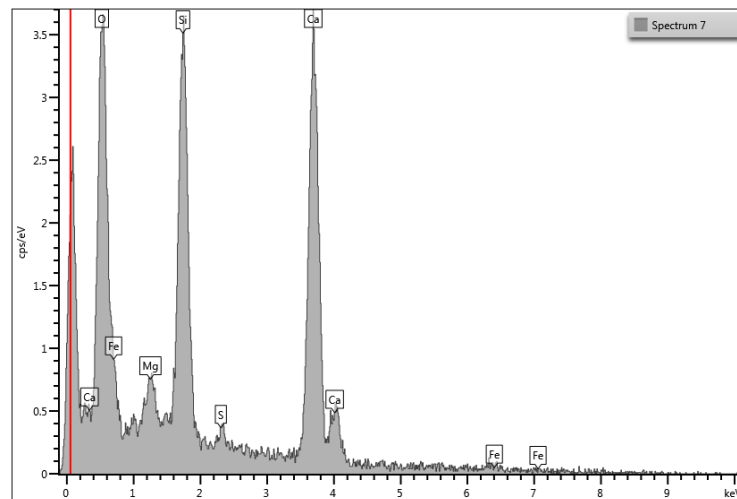
Figure 44 – Backscattered SEM image of a large entrapped slag particle in the sample taken after degassing, showing F and S containing phases. (a) Backscattered image, (b) EDS mapping showing different phases in the inclusion – MgO, CaS and cuspidine in a Ca-silicate matrix.

Figure 46 shows a very small micro-inclusion with no Ca, but showing Mg and Al. Due to its small size and the presence of a small Ti peak in the EDS spectrum, the inclusion depicted might have formed during cooling and solidification. Figure 47 shows one inclusion whose composition is

between C_2S and MgO . These inclusion types complicate the analysis as the separation of different inclusion populations becomes very difficult. Figure 48, the size distribution for the three samples is shown. There are two obvious inclusion populations – 0 to 3 microns (micro-inclusions) and larger than 5 (most likely entrapped slag).

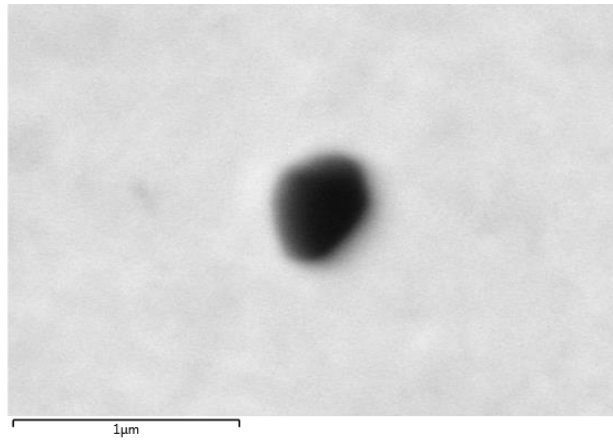


(a)

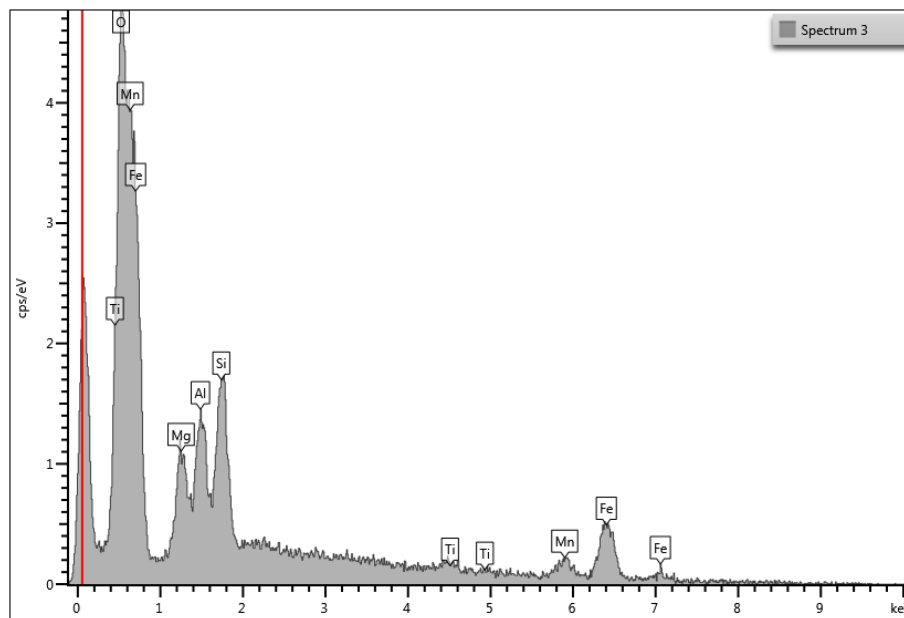


(b)

Figure 45 – Back-scattered SEM image of a large non-metallic inclusion showing a slag-like composition in the EDS spectrum, with high Ca and Si contents and some Mg.

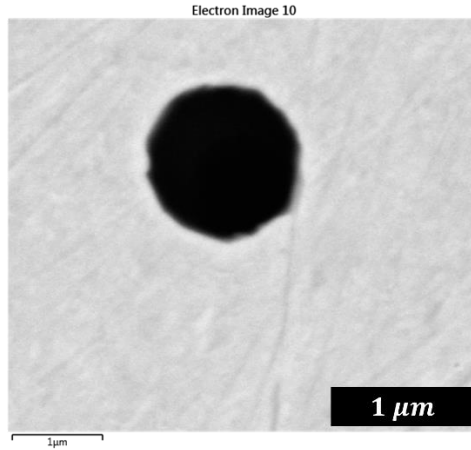


(a)

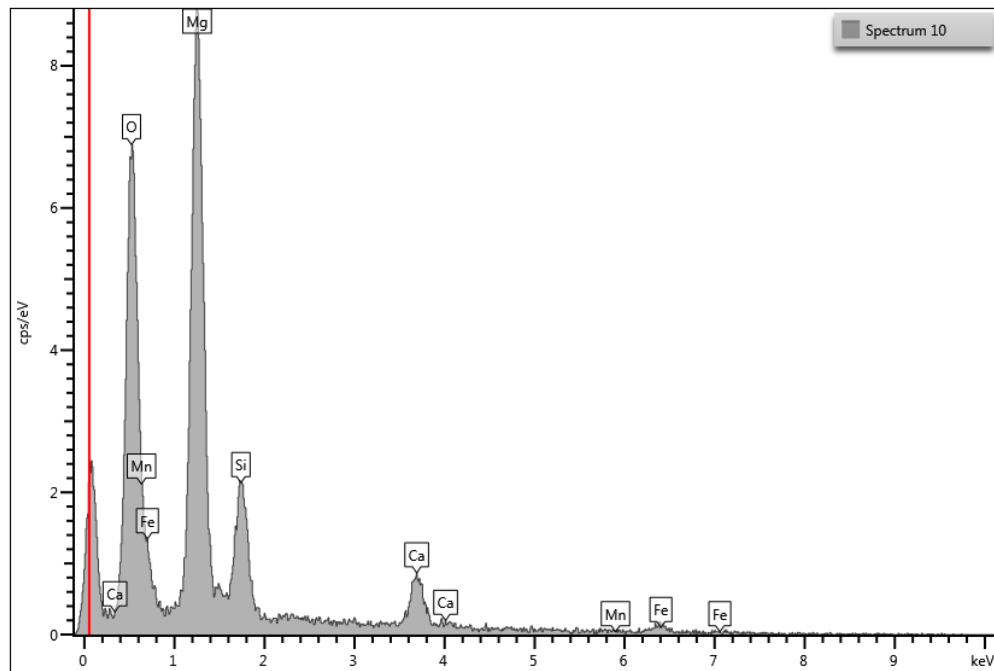


(b)

Figure 46 - Back-scattered SEM image of a micrometer-sized apparently solid non-metallic inclusion showing significant amounts of Mg, Al and Si. The presence of Mn suggests the formation during solidification. (a) Backscattered image, (b) EDS analysis spectrum showing Mg, Al, Si, Ti and Mn.



(a)



(b)

Figure 47 – (a) Back-scattered SEM image of a micron-sized non-metallic inclusion and (b) its correspondent EDS spectrum, showing the presence of Ca and a significant amount of Mg.

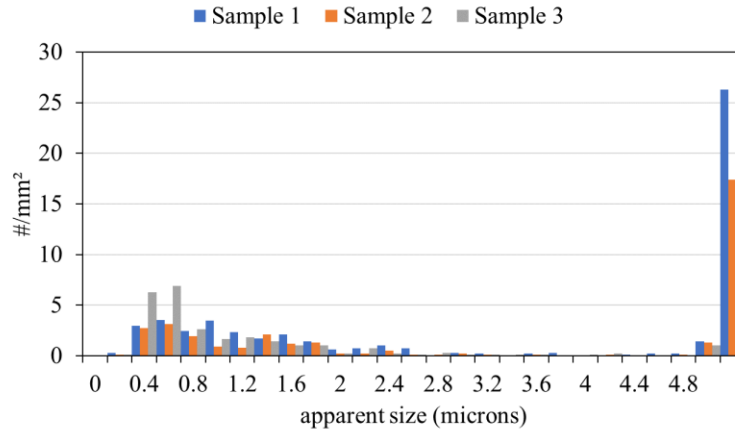


Figure 48 – Size distribution for the three different samples showing distinct populations of micro-inclusions smaller than 3 micron and larger than 5 micron.

The inclusion analysis indicates that there is a spread in chemical composition, especially for smaller inclusions. These inclusions that are richer in Mn and Si appear to have formed when the remaining dissolved oxygen in the melt precipitates, that is, during cooling and solidification. To understand the possible formation of different oxide phases in the lollipop samplers, Scheil solidification simulations were done using FactSage 7.0 using the Equilib model, FSstel and FToxid. FSstel was chosen rather than FTMisc due to the optimized database on solidification of steel, more accurately predicting microsegregation. Solubility of oxygen in solid steel is low and Mn and Si segregate upon solidification. The starting composition was set according to the received chemical analyses. The assumed starting total oxygen was 20 and 40 ppm. The cooling step chosen was 5°C and the analysis was set to stop at 99% solidification due to software limitation on solution convergence. The results for the predicted microsegregation in steel, precipitation of oxide phases and chemical composition of the non-metallic inclusions are shown in Figure 49, Figure 50 and Figure 51 below.

In Figure 49, it is seen that the oxygen concentration in the remaining liquid increases with solidified fraction. This is counterintuitive, since as temperature lowers, the solubility of oxygen decreases. However, at this stage the low oxygen activity is being controlled by elements present in very low quantities, such as Mg, Al and Ca. As the liquid cools, the inclusions precipitate and the liquid steel is depleted in Mg, Al and Ca, increasing solubility of O in the steel. Mn and Si, present in much larger concentrations microsegregate. When the liquid is in the verge of full

solidification, Mn and Si microsegregation decrease the oxygen activity and manganese silicates precipitate as liquid inclusions.

The predicted non-metallic inclusions that precipitate upon cooling and solidification are shown in Figure 50. In Figure 50a the initial oxygen content in steel is 20 ppm, and initial Ca content is 11 ppm from equilibrium calculation using FTmisc and FToxid, assuming CaO and MgO-saturated slag with 15%CaF₂. The predicted initial population of inclusions is a mixture of di-calcium silicate and MgO, with increasing MgO contents until the start of solidification, marked by the grey line showing start of delta-ferrite precipitation. During solidification, liquid inclusions, spinels and olivine (forsterite) start to precipitate. In Figure 50b, it is seen that if the oxygen content is high enough so a liquid slag phase and olivine are predicted rather than a C₂S and MgO mixture. As the steel cools down, there is precipitation of olivine and spinels in the liquid steel, and as it solidifies more liquid inclusions precipitate. The chemical composition of all phases formed during solidification are plotted in the ternaries of Figure 51. The plots also show how the chemical composition of the liquid inclusion varies during solidification. For a starting total oxygen of 20 ppm (Figure 50a), the chemical composition of inclusions ranges from C₂S + MgO to liquid ranging from C₂S to olivine, with more oxidized phases containing Mn and Si appearing in the later stages of solidification. The case for 40 ppm O in Figure 50b shows that the general trend for inclusion modification is similar although the high initial oxygen predicts liquid inclusions with a lower Ca concentration.

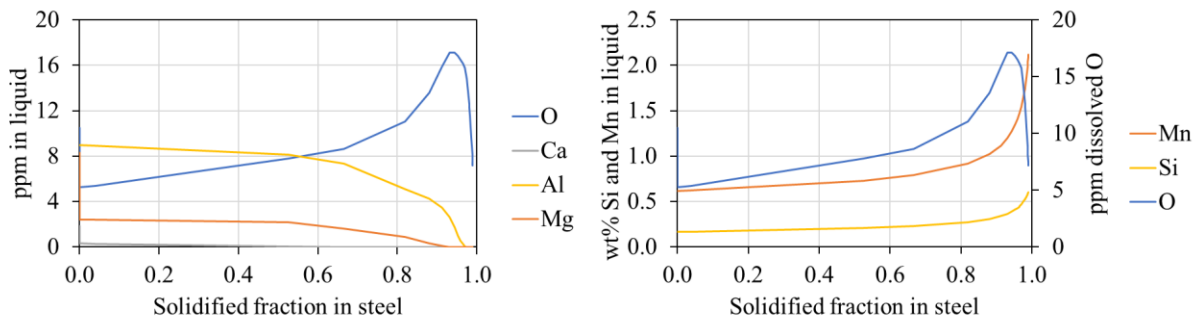
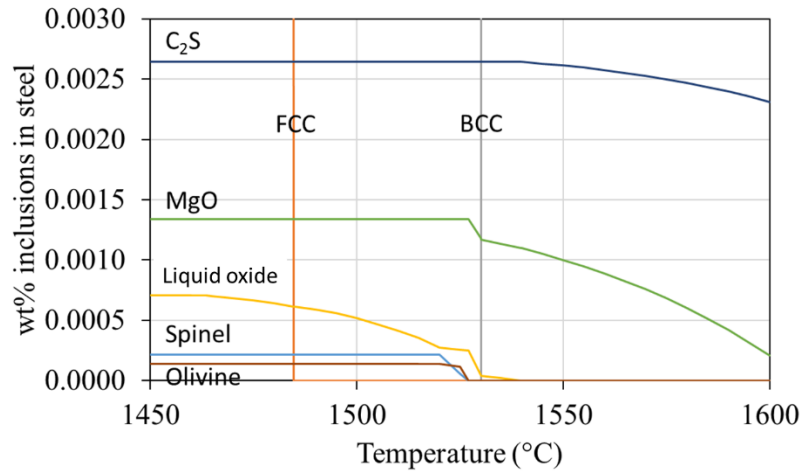
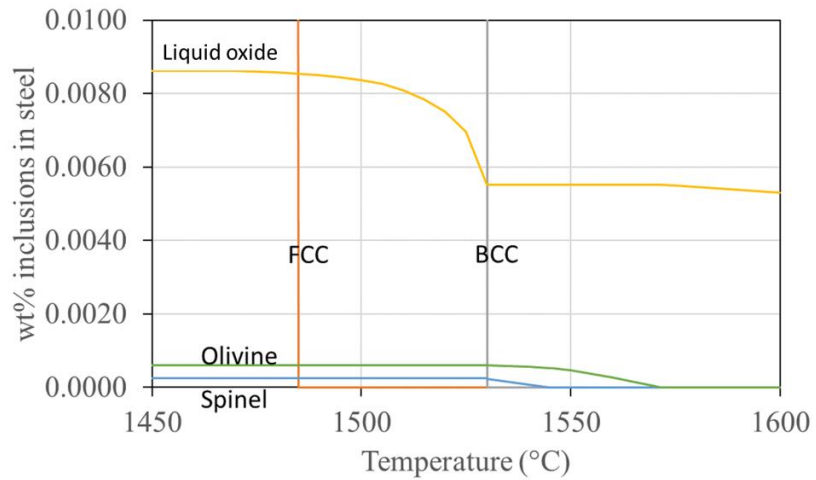


Figure 49 - Microsegregation during solidification of steel as simulated by FactSage using Scheil-type calculation – no back diffusion of solute in the solid and full mixing in the liquid.

Starting total oxygen is 20 ppm.

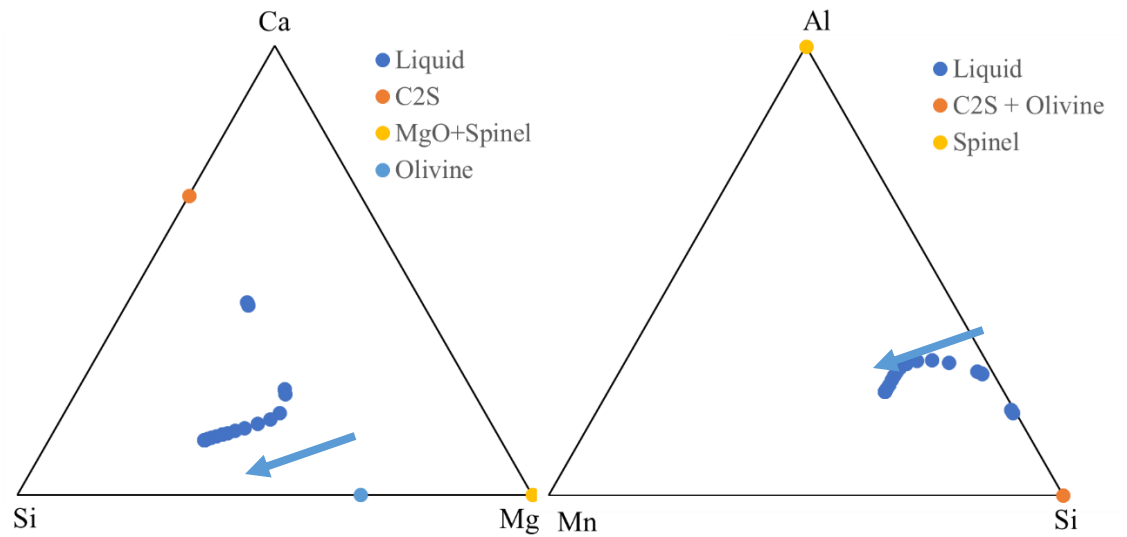


(a)

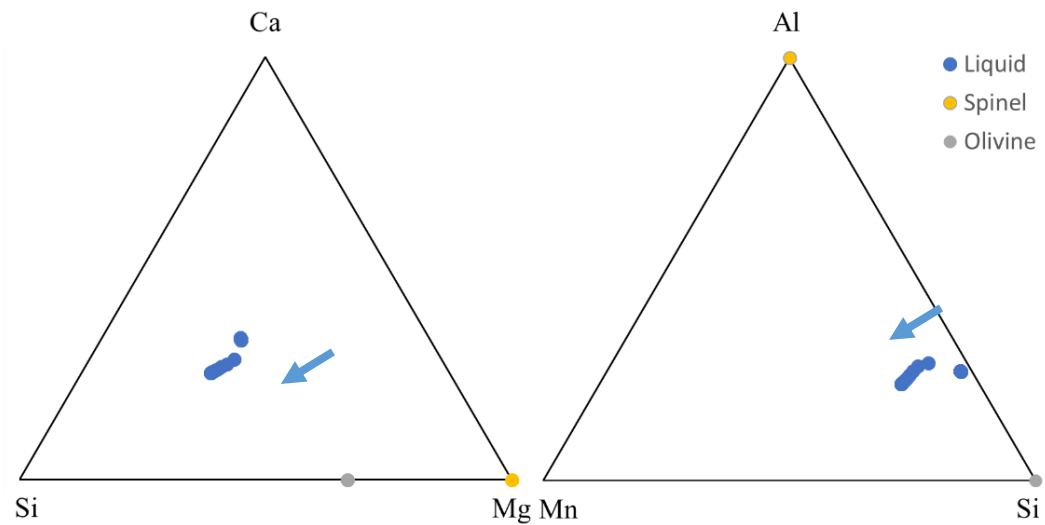


(b)

Figure 50 – Precipitation of oxide phases upon cooling in steel, as predicted by FactSage 7.0 Equilib module using a Scheil-type calculation (full mixing in liquid, no diffusion in solid). (a) Starting total O is 20 ppm, (b) starting total O is 40 ppm.



(a)



(b)

Figure 51- Ternary projections showing the expected chemical composition of different non-metallic inclusion populations as steel is cooled down and solidified. (a) Initial total O content is 20 ppm, (b) Initial total O content is 40 ppm. The blue arrows indicate the direction of composition change of slag phase upon solidification, showing enrichment of Mn and Si in inclusions.

In Figure 52, a comparison is made between the predicted phases formed during solidification and the measured inclusion compositions. The modeling result agrees with the observed trend, confirming the presence of dissolved Mg in the melt and the formation of a large range of inclusion compositions due to a combination of precipitation and microsegregation upon cooling.

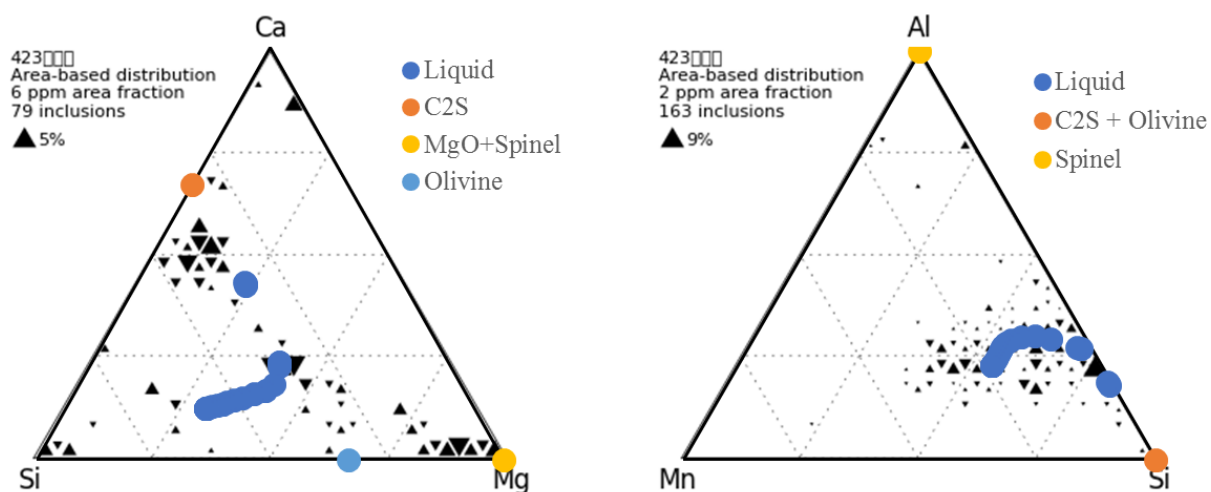


Figure 52 – Comparison between observed and calculated inclusion composition at solidification for Sample 3, inclusions smaller than 1 micron.

Although the likely origin of the different inclusion phases in Si-killed steels after vacuum degassing and desulfurization is explained here, the mechanism for Ca transfer still needs to be understood. Previous experiments using CaO-Al₂O₃-MgO-SiO₂ slags did explain Al and Mg pick-up from slag, but Ca pick-up could not be observed. Therefore, a set of experiments was designed to simulate the chemical composition of slag and steel for this process in the induction furnace.

Oxide inclusion evolution from degassing to casting

For this section, the samples obtained from the vacuum degasser are compared to samples obtained further in the process (after chemical composition adjustment [ferroalloy addition], then after intentional reoxidation in ladle and in tundish before casting) to shed light on the Ca and Mg behavior due to steel-slag reactions. Samples were obtained from a process in which the steel, after poured from the EAF, is decarburized to less than 500 ppm and then desulfurized in a tank degasser, then refined in the ladle station (LMF) for chemistry adjustment (or trimming). The steel

is then reoxidized with oxygen to obtain liquid Mn-silicates while having low S, then brought to the tundish for casting. The summary and timeline of analyzed samples can be seen on Table 4.

Each one of the samples had been analyzed in the plant by optical emission spectroscopy (OES) for bulk chemical composition. Slag after desulfurization was analyzed using XRF, with the sulfur reported as SO_3 . To analyze inclusions in the steel samples, the lollipop samples were cut to reveal a transverse plane. The samples were mounted in conductive epoxy resin and polished to 1 micron using diamond suspension. Each sample was analyzed using Automated Feature Analysis in the ASPEX Explorer. For each sample, the whole thickness of the cross-section was analyzed with a magnification of 1200x at 10kV accelerating voltage, 40% spot size and 16 mm working distance, across an approximate area of 20 mm^2 for the vacuum degasser and after trimming samples, and around 10 mm^2 for the samples after reoxidation and in the tundish (a smaller area was used for the latter samples due to the much higher inclusion concentration in the reoxidized samples).

EDX analysis of fluorine (F) in small inclusions can be a challenge. If the interaction volume of the electron beam is larger than the analyzed inclusion depth, iron peaks are collected. Since the $\text{Fe-L}\alpha$ (0.705 keV) and $\text{F-K}\alpha$ (0.677 keV) overlap in the EDS spectrum, the steel matrix must be removed for accurate identification of fluorine peaks in the inclusions. To avoid the Fe matrix effect, a piece of sample from Heat 01 and from Heat A (after trimming by ferroalloy addition) were electrolytically dissolved using a methanol-tetramethylammonium chloride-acetylacetone solution for 45 minutes. The solution was then vacuum-filtered with a $0.2 \mu\text{m}$ -opening membrane filter. The filter was Pt-coated and observed using the FEI Quanta 600 SEM at 20 kV accelerating voltage and 10mm working distance.

Table 4 – Summary of the plant timeline and processes of the analyzed steel samples

Heats	After VD	After trimming	After reoxidation	Tundish sample
01, 02 and 03	0 minutes	--	--	--
Heat A	0 minutes	50 minutes	133 minutes	192 minutes
Heat B	0 minutes	38 minutes	--	147 minutes

Results and Discussion

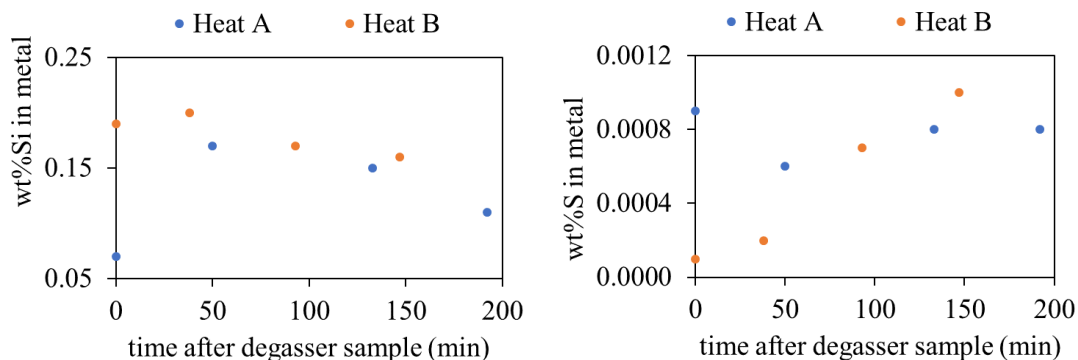


Figure 53 – Evolution of chemical composition of heats after degasser sample. The left plot shows the evolution of silicon in metal and the right plot shows the evolution of sulfur in metal over time. Si fade and S reversal are attributed to the reoxidation procedure. Aluminum is < 20 ppm for all samples.

As expected, the steel is strongly desulfurized as it leaves the vacuum degasser, as seen in Figure 53. In Heat A, the measured sulfur partition coefficient ($L_S = \frac{[\%S]}{[\%S]}$) is 365, while L_S for Heat B after degassing is 3284. The slag masses and initial sulfur content prior to degassing are unknown. The lower concentration of Si after degassing of Heat A suggests that more Si was consumed. Stirring under vacuum can bring the time constant for steel-slag reaction to around 66 seconds (Figure 54), approaching equilibrium 10 minutes from the start of the desulfurization treatment. The expected desulfurization profile can be seen in Figure 54, where soft and strong stirring scenarios, with and without vacuum are compared. In Figure 55, it is seen that L_S has a square-root relationship with [%Si] due to the stoichiometric ratio of 1 mol Si reacting to remove 2 moles of S, so the 10-fold drop in L_S cannot be from the small difference in Si concentration. Slight analytical errors in these low levels of [%S] will strongly influence the measured partition coefficient, though.

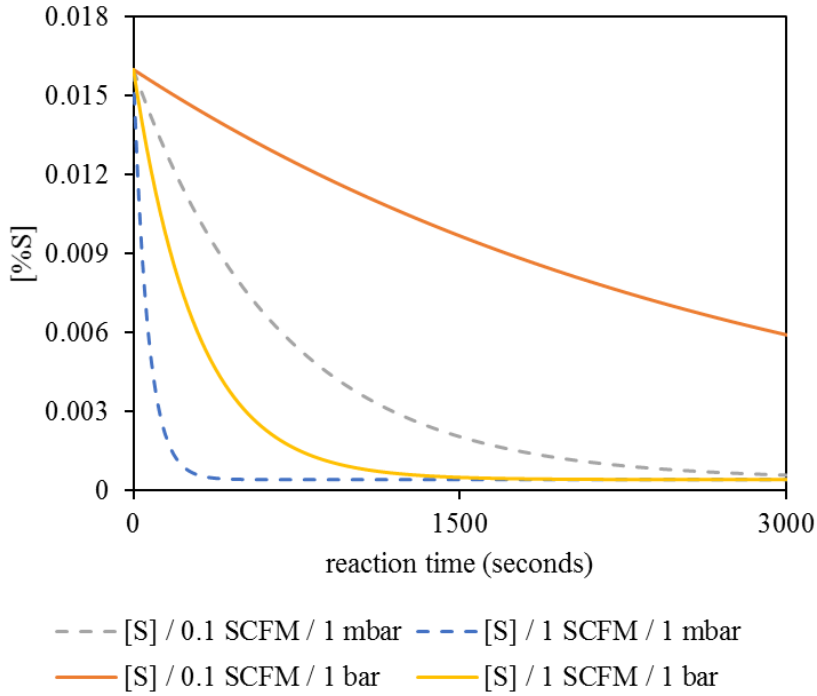


Figure 54 – Calculated desulfurization profile for a 3m diameter, 150t ladle with 2.25t slag, with $L_S = 2500$, $k_{steel}/k_{slag} = 10$ and initial [%S] = 0.016wt%S, under different Ar blowing rate (0.1 SCFM and 1 SCFM) and under variable pressure (1 mbar and 1 bar) [82,107].

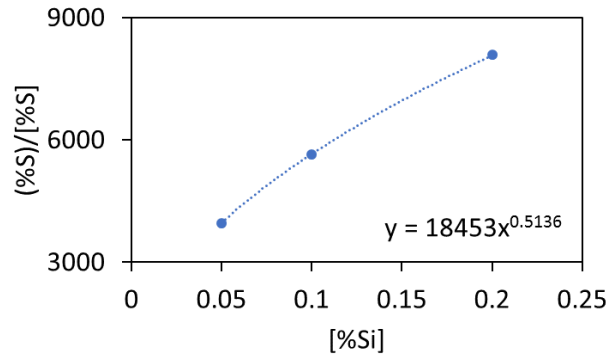


Figure 55 – Calculated effect of Si on the sulfur partition for a CaO-MgO-saturated, 60%CaO-15%CaF₂-5%MgO-20%SiO₂-CaS slag with $a_{cas} = 1$. The equilibrium (%S) content for F-containing slags for the partition coefficient calculation was calculated using the consortium database of FactSage – not commercially available.

The initial non-metallic inclusion composition is compatible with the quasi-equilibrium state of the slag-metal system, as seen on Figure 56 and Figure 57. The inclusions considered for the area

fraction measurement are smaller than 5 microns to minimize the impact of slag-based inclusions. The measured [O] from inclusions in the samples after degassing is on average 2.4 ppm, with 1.4 ppm [Mg] and 0.9 ppm [Ca]. If we assume the same mass transfer coefficient for the steel phase as in Figure 54 and assuming all Ca can react with the steel, in 20 minutes the slag can provide 1.7 ppm Ca taking the arbitrary numbers for Ca equilibrium as $[Ca]_{eq} = 0.1$ ppm, or 17 ppm Ca if $[Ca]_{eq} = 1$ ppm and if all transferred Ca would be gettered by inclusions or dissolved oxygen; it thus appears possible that the Ca in those smaller inclusions are truly originated from steel-slag reduction reactions. The calculated Henrian activity for Ca for comparison, considering steel-slag equilibrium for $h_{Si} = 0.2$, $a_{SiO_2(cristobalite)} = 5.2 \times 10^{-5}$ and $K_{CaO} = 8.4 \times 10^{-9}$, is $h_{Ca} = 1.5 \times 10^{-6}$ (15 ppb). The lower amount of Mg in inclusions than expected can be explained by the low solubility of Mg in Ca-silicate inclusions, meaning the steel might be close to MgO saturation. In Figure 57, one can see that the Mg content of these inclusions can go up to 40%. Inclusions larger than 5 microns have a notably lower Mg content and higher Ca content, indicating that these might be entrained slag (which was confirmed by the inclusion extraction). The smallest, sub-micron inclusions are rich in Mg, Mn and Al and most likely precipitated during solidification.

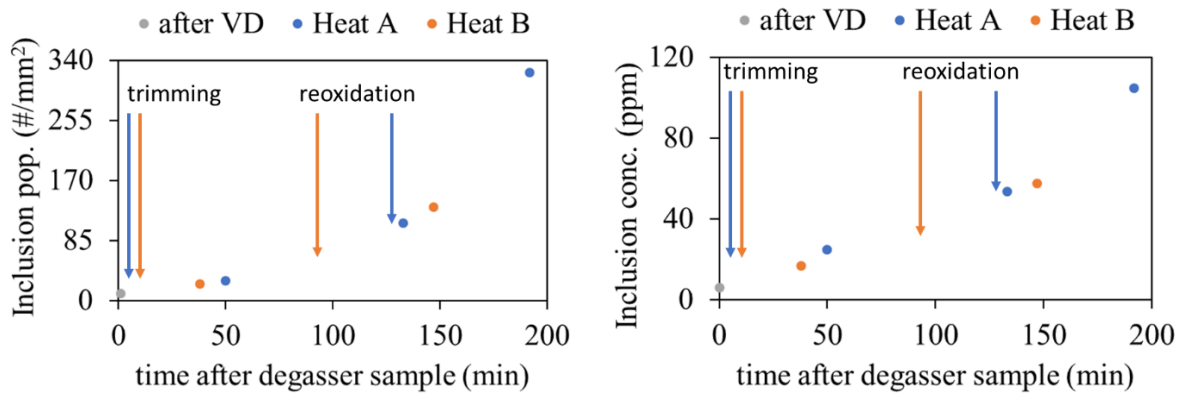


Figure 56 - Evolution of inclusion population in number per square millimeter (left) and inclusion concentration in mass-based parts per million (right). Degasser samples are remarkably clean, and the inclusion amount increases as the steel is reoxidized further in the process. The arrows mark the time of trimming (adding FeSi or SiMn) and reoxidation. The arrows color code follows the color code of the data points.

After trimming (Figure 56 and Figure 57), the inclusion content rises, now to an average of 8 ppm [O] between Heat A and B, with the Mg content dropping to 0.6 ppm, and the Ca content rising to

6 ppm. In these samples, there is a bimodal population of Ca-silicates and Mn-silicates, with distinct sizes (the effect of solidification is further discussed in the next section). Ca is not found in these solidification inclusions, although it is predicted by FactSage model.

Table 5 – Typical chemical composition of ferroalloys used for Si/Mn alloying and deoxidation in the studied process. In FeMn and SiMn, Ca should be present as an oxide while in FeSi it can be present as an intermetallic compound.

Ferroalloy	wt%Si	wt%Mn	wt%Fe	wt%C	wt%Ca	wt%Mg	wt%Al	wt%S
FeMn	0.33	77.3	19	0.5	0.34	0.25	0.063	0.008
FeSi	74.9	0.2	24.3	0.03	0.07	0.004	0.1	0.002
SiMn	15.5	65.9	15.5	2	0.003	0.009	0.006	0.016

The amount of Ca that appears in the form of inclusions as seen on Figure 57c is similar for both heats, around 5 ppm regardless of the ferroalloy used for composition trimming. In Heat A, 109kg FeSi is added, while in Heat B 73kg SiMn is added. Samples were taken around 30-50 minutes after the addition of these ferroalloys. To yield 5 ppm Ca, the amount of Ca in FeSi should be at least 0.46% and the amount of Ca in SiMn should be 0.68%Ca (0.96%CaO). These values are significantly higher than the values provided by the steelmaking company of 700 ppm for FeSi and 30 ppm for SiMn (Table 5).

Ca yield is probably related to the amount of dissolved oxygen in the steel. In this case, since the available oxygen for reaction with Ca is also quite low and there is not a significant population of inclusions after degassing, the melt would incorporate only a few parts per million of calcium as newly formed inclusions. The reacting Ca might instead redissolve Mg into the melt, with dissolved Mg reprecipitating upon solidification; such an effect is seen in Figure 58. Note that, in this case, the total Ca has a trend opposite to Mg when accounting for all samples (Figure 57), so there appears to be little or no reprecipitation of CaO during solidification – in contrast with MgO. This supports the suggestion of low solubility of Ca in the steel.

The smaller inclusions are expected to be secondary inclusions (formed during steel solidification), and due to the depletion of trace deoxidizing elements such as Ca, Mg and Al, the reaction products will appear to have a composition compatible with a higher oxygen potential. In all samples, the

smaller inclusions are richer in Mn and Al. In the sample taken after degassing, not much Ca is available to prevent the precipitation of Mg upon solidification, unlike in the case of the sample after trimming. In the reoxidized and tundish samples, the smaller Mn-silicates are leaner in Al, Mg and Ca and richer in Mn.

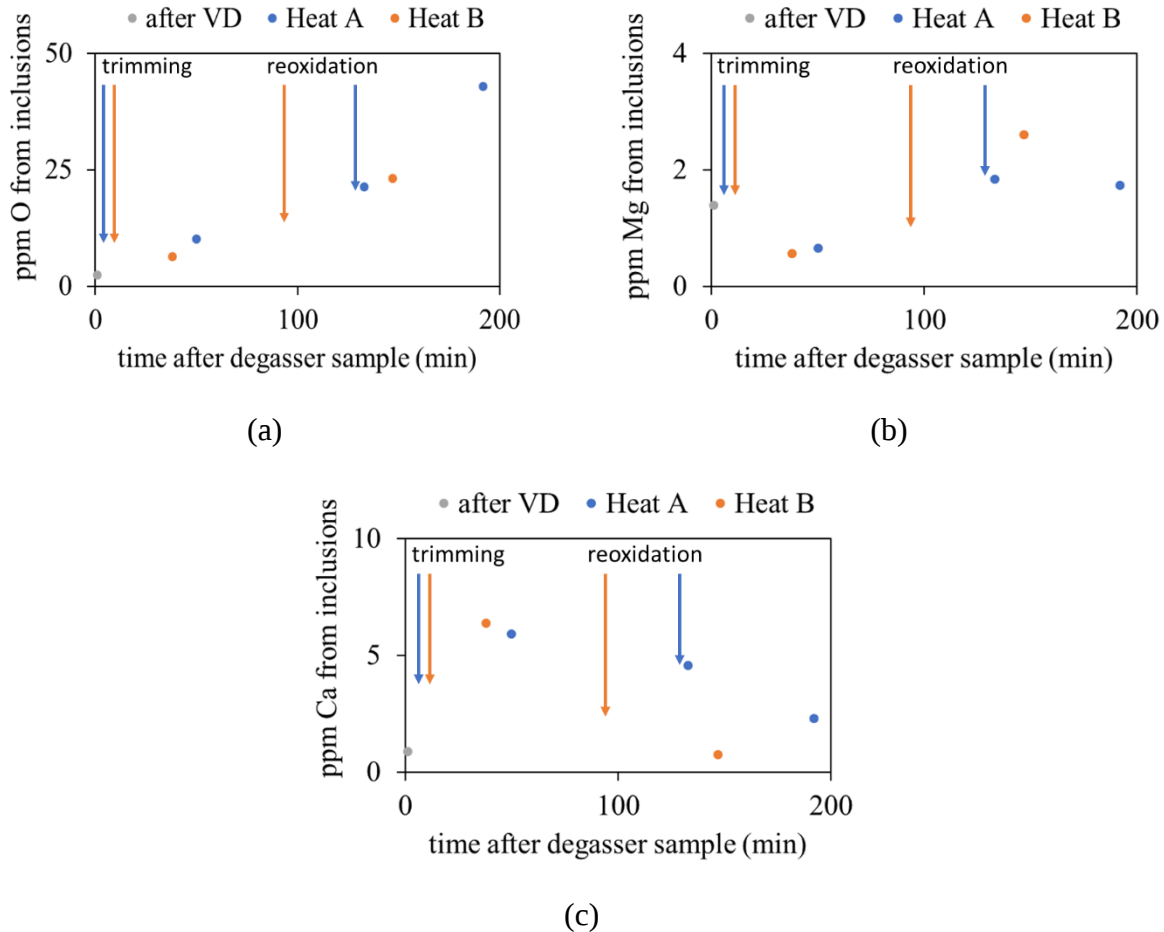


Figure 57 – Estimated total (a) oxygen, (b) magnesium and (c) calcium in the analyzed steel samples from the non-metallic inclusion analysis over time (considering inclusions smaller than 5 micron).

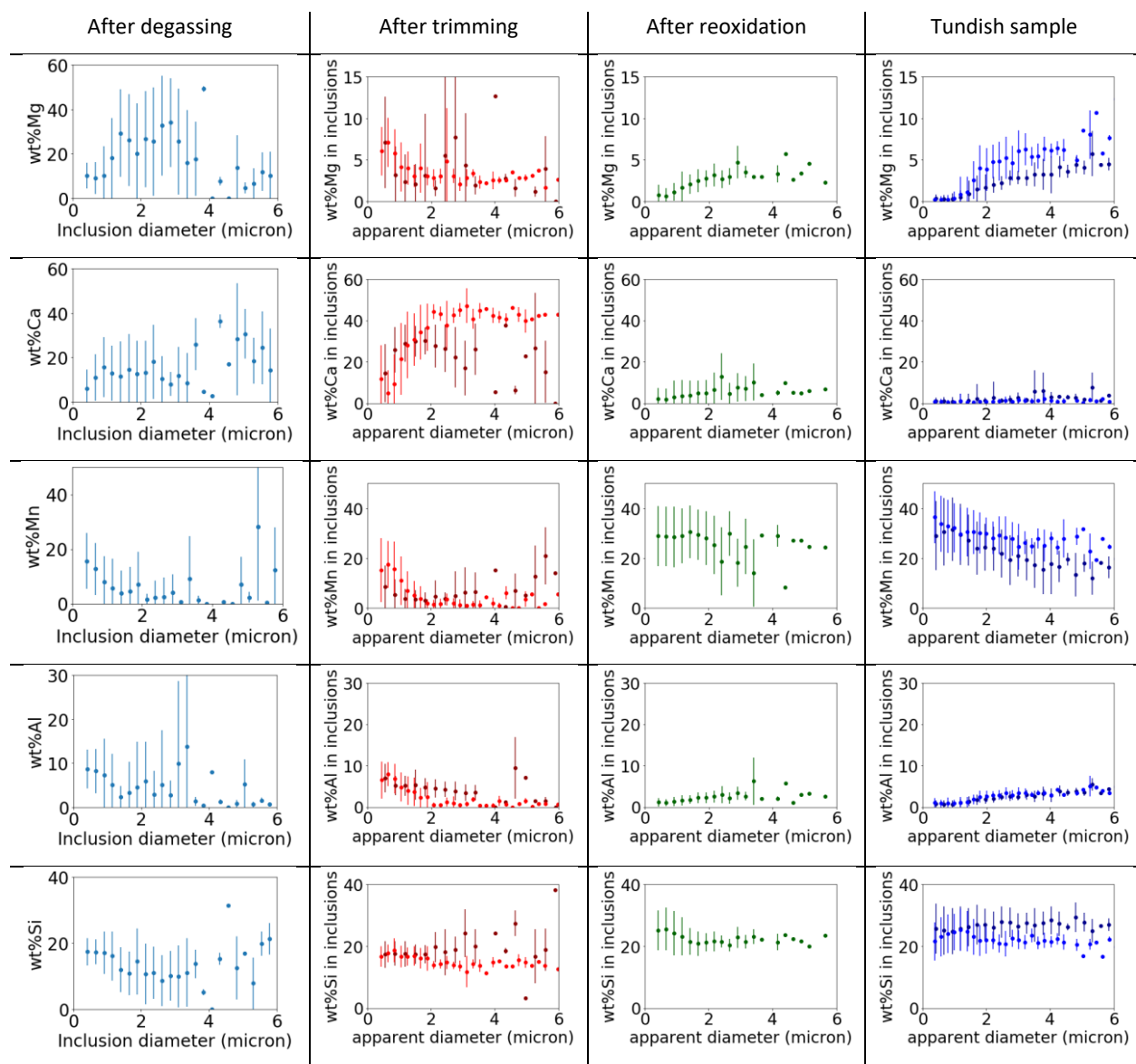


Figure 58 – Non-metallic inclusion analysis results as area-averaged elemental weight percent in inclusions for all samples, showing the evolution of chemical composition along the process and its inclusion size dependence. The error bars are the standard deviation for composition for the binned apparent size. Results for after vacuum degassing are from Heats 01, 02 and 03. Dark-red and dark-blue data points for after trimming and tundish samples are from Heat B. Bright-red, bright-green and bright-blue data points for after trimming, after reoxidation and tundish samples (from Heat A).

The inclusion extraction results help to understand the origin of the different populations of non-metallic inclusions present in the samples after degassing and trimming. These results can be seen

in Figure 59 for the sample taken after degassing, and Figure 60 for the sample taken after trimming, with their respective chemical compositions excluding oxygen. Typically, inclusions larger than 5 microns are mostly $\text{CaO-CaF}_2\text{-MgO-SiO}_2$, with a clear F content. Many reoxidation inclusions (Mn-silicates) are found, with varying Ca and Mg contents. These might be formed by the collision of Mn-silicates with preexisting slag inclusions. Sub-micron inclusions as seen on Figure 59 are secondary Mn-silicates, lean in Ca, containing some Mg and Al. No Ca-silicate inclusions in the range of 1-2 micron were found in this dissolution.

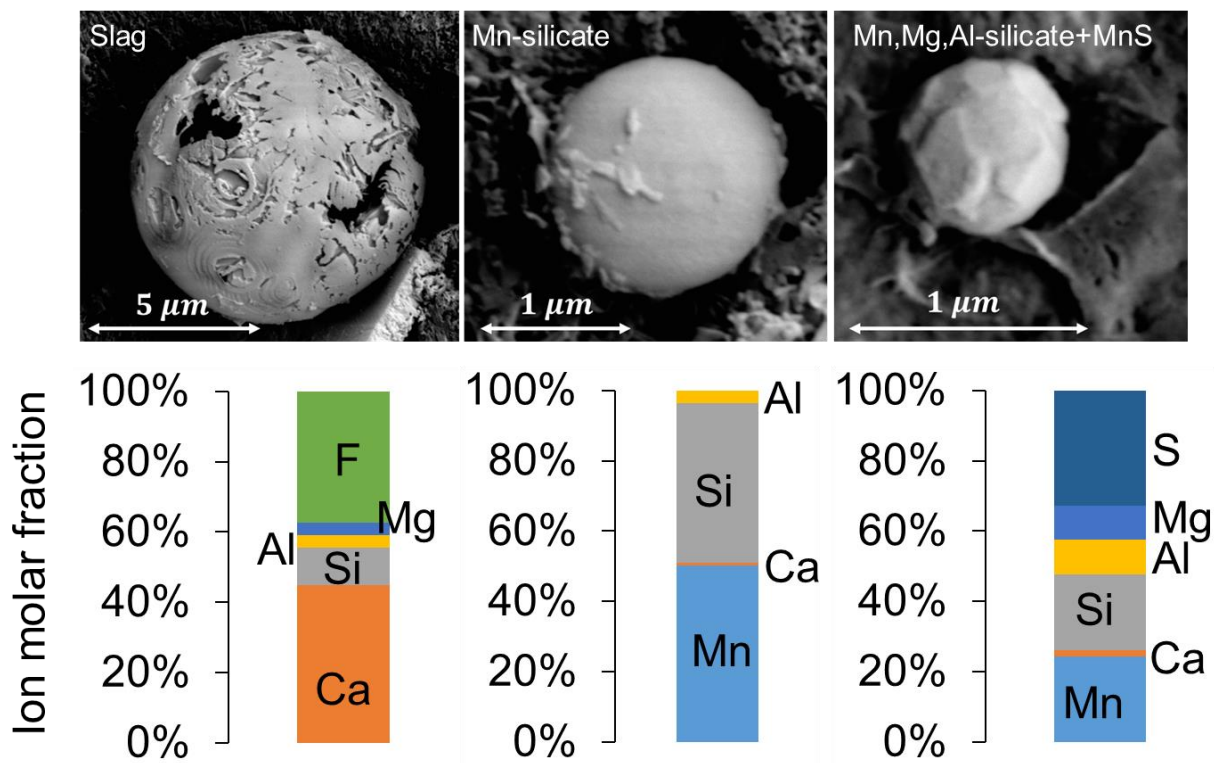


Figure 59 - Typical non-metallic inclusions found after degassing, as extracted. The left image shows a slag-based inclusion, rich in F and S, and high Ca-to-Si ratio. The center image shows a reoxidation inclusion, a Mn-silicate containing Ca and Mg. The right image shows a small Mn-silicate probably formed during the solidification of the sample. The correspondent ion fraction for each inclusion (excluding oxygen) is plotted below.

The Ca-silicates from the steel sample taken after trimming - Figure 60 - do not show any F peak, which implies they are truly a reaction product of $[\text{Ca}]$. Also, they are remarkably homogeneous

in chemical composition. The smaller inclusion depicted in Figure 60 is also a Mg, Al-containing Mn-silicate formed during solidification.

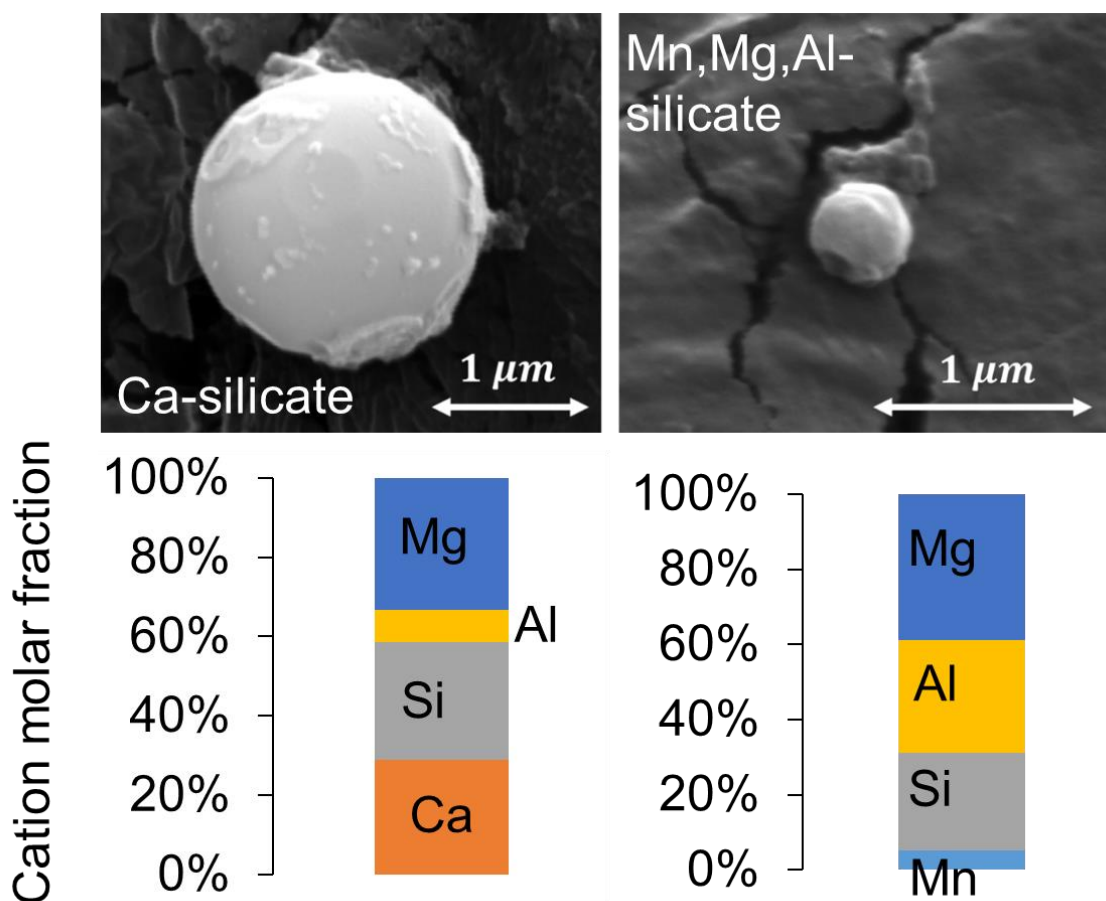


Figure 60 - Typical non-metallic inclusions found after FeSi trimming, as extracted. The left image shows a Ca-silicate inclusion, not containing F, and high Ca-to-Si ratio. The right image shows a small Mg, Mn-silicate probably formed during the solidification of the sample.

Many larger (of the order of 10 micron) Mn-silicate inclusions, with dilute Ca and Mg contents, were also found for samples right after degassing. The hypothesis that Ca may have been reduced from slag is not compatible with the Mn oxides, which should be completely reduced by reaction with Ca, Mg and Al. One possibility is that those inclusions collided during ladle treatment – for 10-micron inclusions colliding with 1-micron inclusions, turbulent collision controls the collision rate ($10^{-13} \text{ m}^3/\text{s}$ for turbulent collision, $10^{-15} \text{ m}^3/\text{s}$ for Stokes collision and $10^{-17} \text{ m}^3/\text{s}$ for Brownian

collision). Given the significantly high collision rate, it is likely that Ca was picked up by some of the inclusions through collision rather than chemical reaction. In the conditions of the induction furnace used in this thesis (around 5.7 cm of internal diameter, 600g molten iron and 140 kHz frequency), the turbulent energy dissipation rate $\epsilon = 10^{-4} \sim 10^{-5} \text{ m}^2/\text{s}^3$ and the turbulent collision is proportional to the square root of the turbulent energy dissipation rate [108]. Therefore, the turbulent collision rate will be $10^{-16} \text{ m}^3/\text{s}$. In this situation, Stokes and Brownian collision are most likely to dominate the collision mechanism.

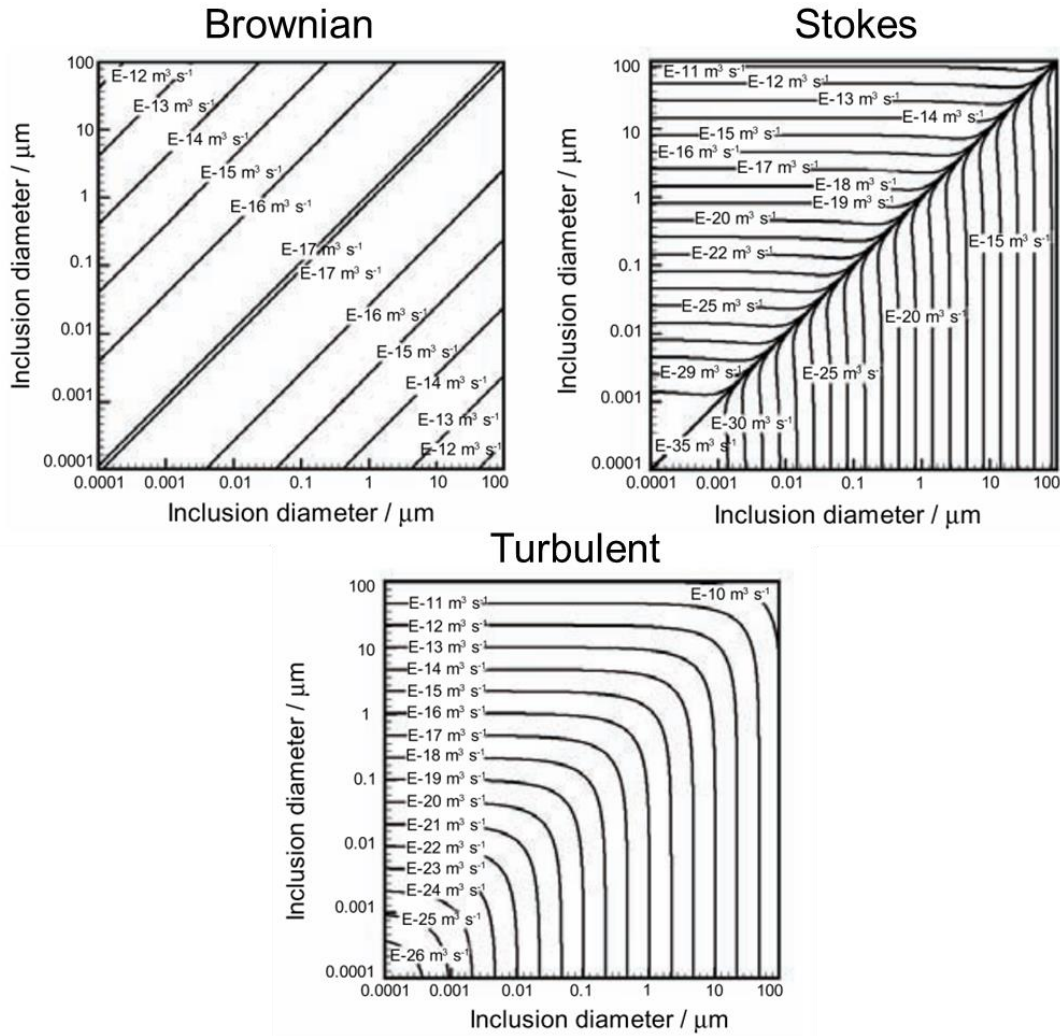


Figure 61 – Calculated coagulation coefficients (β) for different mechanisms – Brownian, Stokes and turbulent collision for liquid steel with $\epsilon = 0.1 \text{ m}^2/\text{s}^3$ (ladle conditions). [109]

Conclusions

- The degassed, desulfurized Si-killed steel is very likely close to steel-slag equilibrium, therefore the relatively high Mg and Ca content in the smaller inclusions can be caused by steel-slag reactions, facilitated by cleanliness (low inclusion concentration, so very sensitive to even a small extent of Ca transfer to the liquid steel) and strong stirring. However, slag-based inclusions can be as small as 5 microns.
- After reoxidation, the rate of Mg pick-up by inclusions is significantly higher than Ca pick-up in inclusions, suggesting Ca solubility in steel is indeed smaller than Mg solubility. CaO in reoxidation inclusions are most likely to be a result of collision of Mn-silicates with the Ca-rich population of inclusions found after trimming – the total insoluble Mg in the steel has an increasing trend whereas insoluble Ca has a decreasing trend.
- Ca-silicates found after trimming are fluorine-free and likely to be reaction products of Ca present in ferroalloys, either as oxides or in metallic form. Ca pick-up by this mechanism was 5-6 ppm.

5.3.2.2. Effect of solidification on the detection of inclusions in Si-Mn killed steel and their chemical composition

It is fundamentally important to control the morphology, composition and concentration of non-metallic inclusions in steel. In Si-Mn killed steels, control of [Ca], [Al] and [Mg] is desired to prevent the formation of solid, non-deformable phases that can disrupt casting by clogging and conformation by reducing toughness [3,5,7,97]. During solidification of Si-Mn killed steels, a significant population of secondary inclusions might appear due to the higher dissolved oxygen compared to typical Al-killed steels. The size, distribution and composition of these secondary inclusions will depend on the local solidification behavior.[68,70,110]. The typical method for steel sampling is using a lollipop sampler, which consists of a 1.8 mm thick steel mold held together by a clip [111]. This is the standard sampling method for most steelmaking processes, and it is widely used to assess the chemical composition and cleanliness of steel. The sampler is often encapsulated in a cardboard cylinder and can be protected from reoxidation by a flushing system using inert gases such as argon [111]. The inhomogeneity in lollipop samples caused by solidification has been studied, differences in solidification time through thickness of a lollipop

should be expected [112]. This section investigates the behavior of minor deoxidizing elements (Ca, Mg) in Si-Mn killed steels upon solidification, and compares the non-metallic inclusion concentration, composition and size to the estimated local solidification time by analyzing the entire thickness of a cross-section of lollipop samples.

Methodology

Steel lollipop samples for this work were obtained from different steel plants. A lollipop sampler is immersed into the molten steel and filled under the influence of ferrostatic pressure and sometimes vacuum. Subsequent solidification is rapid, by radiative cooling from the surface of the steel mold containing the sample. As is shown in Figure 42, the lollipop sample is 12 mm thick and 32 mm wide; the steel sheet forming the mold is approximately 1.8 mm thick. Lollipop samples were sectioned, mounted in graphite-containing hot mounting resin, ground with silicon carbide paper to 800 grit and polished using 1 μm alumina suspension. The polishing surface was parallel to the surface shown in the dotted frame. The samples analyzed for secondary dendrite arm spacing (SDAS, as indication of solidification rate) are listed in Table 6. Sample A is a ladle sample of an Al-killed steel, while B and C are ladle samples of a Si-Mn killed steel, sample B containing Ca-silicates as primary inclusions and sample C containing Mn-silicates as primary inclusions. Sample D is an electric arc furnace sample. The solidification range for each one of the compositions was calculated using Thermo-Calc 2017b for equilibrium solidification conditions, Scheil conditions (no back-diffusion in the solid, full diffusivity in the liquid) and Clyne-Kurz conditions (back-diffusion in the solid, full diffusivity in the liquid). For the Clyne-Kurz type simulation, DICTRA package was used with the thermodynamic database TCFE9 and the mobility database MOBFE4 for back-diffusion calculation, assuming a solidification distance of 20 micron, planar solidification morphology and a linear cooling rate of 31 K/s.

The samples were etched to reveal interdendritic segregation for dendritic arm spacing measurement. The solution used was 4 grams of saturated picric acid solution (1.3 wt%; resulting in a much lower picric acid concentration), 1 gram of copper chloride, 4 cm^3 of liquid soap and 200 cm^3 of deionized water [113]. Each sample was etched for 5 minutes. The structures were observed with a ZEISS metallographic microscope with Axio Cam ICC 5 and the secondary dendrite arm spacings were measured using ImageJ. The same cross-section used in metallography of the Si-Mn killed steel samples (B and C) were used for AFA in the ASPEX Explorer.

Table 6 - Chemical composition of analyzed lollipop samples. Solidification range calculated using Thermo-Calc assuming diffusivity of C in the solid. DICTRA values are calculated for

$$0.5\lambda_{SDAS} = 20 \mu m \text{ and } \dot{T} = 31.3 K/s.$$

Sample	C	Mn	Si	S	P	Al	ΔT (K) Scheil	ΔT (K) Equil.	ΔT (K) DICTRA
A	0.18	0.40	0.01	0.0053	0.0096	0.05	81	43	63
B	0.01	0.48	0.11	0.0008	0.0140	< 20 ppm	23	7	12
C	0.01	0.50	0.17	0.0006	0.0140	< 20 ppm	25	7	12
D	0.05	0.07	0.00	0.0370	0.0090	-	234	59	71

Lollipop solidification structures and estimated cooling rate

The solidification structures of the four samples are shown in Figure 62. In all samples, it was observed that the structure was significantly finer at the chilled surface as compared to the center of the lollipop. Figure 62a and Figure 62b compare the solidification structure of Sample A. In Figure 62c and Figure 62d, the chilled-dendritic-equiaxed transitions zones are clearer. For 3 mm away of the chilled surface, the solidification structure is fine and microsegregation was not sufficient to observe interdendritic segregation despite the expected increased Mn, Si and P concentrations. Then, in the inner part of the sample, a clear dendritic zone is observed for both samples B and C, indicating lower cooling rates, thus increased solidification time. The macrostructure of samples B and C also indicates macrosegregation, since the interdendritic segregation is much more apparent closer to the center. Equiaxed grains are found at the centerline of sample B. In Figure 62e and Figure 62f, the difference between the solidification structure in sample D is shown. Since the sulfur content in sample D is significantly higher than the other three samples (370 ppm, before desulfurization), interdendritic segregation is more apparent in all regions of the sample. The secondary dendrite arm spacing measurements and the estimated cooling rate for all four samples are shown in Figure 63. Since the four samples had carbon content smaller than 0.53wt%C, the cooling rate was estimated from the empirical correlation shown in Eq. 53 [74].

$$\lambda_{SDAS} = 148\dot{T}^{-0.38} \quad (54)$$

From the results shown in Figure 63a and Figure 63b, the cooling rate significantly decreases from the surface to the center of the sample. There is a significant difference between the estimated cooling rates at the sample edge for sample A compared to the other three, while all four samples exhibit similar cooling rates at the sample center. The initial solidification of the lollipop will strongly depend on the contact resistance at the steel sample/mold interface, so it is expected that different steel grades will exhibit different initial cooling rates depending on the overall sample volume changes during solidification. Superheat will also influence on the relative size of the chilled/columnar zones, but studies indicate that upon filling of a lollipop sample, superheat becomes negligible, so the impact of superheat is not expected. At the columnar zone of the lollipop, as the steel shell thermal resistance starts to control heat removal from the melt, the SDAS increases and the cooling rate is similar in all four samples, ranging from 10-30 K/s.

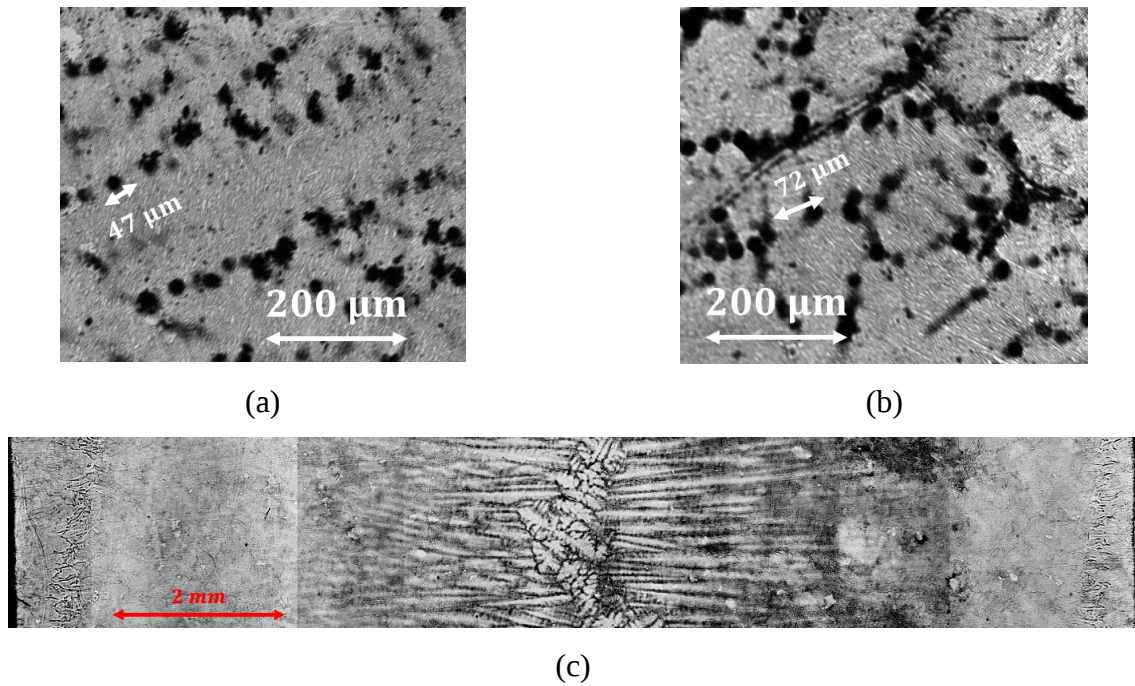
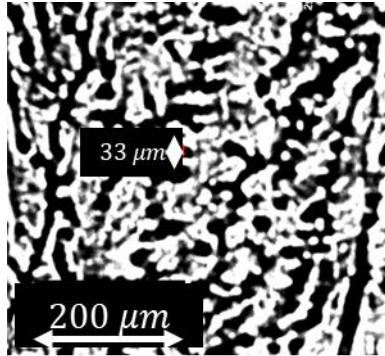


Figure 62 – Metallography results for the lollipop samples showing interdendritic segregation.

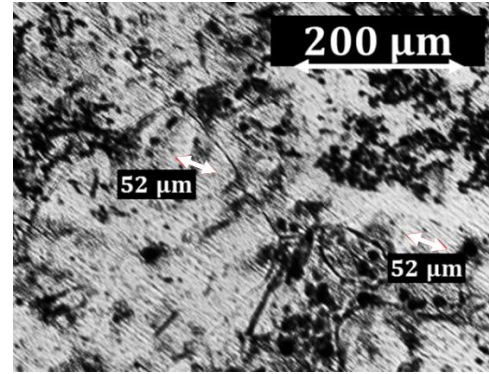
(a) Sample A, close to the edge of the sample; (b) Sample A, closer to the center of the sample. (c) Sample B, through the thickness of the sample. (d) Sample C, through the thickness of the sample. (e) Sample D, close to the edge of the sample, (f) Sample D, close to the center of the sample.



(d)

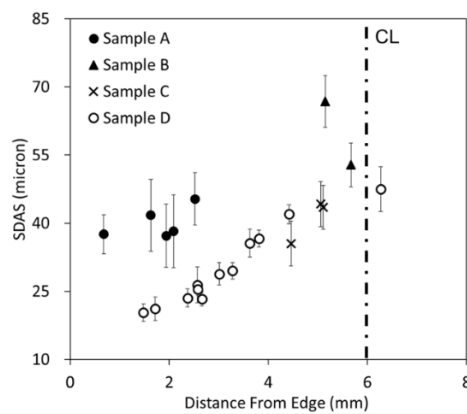


(e)

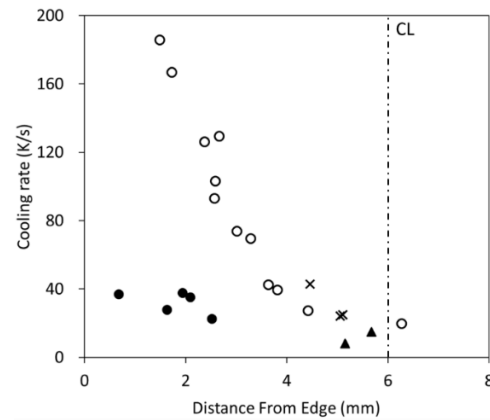


(f)

Figure 62 (cont.) - Metallography results for the lollipop samples showing interdendritic segregation. (a) Sample A, close to the edge of the sample; (b) Sample A, closer to the center of the sample. (c) Sample B, through the thickness of the sample. (d) Sample C, through the thickness of the sample. (e) Sample D, close to the edge of the sample, (f) Sample D, close to the center of the sample.



(a)



(b)

Figure 63 - (a) Measured secondary dendritic arm spacing through the thickness of all samples. Error bars are the standard deviation of the SDAS measurement. (b) Estimated cooling rate based on the measured SDAS using Eq. 1 [74]. The centerline (CL) is marked by the dash-dot line.

Non-metallic inclusion analysis results

The non-metallic inclusion analysis for the Si-Mn killed steel samples B (after trimming) and C (after reoxidation) are shown in Figure 64. In Sample B, two distinct populations of inclusions were found – the larger population, distributed evenly through the sample, is calcium silicates containing smaller amounts of Mg, Al and Mn. The second and smaller population appears to be as secondary inclusions, these are Mn-silicates containing Al and Mg. The position-dependent average chemical composition of the inclusion populations is plotted in Figure 64. The secondary inclusions are only detected by the AFA in the columnar zone of the lollipop. Since the Ca content is strikingly different for the two populations, the element was used as a tracer for primary inclusions. It is seen that for the secondary inclusions, the centerline inclusions are richer in Mn and Si and leaner in Al and Mg while for the primary inclusions, there is a slight increase in Mg, Al and Mn. This suggests that longer solidification times will promote the formation of more phases characteristic of a higher [O]. While significant changes in inclusion composition were found for Sample B due to the presence of Ca, Mg and Al, no significant chemical composition alterations were found in through thickness for Sample C aside from a very slightly higher Mg and Al content in the left side of the plot. The presence of Mn-silicates in sample C indicates the melt was significantly more oxygen-rich than the heat from sample B.

From the measured inclusion concentration and their estimated mass fractions in sample B, it was possible to estimate how much of the trace elements were present in the steel assuming they all precipitated as oxides. The results are compiled in Table 7. With the estimated chemical composition of Table 1 and 2 for sample B, a Scheil-Gulliver simulation was done using FactSage 7.0, stopping the calculation at $f_s = 0.999$. The purpose is to assess the locally equilibrated oxide composition for different degrees of microsegregation. During this calculation, the precipitated phases are removed from the system, therefore, the assumption is the precipitated inclusion will be engulfed by the solidification front and its composition will be frozen. In Figure 65, the results of the simulation are presented. The simulations show that Ca, Mg and Al are depleted from the liquid as it cools down and solidifies. This effect is due to the cooling of the liquid and increasing stability of precipitates, reducing the solubility of these elements. The remaining dissolved oxygen accumulates, and as Mn and Si start to control the deoxidation behavior, oxygen solubility significantly increases, as seen in Figure 65c. Therefore, the final inclusions are Mn-rich.

According to comparisons with measured compositions in Figure 65b and Figure 65d, the FactSage simulation predicted well the final primary and secondary inclusion compositions.

Table 7 – Estimated trace element content in sample B from AFA analysis

ppm [O]	ppm [Ca]	ppm [Mg]	ppm [Al]
14	4	2	5

The number and mass concentration of non-metallic inclusions also vary with position, thus with cooling rate. In Figure 67, it is seen that the secondary inclusions in Sample B precipitated mostly in the dendritic zone. Since the secondary inclusions are significantly smaller than the primary Ca-silicates, the number of Mn-silicate inclusions is comparable to that of primary inclusions, although the mass fraction is very small. There is a contrast in the behavior of the Mn-silicates in Sample C, as seen in Figure 67. In Sample C, there is not a clear trend for the distribution of the inclusions through thickness, but the number of inclusions is higher closer to the edge where cooling rate is significantly higher; the trend is not as visible for the mass concentration.

The observations are in accordance with previous work on the effect of solidification on non-metallic inclusions [68,70,110]. Since the secondary inclusions are mostly divorced from the Ca-silicates, it can be assumed that they homogeneously nucleated in the liquid. Higher cooling rates promote the homogeneous nucleation of inclusions and suppress growth, which is generally limited by diffusivity of the lowest concentration element that constitutes the oxide. In the case of this work, they should be Ca and Mg initially, then O in the later stages of solidification. Higher cooling rates would cause the segregation behavior to be closer to Scheil conditions because of the limited time for segregated elements to back-diffuse into the solid.

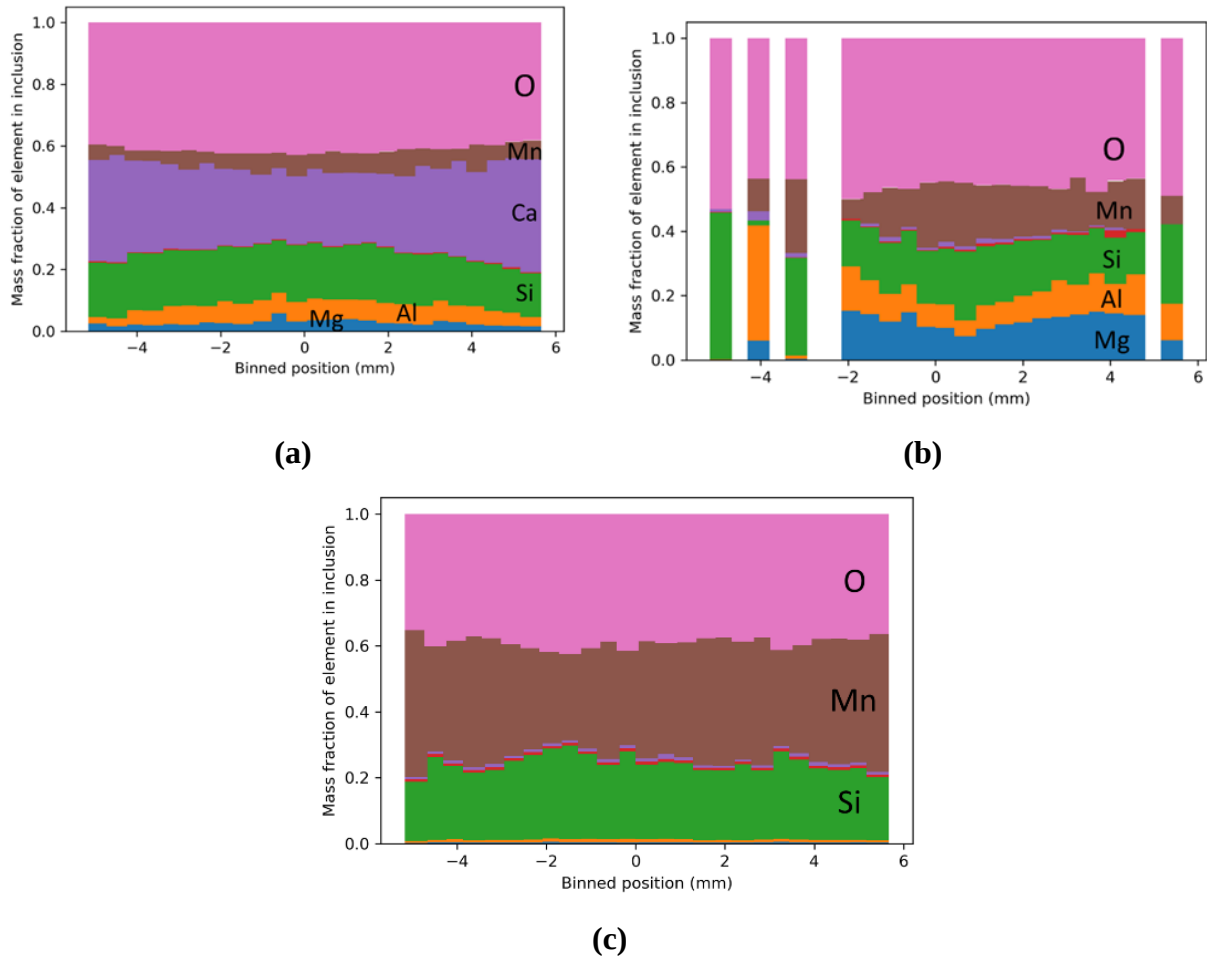


Figure 64 – Area-averaged mass fraction of elements in non-metallic inclusions through the thickness of a lollipop sample. (a) Sample B, primary inclusions; (b) Sample B, secondary inclusions. (c) Sample C, entire analyzed inclusion population.

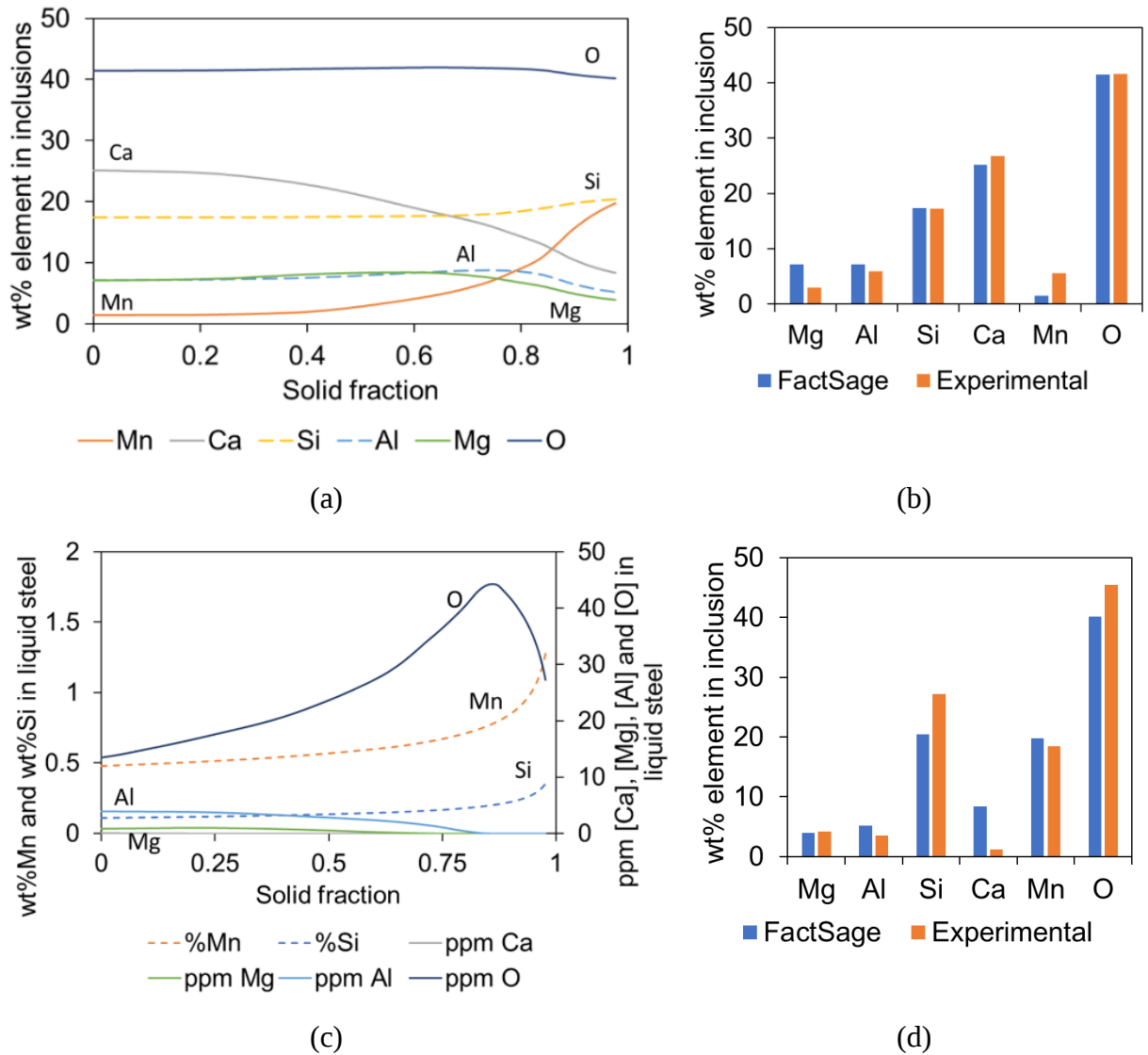
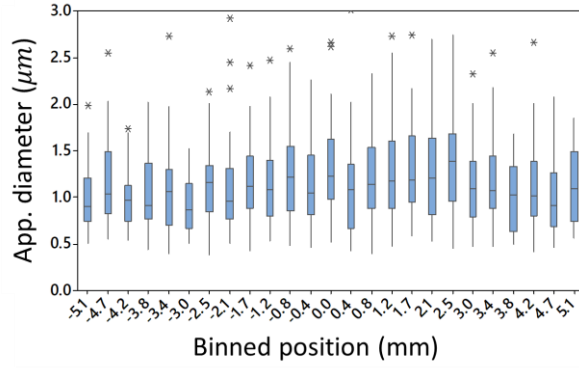
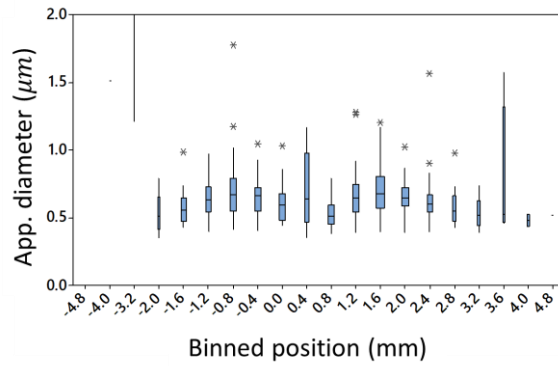


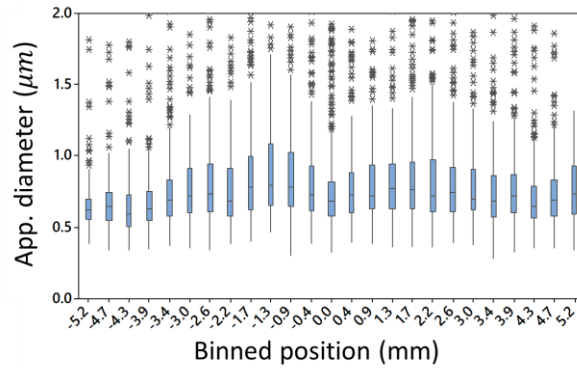
Figure 65 – Solidification model results from FactSage 7.0 using the estimated chemical composition for sample B (Tables 1 and 2). (a) Calculated oxide composition in local equilibrium with liquid steel during solidification. (b) Comparison between predicted and observed primary inclusion composition. (c) Calculated microsegregation profile for Mn, Si and trace elements. (d) Comparison between predicted and observed secondary inclusion composition.



(a)



(b)



(c)

Figure 66 – Boxplot of the size distribution of inclusions through the thickness of a lollipop. Thickness of boxplot is proportional to sample size. (a) Size distribution of primary Ca-silicate inclusions through the thickness of sample B. (b) Size distribution of secondary Mn-silicate inclusions through the thickness of sample B. (c) Size distribution of Mn-silicates through the thickness of sample C.

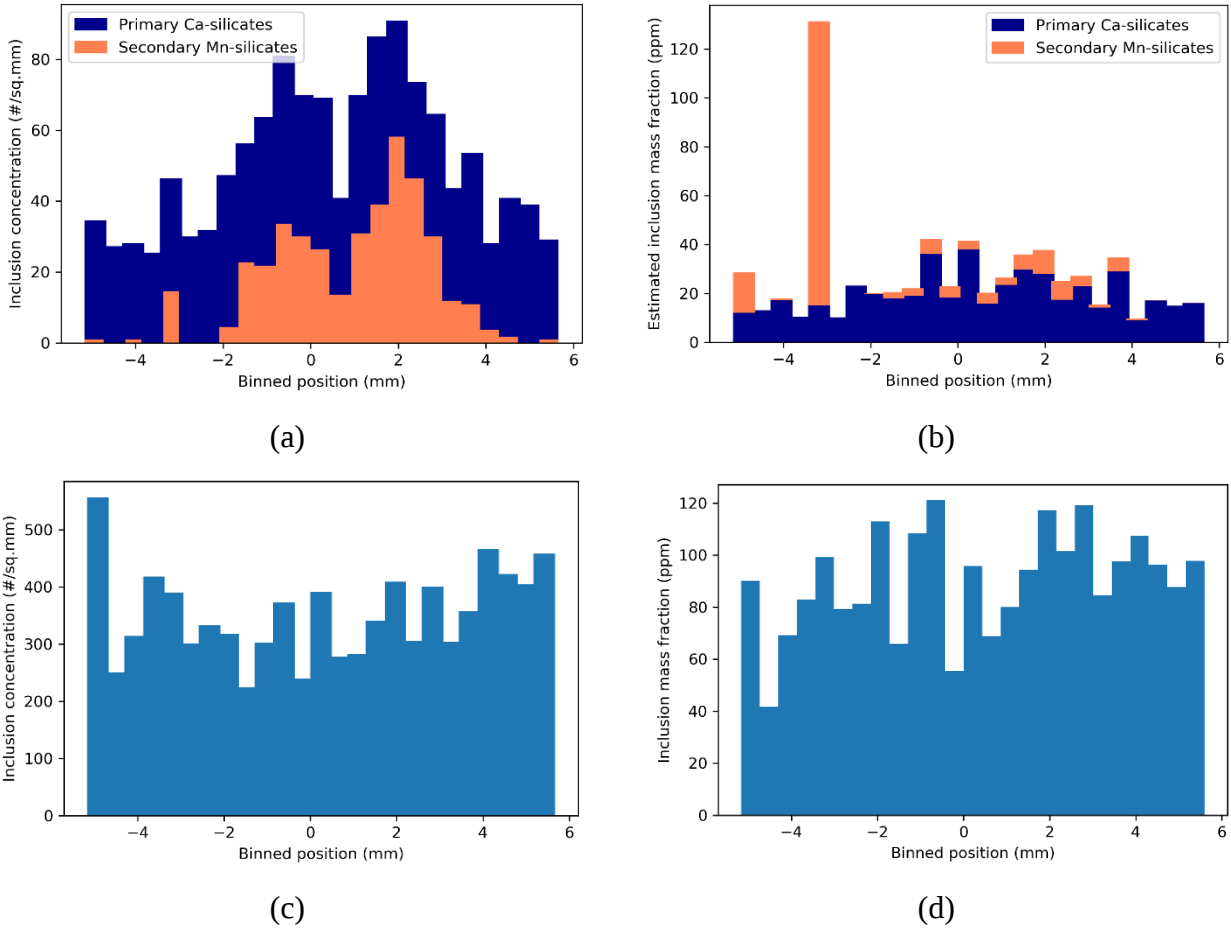


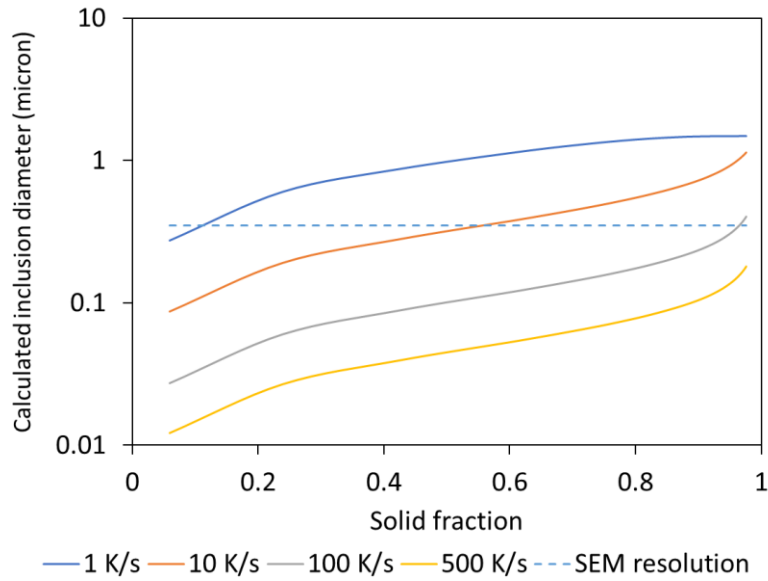
Figure 67 – Number and mass concentration of inclusions through the thickness of a lollipop. (a) Number concentration of primary and secondary non-metallic inclusions in Sample B. (b) Estimated mass concentration of primary and secondary non-metallic inclusions in Sample B. (c) Number concentration of non-metallic inclusions in Sample C. (d) Estimated mass concentration of non-metallic inclusions in Sample C.

The measured size of secondary inclusions is compatible with an inclusion growth calculation, as shown below. Assuming the growth of the secondary Mn-silicates (here taken to be MnSiO_3) are limited by diffusion, their size can be predicted using Eq. 54. The density of iron and inclusions at high temperature (ρ_{Fe} and ρ_{MnSiO_3}) are 7000 kg/m^3 and 3400 kg/m^3 respectively, the diffusivity of oxygen D_O is $3 \times 10^{-9} \text{ m}^2/\text{s}$, M_i is the molar mass of the species, $[\text{wt}\%O]_L$ the oxygen concentration in the bulk liquid and $[\text{wt}\%O]_{eq}$ the equilibrium concentration for the steel-inclusion configuration.

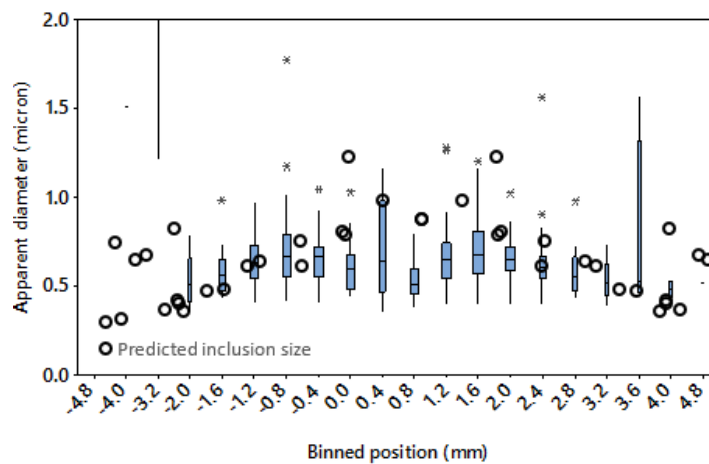
$$r \frac{dr}{dt} = \frac{1}{3} \frac{M_{\text{MnSiO}_3}}{100 M_{\text{O}}} \frac{\rho_{\text{Fe}}}{\rho_{\text{MnSiO}_3}} D_{\text{O}} ([\text{wt}\% \text{O}]_{\text{L}} - [\text{wt}\% \text{O}]_{\text{eq}}) \quad (55)$$

For this calculation, the number of nuclei is taken to be the volumetric concentration of inclusions measured in sample B, which is 5×10^{13} inclusions/ m^3 of steel. The volume of steel per nucleus is then $2 \times 10^{-14} \text{m}^3$ per inclusion. The available oxygen for growth is taken to be the mass of oxygen per available volume of steel. The timestep used for the calculation is the $\Delta T = 1 \text{ K}$ used in the FactSage calculation divided by a fixed cooling rate. The calculation assumes an oxygen concentration difference equal to the remaining concentration of oxygen in the reacting volume (thus assuming that the equilibrium oxygen at the steel-inclusion interface is zero). This approach is used to calculate the maximum inclusion size during solidification for the cooling rates and solidification time from Sample D.

The results are summarized in Figure 68. Based on the calculations, it appears that the apparent smaller concentration of secondary inclusions closer to the edge of the samples might be an analytical artifact caused by the limited growth at high cooling rates. The inclusions would be too small to detect. Figure 68a demonstrates how cooling rate affects the average inclusion size during solidification, compared to the SEM resolution. In Figure 68b, the inclusion sizes calculated using the cooling rates from the lollipop samples (Figure 63b) were compared to the actual AFA measurements through lollipop thickness, although there is room for refinement of this model, such as using the true solidification time with solidification model that accounts for back-diffusion and using more precise values for the oxygen concentrations. These observations can be extended for the Mn-silicates of Sample C; however, they are larger because the higher dissolved oxygen upon solidification will yield larger inclusions. There is no clear distinction between primary and secondary inclusions in those. The presence of Ca, Mg and Al lowers the solubility of O in steel and increasing the nucleation rate compared to manganese silicates.



(a)



(b)

Figure 68 – (a) Calculated effect of solidification rate in the diffusion-limited growth of secondary Mn-silicates. The dashed line is the expected SEM resolution used in the AFA analysis. (b) Predicted inclusion sizes (data points) for the cooling rates observed in the lollipop samples compared to the experimental secondary inclusion size distributions through Sample B thickness (boxplots).

Solidification behavior of steel in a lollipop sampler

To better understand the solidification rate in a lollipop sampler, simulations were done using the software ESI QuikCAST [114]. Based on the dimensions shown in Figure 42, a model of the

lollipop sampler was drawn. The model drawing can be seen in Figure 69. The simulation assumed a filled sampler with initial temperature of 1550°C (1823 K) and no effect of gravity. The material considered for the simulation was a low carbon steel from QuikCAST native database. The boundary conditions for solidification were selected based on the sampler design shown in Figure 70. The schematics for the assumed solidification boundary conditions are given in Figure 71. It is assumed that once the lollipop sampler is fed, which takes less than 0.5 second [115], the thermal resistances from the steel surface to the environment are the interfacial resistance at the mold, conduction through the mold shell and radiation plus natural convection from the outer shell to the environment. It is assumed the emissivity of the steel shell is 0.9 due to high temperature oxidation. The environment temperature is set to be 20°C (298 K). Simulations were done for three different contact resistances and compared to the calculations using experimental data (seen in Figure 72).

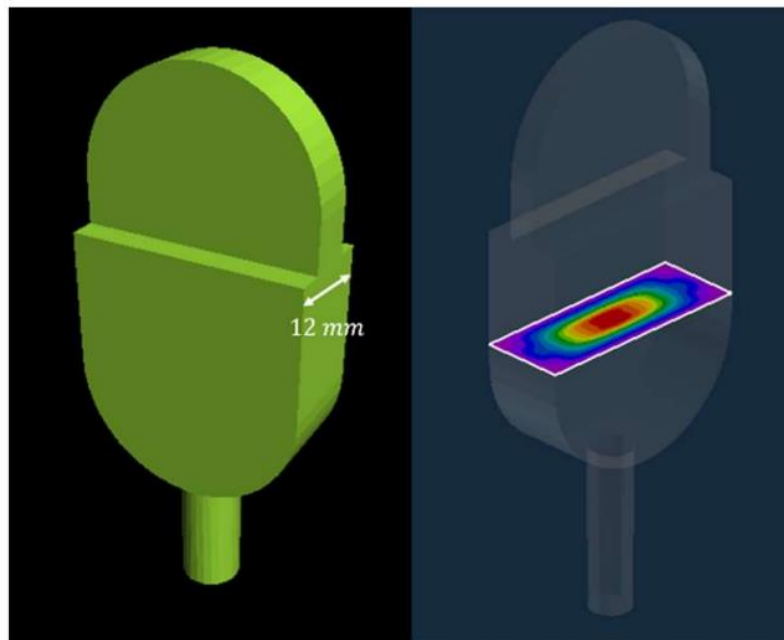


Figure 69 – Model render of lollipop sample used for solidification simulation in ESI QuikCAST (in the left) and a XY-plane slice of the model showing simulated solidification time at the center of the lollipop (in the right).

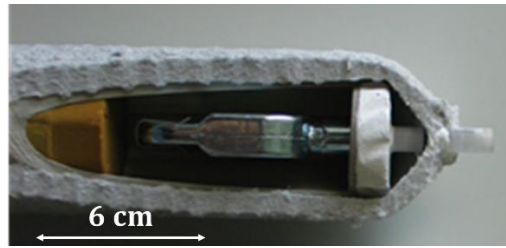


Figure 70 – Lollipop sampler (metallic mold) with cardboard plus refractory casing. The mold is made of carbon steel and is 1.8mm thick.

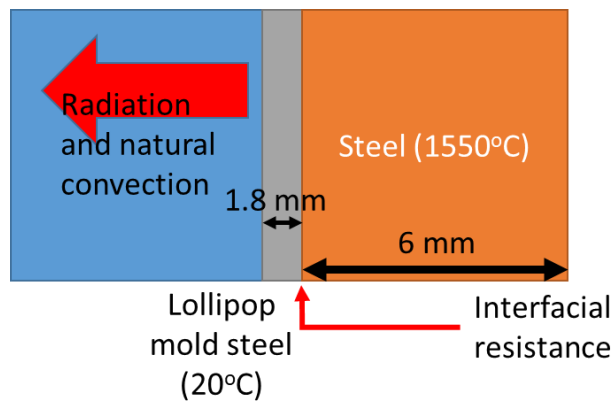


Figure 71 – Schematics of the boundary condition considerations for the solidification simulation of the lollipop sample.

From the results shown in Figure 72, it is seen that the model predicts solidification times of 1 second for $5000 \text{ W/m}^2\text{K}$ to 2.5 seconds for $1000 \text{ W/m}^2\text{K}$ of contact coefficient (the inverse of contact resistance). The three different heats have very different solidification times, within the same range as the simulation. The solidification range for these heats are significantly different due to the differences in C, S, Mn and Si content of these alloys, which affects their solidification time. For this configuration, contact resistance is expected to be the main resistance to heat transfer in the lollipops. Each one of the studied chemistries will have different density changes depending on the phases formed upon solidification, as shown in Figure 73. Heat A is in the peritectic range and has a rapid shrinkage during solidification – the resulting expected increase in contact resistance might explain the increased solidification times as well. Heat D has a high S content and is an EAF sample, so nucleation of CO gas bubbles might also increase surface roughness at the

mold-steel interface as solidification progresses. The sample was also very porous in the center which is an indication of gas evolution during solidification. Heats B and C have very low carbon contents ($< 0.05\%C$) thus they have a small solidification range. Si-Mn killed steels tend to have higher interfacial heat transfer coefficients at chilled surfaces due to the formation of a $MnO-SiO_2$ oxide film [6].

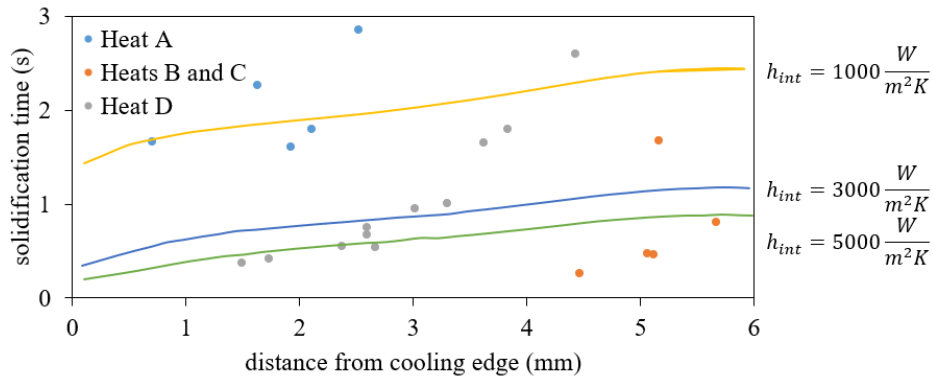


Figure 72 – Comparison between experimental-based solidification time calculations and the simulation results. The lines are the simulation results for different interfacial heat transfer coefficients. The data points are the calculated solidification times based on each samples' solidification cooling rate (estimated from the secondary dendritic arm spacing) and the solidification range as calculated using DICTRA (Table 6).

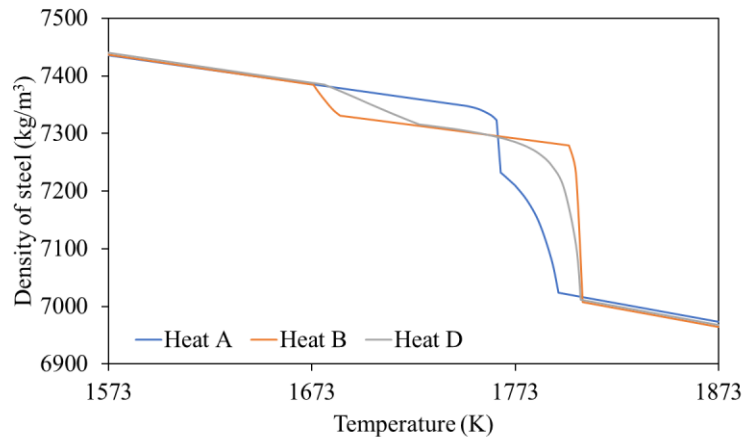


Figure 73 – Equilibrium steel density as a function of temperature for Heat A, B and D (calculated using Thermo-Calc). The curves differ due to their different solidification path.

Conclusions

- Solidification time in lollipop samples can widely vary from the surface to the center. The perceived cleanliness will depend on where the analysis was made through the thickness of the lollipop. To analyze only primary inclusions, the analysis of the surface of the lollipop is recommended. To estimate total oxygen and other minor elements and study micron to submicron-sized inclusions, analysis of the cross-section will yield better results.
- Si-Mn killed steels containing trace amounts of Ca, Mg and Al will precipitate Mn-silicate as secondary inclusions due to microsegregation. The size of secondary inclusions is controlled by the local cooling rate during solidification. FactSage Scheil model accurately predicted the chemical composition of primary and secondary inclusions.
- A simple diffusion-limited growth model could explain the effect of cooling rate on the secondary inclusions.
- Solidification of the lollipop takes 1-3 seconds. For a given superheat of the sample, the solidification time depends on the solidification range and the contact resistance, which depends on the surface roughness and shrinkage of the solidifying steel. Therefore, chemical composition will play an important role in the lollipop solidification.

5.4 Laboratory-scale simulations of ladle furnace treatment

Steel-slag experiments were performed to measure the kinetics of steel and slag reactions and steel and inclusion composition evolution for many typical configurations found in steelmaking. These are summarized in Table 8.

Table 8 – Summary of induction furnace experiments

Number	Steel chemistry	Slag chemistry	Crucible chemistry	General observation
H1	1.25%Mn-0.25%Si – 400ppm O – 7ppm S	(%CaO)/(%SiO ₂) = 5.7, (%Al ₂ O ₃) = 35, 10%MgO	Y ₂ O ₃ - stabilized MgO	Observation of Al and Mg pick-up and model parameter fitting
H2	1.25%Mn-0.25%Si – 400 ppm O – 40 ppm S	(%CaO)/(%SiO ₂) = 5.7, (%Al ₂ O ₃) = 35, 10%MgO		
H3	1.25%Mn-0.25%Si – 400ppm O – 7ppm S-	No SiO ₂ (52%CaO- 41%Al ₂ O ₃ - 7%MgO)		Minimum oxygen potential – no SiO ₂ in slag
H4		H1 + 10%CaF ₂		Observation of surface instability
H5		H1 + 1%MnO		Observation of surface instability and kinetics of reoxidation
H6		H1 + 5%MnO		
H7		(%CaO)/(%SiO ₂) = 5.7, (%Al ₂ O ₃) = 35, 10%MgO		1 kg melt – effect of size in inclusion removal

Table 8 (cont.) - Summary of induction furnace experiments

Number	Steel chemistry	Slag chemistry	Crucible chemistry	General observation
H8	1.25%Mn-0.25%Si – 400 ppm O – 400 ppm S	(%CaO)/(%SiO ₂) =2.3, (%MgO) = 5, 15%CaF ₂	Y ₂ O ₃ - stabilized MgO	Observation of Al, Mg pick-up and model parameter fitting and desulfurization
H8*	1.25%Mn-0.25%Si – 400 ppm O – 350 ppm S	58%CaO- 18%Al ₂ O ₃ - 18%SiO ₂ - 7%MgO	YSM and Al ₂ O ₃	Mass transfer coefficient from desulfurization
H9	1.25%Mn-0.25%Si – 400 ppm O – < 10 ppm S	59%CaO- 27%SiO ₂ - 14%CaF ₂	CaO-3%ZrO ₂ crucible	Reprecipitation of [Ca] through reoxidation
H9	0.5%Si – 400 ppm O – 7 ppm S	No slag	Y ₂ O ₃ - stabilized MgO	Observation of Ca pick-up in non- metallic inclusions from ferroalloy addition
H10	0.1%Al – 400 ppm O - < 10 ppm S + 0.8 g Fe-75%Si- 2%Ca			
H11	1%Mn – 0.2%Si – 400 ppm O - < 10 ppm S + 0.8 g Fe- 75%Si-2%Ca			

5.4.1. Deoxidant preparation

Pure silicon, pure manganese and electrolytic iron were mixed in a graphite crucible and heated to 1300°C to produce a silicomanganese alloy. The target composition was a 7:2:1 mass ratio of Mn:Si:Fe, saturated in carbon and molten at 1300°C.

Table 9 – aimed chemical composition of silicomanganese alloy for deoxidation

wt%Mn	wt%Si	wt%Fe	wt%C _(sat)	T _{melting} [°C]
68.6	19.6	9.8	2	1300

5.4.2. Effect of high basicity, high alumina slag on Si-Mn killed steel inclusion evolution (Exp. H1)

a. Deoxidation

620g of electrolytic iron was melted at 1600°C. Deoxidation was carried using SiMn and medium-carbon (MC) FeMn ferroalloys to achieve the desired Mn/Si ratio of 5.

Table 10 – Typical materials employed in deoxidation experiments

	mass [g]	wt%Si	wt%Mn	wt%Fe	wt%C	ppm O	ppm S
MC FeMn	3.0	0.3	83.1	13.6	1.4	--	--
SiMn	7.5	19.3	67.4	9.6	3.7	--	--
electrolytic Fe	621	--	--	99.96	--	396	7

b. Slag addition and sampling

185g of the desired slag was added to the induction furnace after deoxidation for H1 and H2, while 100g of slag were added for all the other experiments with slag. Sampling was done each 5 minutes with fused quartz sampling tubes of 4mm inner diameter (see the timeline in Figure 74).

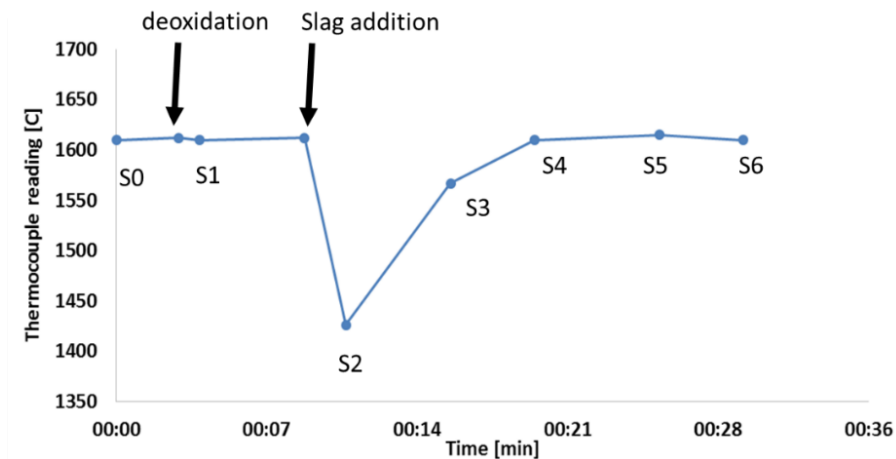


Figure 74 – Temperature-time diagram with sampling and addition events

Results and Discussion

1. Chemical Analysis

Table 11 – elemental chemical analysis of samples taken during experiment

Element wt%	O	C	Si	Mn	Al	Mg
Analytic method	LECO	LECO	ICP	ICP	ICP	ICP
S0	0.0396	--	--	--	--	< 0.002
S1	0.01	0.024	0.18	0.86	< 0.002	< 0.002
S2	--	--	0.20	0.87	0.002	< 0.002
S3	--	--	0.19	0.87	0.003	< 0.002
S4	--	--	0.18	0.79	0.003	< 0.002
S5	--	--	0.17	0.78	0.004	< 0.002
S6	0.002	0.031	0.21	1.08	0.004	< 0.002
Equilibrium FactSage	0.0011	0.051	0.19	1.20	0.0112	0.00017

Table 12 – Definitions of symbols used in the equations below

Variables	Description	Unit
$[\%Al]_i$	weight percent of Al in steel in sample i	%
$[\%Al]_{eq}$	equilibrium weight percent of Al in steel	%
W_{steel}	bulk steel mass	kg
ρ_{steel}	density of steel	kg m ⁻³
A	area of steel-slag interface	m ²
$d_{crucible}$	diameter of crucible	m
m_{Al}	rate constant	m ⁻² s ⁻¹
k_{Al}	mass transfer coefficient	m s ⁻¹

The rate of aluminum pick-up in the steel melt can be written as

$$\frac{d[\%Al]}{dt} = -m * A * ([\%Al] - [\%Al]_{eq}) \quad (56)$$

$$m_{Al} = \frac{k_{Al}}{\left(\frac{W_{steel}}{\rho_{steel}}\right)} \quad (57)$$

Since $W_{steel} = 631.5$ g and $\rho_{steel} = 6954$ kg/m³ and $A = \frac{\pi d_{crucible}^2}{4} = 3.32 * 10^{-3}$ m², we can estimate the mass transfer coefficient through the relationship:

$$m_{Al} = \left(-\frac{d[\%Al]}{dt}\right) * \frac{1}{A * ([\%Al] - [\%Al]_{eq})} \quad (58)$$

For a sample i, we have that:

$$m_{Al,i \rightarrow j} = -\left(\frac{[\%Al]_j - [\%Al]_i}{t_j - t_i}\right) * \frac{1}{A} * \frac{1}{([\%Al]_i - [\%Al]_{eq})} \quad (59)$$

The values of $\frac{d[\%Al]}{dt}$ are taken from the slope between the $[\%Al]$ midpoint values. The calculated values of k_{Al} from each slope are plotted on Figure 75.

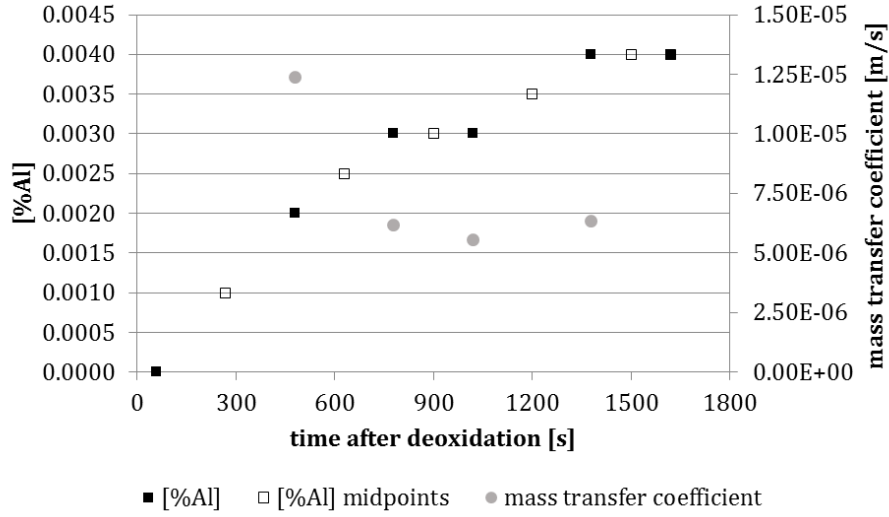


Figure 75 – Variation of aluminum content after slag addition, and calculated mass transfer coefficients

$$\overline{k_{Al}} = (8 \pm 3) * 10^{-6} \text{ m/s} \quad (60)$$

The value of the mass transfer coefficient is used for validation of the steel-slag mass transfer model and to compare its results with the experimentally obtained inclusion composition. The mass transfer coefficient for steel was calculated from the analyzed aluminum with Eq. 3, then FactSage simulations using the calculated mass transfer coefficient were made. The simulation results agree with measured inclusion compositions, indicating that the assumption of steel-to-slag mass transfer limited inclusion modification. The approximate time constant for aluminum is=calculated to be around 3400 s, which shows that the stirring conditions are much slower compared to a real ladle.

2. SEM Automated Feature Analysis (AFA-ASPEX)

The AFA analyses were run in the FEI ASPEX Scanning Electron Microscope as described in Section 5.1. The full cross-section of a sample was analyzed to detect possible inhomogeneity caused by solidification in the sample.

The average results for chemical composition changes through the process are plotted below. Addition of slag was done 360 seconds after deoxidation, which is taken as the effective initial time for steel-slag interaction. The error bars show the elemental atomic fraction standard

deviation for the inclusions in each sample. Initial parameters considered for the model are given in the table below.

Table 13 - Initial parameters for inclusion modification model

T [°C]	wt%Mn	wt%Si	ppm O	ppm S	Interfacial area [m ²]	Mass transfer coefficient [m/s]
1600	1.08	0.21	100	7	0.00257	8×10^{-6}

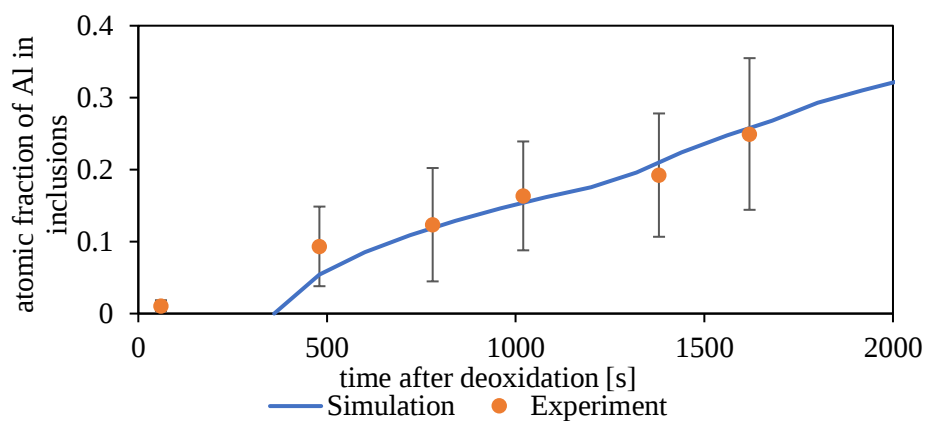


Figure 76 – Average aluminum content in inclusions for the experiment H1 (47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

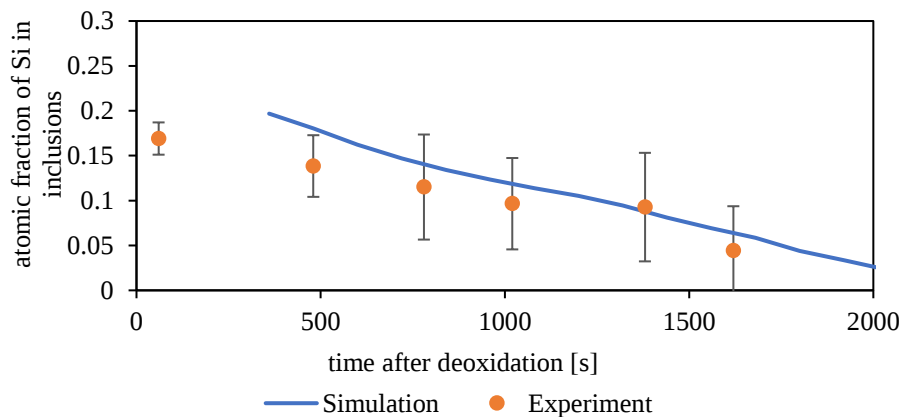


Figure 77 – Average silicon content in inclusions for the experiment H1 (47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

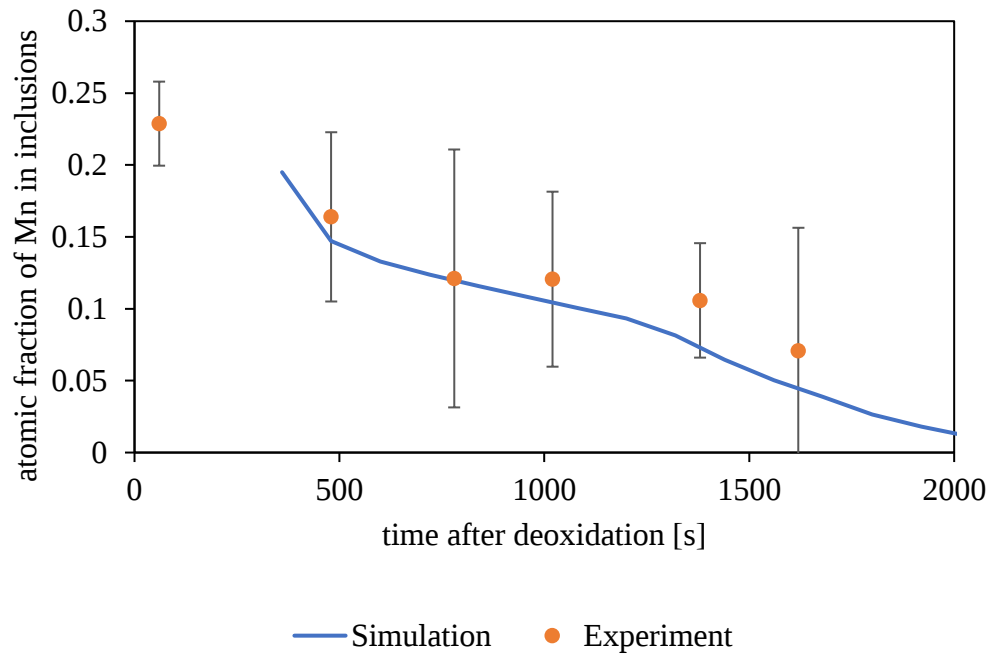


Figure 78 – Average manganese content in inclusions for the experiment H1 (47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

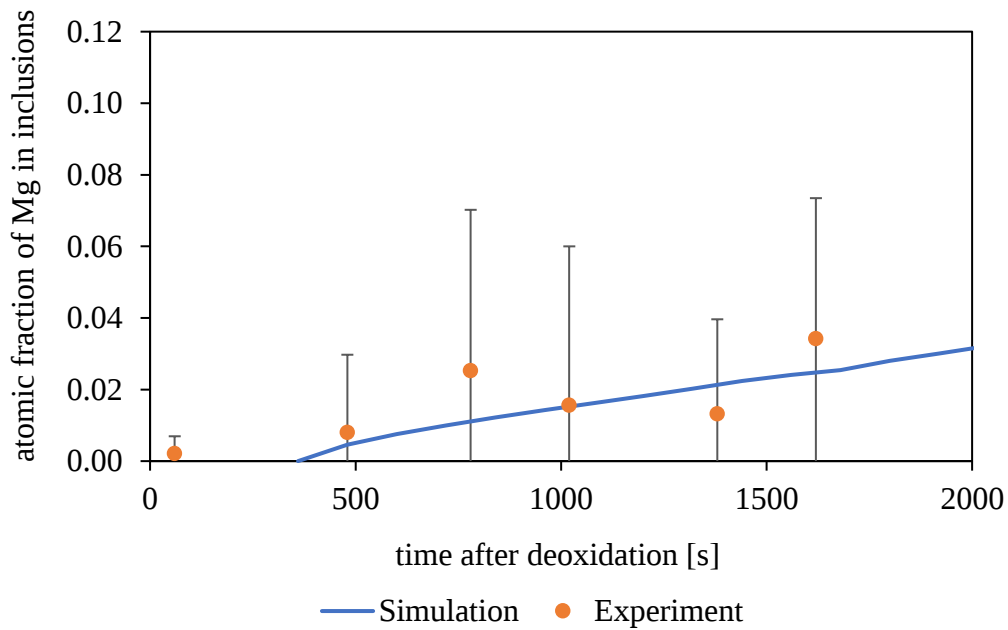


Figure 79 – Average magnesium content in inclusions for the experiment H1 (47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

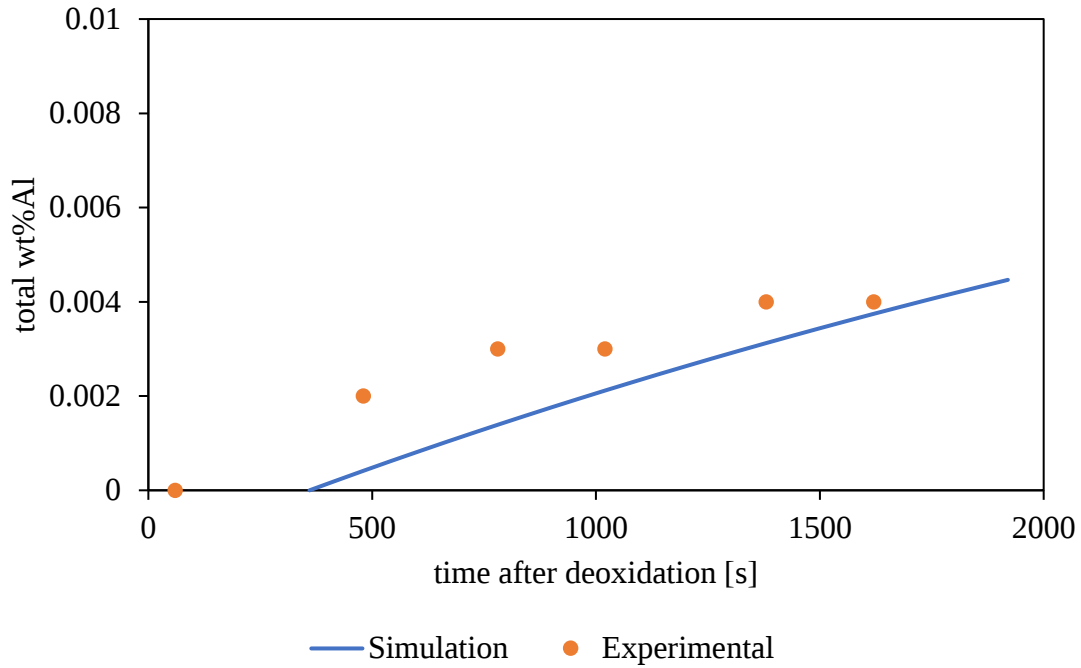


Figure 80 – Measured and predicted total aluminum concentration in steel for the experiment H1
(47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

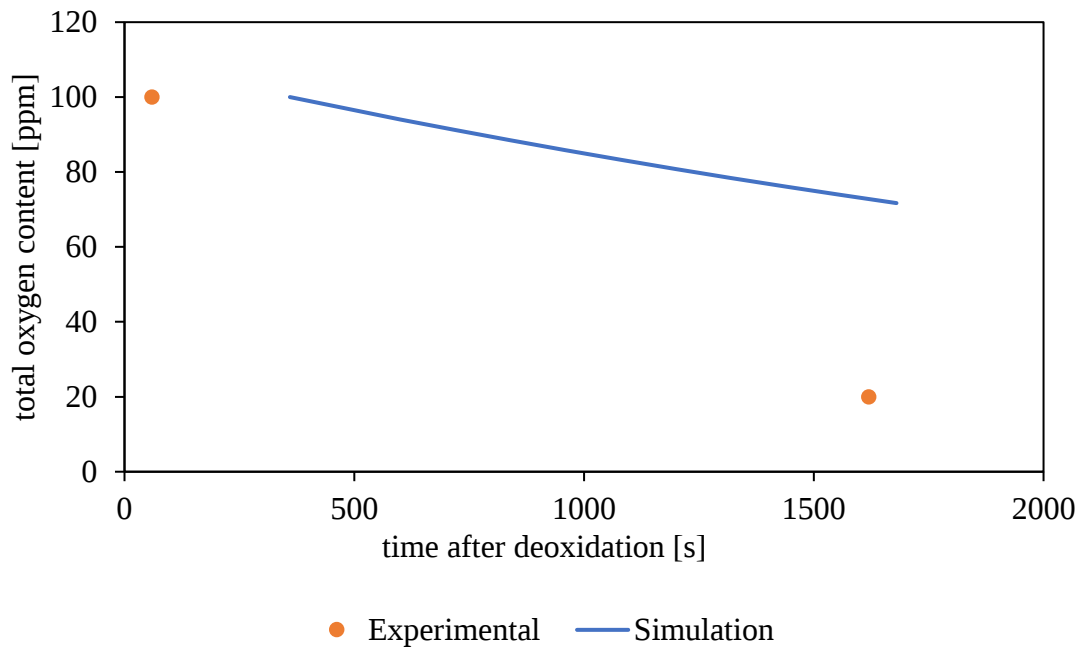


Figure 81 – Measured and predicted total oxygen concentration in steel for the experiment H1
(47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

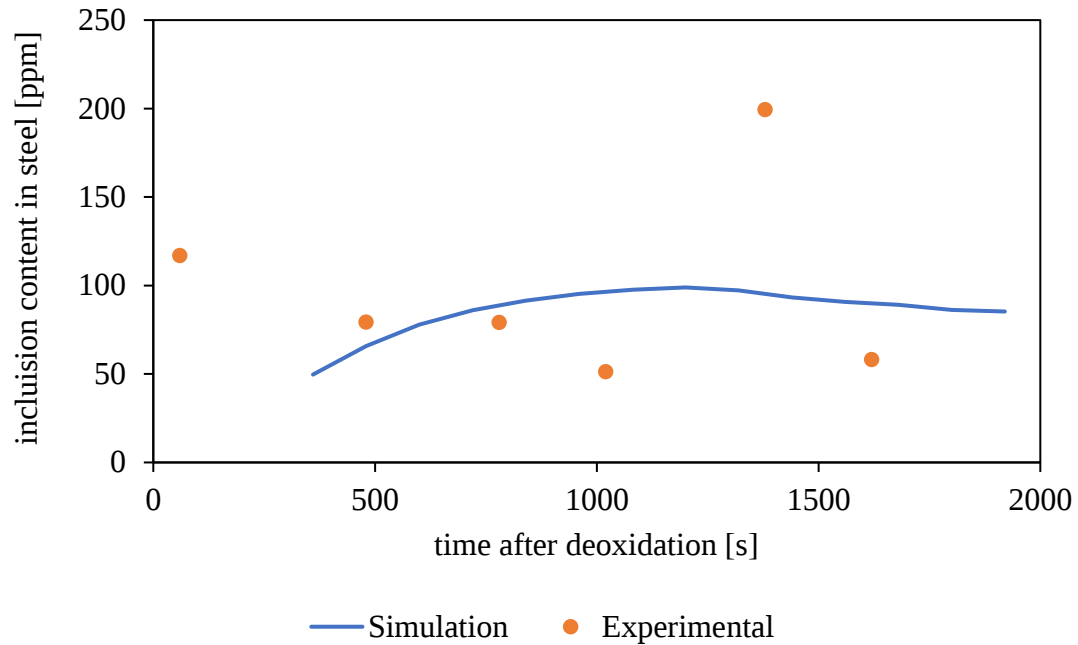


Figure 82 – Inclusion content in steel – simulation and experimental results for the experiment H1 (47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

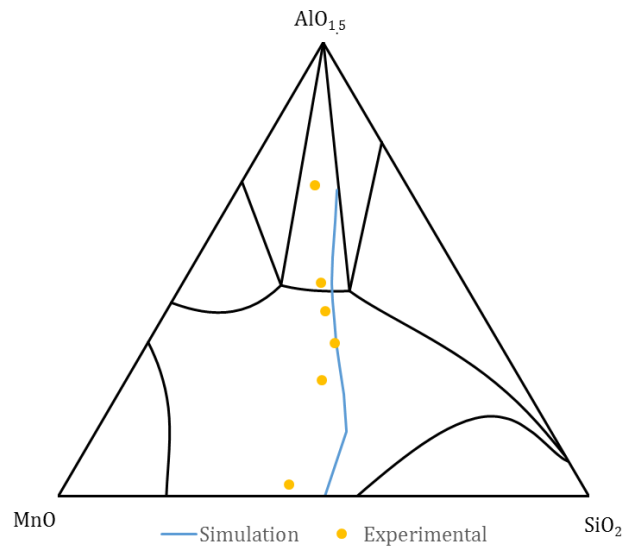


Figure 83 - Atomic fraction ternary diagram (at 1600°C) comparing inclusion modification trajectory between simulated and experimental results. Inclusions leave the liquid region and enter alumina. Experiment H1 (47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

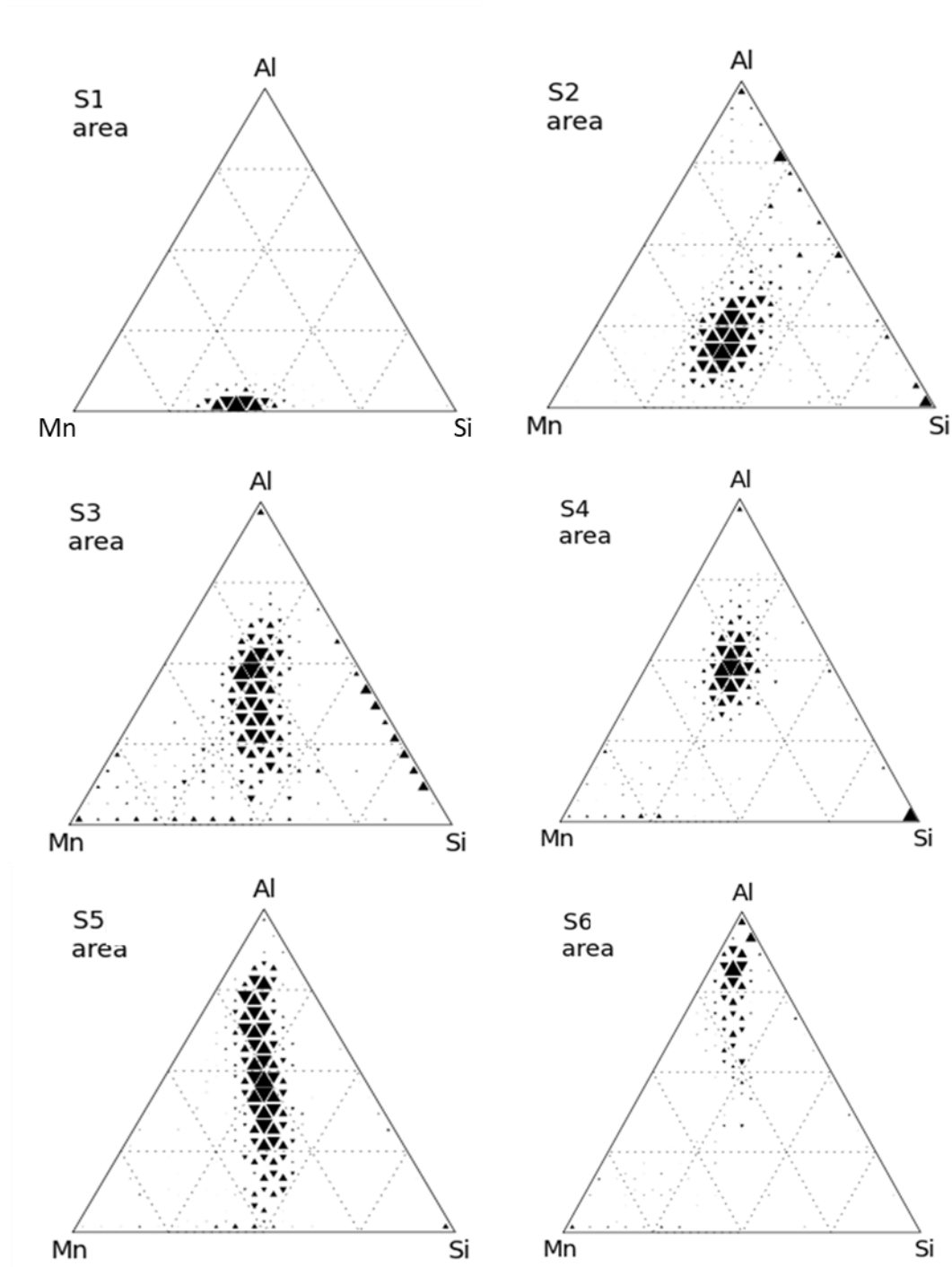


Figure 84 – Atomic fraction ternary diagrams showing inclusion modification with time for the experiment H1 (47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

The obtained inclusion composition values and total aluminum content in steel agree with the model prediction, as shown in Figure 76 to Figure 80. There is a strong deviation from the

predicted and measured concentration of oxygen and total inclusion concentration in steel (Figure 81). Deviation from total oxygen concentration can be caused by increased flotation of inclusions due to agglomeration and measurement variability caused by the limited sample volume and low oxygen content. The compositional spread of the aluminum concentration in inclusions, as seen in Figure 84, can be attributed to the appearance of manganese-silicate inclusions due to microsegregation upon solidification, where the final product of solidification is Al_2O_3 -saturated Mn-Si-Al-O inclusions. The amount of these manganese-silicates is dependent on the previously dissolved oxygen content. It is shown in Figure 85 that although there is a decrease in dissolved oxygen due to Al-pickup, there is still a significant amount of dissolved oxygen. To predict the oxide phases formed during rapid solidification, a Scheil-Gulliver solidification simulation using FactSage is shown in Figure 86. Partitioning of manganese and silicon to the liquid phase results in the precipitation of complex liquid inclusions during solidification in addition to the initial alumina inclusion population.

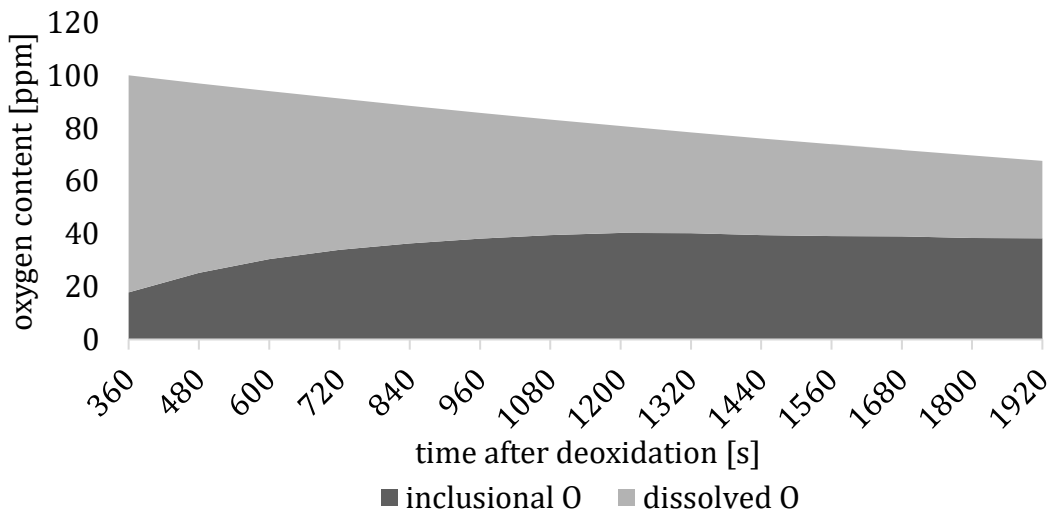


Figure 85 – Predicted inclusion and dissolved oxygen content in steel for the experiment H1
(47%CaO-35% Al_2O_3 -10%MgO-8% SiO_2)

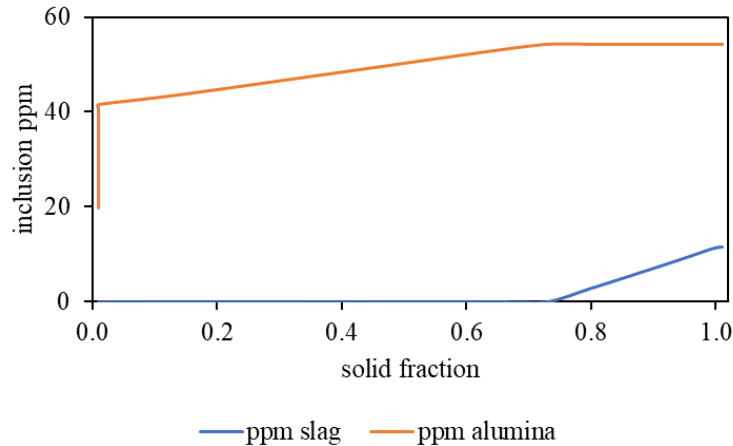


Figure 86 – oxide phases appearing in a 1.25%Mn-0.25%Si-0.03%C-40ppm Al-30ppm O alloy using Scheil-Gulliver solidification model from FactSage; “ppm Al_2O_3 ” refers to the alumina inclusion concentration and “ppm liq” refers to the liquid inclusion concentration in the steel.

The final picture of solidified steel should show us three different inclusion populations in the case shown above:

- 1) initial population of inclusions present in liquid steel due to deoxidation;
- 2) inclusions that are formed during cooling of liquid due to lower solubility of oxygen;
- 3) complex inclusions that precipitate upon microsegregation during solidification.

The segregation of the manganese silicates through the sample diameter is shown on Figure 87 and Figure 88 for sample 5. The inclusions close to the surface are characteristic of a higher [O] content, therefore reoxidation might have happened during sample. Most of the inclusions in the center of the sample are shown to be alumina-rich (Figure 87 and Figure 88). Low aluminum inclusions represent 29% of the area fraction of the total inclusion content in the sample, where they should represent 16.3% of mass fraction according to the Scheil-Gulliver solidification model. The analyzed inclusions appear to be homogeneous (Figure 90 and Figure 91).

The role of alumina as a substrate for manganese silicate precipitation during cooling is also a possibility, creating a complex Al-Si-Mn-O inclusion which would not be liquid at steelmaking temperatures (e.g. mullite). The assessment of the inclusion state of Si-Mn killed steels during steelmaking requires understanding the changes in inclusions occurring during solidification. The prediction of the different inclusion populations appearing during solidification can be made using

a tool as FactSage. Surface reoxidation caused by exposure of red-hot sample to air before quenching were obtained in all samples, with one example shown in Figure 91.

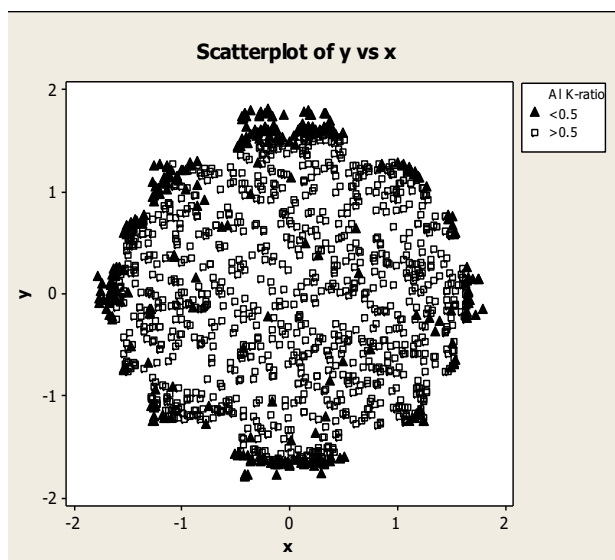


Figure 87 – inclusion map for sample S5; distribution of reoxidation inclusions along the perimeter of the sample. The data points represented by triangles represent the position of inclusions which the Al-K α peaks were more than 50% of the total K α peak counts of Al, Si and Mn for the experiment H1 (47%CaO-35%Al₂O₃-10%MgO-8%SiO₂)

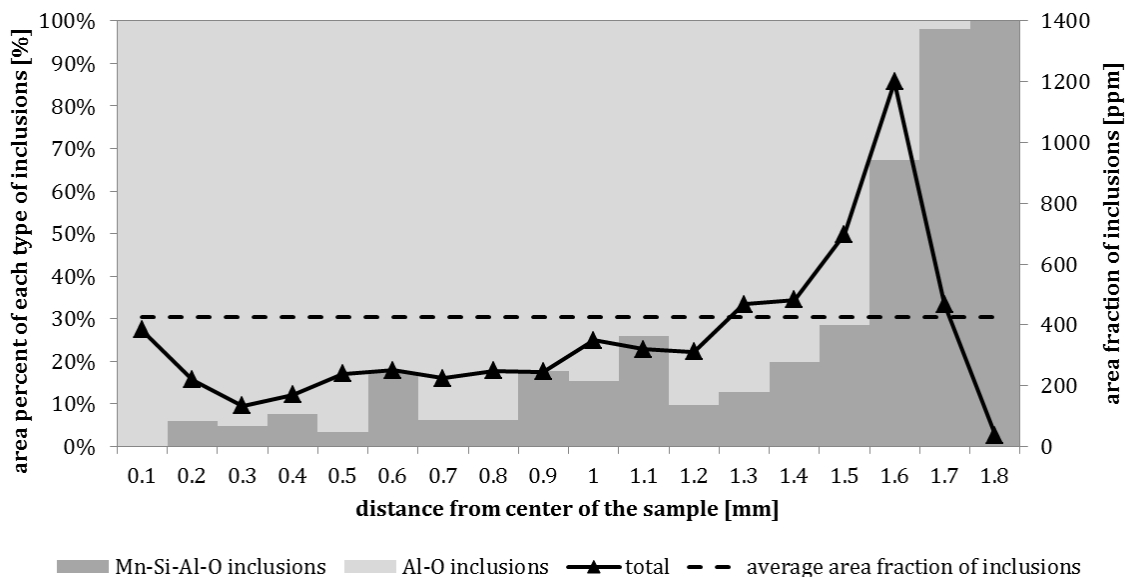


Figure 88 – radial inclusion size distribution for sample S5

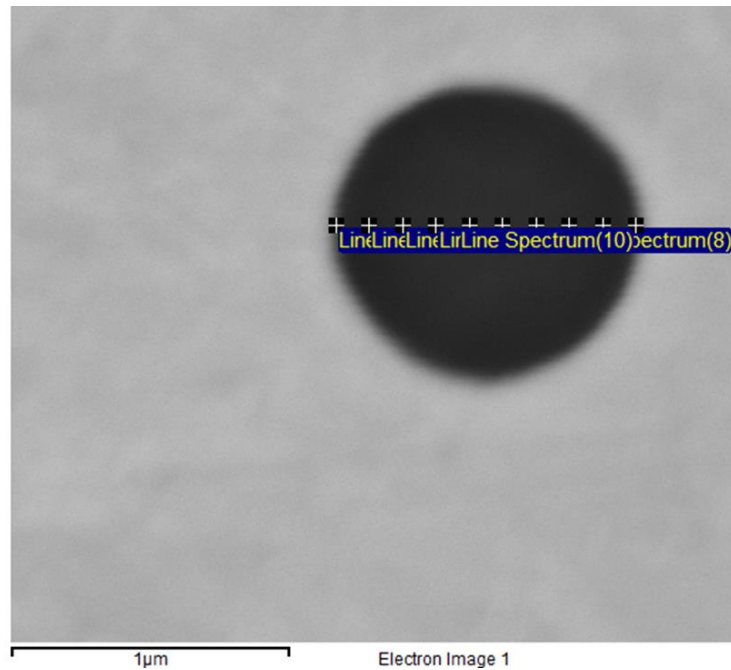


Figure 89 – Complex Al-rich inclusion showing homogeneity in chemical composition (sample S6)

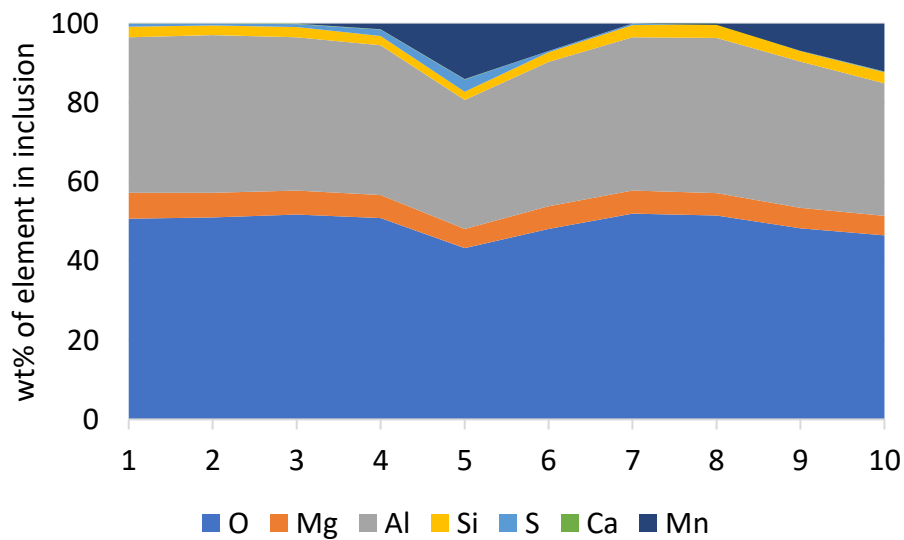


Figure 90 – Composition profile along diameter of Al-rich inclusion from sample S6; EDS sampling positions are from 1 to 10, where 1 is the first and 10 the last from left to right in fig. 19.

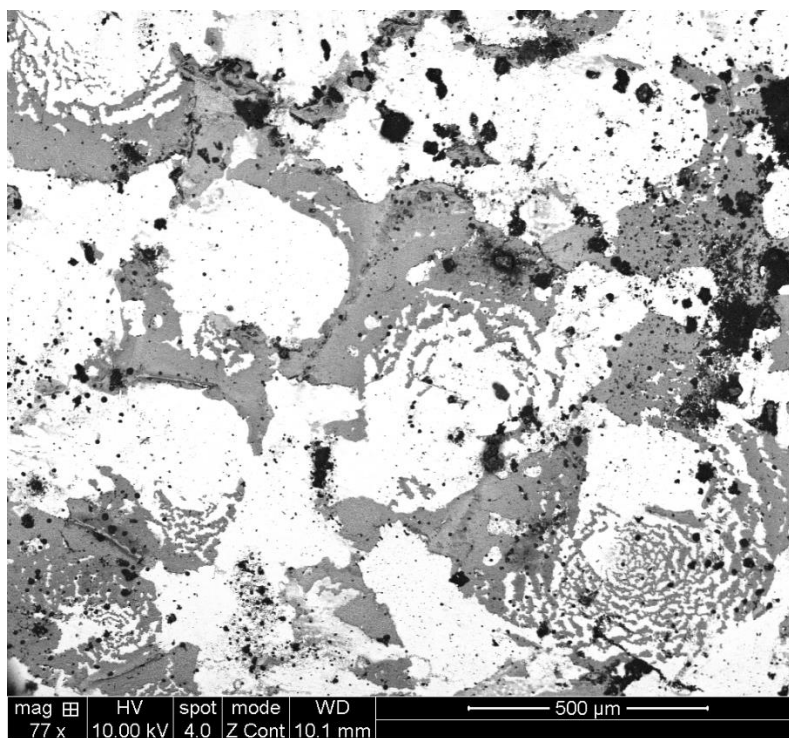


Figure 91 – manganese-silicate oxidation films on sample S6 surface

The experimental work was successful in observing transport of aluminum from slag to steel and the modification of inclusions. The high alumina content in the slag used in this experiment showed transformation of the manganese silicates into aluminates. In practice, higher SiO_2 and lower Al_2O_3 contents should help to reduce the driving force for Al-pickup. Inhomogeneity of inclusion size and composition was observed in this experiment despite the fast solidification and high surface/volume ratio of the sample. Solidification simulations show that different inclusion populations can be formed upon solidification, with high-temperature reoxidation promoting the appearance of Mn-silicate inclusions near the surface of the sample.

5.4.3. Effect of low basicity, low alumina slag on Si-Mn killed steel inclusion evolution (Exp. H2)

According to the equilibrium calculations for both steel-slag systems, presented in Table 14, it is expected that a lower silica concentration and a higher concentration of alumina in slag will strongly affect the extent of aluminum pick-up. The calculated kinetic parameters k' , which is the inverse of time in which reactions reach 62.8% of the expected equilibrium values, are very similar,

which means that any increased rate of aluminum pick-up would reflect differences in equilibrium aluminum content in steel. Pick-up of aluminum should be mostly limited by steel mass transfer. An example of the expected evolution of steel chemical composition for an argon-stirred ladle furnace is given by Figure 92. The expected behavior for the two steel-slag systems was experimentally confirmed, since the reduced SiO_2 /increased Al_2O_3 content in slag effectively increased the extent of inclusion modification, as seen in Figure 93, Figure 94, Figure 95 and Figure 96. Figure 97 shows the calculated oxygen potential at the reaction sites. The oxygen potential for the steel-slag interface for H1 is significantly lower than for H2. Therefore, there should be a larger driving force for the reduction of Al, Mg and Ca for system H1. The inclusions will be modified until the oxygen potential of steel-slag and steel-inclusion interfaces reach equilibrium.

Increased aluminum pick-up will lead to increasing Al_2O_3 content in liquid inclusions ultimately precipitating solid inclusions, as predicted from modeling. The predicted aluminum pick-up rate in inclusions is 9 times faster for low SiO_2 slags. Limited Ca pick-up is predicted by FactSage as seen in Figure 94. However, the SEM results did not show any Ca in the inclusions. Transport of Ca depends on Ca solubility in steel, which is not yet completely understood and quantified. Therefore, the predicted results for calcium transfer is doubtful.

From Table 14, the remaining dissolved oxygen in steel is high enough that a significant population of inclusions will precipitate upon cooling and solidification. It is expected then that the population of inclusions increases as steel solidifies, generating either manganese silicates or manganese sulfides depending on the oxygen and sulfur content of steel. To assess whether the observed inclusions are modified deoxidation inclusions or secondary inclusions from solidification, samples taken from both heats were observed at high temperature in the Confocal Laser Scanning Microscope. The temperature should be high enough that secondary inclusions are redissolved into steel and the excess oxygen will precipitate as inclusions and float on the steel droplet. In Figure 96 it is seen that the samples analyzed from the heat with low silica slag contains inclusions accordingly to their expected phases. Round, liquid inclusions can be seen in sample S2 and solid, clustering inclusions with behavior like that observed for alumina is seen in sample S6 [4].

Table 14 - Relevant equilibrium and kinetic parameters calculated for steel reacting with higher and lower alumina slags

Slag	[Al] _{eq} (ppm)	[O] after deox. (ppm)	[O] _{eq} (ppm)	L _{Al}	k' (10 ⁻⁴ /s)	τ (s)
H1	153	75	8	1342	2.175	4598
H2	9		10	5677	2.055	4866

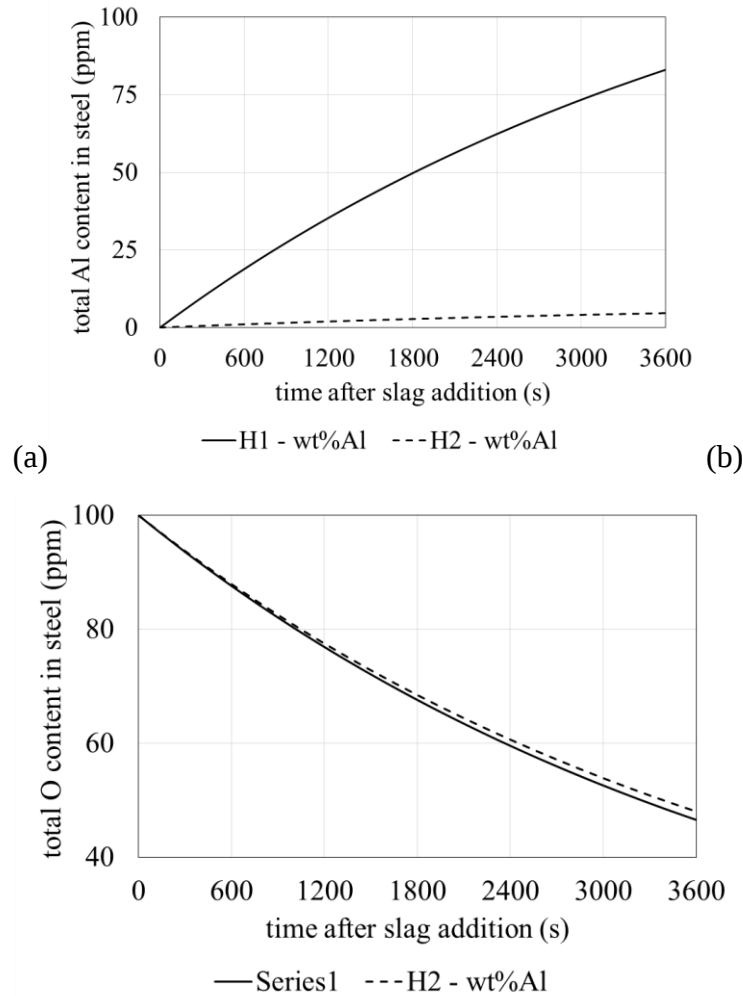


Figure 92 - FactSage simulation of the evolution of (a) total Al content and (b) total O content in steel for both high and low alumina slags. Experiment H1 – 47%CaO-35%Al₂O₃-10%MgO-8%SiO₂, Experiment H2 – 47%CaO-35% SiO₂-10%MgO-8%Al₂O₃.

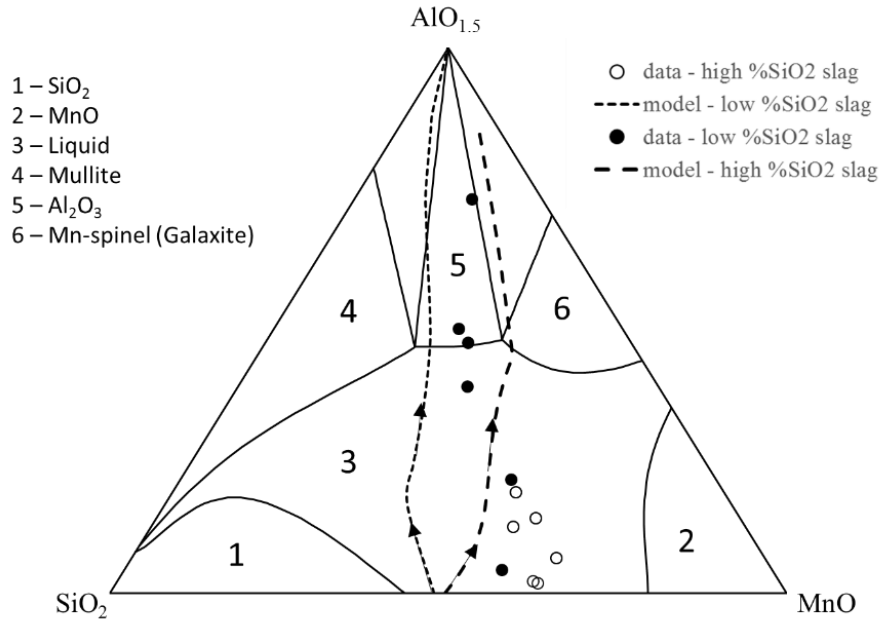


Figure 93 - Isothermal section at 1873 K (1600°C) through the $\text{AlO}_{1.5}$ - SiO_2 - MnO system (compositions plotted as mole fractions; calculated with FactSage 6.4 [5]), together with the inclusion composition trajectories: modeled (broken line) and measured (data points). Experiment H1 – 47%CaO-35% Al_2O_3 -10%MgO-8% SiO_2 , Experiment H2 – 47%CaO-35% SiO_2 -10%MgO-8% Al_2O_3 .

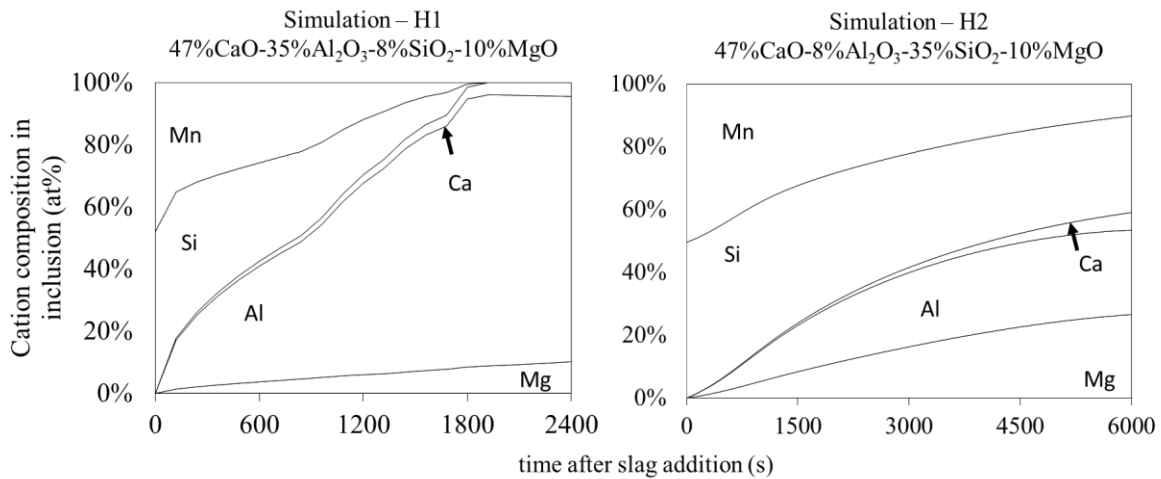


Figure 94 - Calculated cation composition of inclusions for the considered steel-slag systems. Experiment H1 – 47%CaO-35% Al_2O_3 -10%MgO-8% SiO_2 , Experiment H2 – 47%CaO-35% SiO_2 -10%MgO-8% Al_2O_3 .

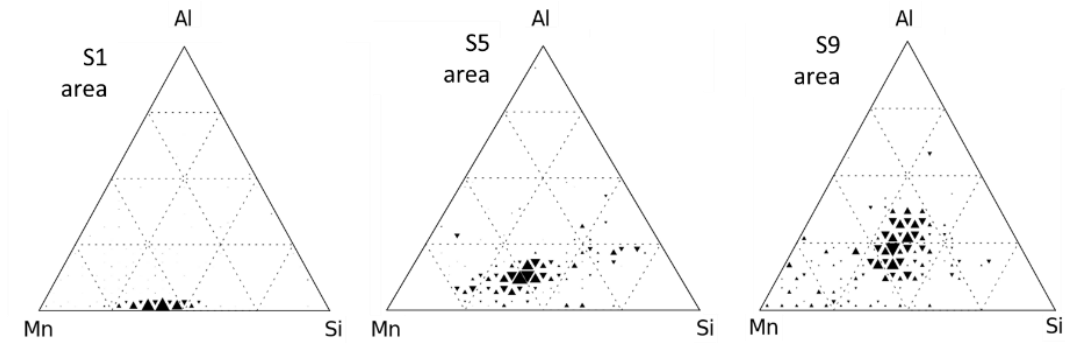


Figure 95 - Proportional symbol plots showing the distribution of compositions of oxide inclusions in steel (exp. H2, low basicity slag) before slag addition (S1), and at various times after deoxidation and slag addition: 60s after deoxidation and 810s before slag addition (S1), 1320s after slag addition (S5), and 4740s after slag addition (S9). Compositions shown as mole fractions.

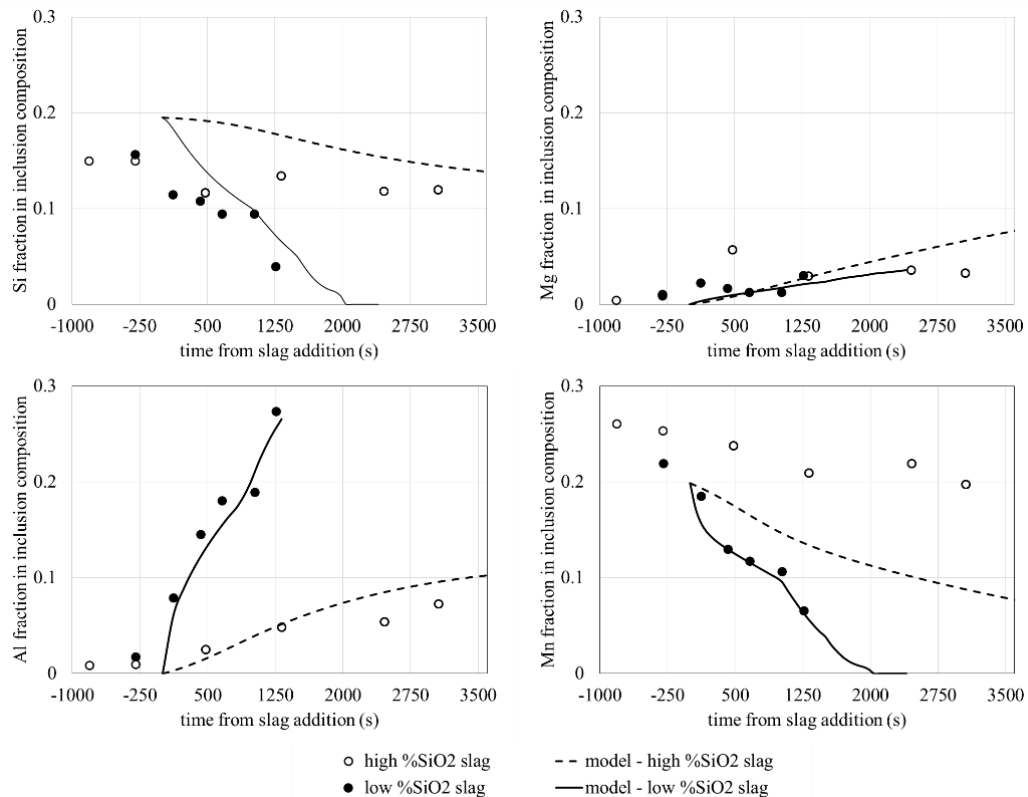


Figure 96 - Change in inclusion composition with time: measured (data points) and modeled (broken lines). Experiment H1 – 47%CaO-35%Al₂O₃-10%MgO-8%SiO₂, Experiment H2 – 47%CaO-35% SiO₂-10%MgO-8%Al₂O₃.

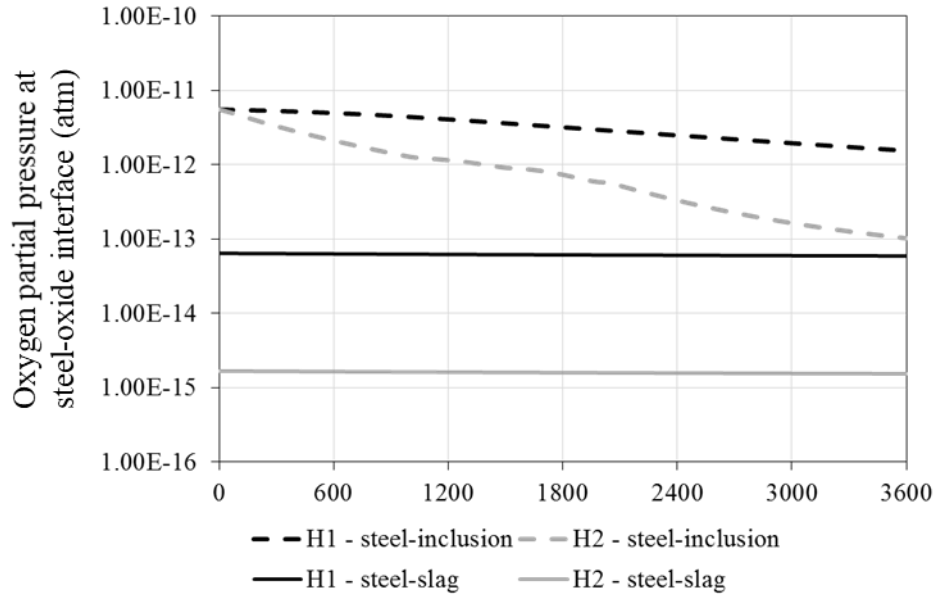


Figure 97 - Calculated changes in oxygen potential at steel-slag interface (full lines) and steel-inclusion interface (dashed lines). Experiment H1 – 47%CaO-35%Al₂O₃-10%MgO-8%SiO₂, Experiment H2 – 47%CaO-35% SiO₂-10%MgO-8%Al₂O₃.

Samples taken from the heat with high silica content in slag did not show any inclusions in CSLM analysis. In line with the high dissolved oxygen in the samples, the inclusions observed in ASPEX are taken to be secondary inclusions. Sampling times for H2 samples were significantly longer than for H1, which means that most of the primary deoxidation inclusions would have floated. The final composition of inclusions at full solidification of steel was calculated using the Scheil-Gulliver solidification model in FactSage 6.4. In this calculation, a fixed temperature drop per equilibrium calculation step is used after which the precipitating phases from the target solution are dropped from the mass balance. Diffusivity in solid phase is assumed to be zero while liquid is assumed to be fully mixed.

In this case, the database FSstel was preferred rather than FTmisc for better partition coefficient modeling. For solidification modeling, the simulated liquid steel compositions at 1260, 2940, 3780 and 4620 seconds after slag addition for H2 were used. The starting temperature was 1600°C and the cooling rate was 10 K/step. The final liquid mass was selected to be 10⁻⁴ g (1 ppm of total simulation mass) for computational time and solution convergence purposes. The expected inclusion composition before and after full solidification is compared to the experimental results

and predicted modified inclusion composition in Figure 98. The Scheil-Gulliver FactSage calculation was also used to predict the inclusion content in solidified steel. The comparison between the calculated values and the experimental results is shown to be reasonable in Figure 99. The dilution of Al and Mg in the experimental results can be explained by the formation of inclusions during cooling and solidification. Due to the local increasing concentration of oxygen, Al and Mg are diluted by Mn and Si reoxidation, which agree with the SEM and CSLM results. Since Ca have very low solubility in steel at steelmaking temperatures, it is not expected that there will be dissolved Ca in steel for precipitation as secondary inclusions. It is also observed that Al and Mg pick-up from steel-refractory-slag reactions have a strong effect on the chemical composition of inclusions formed after solidification.

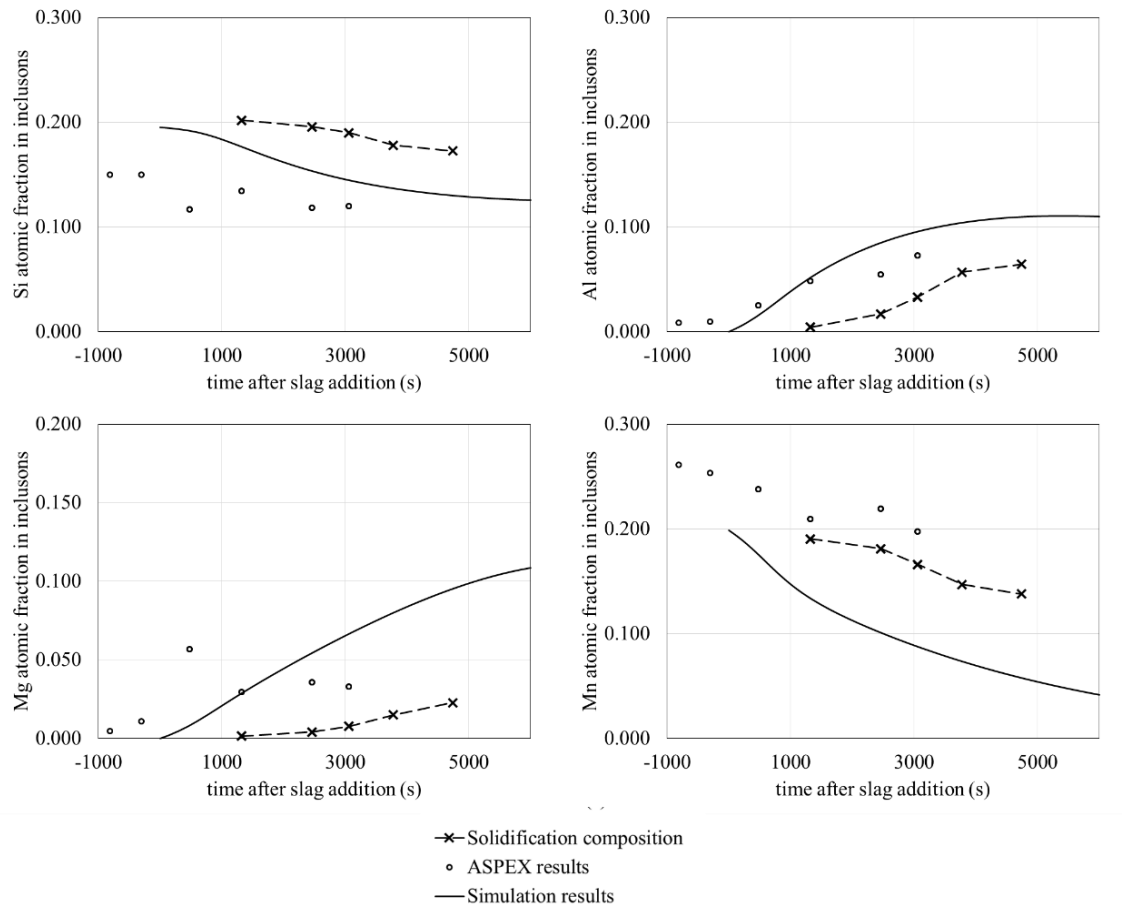


Figure 98 - Comparison of inclusion composition analysis vs FactSage modeling for expected inclusion modification and expected solidification inclusion composition for H2. “Solidification composition” represents the final inclusion composition after solidification. “Simulation results” represents the expected inclusion composition in liquid steel.

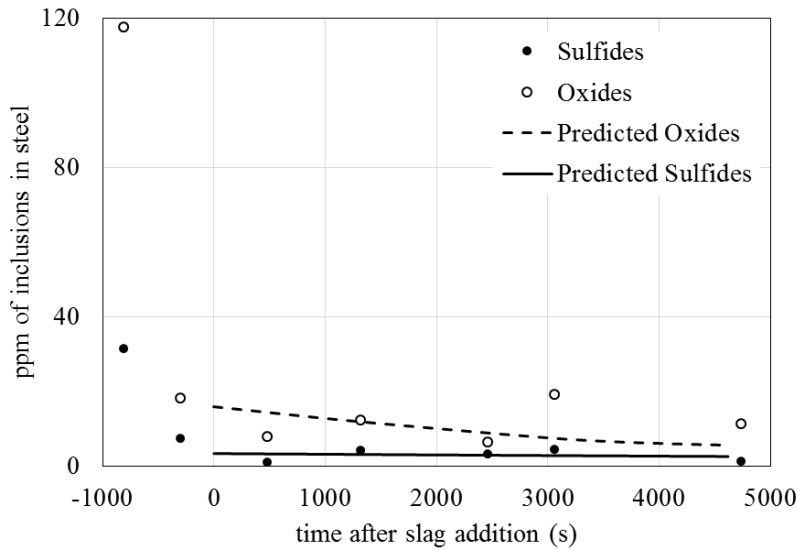


Figure 99 - Comparison between predicted concentration of oxides and sulfides after solidification and experimental data, both for H2. Experiment H1 – 47%CaO-35%Al₂O₃-10%MgO-8%SiO₂, Experiment H2 – 47%CaO-35% SiO₂-10%MgO-8%Al₂O₃.

FactSage calculations show that steel-slag reactions can further modify inclusions and cause the formation of undesired solid phases inside the steel. The experiments successfully showed that slag composition will change the transient inclusion phases as well as the rate of inclusion modification, with substantial changes in inclusion composition, from liquid manganese silicates to partially solid alumina-containing inclusions, because of steel-slag and steel-inclusions reactions. It is shown that basic, high silica slags are less effective in modifying inclusions.

The composition of inclusions formed upon cooling and solidification will depend on the extent of aluminum pick-up in steel, as verified with FactSage and Scheil-Gulliver solidification model. The utilization of this tool reasonably predicted the sulfide and oxide content in solidified steel, agreeing with the CSLM results. The inclusion removal rates are going to be discussed further in this document.

5.4.4. Effect of CaO-MgO-Al₂O₃ slag (minimum a(SiO₂)) on Si-Mn killed steel inclusion evolution (Exp. H3)

In this section, the methodology and results for the experiment H3 is described. This experiment aimed to reach the most reducing conditions for a 0.25wt%Si Si-killed steel, with a double-saturated CaO-MgO-Al₂O₃ slag without initial SiO₂ to maximize reduction of oxides from slag. The expected equilibrium [Al] expected from this experiment is 0.72wt%Al in the steel and 7 ppm Mg according to FactSage steel-slag equilibrium calculations. The induction furnace setup, deoxidation, slag preparation and non-metallic inclusion composition and morphology analysis were as described in the Methodology of the previous chapters.

The inclusion analysis results are presented in Figure 100, together with the FactSage simulations and the inclusion analysis results for H1 and H2. As expected from the initial absence of SiO₂ from the slag, the Mn-silicate inclusions are readily converted to Al₂O₃ by reduction of MnO and SiO₂ from Al pick-up from slag. There was no Ca pick-up detected for this experiment. In the samples taken later during the experiment, many pure MgO inclusion were detected. Al pick-up was similar to the expected values according to the FactSage simulations. In the results presented in Figure 100, it is seen that the kinetic modeling accurately predicts a plateau in the change with time of the Al concentration in inclusions, due to full conversion of inclusions to spinels (MgO.Al₂O₃). The predicted decrease in Al fraction in inclusions at longer times is caused by the predicted increase in Mg and Ca concentrations in inclusions. There is no experimental evidence from these experiments that solid-state diffusion of Mg within solid inclusions is a rate determining step during the conversion of Al inclusions to spinels.

The presence of MgO inclusions also explains the measured increase in overall inclusion Mg content as seen in Figure 100. Since the steel was very clean in the later samples, the presence of MgO inclusions affected the average chemical composition of inclusions. There is evidence of MgO inclusions reacting with liquid steel, showing an Al-rich shell as seen in Figure 101 (probably a solidification product). The calculated stability of MgO inclusions is shown in Figure 102 for both absence and presence of dissolved Al in steel. From these calculations, and the observed reaction product around MgO inclusions, it appears that MgO particles entered the steel and reacted with dissolved aluminum. Therefore, it appears that there was an external supply of MgO, which partially reacted with the melt. This observation is also supported by the larger apparent diameter of MgO inclusions as compared to spinels (in the order of 3 μm larger).

Further analysis of the steel-crucible and slag-crucible interfaces shows that for these slip-cast Y_2O_3 -stabilized MgO crucibles the slag wetted the MgO grains to hundreds of micrometers into the crucible wall. It is also seen that the crucibles became more porous after the experiments due to corrosion of the MgO grains. It appears that the crucible can be a source of MgO particles that are too small to float out of the liquid steel. Therefore, these MgO inclusions are captured during sampling. The steel-crucible interface features are shown in Figure 103.

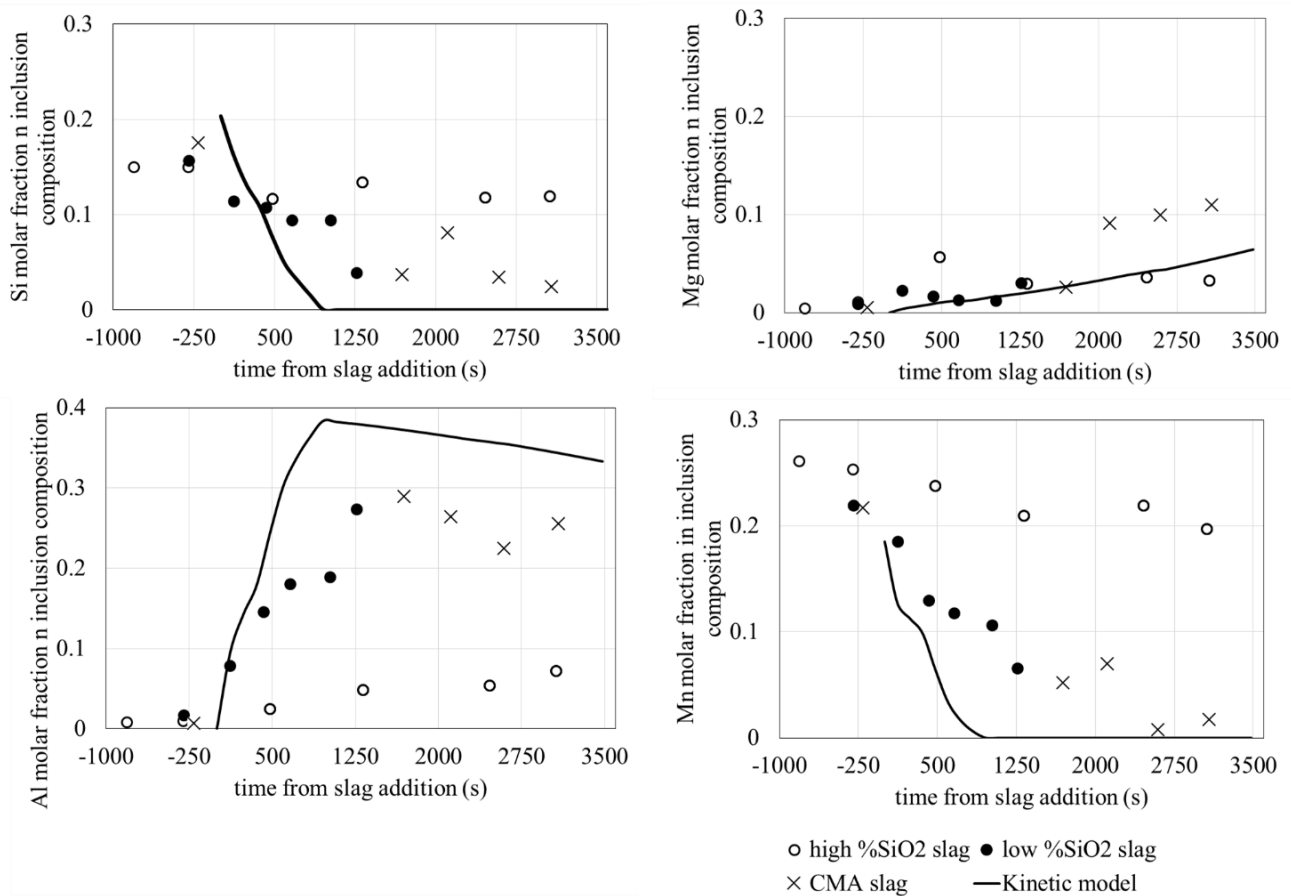


Figure 100 - Non-metallic inclusions: measured change in average chemical composition over time for three different slag compositions (low %SiO₂ slag data points are from exp. H1, high %SiO₂ slag data points are from exp. H2, CMA slag refers to exp. H3). The black line represents the kinetic model prediction for the CMA (H3) slag case. H3 – 52%CaO-41%Al₂O₃-7%MgO

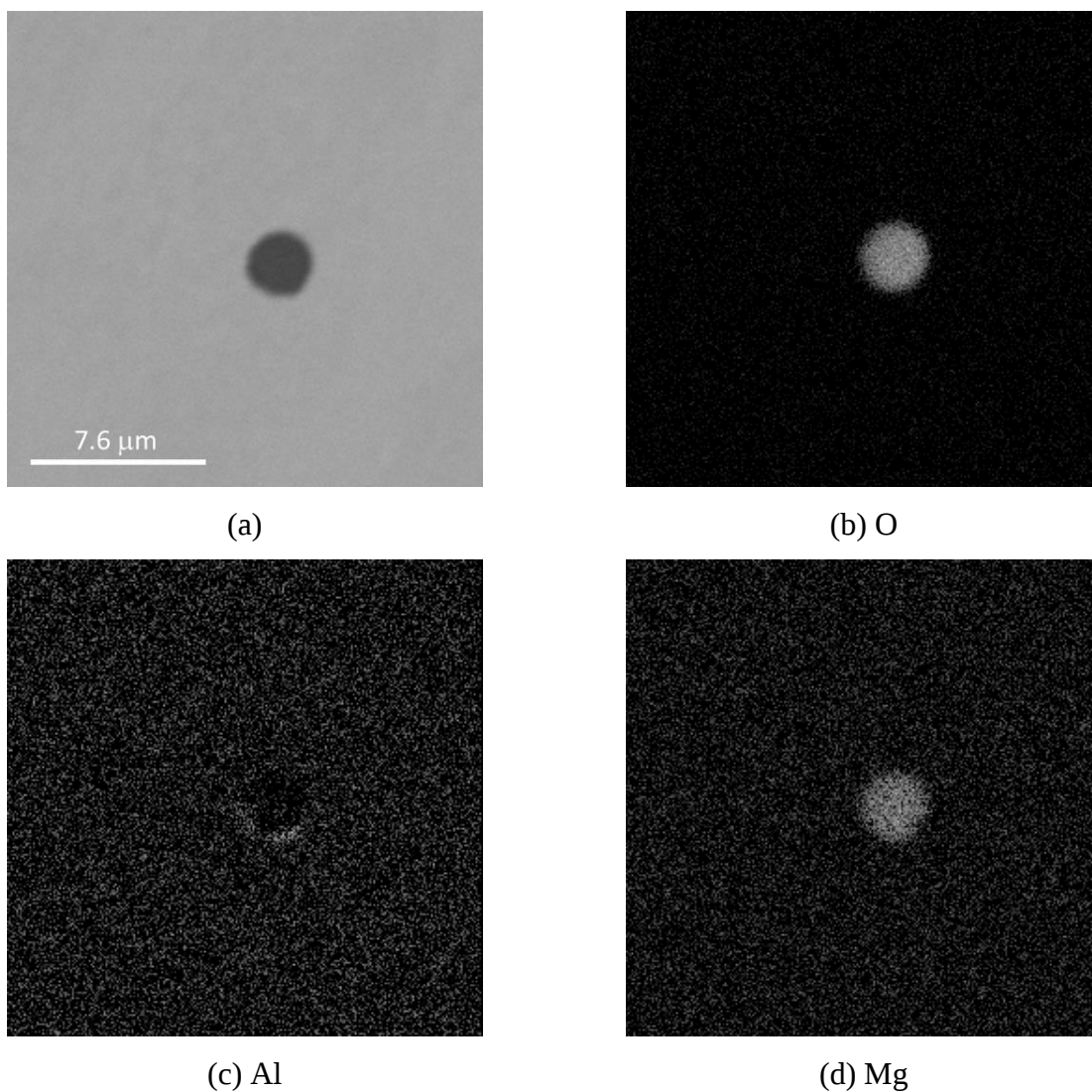


Figure 101 – X-Ray mapping of MgO inclusion found in Sample S5 of CMA slag heat. (a) Backscattered electron image of the inclusion. (b) Oxygen map; (c) Aluminum map; (d) Magnesium map. The MgO particle appears to have reacted with steel forming an Al-rich shell.

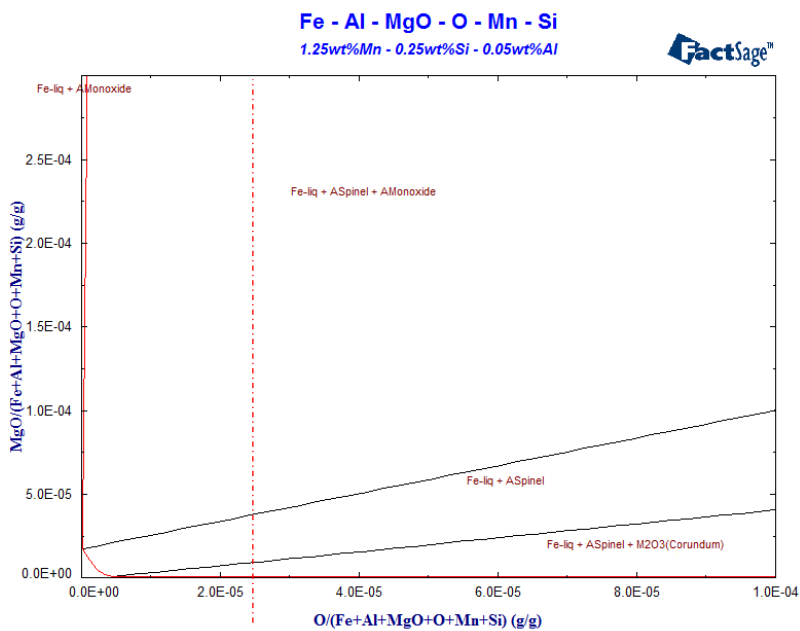
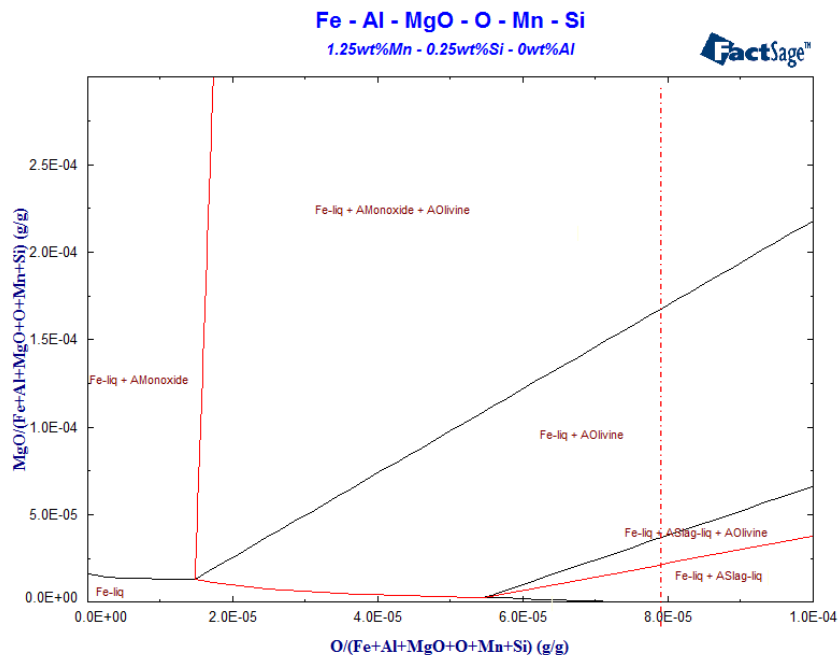
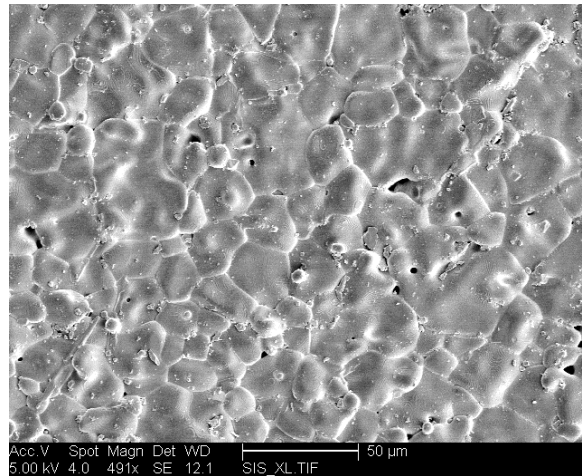
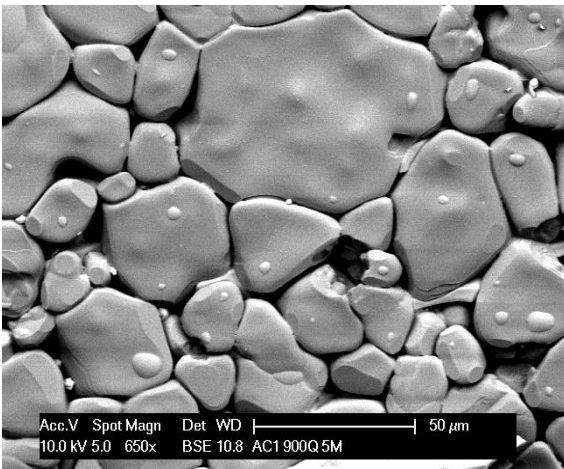


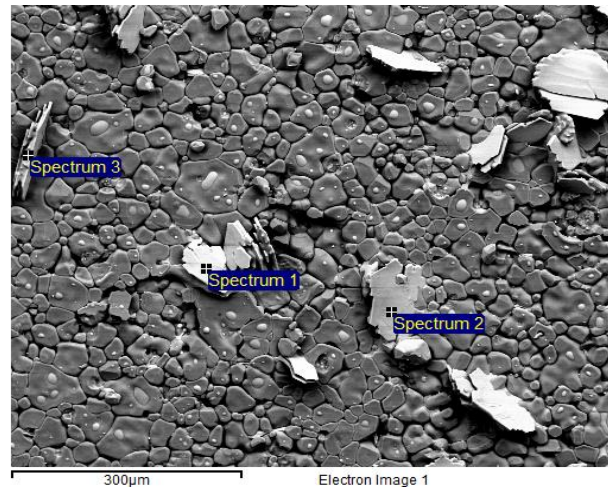
Figure 102 – Stability diagram of MgO vs total oxygen content in steel, calculated with FactSage at 1600°C and 1 atm. (a) No Al in the system; (b) 0.05wt%Al in steel. The dashed red lines represent the typical total oxygen content for Si-Mn killed steels (a) before and (b) after Al pick-up to 500 ppm.



(a)



(b)



(c)

Figure 103 – Inner surface of MgO crucible. (a) Unused MgO crucible; (b) MgO crucible after steel-slag experiment (H2). Corrosion on grain boundaries and missing grains are observed. (c) MgO crucible after steel-slag experiment (H2). Plate-like slag solidification features growing from intergranular spaces.

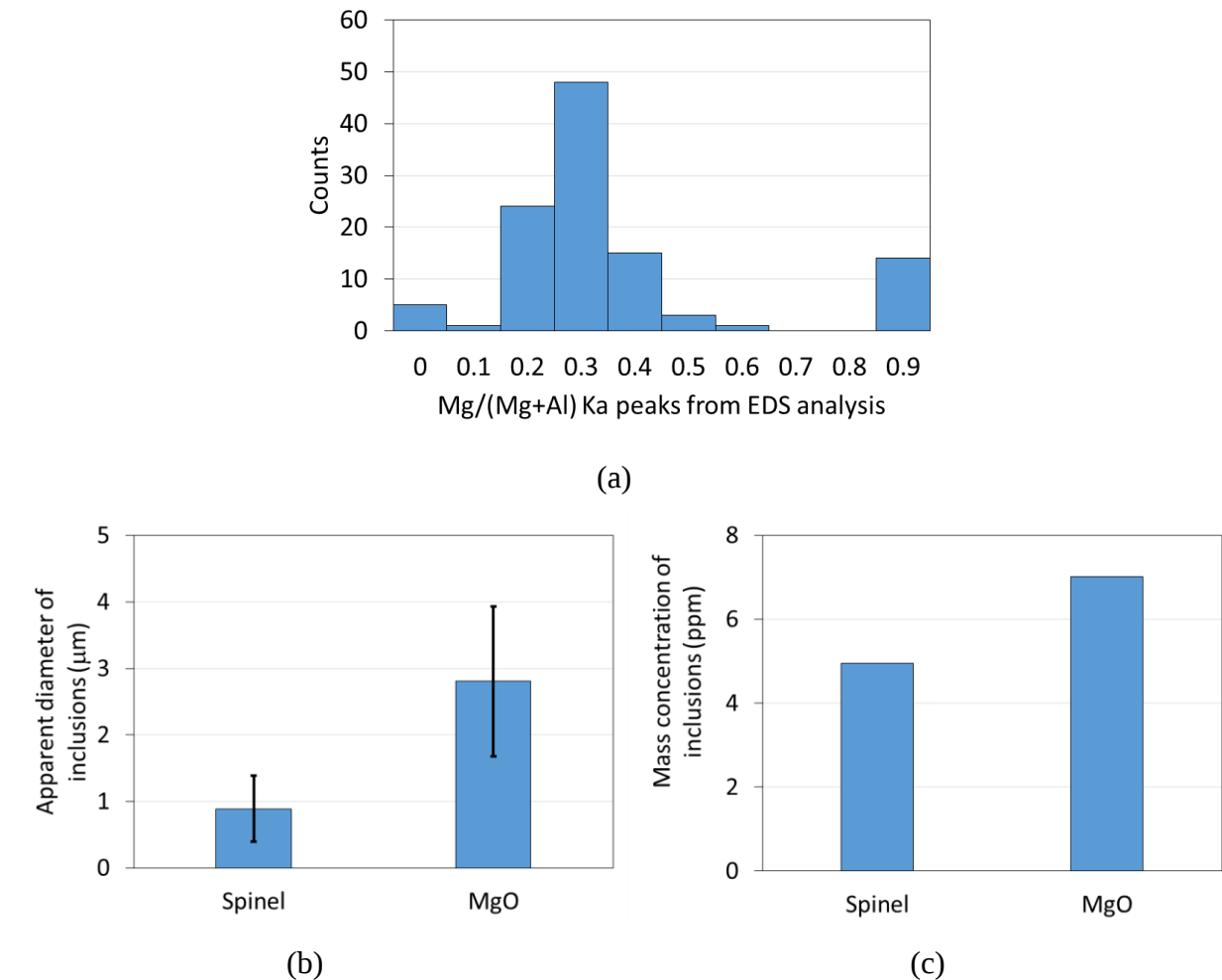


Figure 104 – Statistics of non-metallic inclusions found in latest sample taken from CMA slag experiment. (a) Histogram showing distinct populations of Mg-containing inclusions (mainly spinels and pure MgO). (b) Comparison of mean (columns) and standard deviation (error bars) of non-metallic inclusion apparent diameter between spinel and MgO inclusions; (c) Comparison of mass concentration of spinel and MgO inclusions based on the measured area fraction.

5.4.5. %MnO and %CaF₂ effect on steel-slag-inclusion reactions (Exps. H4, H5 and H6)

In this experiment, MnO and CaF₂ were added to the same base slag composition of H1 to test the idea whether the reduction of MnO from the slag by Si and the subsequent oxygen transfer would translate into interfacial breakup, leading to increase in the mass transfer rate and slag entrapment due to interfacial breakup. The addition of CaF₂ is to test the effect of decreased viscosity of the slag and its impact on the kinetics of inclusion transformation.

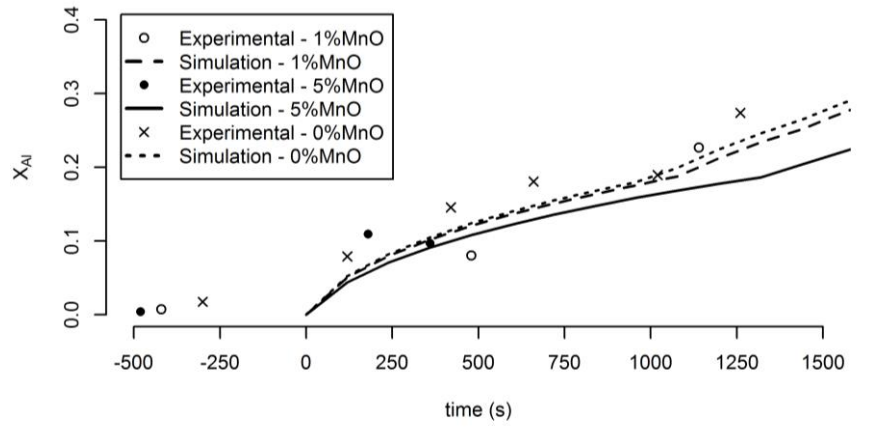
Figure 105 compares the evolution of measured inclusion chemical compositions with simulations. The measurements and simulations agree. There is very little apparent influence of (%MnO) in the slag on the inclusion composition evolution, both experimentally and theoretically. All the results show progressive reduction of MnO and SiO₂ from the inclusions and pick-up of MgO and Al₂O₃. No noticeable CaO pick-up by the inclusions was found. The third data point for the experimental results of 5%MnO slag shows an unusually high MgO content in inclusions. This might be due to erosion and detachment of MgO particles from the crucible; high (%MnO) in the slag can promote slag-crucible reaction through the local formation of (Mn,Mg)O solid solution [118]. It is not the formation of solid solution that is expected to erode the crucible, but the subsequent reduction of MnO by Si in the steel.

Figure 106 similarly compares changes in inclusion chemical composition for steel in contact with 0%CaF₂ (H4) and 10%CaF₂ (H5) slags. The results confirm that the added CaF₂ does not have a strong effect on alumina and silica activities in the slag, since the experimental results with both slags are very similar (Figure 106b). In all these cases, steel-slag reactions are controlling inclusion modification and the one-parameter kinetic modeling successfully predicts inclusion modification. (The one parameter is the mass transfer coefficient in the steel to the steel-slag interface, with the corresponding mass transfer coefficient in the slag taken to be 0.1 times as large.) Figure 107 show the change in total inclusion concentration, based on inclusion analysis and from simulations, also showing no obvious effect of CaF₂ and MnO (in the slag) on the rate in which the inclusions are captured by the slag. The kinetic model assumes that all inclusions in the sub-volume of steel that reacts with slag are incorporated by the slag, the rate-limiting step being the mass transfer of steel to the steel-slag interface (as is the case for dissolved elements). The trends exhibited by the experimental results suggest that the decay in inclusion content is indeed controlled by mass transfer in liquid steel.

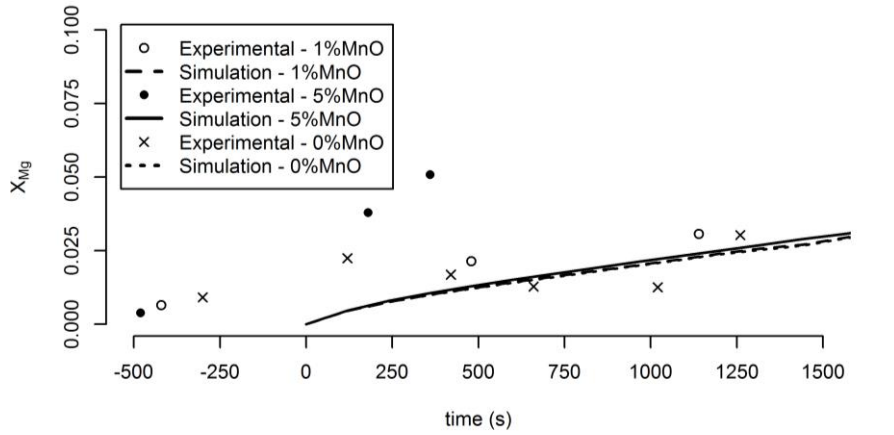
The lack of any significant effect of MnO in the slag on changes (over time) in the inclusion composition appears surprising, given that previous work using a similar modeling approach predicted an effect of FeO and MnO on ladle desulfurization (and Si pick-up by steel) [8]. However, that work considered Al-killed steel, in which the concentration of deoxidizer in liquid steel is around one order of magnitude smaller than for Si-killed steel. For Si-killed steel, the much higher concentration of deoxidizer means that mass transfer of MnO in the slag is more likely to

be rate-determining than Si mass transfer in the steel. In support of this suggestion, Figure 108(a) shows little difference between the calculated oxygen activities for slags with and without MnO. In Figure 108(b), the steel-slag interfacial [%Si] decreased slightly with increasing MnO, but the concentration is still sufficiently high to maintain the low oxygen activities seen in Figure 108(a). From the mass transfer coefficients and densities of the liquid phases, the amount of steel relative to slag reacting to local equilibrium is 28:1. Using a simple mass balance assuming all MnO will be reduced by Si, a consumption of 4.8%MnO from the slag is equivalent to $\Delta[\%Si] = -0.03\%$, which is not enough to either decrease Si or increase SiO₂ activities significantly. Even for 0%MnO slags, there is consumption of Si at the interface due to reduction of Al₂O₃, MgO and potentially CaO. The initial bulk chemical composition of 0.25%Si is denoted in Figure 108(b) as well. For Si-killed steel, the oxygen potential is governed by the reaction between Si and O; unlike the case for Al-killed steel, the concentration of Si in the steel does not change significantly (for the simulated conditions) nor does the slag composition change significantly regarding the concentrations of stable oxides such as CaO, Al₂O₃, MgO and SiO₂. The result is a nearly constant interfacial oxygen activity, independent of the initial (%MnO) in the slag. (The oxygen activity at the steel-inclusion interface decreases over time, approaching that at the steel-slag interface, as the system approaches overall equilibrium through transfer of Al from the steel-slag interface to the bulk steel, followed by reaction with the inclusions).

The conclusions are similar for industrial conditions based on calculations. As examples, Figure 109 and Figure 110 show insignificant effects of the initial (%MnO) in the ladle slag on the change in the calculated total oxygen, and silicon fade.

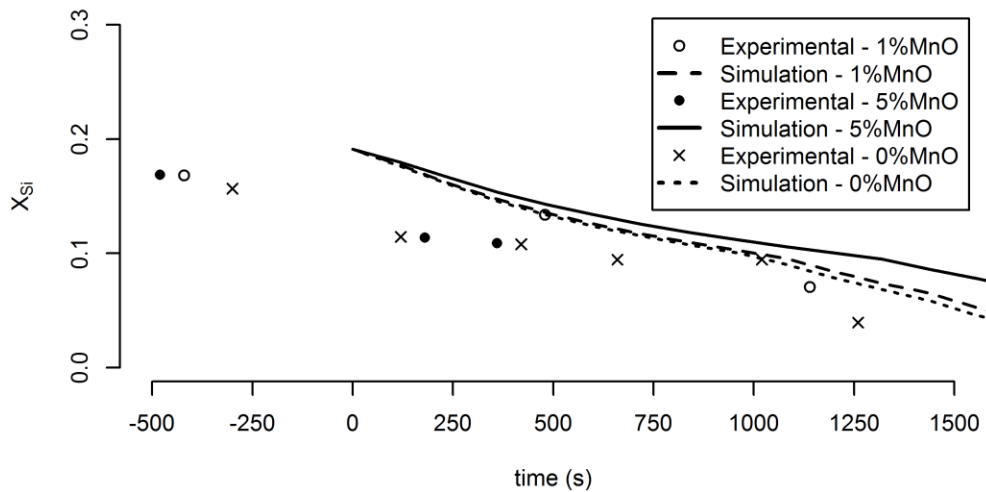


(a)

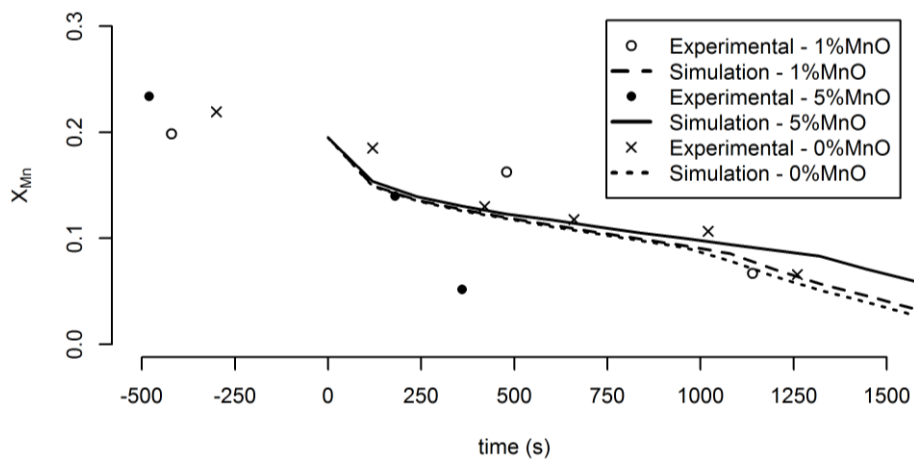


(b)

Figure 104 - Experimental versus modeling results for the mole fraction of elements in non-metallic inclusions for different starting MnO contents in slag. Data points are the area-averaged compositions as measured by SEM-EDS and the lines correspond to FactSage kinetic modeling results. Time zero is the moment when slag is added to the system. (a) Aluminum, (b) magnesium, (c) silicon and (d) manganese.

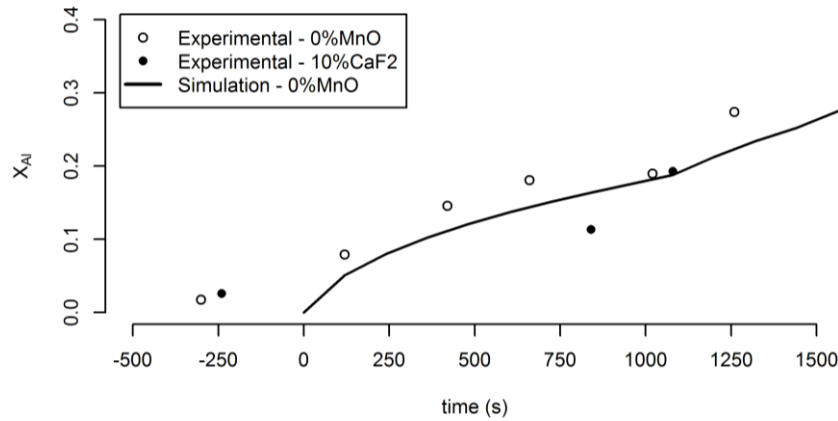


(c)

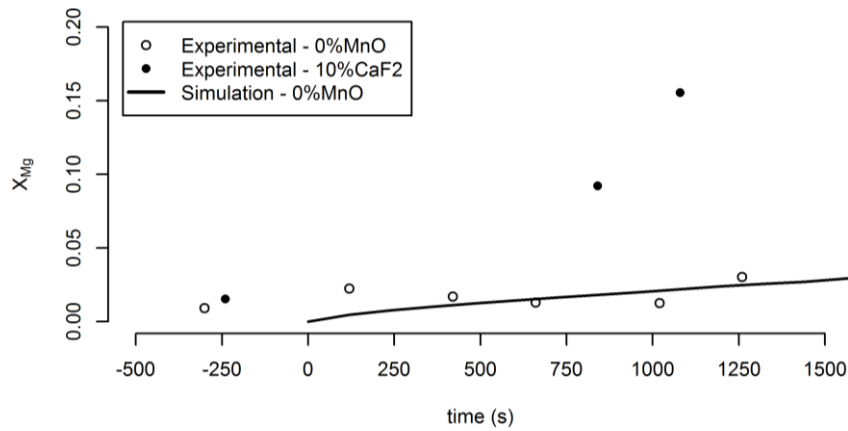


(d)

Figure 105 (cont.) - Experimental versus modeling results for the mole fraction of elements in non-metallic inclusions for different starting MnO contents in slag. Data points are the area-averaged compositions as measured by SEM-EDS and the lines correspond to FactSage kinetic modeling results. Time zero is the moment when slag is added to the system. (a) Aluminum, (b) magnesium, (c) silicon and (d) manganese.

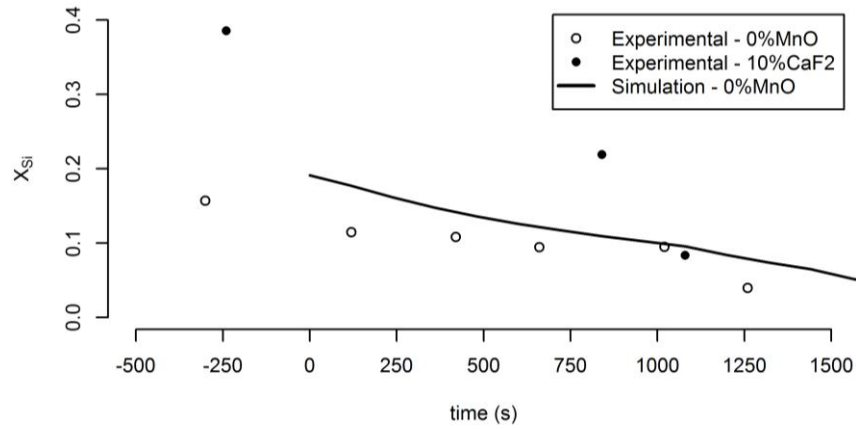


(a)

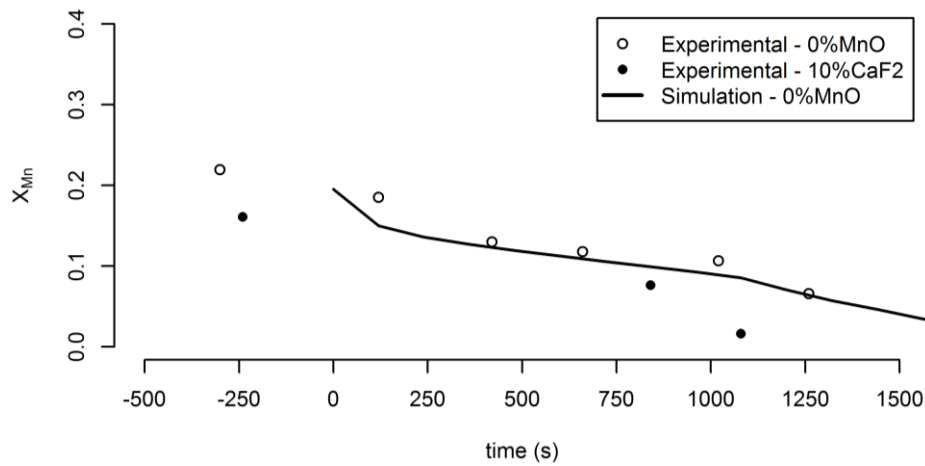


(b)

Figure 105 – Experimental versus modeling results for the mole fraction of elements in oxide inclusions for 0%CaF₂ and 10%CaF₂ contents in slag. Data points are the area-averaged compositions as measured by SEM-EDS and the lines correspond to FactSage kinetic modeling results. Time zero is the moment when slag is added to the system. (a) Aluminum, (b) magnesium, (c) silicon and (d) manganese.

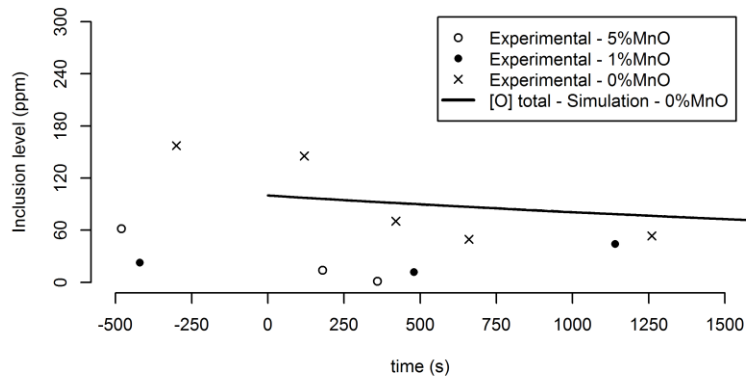


(c)

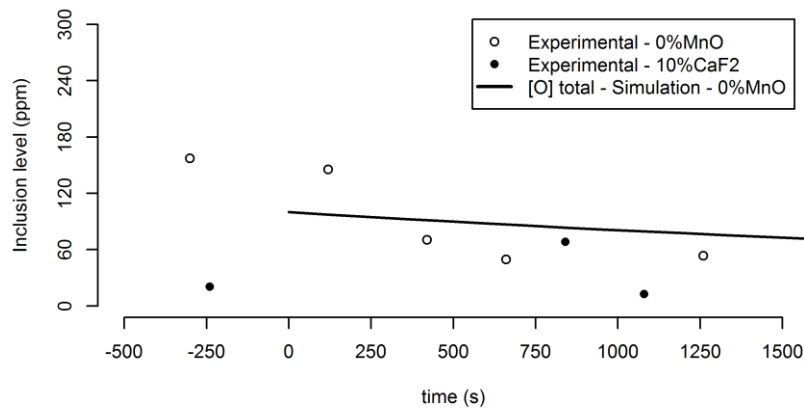


(d)

Figure 106 (cont.) – Experimental versus modeling results for the mole fraction of elements in oxide inclusions for 0%CaF₂ and 10%CaF₂ contents in slag. Data points are the area-averaged compositions as measured by SEM-EDS and the lines correspond to FactSage kinetic modeling results. Time zero is the moment when slag is added to the system. (a) Aluminum, (b) magnesium, (c) silicon and (d) manganese.

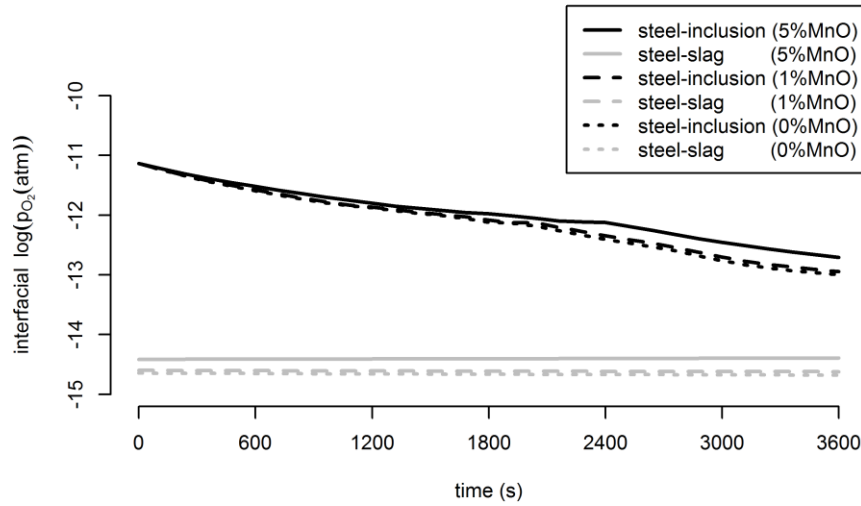


(a)

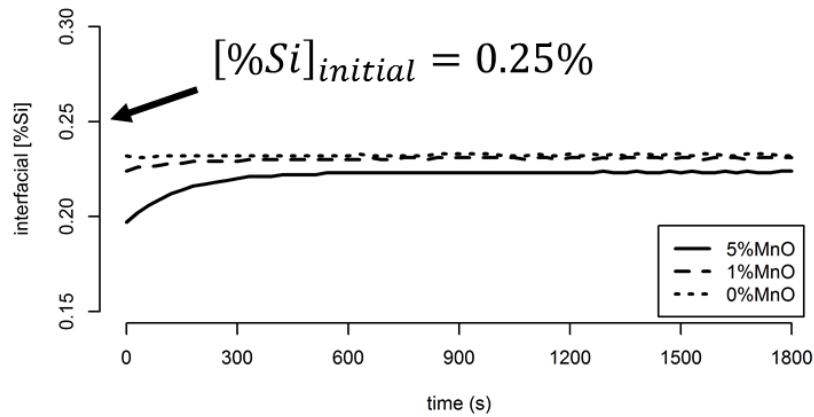


(b)

Figure 107 – Experimental versus modeling results for steel cleanliness for different slag compositions. The data points are the total mass fraction of inclusions in steel as measured by ASPEX, while the solid line is the oxygen (dissolved + bound) concentration in steel as simulated by FactSage. Time zero is the moment when slag is added to the system. (a) Different MnO contents in slag are compared, (b) different contents of CaF_2 are compared.



(a)



(b)

Figure 108 – FactSage kinetic modeling results for experimental conditions showing interfacial chemical composition changes with time in respect to the steel-inclusion and steel-slag reaction sites. (a) Oxygen potential changes in respect to steel-slag and steel-inclusion interfaces. (b)

Concentration of Si at the steel-slag interface at local equilibrium. Black lines represent conditions for steel-inclusion interfaces while grey lines represent conditions for steel-slag interfaces. Solid lines represent 5%MnO slag, dashed lines represent 1%MnO slag and dotted lines represent MnO-free slag.

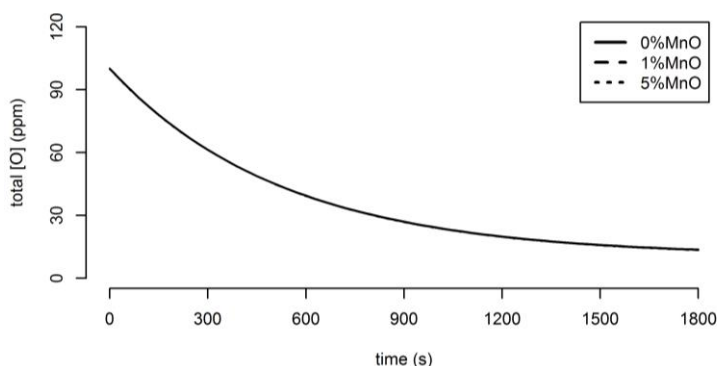


Figure 109 - FactSage kinetic modeling results showing the evolution of total oxygen in steel under industrial conditions for ladle slag containing different MnO contents. Black lines represent 0%MnO, dashed lines represent 1%MnO slag and dotted lines represent 5%MnO slag. The lines are superimposed: the results are not sensitive to (%MnO).

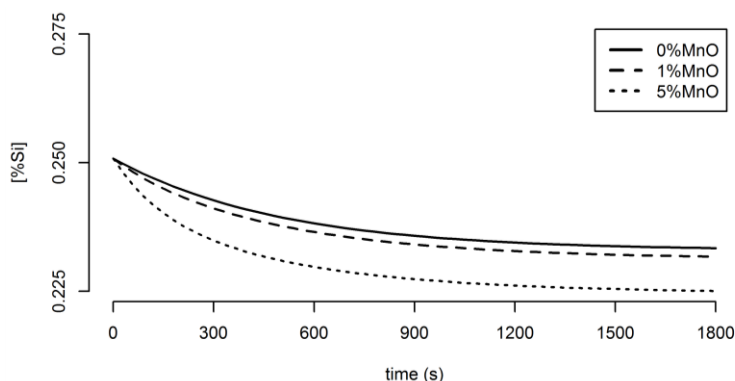


Figure 110 – FactSage kinetic modeling results showing the predicted silicon fade in steel under industrial conditions for ladle slag initially containing 0%, 1% and 5%MnO.

5.4.6. Inclusion evolution during Al_2O_3 -free secondary refining

5.4.6.1. Effect of $\text{CaO-SiO}_2\text{-MgO-CaF}_2$ (CSMF) slag in Si-Mn killed steel in a MgO crucible (H8)

The goal for this experiment was to replicate the steel-slag conditions for desulfurization of Si-killed steels without Al_2O_3 addition in the slag, using a $\text{CaO-SiO}_2\text{-MgO-CaF}_2$ slag instead and observing how the inclusion composition will evolve over time. In industrial conditions, this system yielded CaO and MgO-rich inclusions. The inclusion evolution composition in the absence of intentionally added Al will be analyzed – if there is any reduction of MgO and CaO from the slag, the impact of Ca and Mg on the Mn-silicate chemical composition is expected to be more apparent.

Experimental setup

Desulfurization of Si-killed steels was simulated under laboratory using an RF-induction furnace with a graphite crucible as a susceptor, kept under Ar atmosphere. 600 g of electrolytic iron containing 100-200 ppm O and 40 ppm S were placed inside a Y₂O₃-stabilized MgO crucible with 0.6 g of Fe(II) sulfide (FeS) powder to achieve the starting composition of 400 ppm S. The aimed slag composition is shown in Table 1, and the expected phases at 1600°C – liquid slag, CaO and MgO - can be seen in Figure 111. The chemical composition was chosen to be saturated in CaO and MgO at 1600°C. The MgO crucible containing the electrolytic iron and FeS mixture was heated to 1600°C and when molten a sample was taken. Deoxidation was done using 10g of a laboratory-prepared SiMn alloy containing 68.6%Mn-19.6%Si-9.8%Fe-2%C). A sample was taken 1 min after deoxidation, and then 100 g of the slag powder was added to the system. After the temperature reading went back to 1600°C (after 15 minutes), samples were regularly taken until 3 hours of processing. Three pieces of electrolytic iron of 2.7 to 3 grams previously reoxidized at 800°C in a muffle furnace to contain approximately 0.02 g O each (measured with a 0.0001g resolution balance before and after reoxidation) were then added to the melt to reoxidize the steel to precipitate minor elements such as Ca and Mg (if there were any in solution). Samples were taken immediately after reoxidation then two more within five to ten minutes of each other. The collected samples had their chemical compositions analyzed for metals (Si, Mn, Al, Ca, Mg) with ICP-MS by the courtesy of the RJ Lee Group and for O, S, C and N by LECO combustion analyses by the courtesy of the US Steel Research Center. The non-metallic inclusions were quantitatively analyzed using ASPEX Explorer Automated Feature Analysis and FEG-SEM FEI Quanta600 Aztec feature analysis at 10 kV.

Table 15 - Aimed steel composition at deoxidation laboratory trial.

C	Si	Mn	O	S	Fe
0.03%	0.33%	1.15%	100-200 ppm	400 ppm	Bal.

Table 16 - Aimed slag composition for laboratory trial.

CaO	SiO₂	MgO	CaF₂
56%	24%	5%	15%

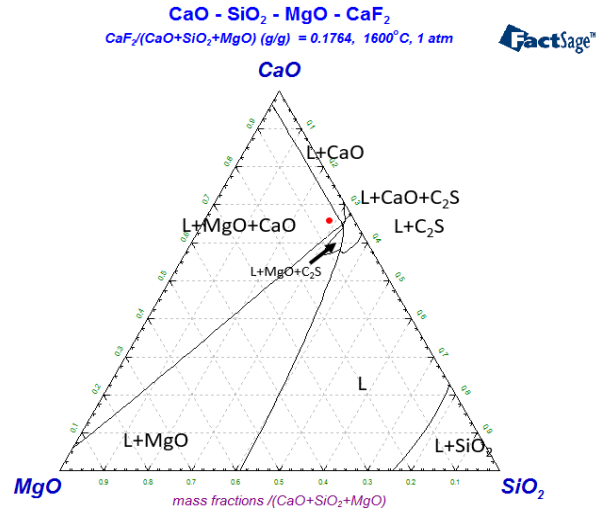


Figure 111 – Pseudo-ternary diagram showing the expected phases at 1600°C for the system CaO-MgO-SiO₂-15%CaF₂ calculated using the FToxid database and the SLAGH solution model for slag. The red dot demonstrates the chosen chemical composition for the experimental setup.

Table 17 – Chemical composition of slag – aimed, before and after the experiment. Analysis was done by XRF using a Bruker XRF Analyzer.

	wt%Ca ²⁺	wt%Si ⁴⁺	wt%Mg ²⁺	wt%Al ³⁺	wt%S
Aimed	48	11	3	0	0
Initial	51	8	2.5	0.4	0.09
Final	50	9	3.3	0.1	0.19

Results and Discussion

In Figure 113 to Figure 116, the evolution of non-metallic inclusions is reported. The inclusions start as liquid, close to equimolar Mn-silicates (MnO.SiO₂) and as processing continues there is continuous pick-up of Mg, and the inclusions follow a straight line between MnO.SiO₂ and forsterite (Mg₂SiO₄). In the first two samples, there is a significant fraction of small MnS particles formed during solidification that are smaller than ASPEX Explorer resolution. Since these inclusions disappear over time, this is an indication that desulfurization is effective. After 30

minutes, most of the inclusions are modified to forsterite, and only 1.4 inclusions per square millimeter were found in sample 8 (Figure 115e).

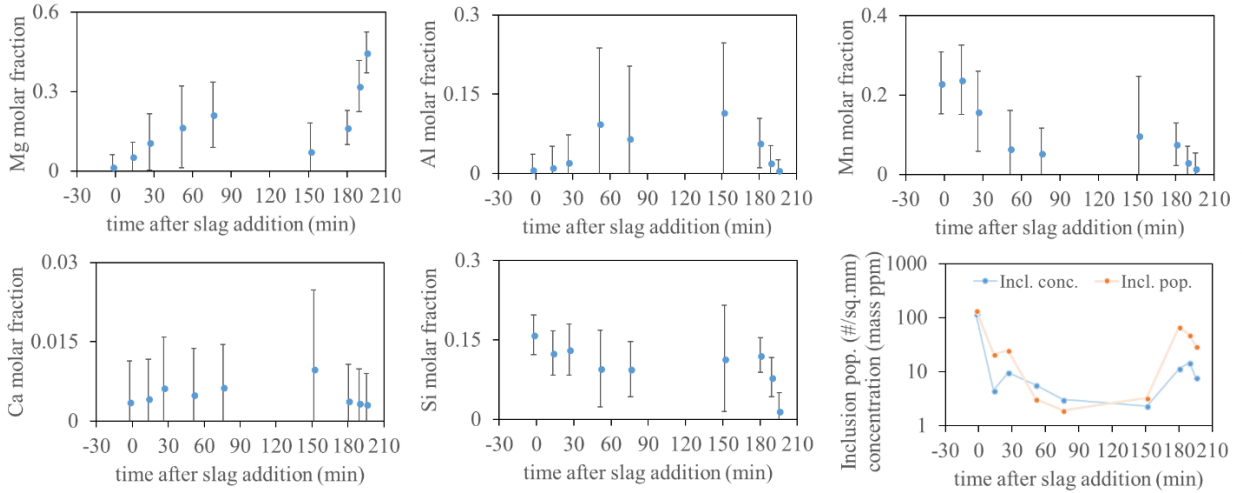
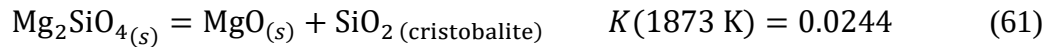


Figure 112 – Summary of oxide inclusions chemical composition for experiment H9 (CaO-SiO₂-CaF₂-MgO). The error bars represent the standard deviation for the chemical composition for each sample. The reoxidation event happened at the 180.3-minute mark.

After reoxidation, 25 ppm of inclusions apparent to ASPEX form as forsterite and are reduced back to MgO in 10 minutes. The stability of forsterite and MgO in the steel can be studied through the following equation:



If forsterite and MgO are mutually stable ($a_{\text{Mg}_2\text{SiO}_4} = a_{\text{MgO}} = 1$), the equilibrium activity of cristobalite in the melt would be 0.0244. However, for the present slag, $a_{\text{SiO}_2(\text{cristobalite})} = 5 \times 10^{-5}$ and $a_{\text{MgO}} = 1$, then the activity of forsterite is 0.0021. This means that forsterite should not be stable if the steel is equilibrated with the present slag. The estimated dissolved oxygen concentration for a 0.2%Si steel equilibrated with MgO and forsterite is around 20 ppm [O] ($p_{\text{O}_2} = 2.7 \times 10^{-13} \text{ atm}$), and for $a_{\text{MgO}} = 1$ and $a_{\text{SiO}_2} = 5 \times 10^{-5}$ the [O] is 5.8 ppm according to

FactSage ($p_{O_2} = 5 \times 10^{-16} \text{ atm}$). Therefore, MgO inclusions are expected to be stable in this system.

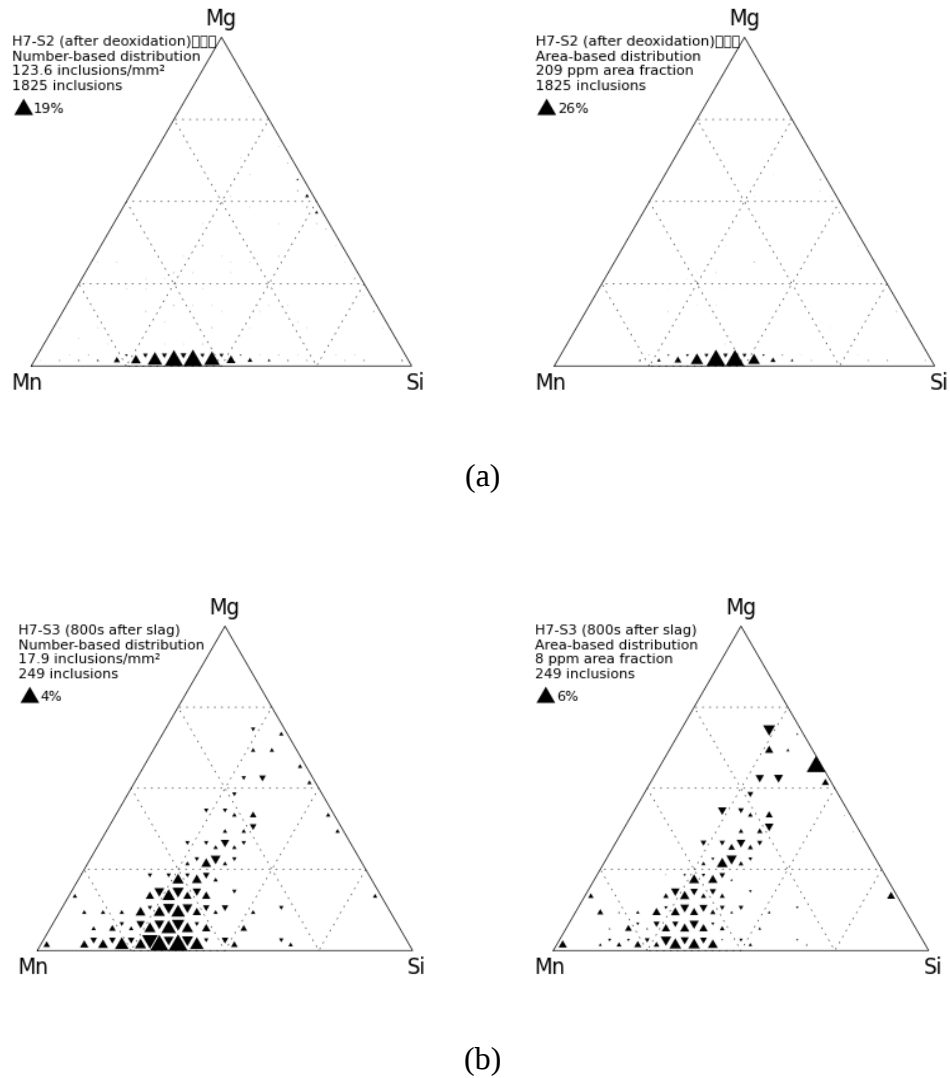
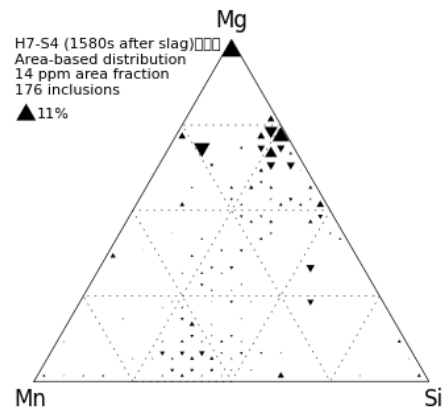
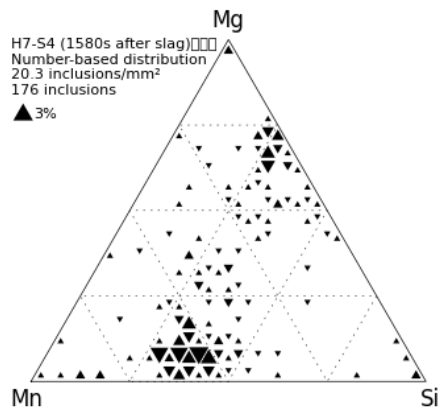
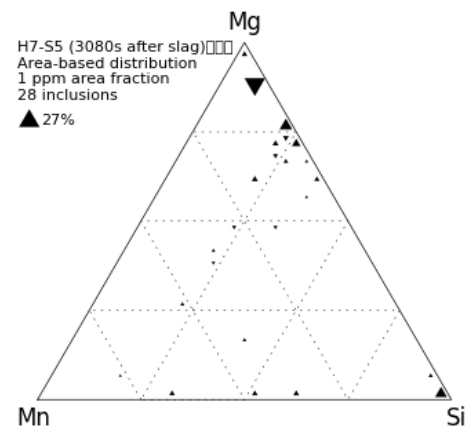
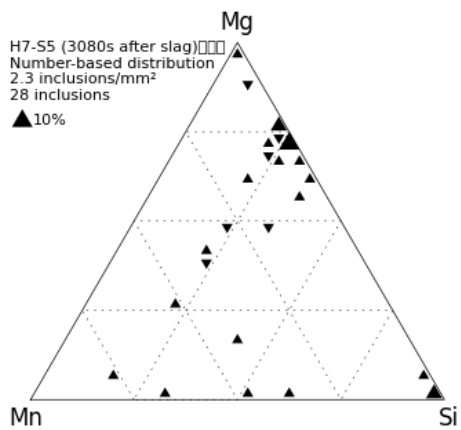


Figure 113 – Ternary diagrams showing chemical composition evolution of inclusions in Si-Mn killed steel during desulfurization with CaO-MgO-SiO₂-CaF₂ slag. Left-hand side diagrams show the number-based distribution of inclusions and the right-hand side show the area-based distribution. (a) Sample taken 108s after deoxidation; (b) 800s after slag addition;

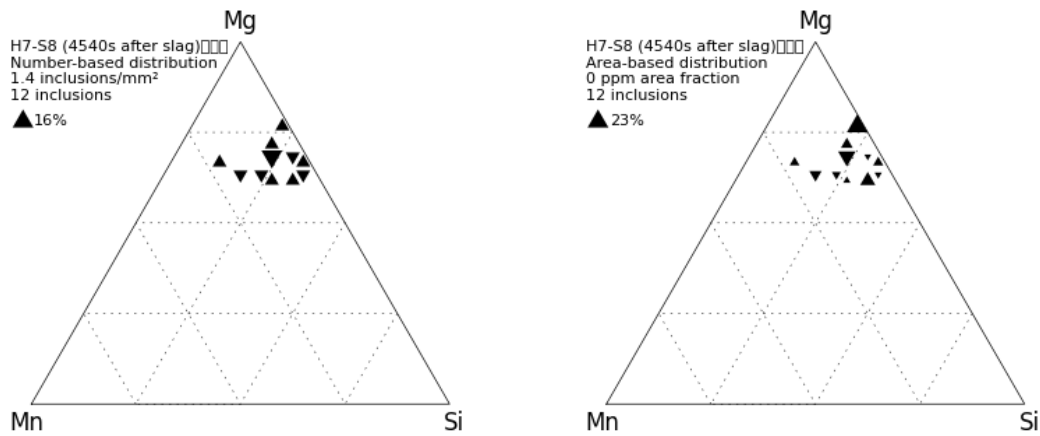


(c)

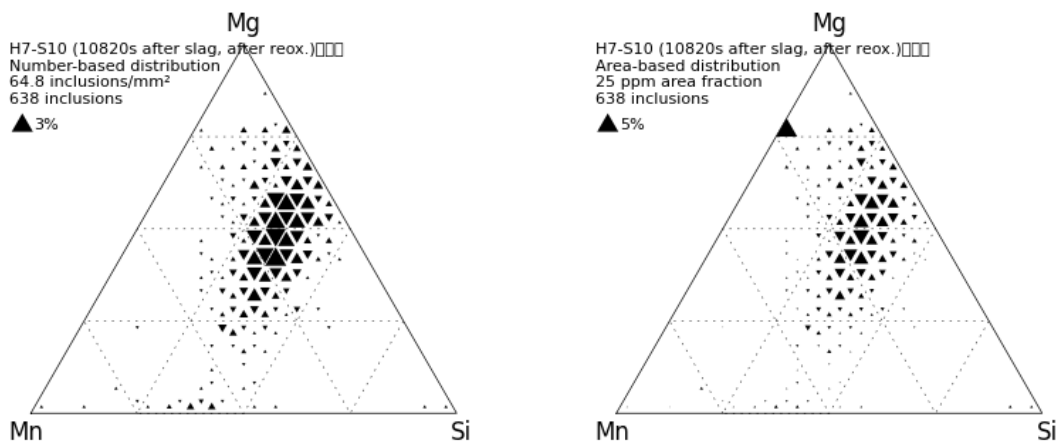


(d)

Figure 114 – Ternary diagrams showing chemical composition evolution of inclusions in Si-Mn killed steel during desulfurization with CaO-MgO-SiO₂-CaF₂ slag. Left-hand side diagrams show the number-based distribution of inclusions and the right-hand side show the area-based distribution. (c) 1580s after slag addition; (d) 3080s after slag addition;

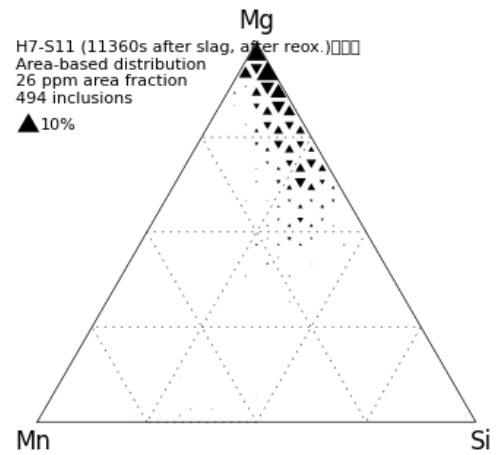
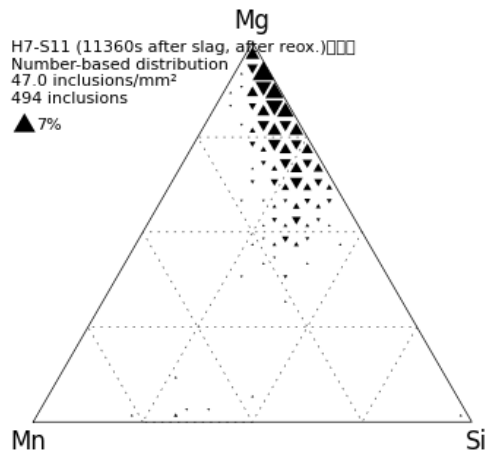


(e)

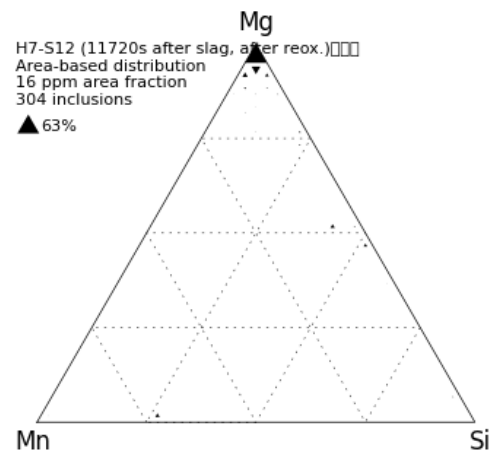
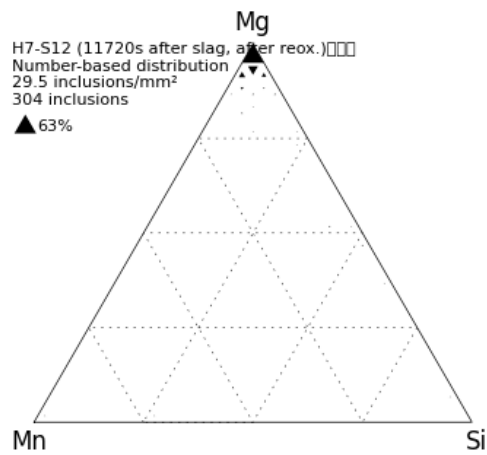


(f)

Figure 115 – Ternary diagrams showing chemical composition evolution of inclusions in Si-Mn killed steel after desulfurization with CaO-MgO-SiO₂-CaF₂ slag. Left-hand side diagrams show the number-based distribution of inclusions and the right-hand side show the area-based distribution. (e) 4540s after slag addition; (f) 10820s after slag addition and immediately after reoxidation;



(g)



(h)

Figure 116 – Ternary diagrams showing chemical composition evolution of inclusions in Si-Mn killed steel after desulfurization and reoxidation with CaO-MgO-SiO₂-CaF₂ slag. Left-hand side diagrams show the number-based distribution of inclusions and the right-hand side show the area-based distribution. (g) 11360s after slag addition and 600s after reoxidation; (h) 11720s after slag addition and 960s after reoxidation.

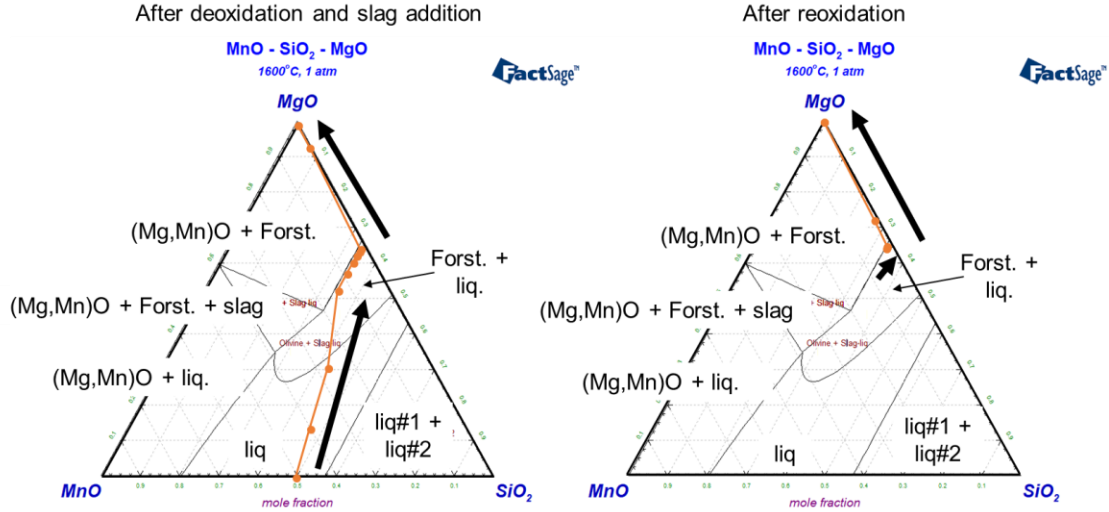


Figure 117 – FactSage kinetic simulation results for the experiment with Si-Mn killed steel in contact with a 56%CaO-24%SiO₂-15%CaF₂-5%MgO slag before and after reoxidation. The connected data points are the predicted inclusion chemical composition. The arrows indicate the direction of chemical composition changes – the inclusions are initially liquid Mn-silicates, which pick-up Mg, forming forsterite and ending as MgO inclusions.

In Figure 118, the chemical compositions for different experiments with regards to Si and S are plotted. The measured Ca, Mg and Al contents were less than 4.5 ppm for all samples, except for the last sample of the heat where the total Mg content was found to be 5.9 ppm. It is seen that there was a very strong Si and S fade. Since the final composition is 4.1 ppm S and the masses of steel and slag are known, the sulfide capacity for this slag can be estimated.

$$W_{S,slag} = 600 * (400 - 4.1) * 10^{-6} = 0.238 \text{ g} \quad (62)$$

$$L_S = \frac{(\%S)}{[\%S]} = \frac{0.238\%}{0.00041\%} = 581 \quad (63)$$

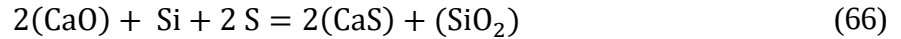
The kinetics of Si and S removal can be written as:

$$\ln \left(\frac{([i] - [i]_{\infty})}{[i]_0 - [i]_{\infty}} \right) = -k't \quad (64)$$

The value of k' is 0.0011 1/s . The value of k' is given by:

$$k' = \frac{k_{eff} \rho_{steel} A}{W_{steel}} \left(1 + \frac{W_{steel}}{W_{slag} L_S} \right) \quad (65)$$

The values considered are $\rho_{steel} = 6962 \text{ kg/m}^3$, $A = 0.002565 \text{ m}^2$, $W_{steel} = 0.6 \text{ kg}$, $W_{slag} = 0.1 \text{ kg}$, $L_S = 581$ and $k' = 0.0011 \text{ 1/s}$. The calculated $k_{eff} = 3.66 \times 10^{-5} \text{ m/s}$ is the same order of magnitude of calculations from previous experiments ($k_{steel} = 8 \times 10^{-6} \text{ m/s}$) but 4.6 times larger. There is, however, an imbalance between Si and S. The extent of Si and S fade is given below. Some Si is inherently consumed during desulfurization. The reaction can be written as the following:



Desulfurization by Si consumes 1 mol Si for 2 moles of S, so the observed Si fade is 6.2 times larger than the expected value of 173 ppm. Then, the required Si to desulfurize the steel should be 0.0037 moles of Si, equivalent to 0.103 g Si. The observed fade is 6 times larger than the expected. This means that there is another oxide being reduced by Si from slag. The only reducible oxide left is MgO, so Si loss might have been caused by Mg evaporation, as well as reoxidation during sampling.

$$[\%S]_f - [\%S]_0 = -395.9 \text{ ppm} \equiv -0.238 \text{ g S} = -0.0074 \text{ mol S} \quad (67)$$

$$[\%Si]_f - [\%Si]_0 = -0.107\% \equiv -0.642 \text{ g Si} = -0.0229 \text{ mol Si} \quad (68)$$

After the experiment, there was an increase in both SiO_2 and MgO as seen in Table 17. The increase in SiO_2 is related to the consumption of $[\text{Si}]$ as seen on Figure 118. The increase in MgO content can be related to wear of the crucible caused by slag penetration.

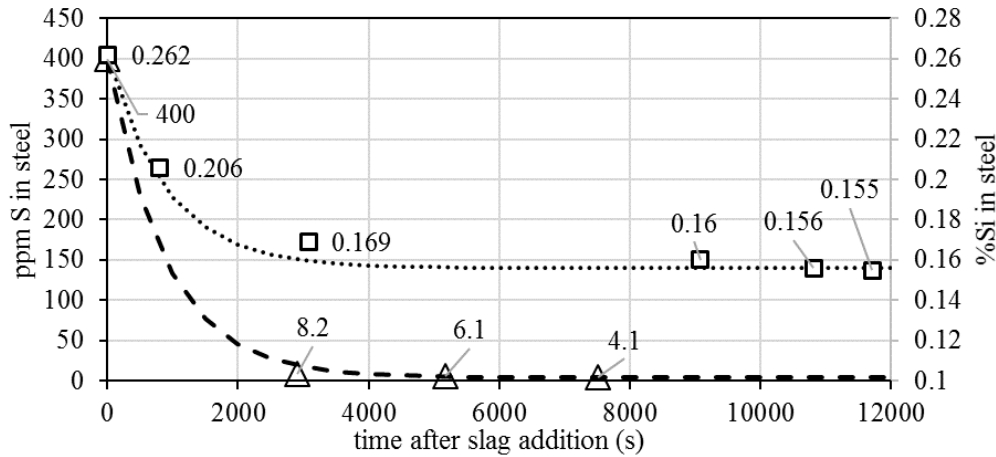


Figure 118 – Chemical analysis for the desulfurization experiment showing Si and S fade. Triangles represent measured ppm S in sample while squares show measured wt%Si. The dashed lines are fitted to the observed values using the same kinetic parameters.

Therefore, we can conclude that:

- Refinement of Si-killed steels with very basic, high CaF_2 slags can drive the steel to very low levels of oxygen and sulfur. Vacuum degassing can guarantee strong mixing for desulfurization.
- Experimental results showed the same trends from industrial practice – strong desulfurization, ending with clean steel and with very low inclusion levels. Mg pick-up happens transforming Mn-silicates into forsterite. The final inclusion compositions are very dependent on the dissolved oxygen in ladle.
- Si fade in the experiment is much higher than expected. This effect is most likely to be caused by reoxidation of the melt.

5.4.6.2. Effect of CaO-SiO₂-CaF₂ (CSF) slag in Si-Mn killed steel in a CaO-3%ZrO₂ crucible Oxide inclusion modification of Si-Mn killed steel in CaO crucible in presence of CaO-SiO₂-CaF₂ slag

Since there was no observable Ca pick-up in any of the previous experiments, this experiment intended to assess whether the reduction of MgO from slag and refractories masked the reduction of CaO from slag by Si in the steel, and if reoxidation of the steel would reprecipitate whatever Ca that is dissolved in the steel. Since Mg was readily reoxidized in the previous section, if Ca has a similar solubility than that of Mg, the observed behavior upon reoxidation should be the same (that is, the observable precipitation of Ca-silicates). In this experiment, a CaO-saturated CaO-SiO₂-CaF₂ slag is added on top of a Si-killed steel, contained inside a CaO-3%ZrO₂ crucible.

Experimental

200g of electrolytic iron containing around 300 ppm of oxygen and less than 10 ppm of sulfur was molten and heated to 1600°C in a calcium oxide crucible. After molten, the steel was deoxidized with 4.7 g of laboratory-made silicomanganese alloy (70%Mn-20%Si-10%Fe) to achieve an aimed chemical composition of 1.3%Mn and 0.3%Si and form liquid manganese silicates as the primary deoxidation product. 57g of pre-molten CaO, Ca₂SiO₄-saturated CaO-SiO₂-CaF₂ slag (59%CaO-27%SiO₂-14%CaF₂) was then added to the system and let react for over two hours and half to reach equilibrium. Afterwards, two oxidized electrolytic iron pieces were added to the system. The pieces had been reoxidized in a muffle furnace at 800°C for 15 minutes. The weight gain due to reaction with oxygen was measured as 0.047g. Steel samples were taken 1) after slag addition, 2) before reoxidation and 3) after reoxidation. The steel-crucible interface was then analyzed using SEM/EDS to investigate what is the resulting reaction product. A cross-section of the crucible was also prepared using cold mounting resin and polished to 1 micron and analyzed using the SEM.

Results and Discussion

For the studied system, the activity of SiO₂ is equal to 6.2×10^{-5} . Given that the steel contained 0.3%Si, the equilibrium oxygen partial pressure at steel-slag interface is $4.6 \times 10^{-16} \text{ atm}$, with oxygen activity of 0.64 ppm O. The oxygen activity is comparable to a steel containing 0.28%Al in equilibrium with pure alumina.

Figure 119 gives a summary of how the inclusion number changed after deoxidation and slag addition. The mass fraction was estimated, by taking the area fraction to be the same as the volume fraction and an average inclusion density of 3.5 g/cm^3 . In the first sample taken 11 minutes after slag addition, the inclusions were manganese silicates with slight Al and Mg pick-up. After 2.5 hours, there was only 1 ppm of area fraction of inclusions in the analyzed cross section, with 1.6 inclusions per square millimeter. After addition of the electrolytic iron pieces, there was an apparent increase of 7 ppm of oxygen as estimated from the inclusion analysis. If all the oxygen present in the oxidized electrolytic iron was converted to inclusions, an increase of 235 ppm in O should be expected. However, most of the developed scale is dissolved when penetrating the slag layer on top of the steel. After reoxidation, there was a slight reduction in size (Figure 120).

Figure 121 to Figure 124 demonstrate how non-metallic inclusion composition evolved over time. In Figure 121, the chemical composition of the inclusions is plotted as cation fractions. At 11 minutes after slag addition, there is a slight Mg and Al pick-up. Figure 122 shows the manganese silicate composition in the $\text{MnO-SiO}_2\text{-AlO}_{1.5}$ ternary diagram.

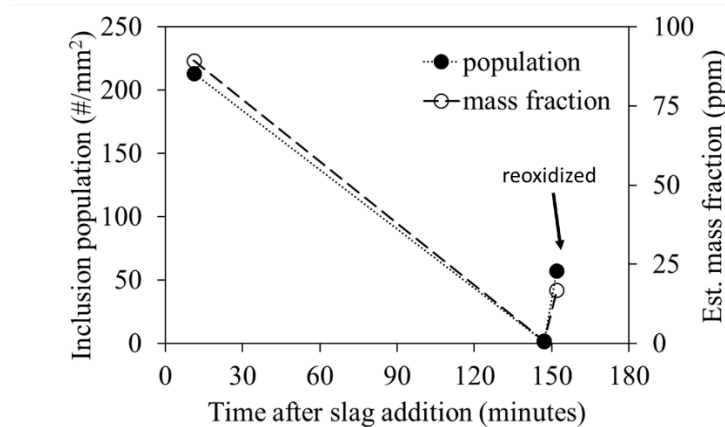


Figure 119 – Oxide inclusion population and estimated mass fraction evolution after slag addition. Full circles represent the inclusion population and hollow circles represent the estimated mass fraction for each sample.

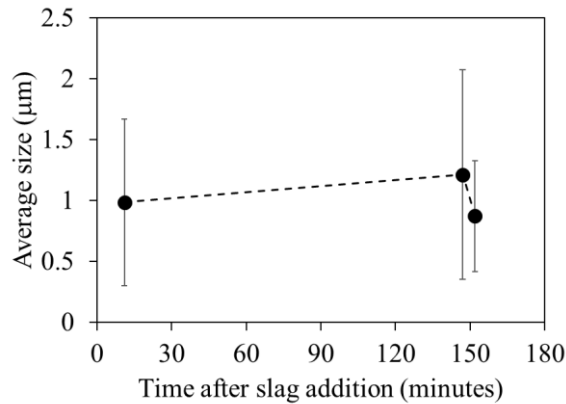


Figure 120 – Oxide inclusion apparent diameter evolution after slag addition. Error bars are the standard deviation of the apparent diameter in each sample.

After 147 minutes, the few inclusions remaining are silicates containing Ca, Zr, Mg and Al. These elements were picked up from reaction from slag and crucible, and the source of these elements was found once the crucible is analyzed. However, the very small number of such inclusions does not provide statistically relevant information about what is in the melt. At this stage, the residuals such as Ca, Zr, Mg and Al should be in equilibrium with the oxides in the slag. In Figure 123, the oxide ternary diagrams show that the inclusion compositions are very scattered, although there are some inclusions consistently in the spinel range of $\text{MgO-Al}_2\text{O}_3$ diagram with some ZrO_2 and CaO . The measured average composition was calculated by FactSage 7.1 to be 95.9% liquid and 4.1% tetragonal ZrO_2 , although the predicted SiO_2 (cristobalite) activity for this system is calculated to be 0.86, which is too high to be stable in the experimental conditions. This is also a result of the low inclusion concentration and does not affect the reoxidation results.

The reoxidation of the melt precipitated oxides containing Zr, Ca, Al and Mg. The precipitation of Al and Zr was notable, indicating the presence of these dissolved elements in the melt prior to reoxidation, as was Ca. That indicates that Ca had indeed been reduced from the surrounding oxide system and dissolved in the steel. The average composition is calculated by FactSage 7.1 to be 92% liquid, 5% tetragonal ZrO_2 and 3% mullite. Again, the calculated SiO_2 activity is much higher than expected (0.3). In Figure 124, it's seen that most inclusions belong to $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2\text{-(CaO)-(MgO)}$ system, with a lower number of smaller Mn-silicates. The precipitation of Mn-containing inclusions indicates that most of the most reducing metals such as Ca, Mg and Zr could be reoxidized. Figure 125 shows one individual oxide inclusion containing Mg, Al, Zr, Ca and Si,

with a distinct brighter region correspondent to ZrO_2 . The estimated concentrations of Ca, Zr, Al and Mg dissolved in steel based on the inclusion analysis after reoxidation is given in Table 18.

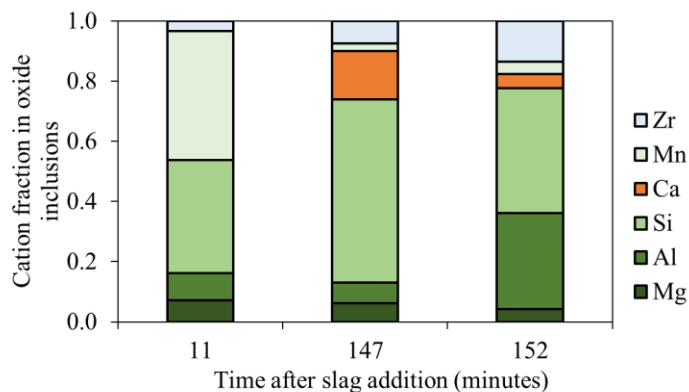


Figure 121 – Area graph representing the evolution of cation mass fraction in non-metallic inclusions over after addition of $\text{CaO-SiO}_2\text{-CaF}_2$ slag.

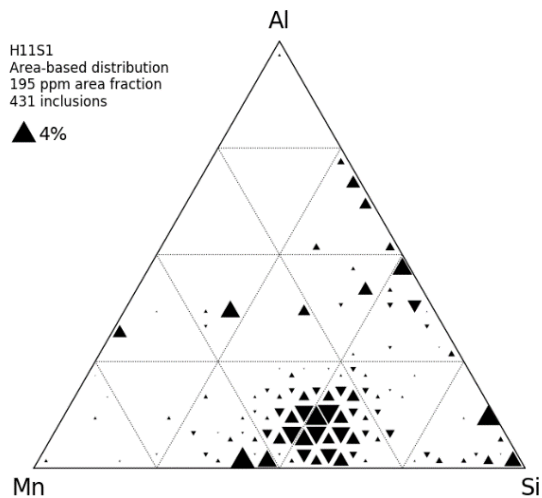


Figure 122 - Ternary diagram showing area-based chemical composition distribution of inclusions in Si-Mn killed steel 11 minutes after addition of $\text{CaO-SiO}_2\text{-CaF}_2$ slag.

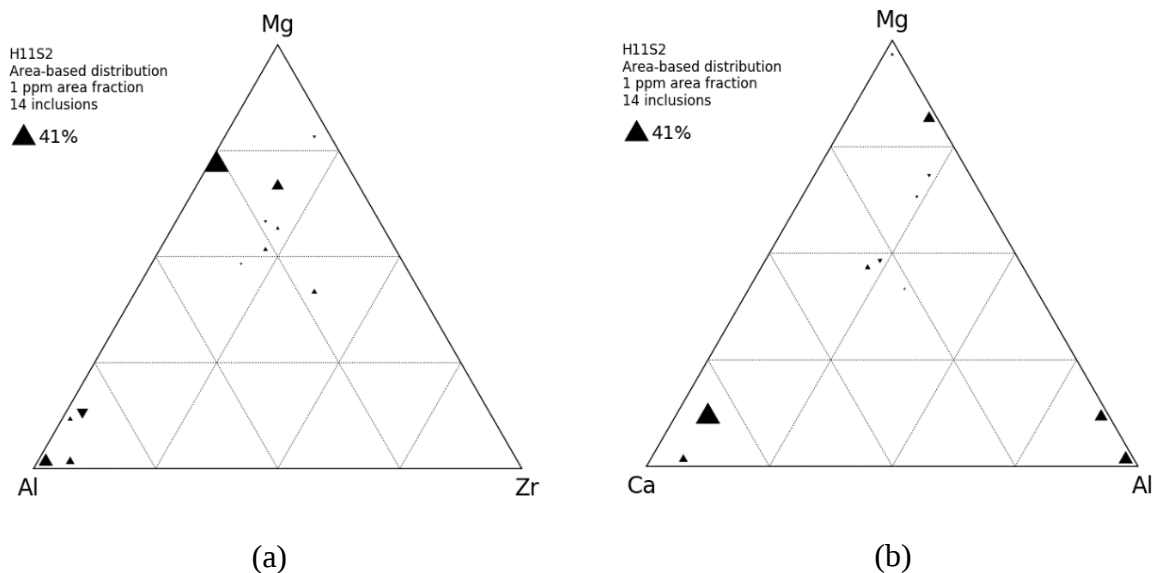


Figure 123 - Ternary diagrams showing chemical composition of inclusions in Si-Mn killed steel 147 minutes after addition of CaO-SiO₂-CaF₂ slag. (a) MgO-AlO_{1.5}-ZrO₂ (b) MgO-AlO_{1.5}-CaO.

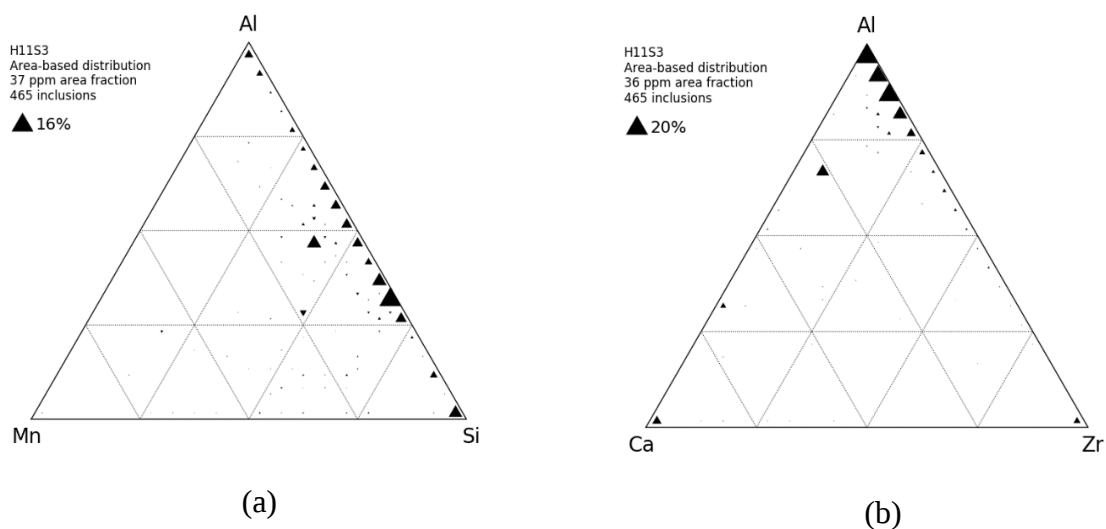


Figure 124 - Ternary diagrams showing chemical composition of inclusions in Si-Mn killed steel 152 minutes after addition of CaO-SiO₂-CaF₂ slag and 2 minutes after reoxidation. (a) MnO-AlO_{1.5}-SiO₂ (b) CaO-AlO_{1.5}-ZrO₂

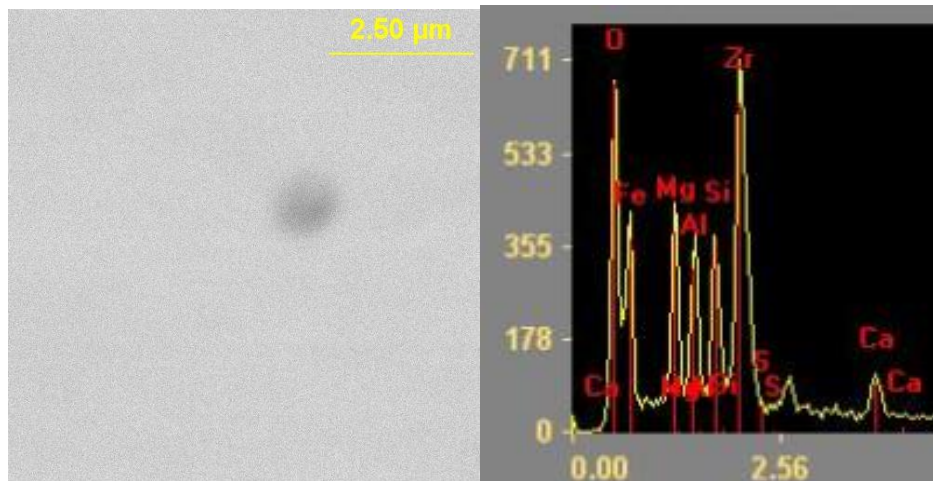


Figure 125 – Non-metallic inclusion containing Ca, Zr, Mg, Si and Al, found in the sample after reoxidation.

Table 18 – Estimated concentrations of Ca, Zr, Al and Mg dissolved in steel before reoxidation

Ca	Zr	Al	Mg
0.3 ppm	0.8 ppm	2 ppm	0.3 ppm

Since the slag was produced from reagent-grade chemicals (CaF_2 , SiO_2 and CaO), the crucible was investigated as a source of residual Mg, Al and Zr. Figure 126 depicts the steel-crucible interface, and it is glazed in slag. Since the slag wets the refractory and is expected not wet the steel, a glaze is formed over the whole inner surface of the crucible. In the same figure, the spectrum shows small concentrations of Mg and Al, but no Zr. ZrO_2 has limited solubility in $\text{CaO-SiO}_2\text{-CaF}_2\text{-(MgO)}$ slags [119]. Throughout the steel-crucible interface, CaZrO_3 inclusions were found and these can be identified as the main Zr supply to the steel. One example can be seen in Figure 127. The strongly wetting behavior of this slag can be perceived in Figure 128, which is from the crucible polished cross-section. The slag penetrates the entirety of the crucible wall thickness, accessing CaZrO_3 and possibly other impurities responsible for Zr, Mg and Al transfer.

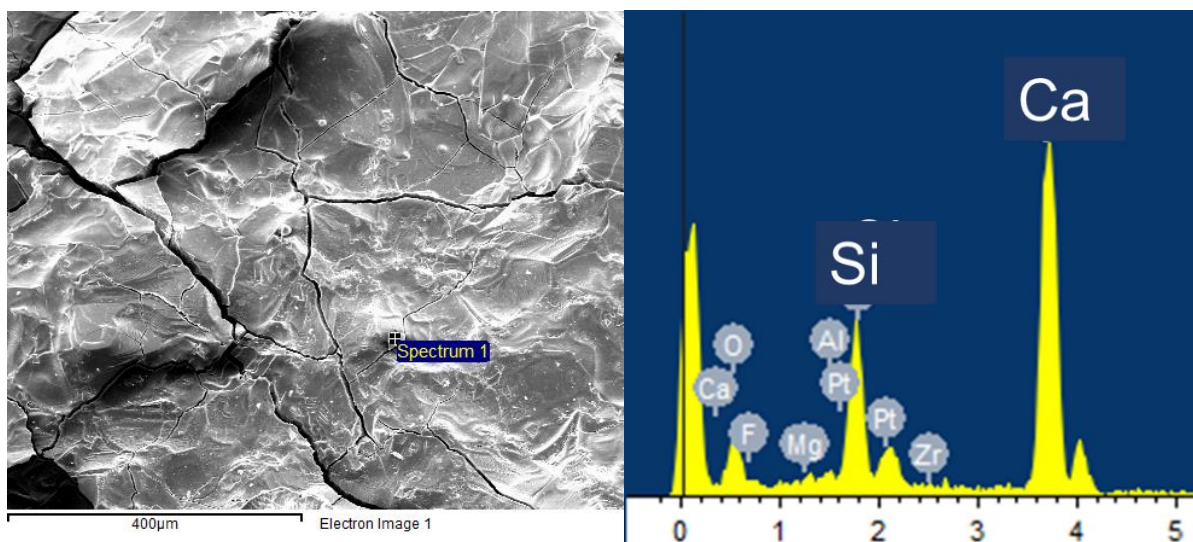


Figure 126 – Secondary electron image (left-hand side) of the steel-crucible interface after the experiment, showing a slag glaze covering the crucible’s surface. In the right-hand side image, the EDS spectrum shows the chemical composition of the glaze.

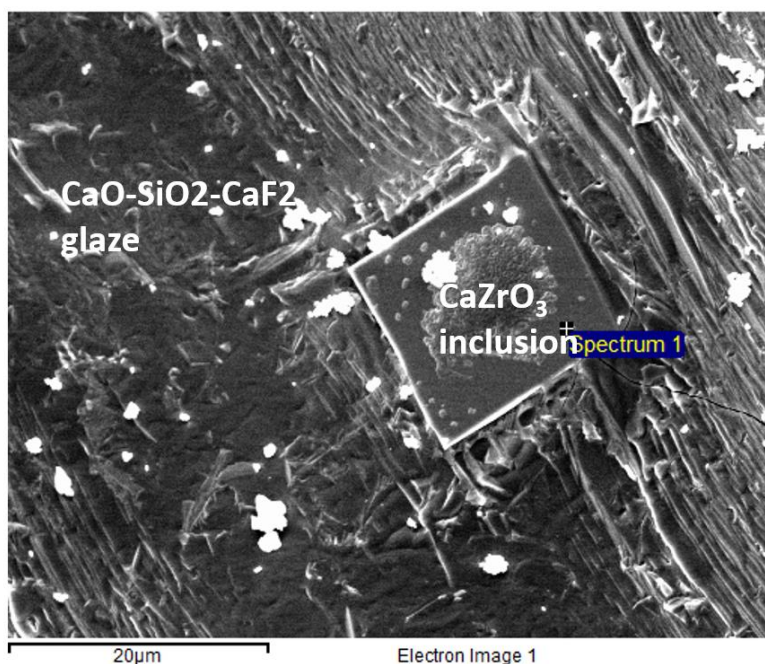


Figure 127 - Secondary electron image of the steel-crucible interface after the experiment, showing a CaZrO_3 crystal amidst the slag glaze covering the crucible surface.

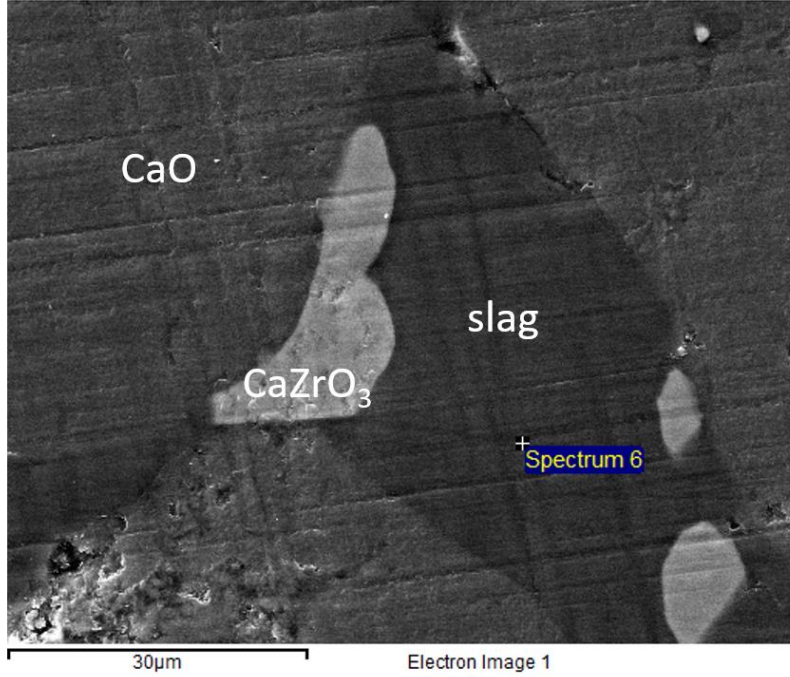


Figure 128 - Secondary electron image of the CaO crucible polished cross-section after the experiment, showing extensive slag penetration into the crucible wall thickness and the presence of CaZrO_3 at the grain boundaries.

Using the non-metallic inclusion composition and concentration, the concentration of precipitated Ca is estimated to be 0.3 ppm (much smaller than the predicted FactSage value of 12 ppm), Zr is 0.8 ppm, Mg is 0.3 ppm and Al is 2 ppm. The calculated CaO activity for the measured inclusion composition is 1.77×10^{-4} and the steel is surrounded by slag saturated in CaO, therefore $a_{\text{CaO}} = 1$ for the conditions before reoxidation. Assuming $p_{\text{O}_2} = 4.6 \times 10^{-16} \text{ atm}$, calculation of Ca activity is straight forward [120][2].

$$K_{\text{CaO}} = \frac{a_{\text{CaO}}}{h_{\text{Ca}}h_{\text{O}}} = \frac{1}{f_{\text{Ca}} * (3 \times 10^{-5}) * (6.3 \times 10^{-5})} = 8.4 \times 10^9 \quad (69)$$

$$f_{\text{Ca}} = 0.056 \quad (70)$$

Conclusions

- Ca, Mg, Al and Zr are reduced from surrounding oxide system due to very reducing conditions. The oxygen activity is controlled by the ratio $[\text{Si}]/(\text{SiO}_2)$.
- Impurities in crucible can significantly impact on non-metallic inclusion composition since most oxides will be reduced. Solubility of Al is high at this oxygen activity.
- Even under these highly reducing conditions, the concentration of Ca is still too low ($[\text{Ca}] = 0.3 \text{ ppm}$, $f_{\text{Ca}} = 0.06$) to explain amount of Ca pick-up by inclusions observed in industrial trials.

5.4.7. Steel-crucible reaction investigations

5.4.7.1. Si-Mn killed steel in contact with MgO crucible in the absence of slag

In the previous sections, significant Mg pick-up by the inclusions have been observed in most of the experiments. Moreover, the slag-crucible interactions can also induce pick-up of impurity elements from the crucible in the inclusions, such as the case of Zr, Mg and Al in the CaO crucible experiments. In this section, the reactions of Si, Mn-killed steel with crucibles without intentional slag addition are studied.

Experimental

600 g of electrolytic iron containing around 300 ppm of oxygen and less than 10 ppm of sulfur was added into a slip-cast $\text{MgO-2\%Y}_2\text{O}_3$ crucible. The melt was deoxidized using laboratory-made silicomanganese alloy (70%Mn-20%Si-10%Fe-sat. C) and let react with the crucible for one hour without slag addition. As in the previous section, the steel-crucible interface was analyzed using SEM/EDS to investigate what is the resulting reaction product. A cross-section of the crucible was also prepared using cold mounting resin and polished to 1 micron and analyzed using the SEM.

Results and Discussion

In Figure 129, it can be seen from the non-metallic inclusion composition that both Mg and Al were reduced from the refractory. The model line in Figure 129 was fitted using $m_{\text{steel}} * A_{\text{steel-refractory}} = 6 \times 10^{-9} \text{ m/s}$. There was an observable Al pick-up (Figure 129). From the manufacturer's table, it is estimated that impurities in the crucible are 0.6%CaO, 0.2%SiO₂, 0.4%Al₂O₃, 0.1%Fe₂O₃ and 0.01%B₂O₃. During the experiment, the crucible slag deoxidized the

sample as seen from Figure 130 – the Mn content decreased over time. After reduction, the composition of this mixture of impurity oxides is similar to a ladle slag, therefore enhancing reactions with refractory and promoting Al and Mg pickup due to low SiO_2 activity in this liquid mixture. The SiO_2 content in this intergranular slag will increase since it is the reaction product of the reduction of the other oxides by Si. While Figure 131 exhibits the refractory as is, a MgO matrix (grey) showing some porosity (black) and Y_2O_3 inclusions (white), Figure 132 demonstrates the state of the refractory after use, showing again a MgO matrix (dark grey) with grain boundaries decorated with both Y_2O_3 (white) and slag (lighter grey).

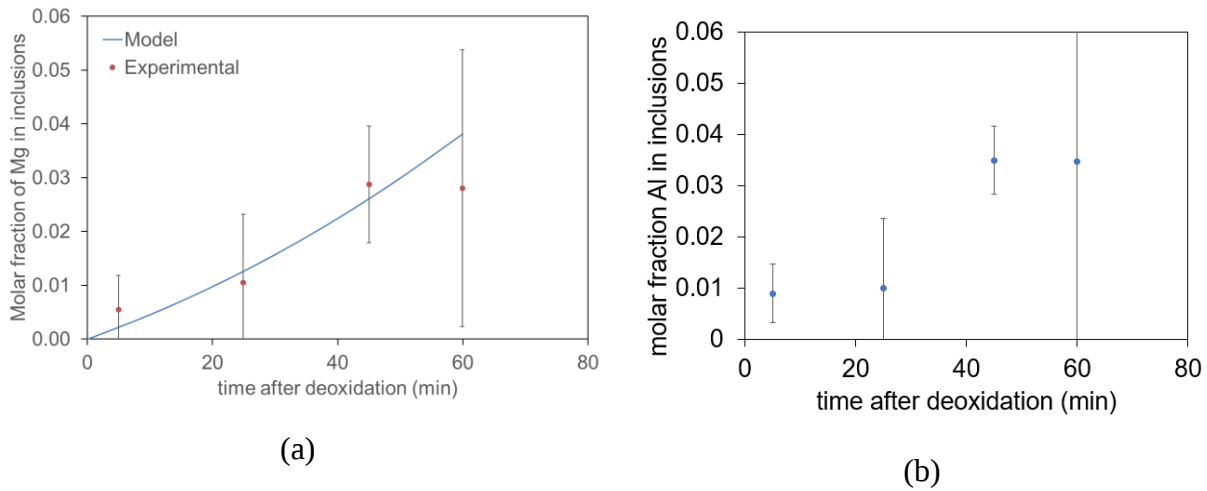


Figure 129 – Molar fraction of (a) Mg and (b) Al in manganese silicates after steel-crucible reactions. Error bars are the standard deviation for the molar fractions and the solid line in (a) is the model fit for the Mg pick-up from crucible.

In Figure 133, the steel-crucible interface after reaction is shown. The expected reaction product is a Mg-silicate layer; however, the picture shows a complex slag containing Ca and Al covering the grains. Figure 134 again shows a complex Ca-silicate slag in the grain boundary of the refractory. In Figure 135, it is seen that the uncovered refractory surface is MgO. The Ca/Si ratio from the EDS analysis is significantly higher than the manufacturer's analysis. This is the result of the reduction by Si of Al_2O_3 and MgO from the slag layer to the steel melt.

This observation is essential to understand the kinetics of steel-refractory reactions for these laboratory experiments, which have a significantly larger surface-to-volume ratio than a real ladle furnace ($A/V = 92.7 \text{ m}^2/\text{m}^3$ for the current 5.71 cm inner diameter crucible with 600g of molten steel versus $A/V = 1.65 \text{ m}^2/\text{m}^3$ for a 3m diameter 150t ladle). In the presence of slag, most likely

the slag will wet the entirety of the steel-crucible interface, therefore mediating their chemical reactions. This is very significant in the case where a solid product layer is expected for Al-killed steels, Al will react with MgO forming a spinel (MgAl_2O_4) layer [121]. Diffusion of Mg and Al through this layer will become the rate-limiting step for the reaction, and the MgO activity will significantly decrease – therefore Mg transfer will be slowed down. However, in the presence of a liquid slag wetting the crucible, the spinel will dissolve in this slag, and the steel will be always exposed to an MgO saturated liquid with enhanced mass transfer rates since now the rate-limiting step would be the mobility of Mg and Al through a *liquid* instead of a *crystalline solid*. In this case, the steel will pick up Mg very quickly. This mechanism is shown schematically in Figure 136.

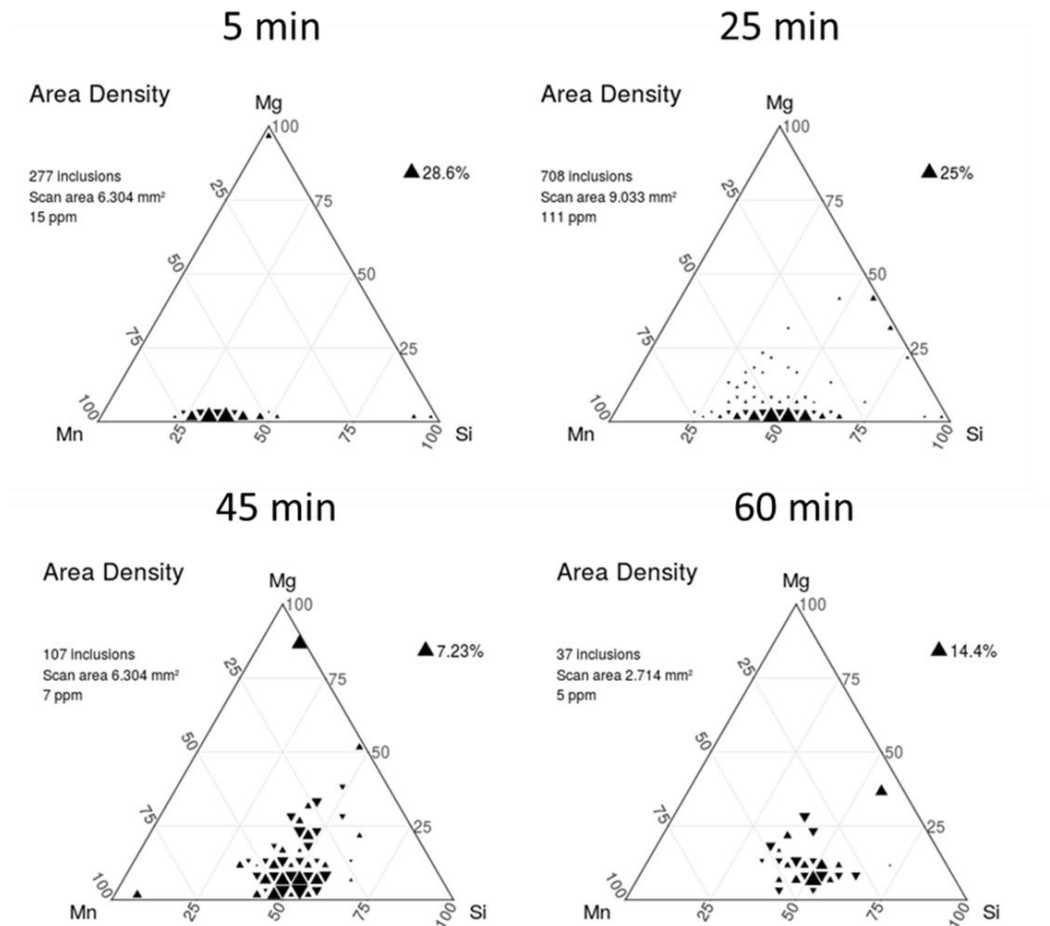


Figure 130 – Evolution of oxide inclusion composition during 1 hour of steel-crucible reactions plotted as MnO-SiO₂-MgO ternaries in a molar basis.

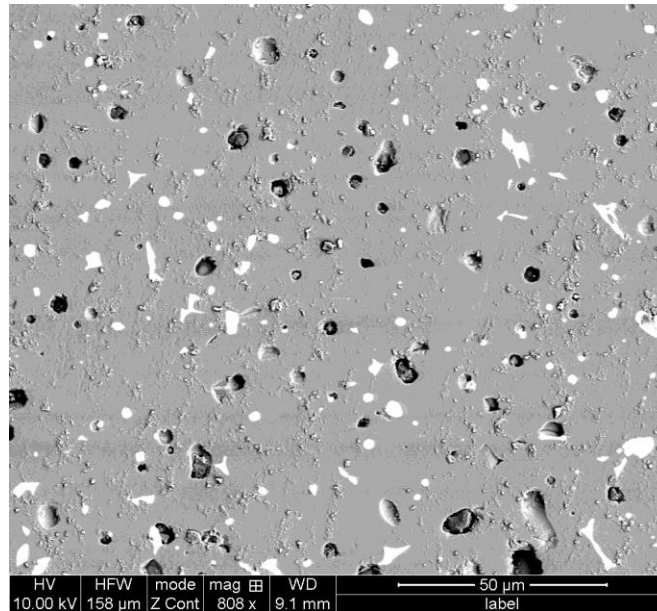


Figure 131 – Back-scattered electron image of MgO crucible as-is. Grey area is the MgO matrix, white regions are Y_2O_3 deposits and dark spots are open porosity.

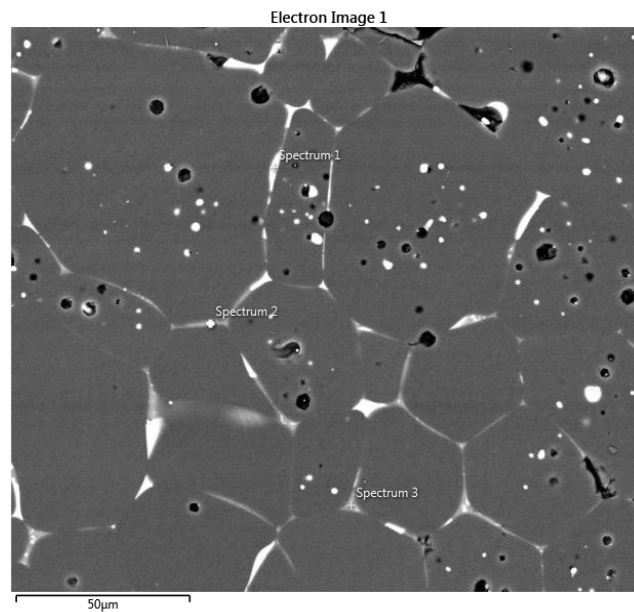


Figure 132 – Back-scattered electron image of MgO crucible after steel-crucible experiment. Grey area is the MgO matrix, white regions are Y_2O_3 deposits and dark spots are open porosity. Lighter grey areas marking the grain boundaries are slag produced from the MgO crucible impurities.

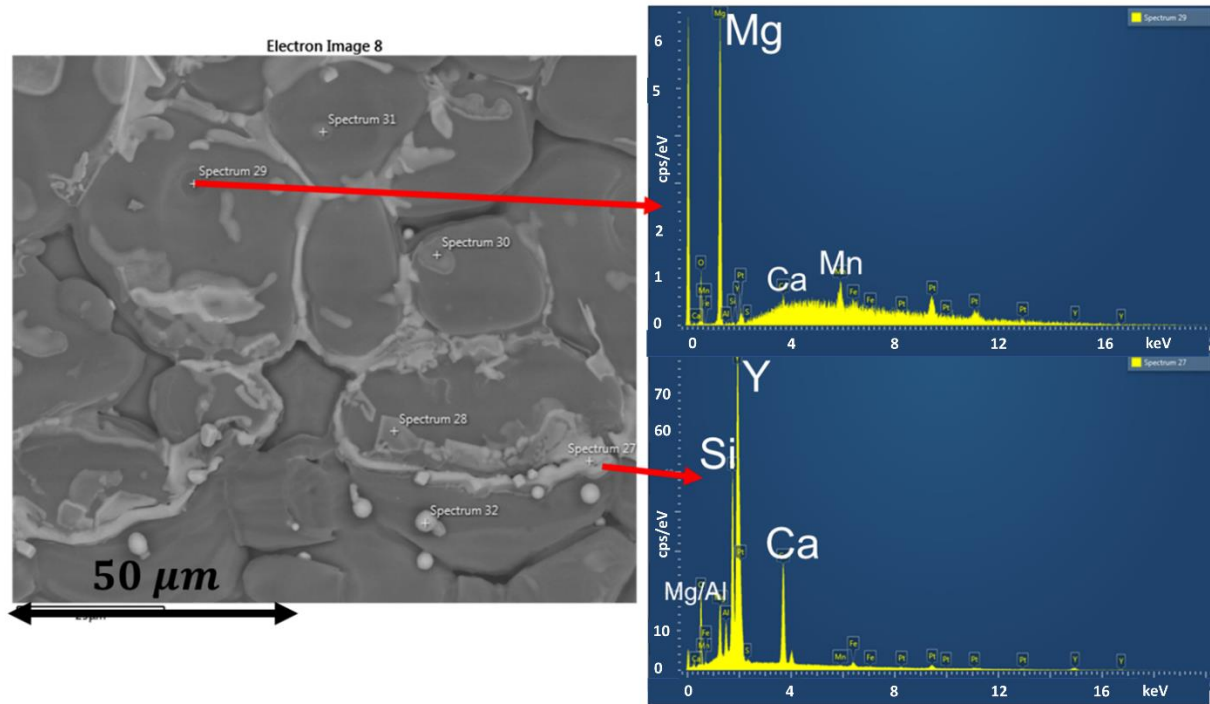


Figure 133 – Back-scattered electron image of the steel-crucible interface after the experiment, showing liquid slag wetting the grains. The spectra on the right shows the presence of MgO and Ca, Si, Al, Mg, Y-containing liquid.

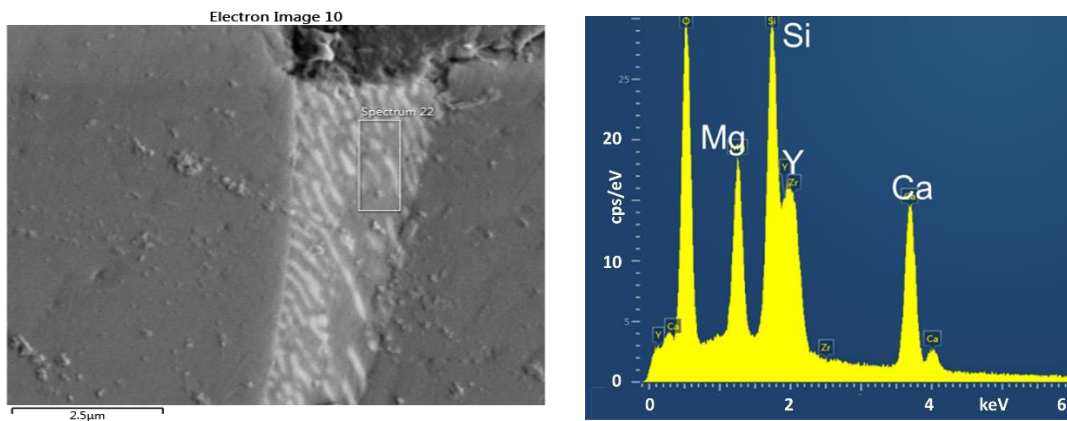


Figure 134 – Back-scattered image showing Ca, Si, Mg-containing slag at the grain boundary as visible from the crucible cross-section. Spectrum on the right shows the chemical composition of the apparently liquid phase.

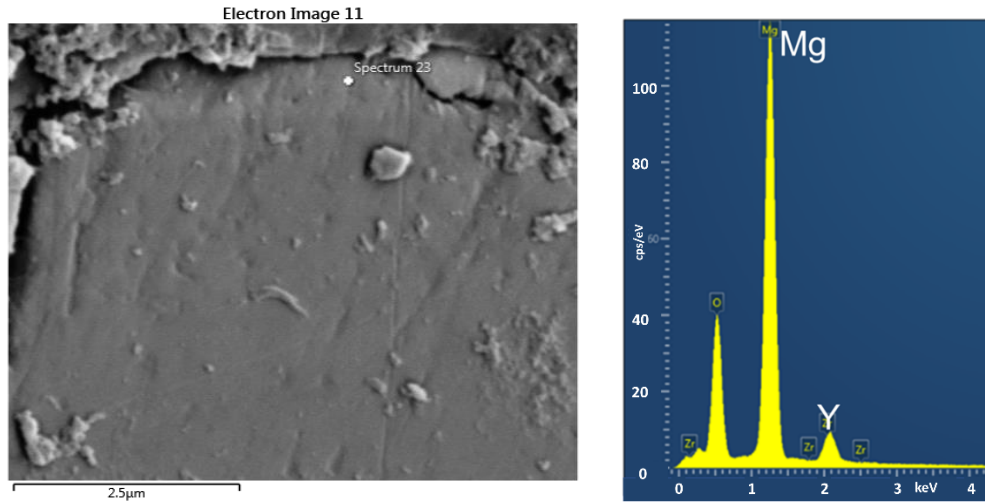


Figure 135 - Back-scattered image showing a cross-section of the used MgO refractory close to the steel-crucible interface. Spectrum on the right shows the chemical composition of the refractory, which shows as almost pure MgO.

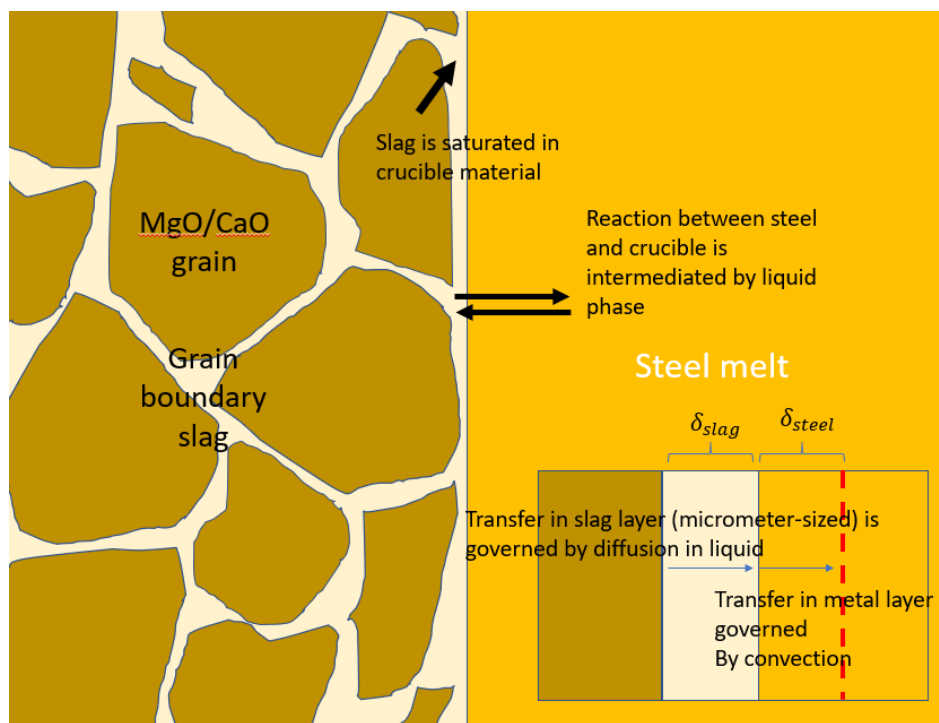


Figure 136 – Proposed mechanism for steel-crucible interaction mediated by liquid slag.

Conclusions

- Pure crucible + steel reaction will transfer Mg from crucible matrix and Al from impurities to the steel. Fitted mA for the steel-crucible reaction is $6 \times 10^{-9} \text{ m}^3/\text{s}$.
- The reaction is intermediated by liquid formed from the crucible impurities or added slag, which might change both the apparent overall mass transfer and activity of MgO in contact with steel. Also, the slag-like layer formed at the steel-crucible interface will enhance transfer of other elements such as Al and Zr.

5.4.8. Inclusion removal kinetics for different steel-slag systems

In the literature review, it was observed that the oxygen removal from the melt can be calculated as a first-order reaction with a mass transfer coefficient with units $L * t^{-1}$. The inclusion removal kinetics for the different steel-slag experiments were analyzed as first-order processes. In Figure 137, the mass-based population (in inclusion ppm) is plotted versus the time of sampling. A summary of the fitted mass transfer coefficient for the mass concentration of inclusions is shown in Figure 138. It is seen that the mass transfer coefficient for inclusion removal is approximately 0.001 s^{-1} . Assuming the mass of the melt being 600g, the density of steel 7 g/cm^3 and the internal diameter of the crucible as 5.71 cm, the mass transfer coefficient is calculated to be in the range of $4 \times 10^{-5} \text{ m/s}$, which is 5 times larger than the measured mass transfer coefficient for the pick-up of Al (see section 5.3.3) but close to other measured mass transfer coefficients in the same furnace configuration, if only inclusion absorption by slag is taken in account. If the lateral area is also considered for inclusion removal (which is a reasonable assumption, since there is slag at the steel-crucible interface), the calculated mass transfer coefficient for inclusion removal is very similar to the mass transfer coefficients for steel-slag reactions measured in this work (and compared in the next section). That is consistent with the hypothesis that inclusion removal is mass transfer-limited.

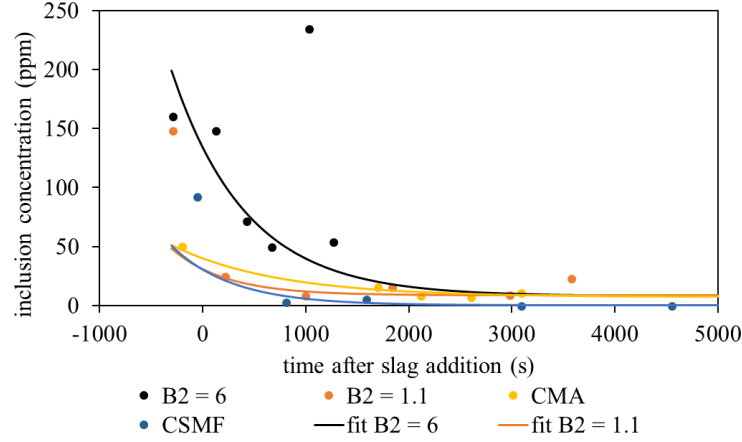


Figure 137 – Inclusion mass-based population evolution for experiments with different slag compositions. Data points are experimental results from AFA data and lines are first-order reaction fits to the data points.

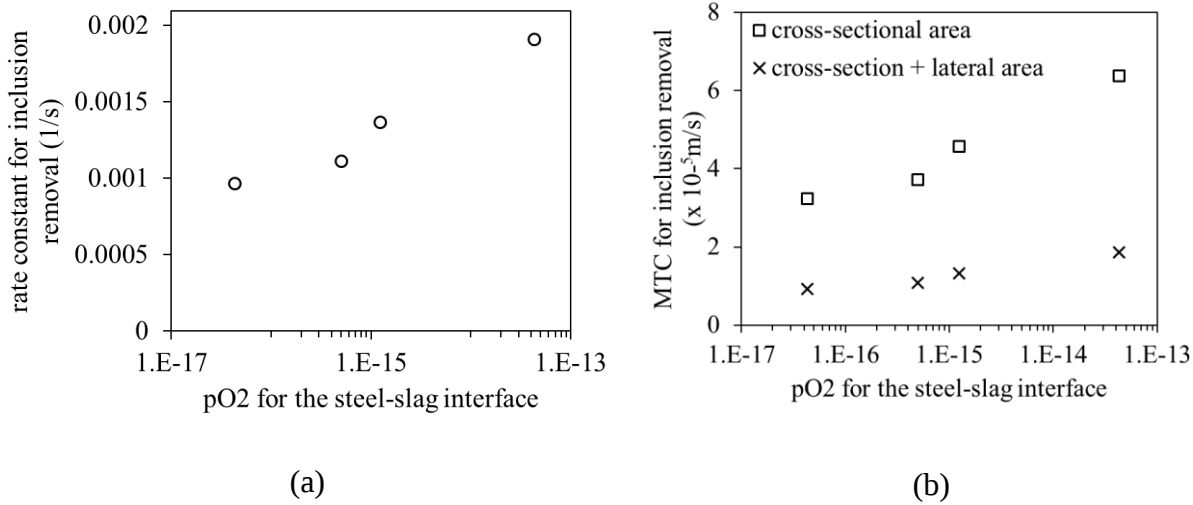


Figure 138 – Mass-based inclusion removal (a) rate constant and (b) mass transfer coefficients for different slags (plotted in respect to steel-slag interfacial pO_2). In (b), the mass transfer coefficients are plotted considering both the cross-sectional area of the crucible and the cross-sectional with the lateral area.

5.4.9. Analysis and comparison of measured mass transfer coefficients

The average steel mass transfer coefficient for steel-slag reactions, as measured in this work from various methods as described earlier, is $mA = 0.06 \pm 0.03 \text{ cm}^3/\text{s}$. Corresponding values for the similar experimental setups are summarized in Table 19. The mass transfer coefficient compares

to the values obtained by Manning and Fruehan and to the lower end of the values obtained by Kumar and Roy, although at least one number (measured Al pick-up in H1, no added sulfur) is one order of magnitude smaller than the typical values.

Two experiments were performed in the same fashion as the experiment H1 to measure the mass transfer coefficient based on the desulfurization rate, but with a slag containing 57%CaO-18%SiO₂-18%Al₂O₃-7%MgO. The desulfurization profiles as shown below, where $S = \ln([S] - [S]_{eq}) / ([S]_0 - [S]_{eq})$. One of the experiments was performed in an MgO crucible and the other in an alumina crucible. For the alumina crucible experiments, only the initial data points were considered, since by the end of the experiment the slag would be close to spinel saturation with $[\%S]_{eq} = 120$ ppm compared to 3 ppm in equilibrium with the initial slag composition, with 1%Mn and 0.25%Si.

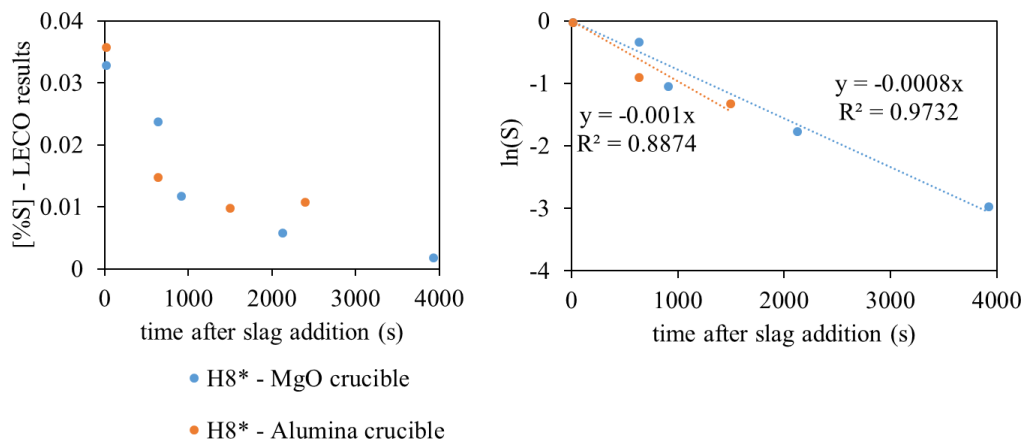


Figure 139 – Desulfurization results for 600g steel containing 1.25%Mn-0.25%Si, in two different crucibles for steel mass transfer calculation.

Considering the steel volume of 600g to be 86 cm³, the mA , taken to be k'/V_{steel} , had an average of 0.07 ± 0.01 cm³/s.

There are many factors that may account for the differences observed:

- Increased slag mass will slow down steel velocity at the interface thus reducing the mass transfer coefficient;
- The use of a refractory lid at the top of the crucible reduces heat loss by radiation and slow down convective stirring in the melt due to heat transfer;

- Less oxygen transfer across the interface as compared to Al containing experiments with active reduction of SiO₂ from the slag. Oxygen and sulfur transfer changes the interfacial tension of the steel-slag interface, leading to instabilities and changing the effective steel-slag interfacial area;
- Difficulties of chemical analysis for Al levels smaller than 200 ppm for the provided sample masses (generally 5-10g due to sampler size) using ICP-MS. Trials where the observed inclusions were in the spinel range had unrealistically Al contents (< 20 ppm).

Table 19 – Comparison of steel mass transfer coefficients measured in this work and the work of others in similar induction furnace setup

Experiment	mA (cm ³ /s)	Setup
H1 – 180g slag (Al pick-up)	0.02	5.7 cm ID, graphite susceptor, alumina lid, 600g of steel, Si-killed
H8* - 100g slag (de-S)	0.07	
H8 - 100g slag (de-S)	0.09	
Inclusion removal	0.05 (slag) / 0.01 (slag + refractory)	
Kumar (Al-Si reaction) [54]	0.13-0.17	As above, 0.3%Al
Roy [122] – 100g slag (de-S)	0.1-0.2	4.9 cm ID, graphite susceptor, no lid, 1000g of steel, Al-killed
Manning and Fruehan [123] (de-P)	0.05-0.1	4.9 cm ID, Mo wire susceptor, lid, 200g of steel

5.4.10. Effect of Ca-containing FeSi75 in deoxidation, Al-killed and Si-killed steels

The steel-slag reaction experiments did not show the same FactSage-predicted Ca pick-up in the inclusions. In the experiments described in this section, Ca is added to the steel as an impurity in ferrosilicon. The structure of the laboratory-made ferroalloy containing 75wt%Si and 2wt%Ca and the effects of Ca in the steel cleanliness for non-deoxidized, Al-killed and Si-killed steels are studied and reported.

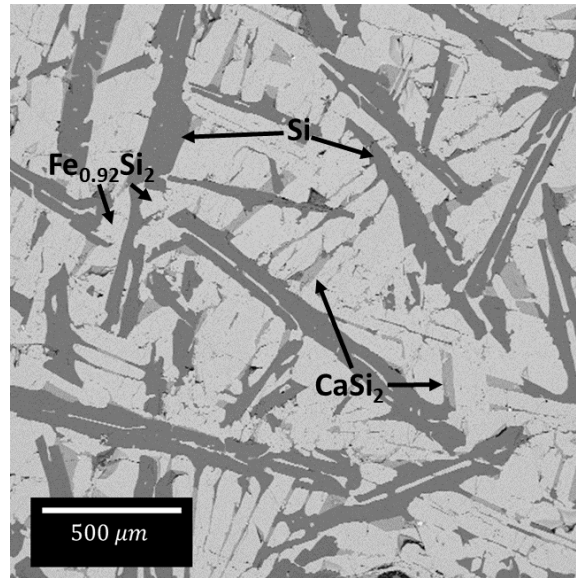
5.4.10.1 – Ca-Si deoxidation

In this experiment, Ca-containing FeSi was prepared for use as a deoxidant, melting 2.4g of CaSi_2 , 36g of pure Si and 11.3 g of electrolytic iron, to yield a ferroalloy with 75wt%Si-23wt%Fe-2wt%Ca. The mixture was placed in a graphite crucible and molten in an induction furnace, using Ar as a protective atmosphere. Due to the solubility of Ca in molten Si, the yield was close to 100% (EDS analysis show around 2wt%Ca). The solidification microstructure of the alloy is shown in Figure 140. In Figure 140b, the Ca-rich phases are evenly distributed throughout the matrix in the interdendritic spaces. The phases formed as shown in the picture are pure, primary Si, $\text{Fe}_{0.92}\text{Si}_2$ and CaSi_2 . The microstructure is in accordance with the phase diagram predictions (Figure 141).

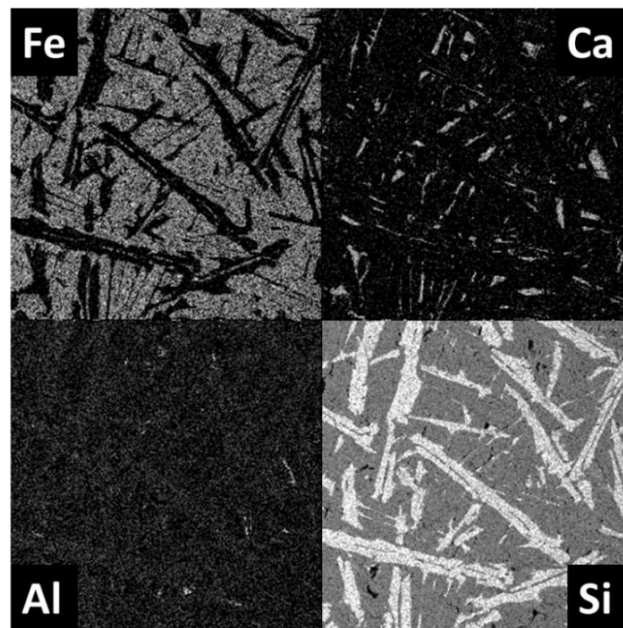
The deoxidation experiment was carried using 600 g of electrolytic iron containing 400 ppm O and 7 ppm S. After molten and kept at 1600°C , 4 grams of the ferroalloy was added to the melt to yield 0.5%Si. Samples were taken no more than 60 seconds after deoxidizer addition, then at 300 s and 600 s after deoxidation.

Figure 142 shows the proportional ternary plots showing the average chemical composition of the resulting inclusions. The initial composition of the inclusions is, on average, 71% SiO_2 -29%CaO. Typically, when CaSi_2 powder is added to steel for Ca treatment, the yield is around 1% for Al-killed steels.

The presence of a Fe-Si alloy matrix and very fine CaSi_2 particles would limit the availability of O to react with Ca, thus reducing the supersaturation. This effect can be confirmed by the size distribution analysis of the sample, as shown in Figure 144. From the first sample to the second samples, although the number-based concentration of inclusions decreased, there was an increase in area fraction from Sample 1 to Sample 2. From the size distribution histograms in Figure 144, the maximum inclusion size and the mode increased. This is a clear indication of non-metallic inclusion growth. Therefore, the conclusion is that there were inclusions and nuclei smaller than the cutoff size of $0.3\ \mu\text{m}$ for these analyses (in Sample 1). As inclusions grew, the number density gets smaller and the area fraction increases from Sample 1 to 2, but then decreases from Sample 2 to 3 by inclusion flotation. The concentration of minor elements in steel from the inclusion analysis and the inclusion population and concentration evolution are plotted in Figure 143.



(a)



(b)

Figure 140 – Microstructure of the FeSi(Ca) ferroalloy showing its solidification structure. Figure 140b shows the chemical composition of the distinct phases, showing the pure, primary Si dendrites, the iron-silicon intermetallic dendrites and the dispersed CaSi_2 formed from the solidification of the eutectic. Aluminum was also detected as a minor impurity in the ferroalloy.

Since 4 grams of FeSi was added, 0.08g was added to the steel, which is equivalent to 133 ppm Ca. From the inclusion analysis of the first sample, 39.1 ppm of Ca was fixed in the Ca-silicate inclusions. The Ca yield was 29%, but it should be higher due to the small inclusions not analyzable by ASPEX in the settings described in this section.

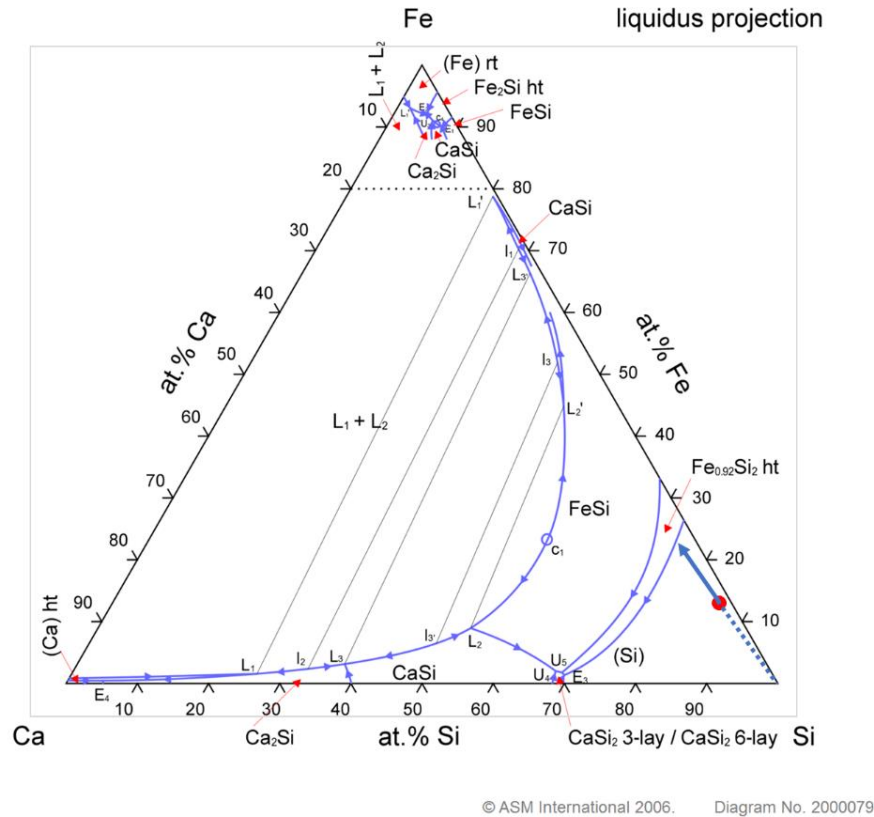


Figure 141 – Ternary diagram showing the liquidus projections for the Ca-Si-Fe system [124].

The red point marks the starting composition of the liquid, and the blue arrow indicates the direction of liquid composition change upon solidification. The primary phase formed will be Si, followed by the precipitation of $\text{Fe}_{0.92}\text{Si}_2$ culminating in the formation of the eutectic, containing Si, $\text{Fe}_{0.92}\text{Si}_2$ and CaSi_2 .

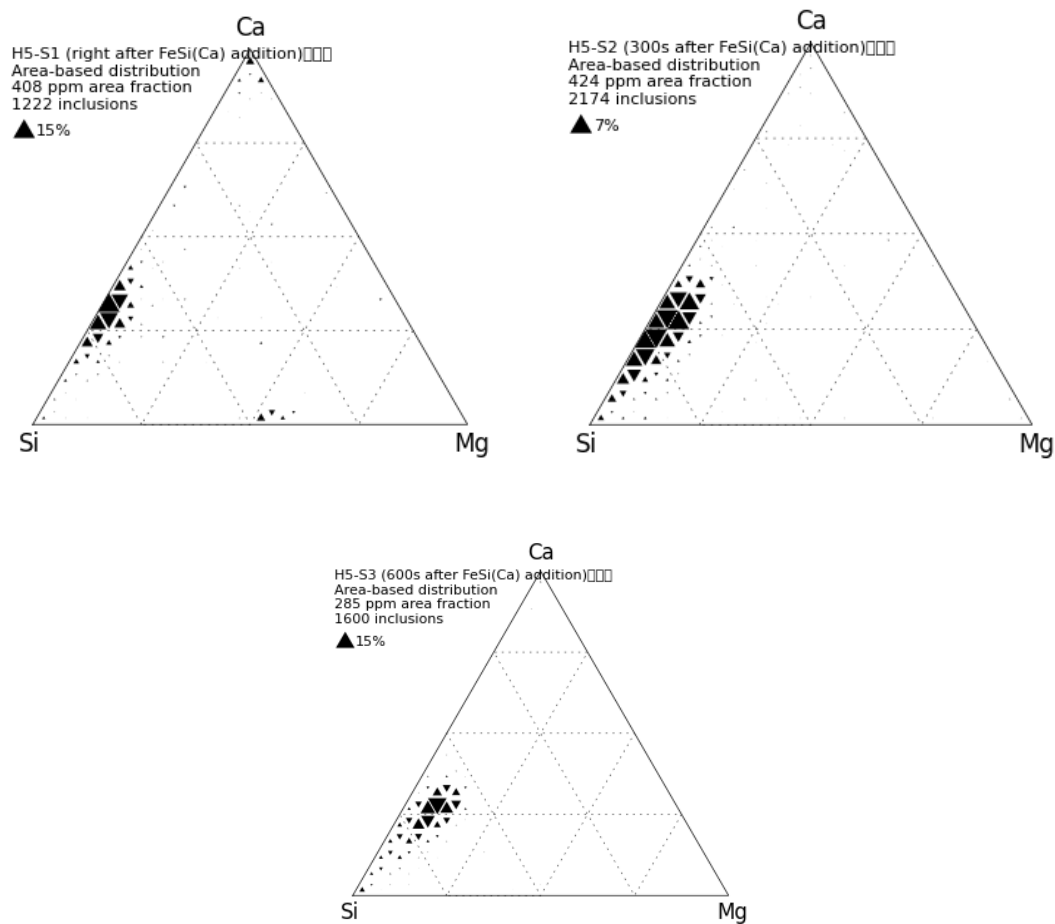


Figure 142 – Ternary diagrams showing the chemical composition of non-metallic inclusions. Samples were taken after 0 seconds, 300 seconds and 600 seconds after FeSi(Ca) addition.

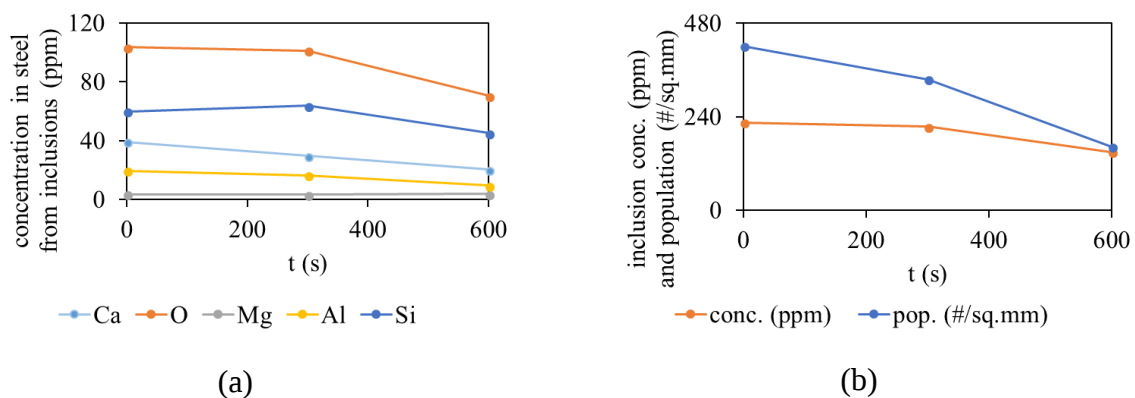
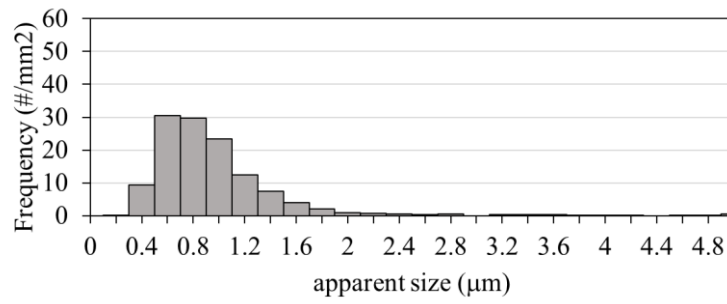
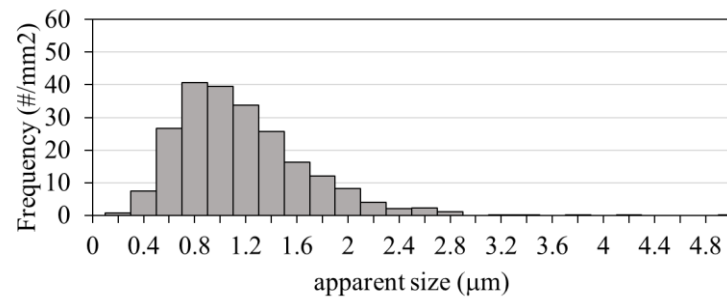


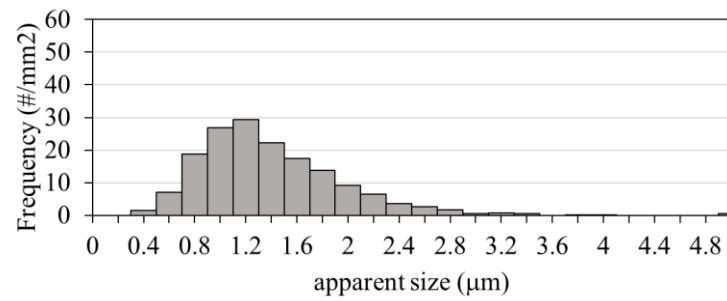
Figure 143 – (a) Concentration of minor elements in steel from inclusion analysis. (b) Inclusion population and concentration over time.



(a)



(b)



(c)

Figure 144 – Size distribution of inclusions from (a) Sample 1, (b) Sample 2, (c) Sample 3 after Ca-Si deoxidation.

In the next sections, the efficiency of Ca in FeSi are tested against less oxidized melts such as Al or Si-Mn killed steels.

5.4.10.2 – FeSi75-based Ca-treatment of Al-killed Steels

The behavior of Ca present as an impurity in FeSi75 was discussed as one of the possible causes of Ca-silicate formation after trimming. Since these Ca impurities can significantly disrupt (or enhance) casting by formation of new compounds such as CaS or Ca-aluminates [1,20,89], it is important to understand the mechanism by which these new phases form in highly reduced systems, such as a deeply-deoxidized Al-killed steel. One experiment was performed, in which 2%Ca-FeSi75 was added to an Fe-0.05%Al melt contained in an MgO crucible.

To simulate Ca-treatment of Al-killed steel through the addition of FeSi, 600 grams of electrolytic iron ($[S] < 10$ ppm) was molten in a MgO crucible and heated to 1600°C. 0.55 grams of aluminum (as a single shot) was added to the melt, and one sample (S1) was taken using a 4mm inner diameter silica tube one minute after deoxidation. To test this, one minute after sampling, a single lump of 0.85 grams of laboratory-made FeSi with composition 75%Si-23%Fe-2%Ca was added to the melt. The amount of calcium added (28 ppm) was intentionally smaller than the expected total oxygen in the sample (usually 100 ppm after deoxidation) to maximize calcium reaction yield and prevent evaporation. Samples were taken 1, 3 and 6 minutes after the addition of FeSi. The results and discussion are presented below.

Results and Discussion

From the ASPEX analyses (Figure 145), there is a drastic drop in the inclusion number after FeSi(Ca) addition (population), followed by an increase in the inclusion population again after 2 minutes – in contrast, the inclusion concentration (volume fraction) consistently decreases over time. The analysis for the first sample after Ca-treatment was repeated using a higher resolution microscope, the FEI Quanta600 to capture inclusions down to 0.2 micron equivalent diameter. This analysis reveals 270 inclusions/mm² more that was not detected by ASPEX analysis. This population of small inclusions were all Ca-aluminates. The chemical composition of the inclusions as measured by ASPEX can be seen on Figure 146 and Figure 147.

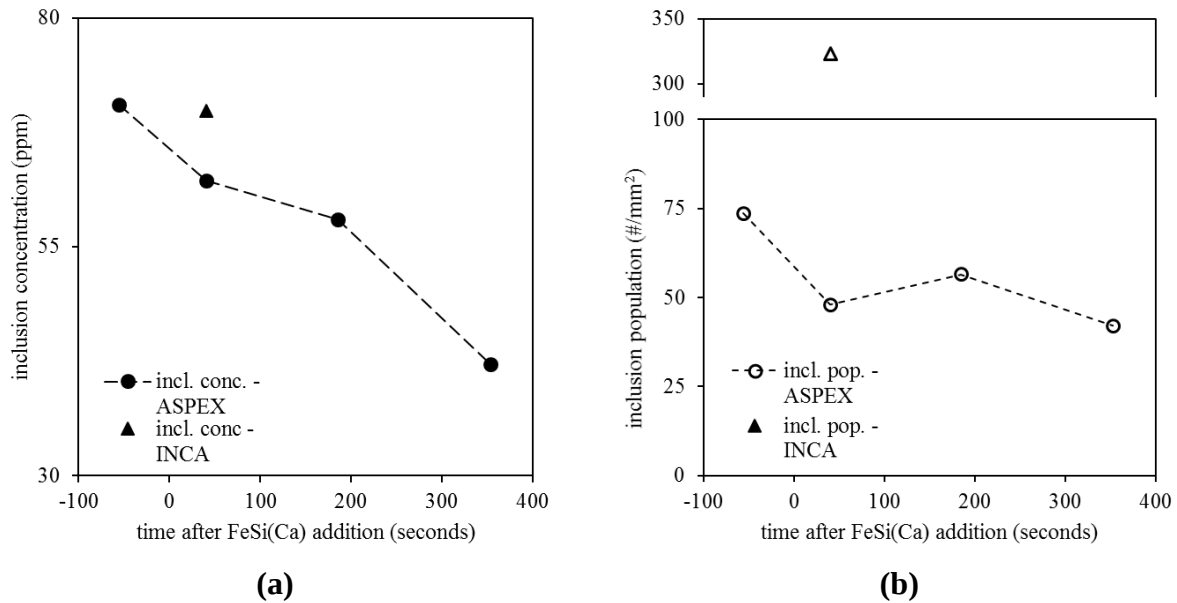


Figure 145 - Evolution of non-metallic inclusions a) concentration and b) population (number) in steel after Al-deoxidation and FeSi addition. Full black dots represent the inclusion mass concentration (in ppm) and the black circles represent the inclusion number (in inclusions per square millimeter) as measured from the ASPEX Explorer analysis. Triangles are from INCA analysis using FEI Quanta600.

The non-metallic inclusions found in all samples, as seen in Figure 148, can be broken down in four different groups: 1) alumina inclusions, 2) spinel inclusions, 3) partially treated Ca-Mg-aluminates, 4) fully treated Ca-aluminates. The initial alumina inclusions are around 1.5-3 microns in diameter. After treatment, due to steel-crucible reactions, Mg is picked up by the melt and the alumina inclusions are transformed to spinel. There is a size dependence to the extent of spinel transformation as captured by the first sample taken 40 seconds after FeSi(Ca) addition. There is around 10 ppm in mass of fully treated, liquid Ca-aluminates, and around the same amount of partially treated Ca-aluminates, closer to the alumina corner as seen in Figure 148. The higher-resolution Quanta 600 analysis measured an extra population of 14 ppm of Ca-aluminates, with size smaller than 0.4 micron. As shown in Figure 149, over time the alumina population significantly decreases due to floatation and reaction to spinel. The amount of spinel initially increases due to steel-crucible reaction, but then decreases due to floatation. These tendencies of agglomeration and floatation of alumina and spinels can be seen in Figure 149, where the PDFs (population distribution function) of Ca-containing inclusions and Ca-free inclusions are plotted.

The fully treated Ca-aluminates tell a more complex story. At 185 seconds after Ca-treatment, the nuclei identified in the first sample grow, leading to an apparent increase in mass ppm and decrease in number. That is supported by the PDF plot in Figure 149 as well. Additionally, the chemical composition of these Ca-aluminates slightly shifts towards Al_2O_3 , as seen on Figure 147. After 353 seconds, the fully treated inclusions are richer in Al, there is a decrease in the concentration and a steeper decrease in the number population, which suggests removal by flotation and growth, respectively. The untreated Ca-aluminates continuously increase in concentration (Figure 148), and they also appear to grow (Figure 147). The equilibrium inclusion content as calculated by FactSage 7.2 (FTmisc + FToxid) using the final sample composition - 6 ppm Ca, 15 ppm O, 3 ppm Mg, 500 ppm Al - was spinels and Al_2O_3 -rich liquid ($X_{\text{AlO}_{1.5}} = 0.67$, $X_{\text{CaO}} = 0.27$, $X_{\text{MgO}} = 0.06$). It is expected that the non-equilibrium inclusions would react towards that composition. The partially treated inclusion population is the growing (equilibrium) population, increasing at the expense of the spinels. However, the shift in composition of the fully treated Ca-aluminates seems to indicate there is Al and O pickup by these inclusions. Since the Al_2O_3 activity in both partially and fully-treated inclusions is less than unity, there is a deoxidation driving force at the Ca-containing inclusion/steel interface. Therefore, this seems to support the suggestion that the mechanism for Ca treatment is that dissolved Al and O precipitate on CaO or CaO-rich calcium aluminates. The resulting lower concentration of dissolved oxygen would cause untreated alumina (and spinel) to dissolve. The relative movements of the detected inclusion populations on the CaO-MgO- $\text{AlO}_{1.5}$ phase diagram can be seen on Figure 150.

The amount of Ca in the melt/inclusions stays relatively constant through the whole experiment, around 6-7 ppm, until removal by flotation. The total Ca addition from the ferroalloy was 28 ppm, therefore the Ca yield is 21%-25%. Mg is constantly picked up by reduction of MgO crucible by Al. There is an increase in the measured total O in the sample right after Ca treatment, as seen by Figure 148c – indicating that the added Ca reacted with the remaining few ppm of dissolved oxygen in the steel.

Thus, the proposed mechanism of Ca transfer from the ferroalloy is as follows:

1. Ferroalloy melts within seconds in the unstirred melt [41];
2.
 - a. Ca, from FeSi, readily reacts with O in steel, forming unresolved nuclei (CaO, due to the absence of S), which promptly transform to Ca-aluminates. The rate of transformation is limited by the O availability in the melt.
 - b. In parallel, alumina inclusions near the ferroalloy dissolution front react and are fully treated. The decrease in size of inclusions indicates the instability of Al_2O_3 .
3. Different populations will then progressively react until equilibrium. If reactions are limited by mass transfer in liquid steel, these populations would reach equilibrium much faster than the observed rates. The rate constant for the steel-inclusion reaction can be estimated from the following equation, where D_i is the mass diffusivity of elements in liquid iron, W_{incl} and W_{steel} are the masses of inclusions in the steel and of steel itself, ρ_{incl} and ρ_{steel} the average density of inclusions and the density of steel respectively, r_{incl} is the average radius of inclusions.

$$\begin{aligned}
 \frac{1}{\tau} &= \frac{m_{steel-inclusion} A_{inclusions}}{V_{steel}} \\
 &= \frac{\left(\frac{D_i}{r_{incl}}\right) \frac{\left(\frac{W_{incl}}{\rho_{incl}}\right) (4\pi r_{incl}^2)}{\left(\frac{4}{3}\pi r_{incl}^3\right)}}{\left(\frac{W_{steel}}{\rho_{steel}}\right)} \\
 &= 3 \left(\frac{W_{incl}}{\rho_{incl}}\right) \frac{D_i}{r_{incl}^2} \frac{\rho_{steel}}{W_{steel}}
 \end{aligned} \tag{71}$$

Assuming 1 kg of steel with 30 ppm of inclusions with density 2.7 g/cm^3 , D_i as $3 \times 10^{-9} \text{ m}^2/\text{s}$ and average radius of 1 micron, the time constant (the inverse of the rate constant) is approximately 1.5 seconds (that is, to reach 62.8% of the equilibrium reaction extent).

There is a possibility of inhomogeneity of the steel chemical composition, especially of very low solubility species such as Ca. Also, the effect of O starvation in the melt must be modeled with more precision.

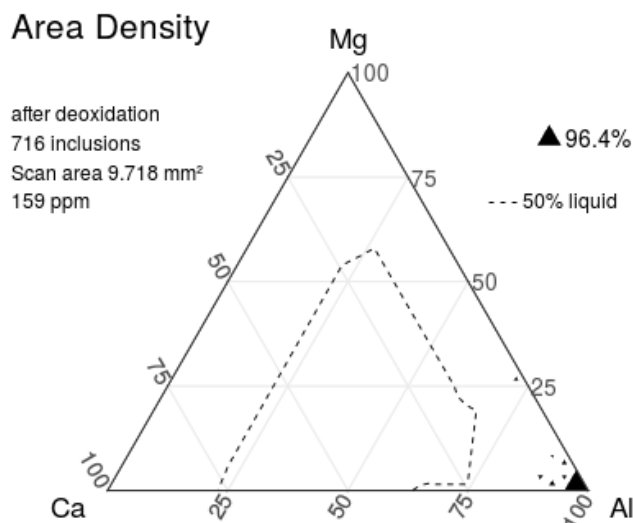


Figure 146 – Chemical composition of non-metallic inclusions from sample taken after deoxidation, showing mostly alumina inclusions.

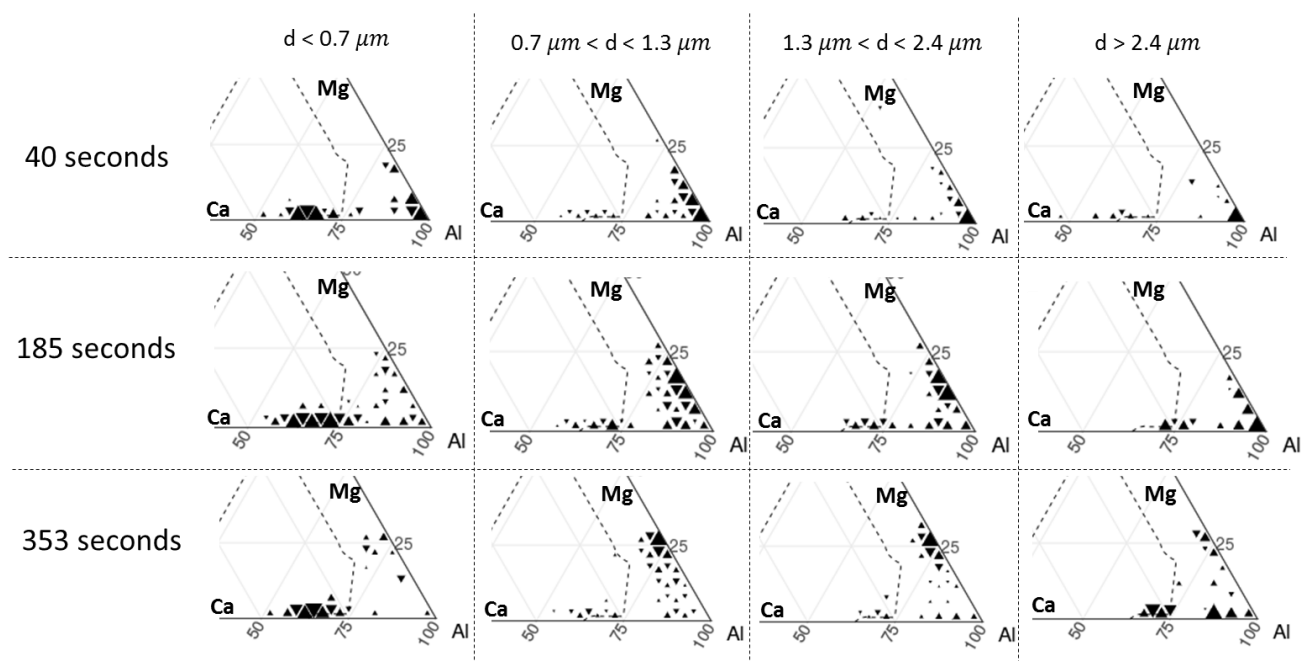


Figure 147 – Breakdown of non-metallic inclusion composition after FeSi-based Ca-treatment, showing the distribution of chemical composition (Ca, Mg and Al) for different inclusion sizes (columns). Each row is a different sample taken at a different time during the experiment. No CaO/CaS was found in these analyses.

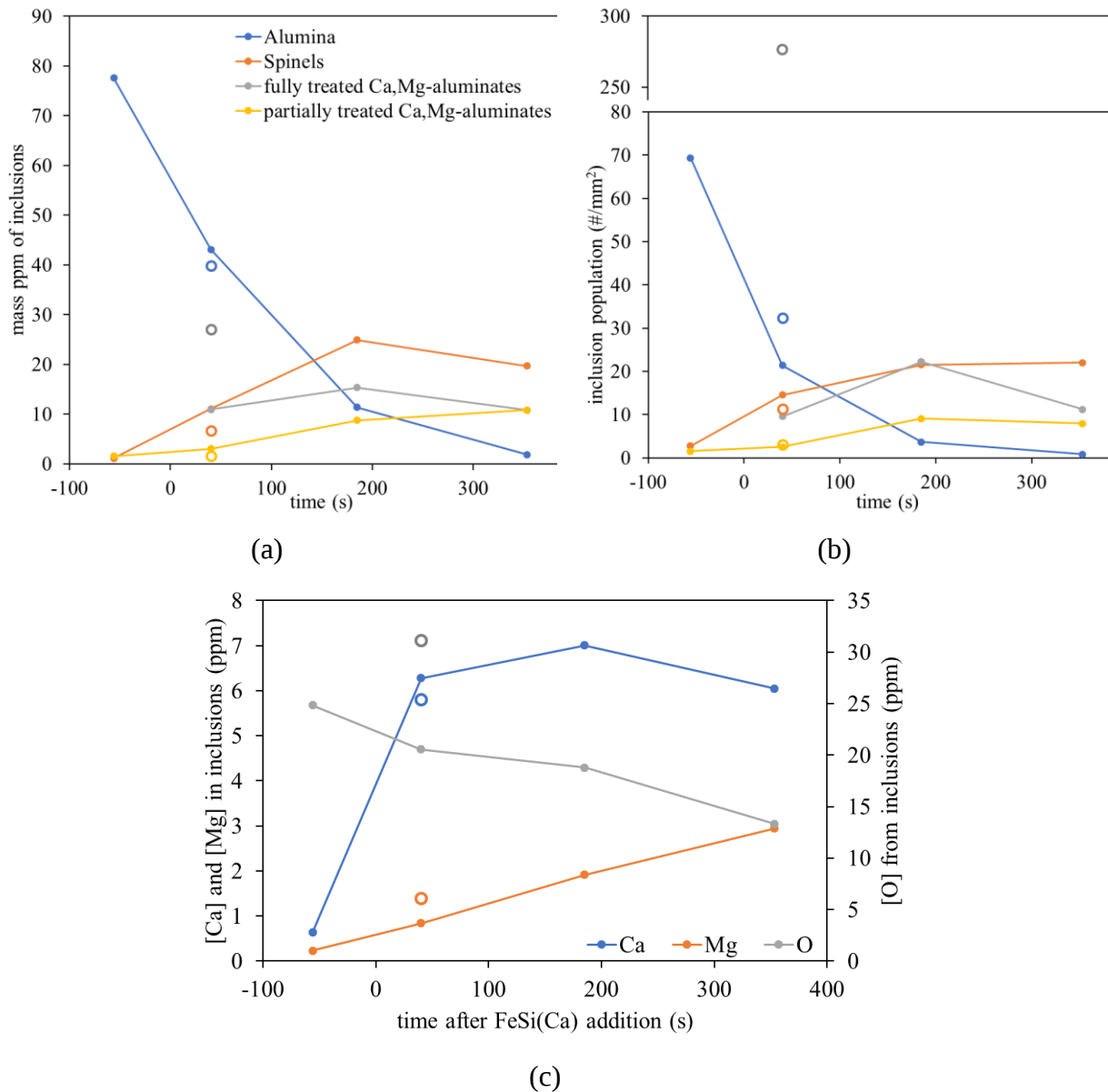


Figure 148 – Evolution of (a) inclusion concentration in ppm, (b) inclusion population in number per square millimeter broken down by non-metallic inclusion type and (c) evolution of Ca, Mg and total O over time. The hollow data points are taken with FEI Quanta600 using INCA – other data points are taken from ASPEx Automated Feature Analysis.

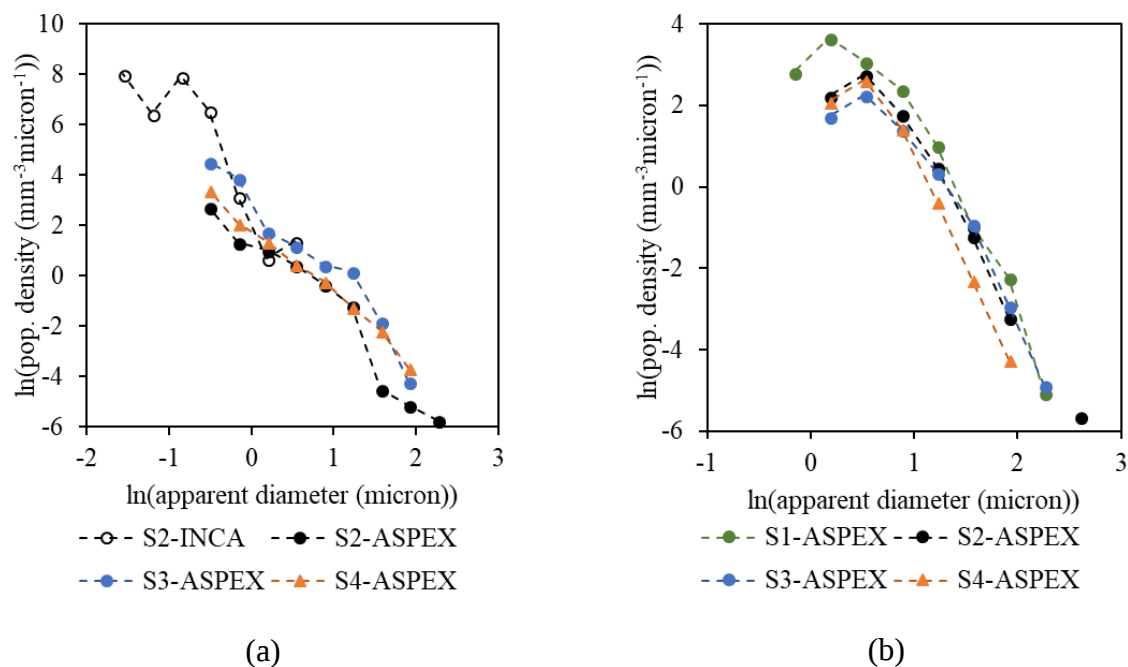


Figure 149 - PDF plots of a) Ca-containing inclusions and b) Ca-free inclusions (alumina). Data was generated from the ASPEX analyses and CSDCorrections software for 3D distribution correction from 2D data [125].

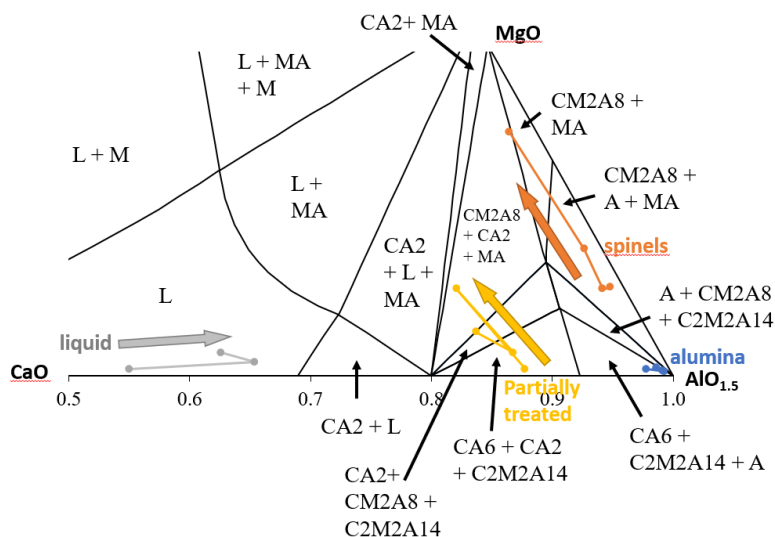


Figure 150 – The evolution of chemical composition of the four identified inclusion populations over time, compared to the partial CaO-MgO-AlO_{1.5} ternary diagram as calculated by FactSage 7.2 (FToxid) at 1873.15 K, plotted in terms of molar fraction.

Conclusions

- Ca-containing FeSi will readily modify alumina inclusions in Al-killed steels, with a perceived calcium yield of 23% (much higher than the ~1% calcium yield when adding calcium silicide other similar laboratory experiments). The yield will depend on available oxygen in the melt.
- This method of Ca-treatment, with more gentle dissolution of Ca in the melt, provides more information about the mechanism of Ca-treatment. Several nuclei of Ca-aluminates are generated then grow to be apparent to automated feature analysis.
- Different inclusion populations persist for a long time – fully-treated inclusions and alumina/spinels will progressively react, forming new partially-treated inclusions, until the equilibrium is reached. These reactions have a timescale on the order of several minutes, for the laboratory conditions used in this work.

5.4.10.3 – FeSi75-based Ca-treatment of Si/Mn-killed Steels

When Al-killed steel was Ca-treated using FeSi in the experiment described in the previous section, the inclusions did not reach equilibrium even after several minutes. To test the idea that [O] controls inclusion-inclusion kinetics and the Ca treatment yield, the experiment described in this section will assess the inclusion evolution for a Ca-treated Si, Mn-killed steel, the time for the reactions to reach equilibrium and the total amount of Ca transferred from FeSi to inclusions compared to the total added Ca.

This experiment followed the same procedure as the Ca-treatment of Al-killed steels, however 10g of SiMn was added upon deoxidation, and 0.7g of FeSi containing 2%Ca was added to the melt 100 seconds after deoxidation. The samples were taken after deoxidation and 60, 180, 360 and 540 seconds after FeSi Ca-treatment. The sample 60s after Ca-treatment was also analyzed using INCA Feature Analysis with FEG-SEM FEI Quanta600 at 10 kV, 10 mm working distance and 2000x field magnification with pixel size of 0.2 micron since ASPEX Explorer could not resolve the inclusions in that sample.

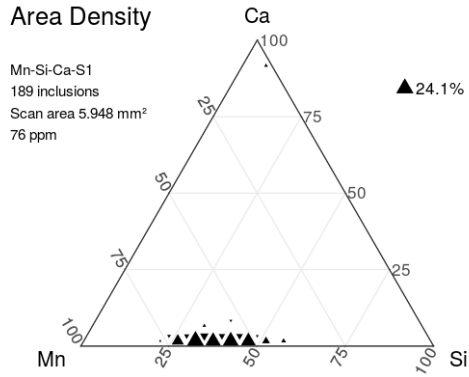
The results for chemical composition of the inclusions over time before and after treatment are shown in Figure 151. The inclusions start as Mn-silicates, and immediately after Ca treatment, there is a very large number of inclusions that precipitate of mixed Mn-Si-Ca oxide composition.

Over time, the Ca/Si ratio in the inclusions remain constant and Mn content decreases over time. The smaller MnO concentration in the inclusions is an indication that the melt was further deoxidized by the FeSi(Ca), avoiding the formation of secondary manganese silicates during solidification.

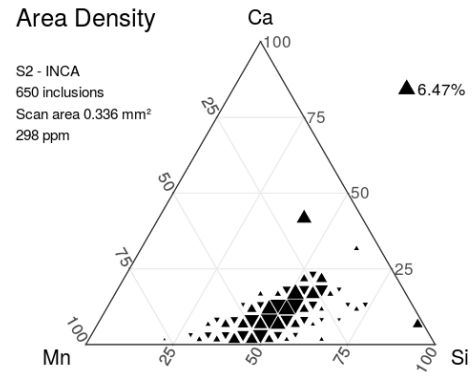
Unlike Ca-treatment of Al-killed steels, there aren't separate population of inclusions, which are all expected to be liquid at 1600°C (the MnO-SiO₂-CaO ternary diagram is plotted for reference in Figure 152. In Figure 153, from the sample before to after deoxidation, there is a significant increase in the number of very small inclusion nuclei (invisible to typical ASPEX automated feature analysis configurations, as seen in Figure 154 and Figure 155). The inclusions then grow to be detectable by ASPEX by 3 minutes after Ca addition; after this, the inclusion number starts to decline, suggesting that steady-state growth and removal rates have been achieved. Since Ca is such a strong deoxidant, Ca supersaturation and the availability of [O] (79 ppm for 1%Mn-0.25%Si) allowed most of the added Ca to react with the neighboring oxygen. Since the steel is not fully deoxidized, the rate in which these nuclei will ripen is almost two orders of magnitude larger than for an Al-killed steel, where the available oxygen for reaction comes mostly from neighboring inclusions and the small amount of remaining [O] (around 3 ppm).

The amount of Ca added was 23 ppm, and the Ca concentration in steel from the inclusion analysis is around 9 ppm. The Ca yield is 40%, larger than the yield obtained for the Al-killed steel (7 ppm for 28 ppm Ca added, 25%) likely due to higher availability of oxygen. From these two sets of experiments, the dissolved oxygen in the steel can play a very important role in the kinetics of Ca-containing inclusion-inclusion reactions.

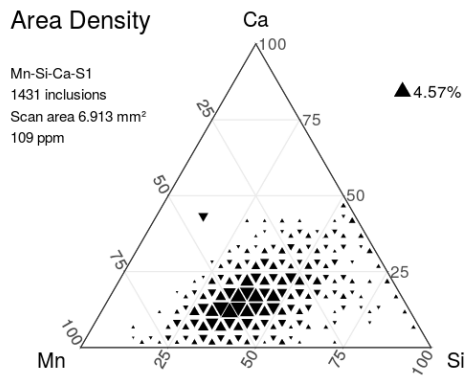
With time, the population of Mn-containing inclusion decreases, either because of the lower oxygen activity for CaO-containing inclusion-steel systems (decreased SiO₂ activity) or deoxidation for steel-refractory reaction.



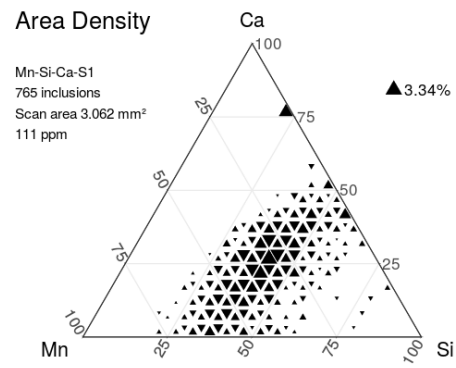
(a)



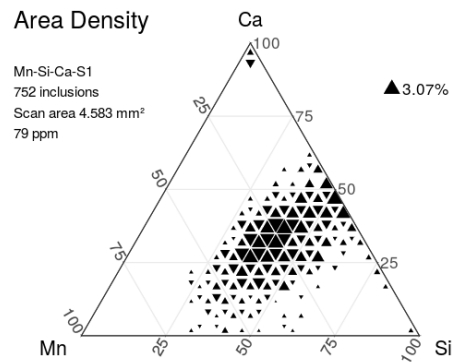
(b)



(c)



(d)



(e)

Figure 151 – Evolution of oxide inclusion compositions for Si-Mn killed steels after FeSi-based Ca-treatment. (a) After deoxidation; (b) 1 minute after FeSi(Ca) addition; (c) 3 minutes after FeSi(Ca) addition; (d) 6 minutes after FeSi(Ca) addition; (e) 9 minutes after FeSi(Ca) addition.

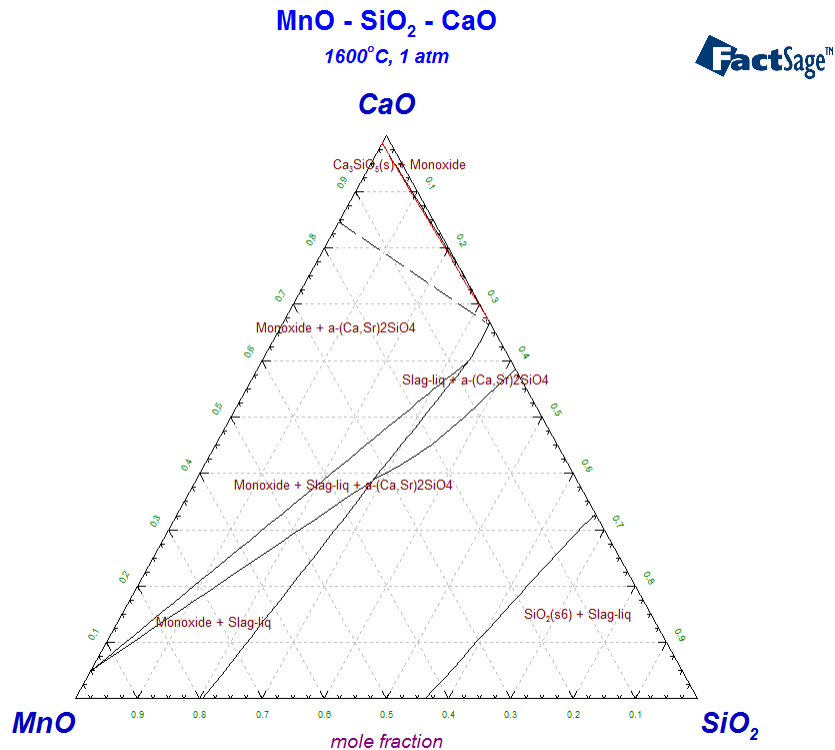


Figure 152 – Isothermal ternary diagram for the MnO-SiO₂-CaO oxide system at 1600°C.

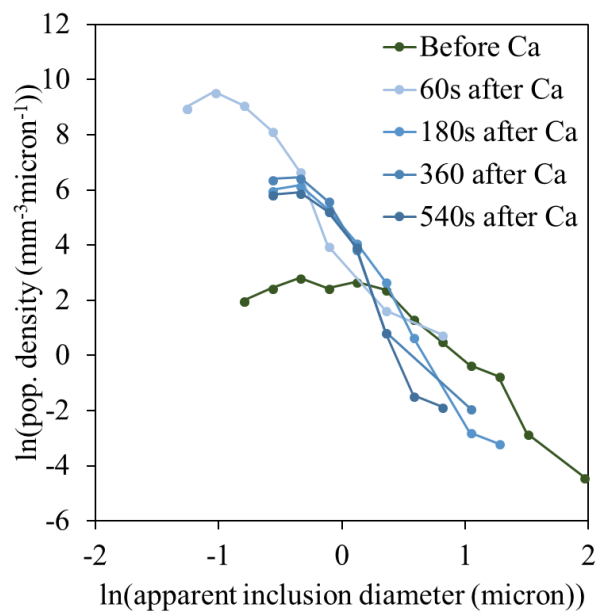
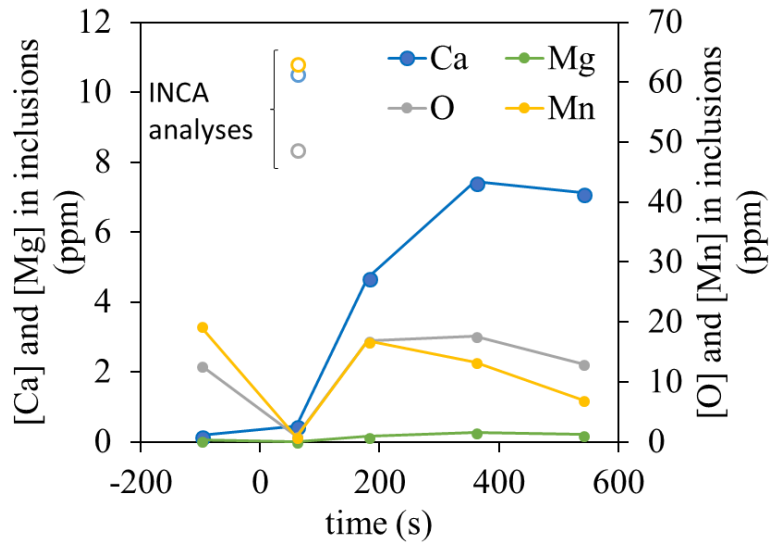
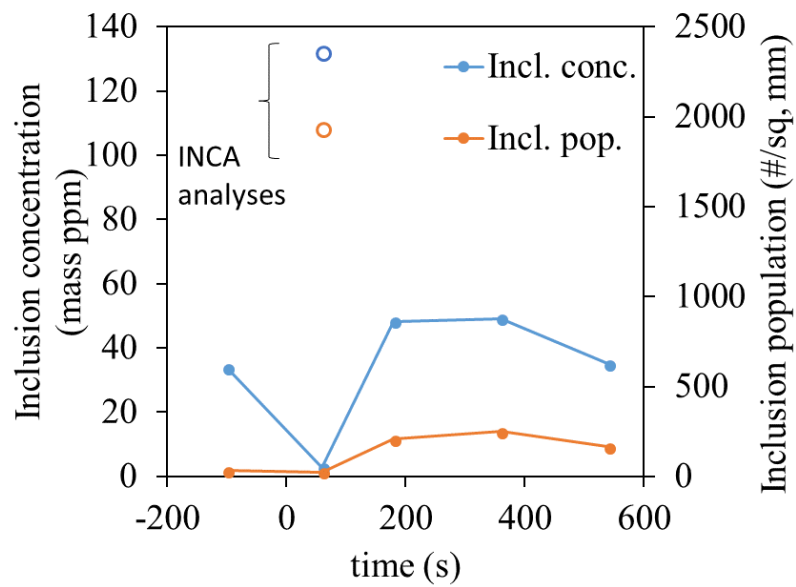


Figure 153 – PDF plots for the evolution of Ca-treated inclusions in Si-Mn killed steel. There is an abrupt increase of small inclusions that eventually grow, while larger inclusions float and leave the system.



(a)



(b)

Figure 154 – Measured (a) concentration of bound Ca, Mg, O and Mn in the steel and (b) measured inclusion concentration and population of inclusions over time from the SEM inclusion analyses.

5.4.10.4. Modeling inclusion-inclusion reactions after Ca-treatment

As seen previously in the previous sections, there seems to be a limiting factor for inclusion-inclusion reactions that depends on the concentration of the oxide constituent elements in solution in the surrounding steel. A model was developed using FactSage macros for the steel mass transfer-limited inclusion-inclusion reactions for two distinct initial inclusion compositions assuming the steel-inclusion reaction volume per timestep of simulation are the following, where D_i is the mass diffusivity of the species in steel, r is the radius of the inclusion, and N is the total number of inclusion nuclei in the steel. It is assumed that the number of inclusion nuclei in the steel is fixed and the average density of an inclusion is 4 g/cm^3 , so the inclusion size changes with the changing mass of the inclusion population, therefore changing the inclusion surface area and the steel mass transfer coefficient. It is also assumed that the bulk steel composition is homogeneous.

$$m_{steel-inclusion} = \frac{D_i}{r} \quad (72)$$

$$\Delta W_{steel} = mA\rho \Delta t = \frac{D_i}{r} N_{incl} (4\pi r^2) \rho_{steel} \Delta t = D_i N_{incl} 4\pi r \rho_{steel} \Delta t \quad (73)$$

The total number of inclusions in the steel is the total volume of inclusions, given by the total volume of inclusions divided by the volume of an individual inclusion:

$$N_{incl} = \frac{W_{inclusions}}{\rho_{inclusions}} \frac{3}{4\pi r^3} \quad (74)$$

$$r = \left(\frac{3W_{inclusions}}{4\pi N_{incl} \rho_{inclusion}} \right)^{\frac{1}{3}} \quad (75)$$

Combining the equations, the amount of steel reacting can be written as the following:

$$\Delta W_{steel} = D_i (4\pi N_{incl})^{\frac{2}{3}} \left(\frac{3W_{inclusions}}{\rho_{inclusion}} \right)^{\frac{1}{3}} \rho_{steel} \Delta t \quad (76)$$

The total number of inclusions for each of the inclusion populations is given by the FactSage equilibrium calculation. The diffusivities, densities and calculation timestep are fixed.

Two conditions were simulated using this modeling approach. For both simulations, the average inclusion density was taken to be 4 g/cm^3 and the average initial inclusion size as 3 micron. The temperature was 1600°C in both cases.

- Case 1:
 - bulk steel composition containing 0.05%Al + 3 ppm O, with the inclusion population #1 being 0.036g Al_2O_3 and inclusion population #2 being 0.021g liquid calcium aluminate (50wt%CaO-50wt% Al_2O_3).
- Case 2:
 - Bulk steel composition containing 1%Mn + 0.2%Si + 80 ppm O, with the inclusion population #1 being 0.05g $2\text{CaO} \cdot \text{SiO}_2$ and inclusion population #2 being 0.01g liquid manganese silicate (50wt%MnO-50wt% SiO_2).

The results for Case 1 are presented in Figure 155, and for Case 2 are presented in Figure 156. It is seen that, for Case 1, the inclusions reached equilibrium in around 20 seconds. The model predicts that, over time, Al and O from the original Al_2O_3 population are transferred to the Ca-aluminate inclusions, while Ca is also transferred from the Ca-aluminates to alumina. The decreasing Al_2O_3 population suggests that O transfer is faster than Ca transfer for this case due to the higher [O] in steel compared to [Ca]. Since it is likely that the associate model in FactSage overpredicts the dissolved Ca and O in steel, this might be one of the reasons why this model under-predicts the equilibrium time for these inclusion-inclusion reactions, while in steelmaking and in the experimental results these reactions can take a few minutes to reach equilibrium.

In Case 2, equilibrium is reached within 5 seconds. There is further deoxidation of the steel ([O] drops from 80 ppm to 60 ppm), and the Mn-silicates are destabilized, [O] is transferred to the lower O_2 -potential interface, which is at the Ca-silicate inclusions. This result shows how critical [O] is to Ca-treatment, and that inclusions with more-reducing interfaces can efficiently act as oxygen sinks and become mixed-composition inclusions. This might explain the presence of Ca-containing Mn-silicates found in some of the heats analyzed in Section 5.2.

Once there is better understanding of the solution thermodynamics of Ca in steel, the kinetics for inclusion-inclusion reactions can be better understood.

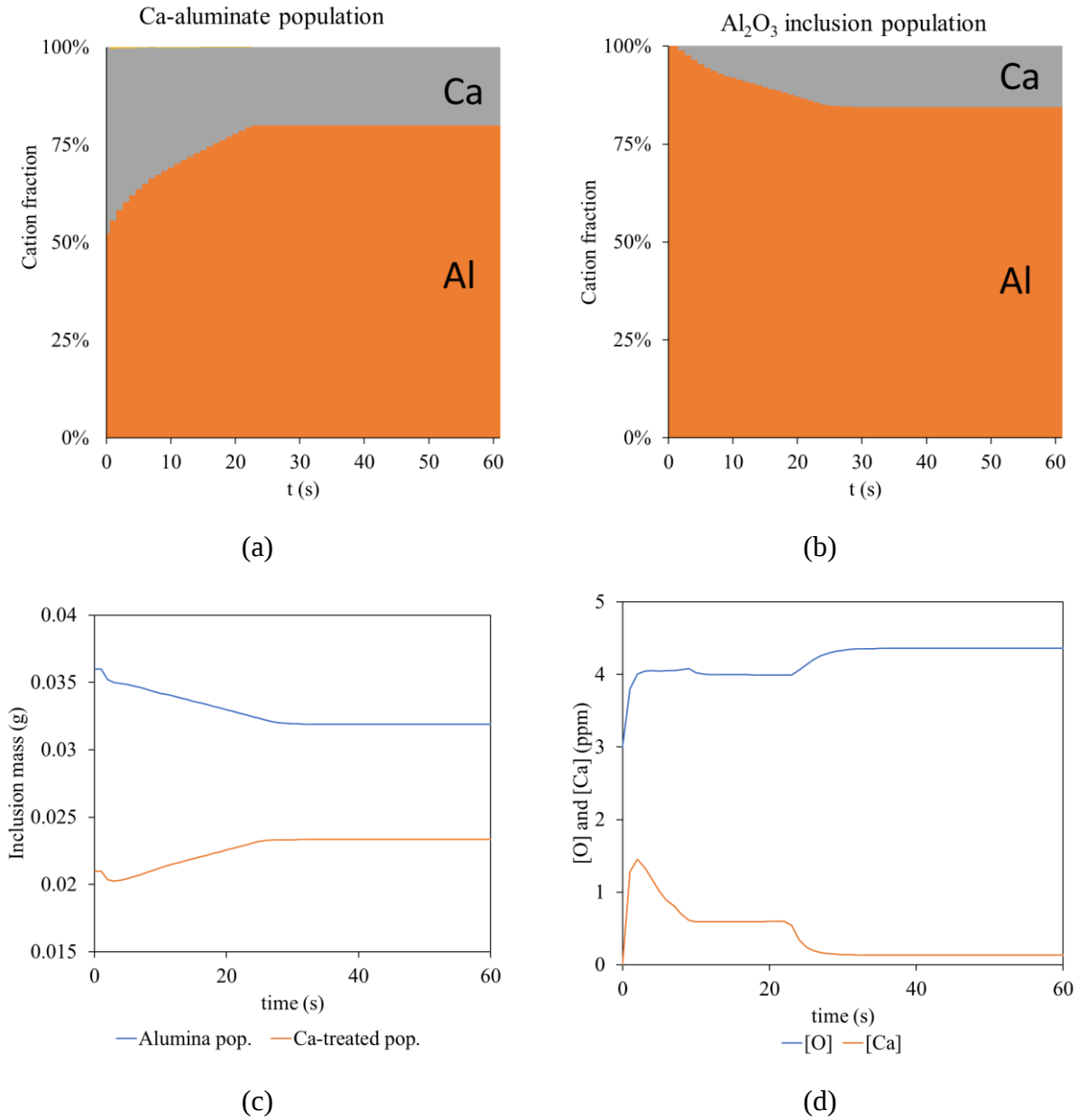
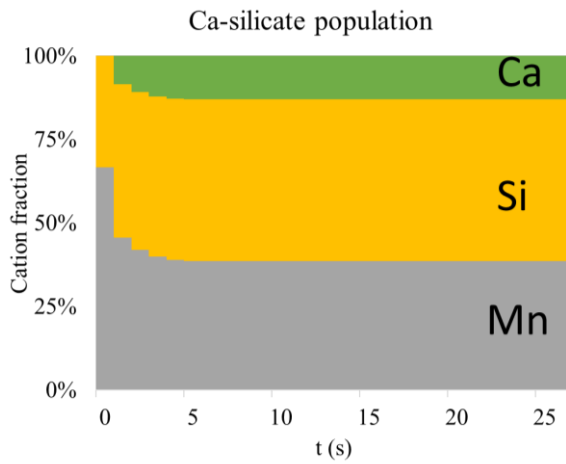
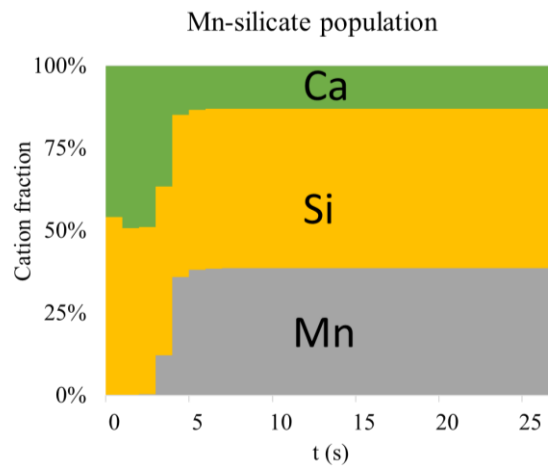


Figure 155 – Oxide inclusion composition evolution after FeSi(Ca) treatment of Al-killed steel.

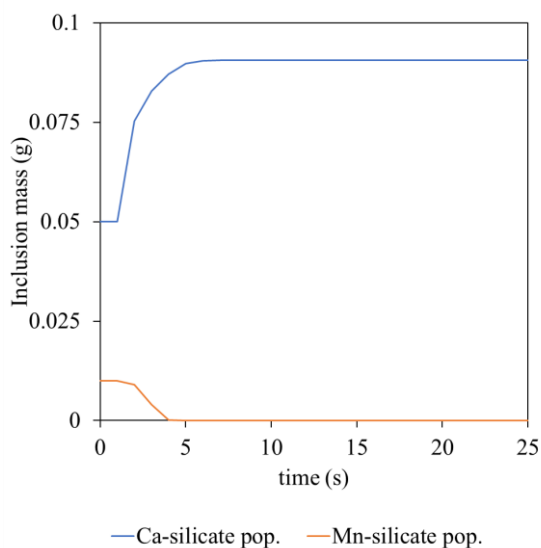
(a) The figure shows the cation fraction (Ca, Al) with time for the initial Ca-aluminate population, and (b) shows the cation fraction evolution for the initial alumina population. (c) The evolution of the concentration of inclusion populations in steel are shown in the plot. (d) The plot shows the evolution of [Ca] and [O] dissolved in steel over time.



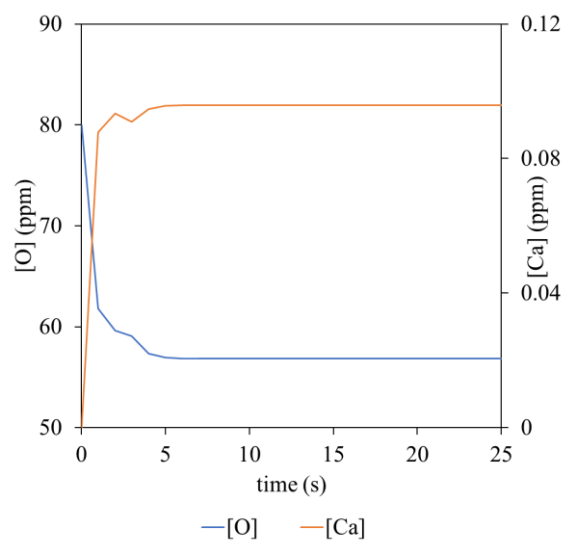
(a)



(b)



(c)



(d)

Figure 156 - Oxide inclusion composition evolution after FeSi(Ca) treatment of Si, Mn-killed steel. (a) The figure shows the cation fraction (Ca, Si, Mn) with time for the initial Ca-silicate population, and (b) shows the cation fraction evolution for the initial Mn-silicate population. (c) The evolution of the concentration of inclusion populations in steel are shown in the plot. (d) The plot shows the evolution of [Ca] and [O] dissolved in steel over time.

5.4.11. Effect of melt depth in experimental mass transfer coefficient: CFD simulation and experimental work

In this section, possible factors that influence the mass transfer coefficient in the induction furnace setup are studied. It is expected that convection drives mixing in the liquid, so COMSOL simulations are done using heat transfer and fluid flow physics modules to compare the computed surface velocities of steel for different steel masses (and consequentially, different melt heights). An experiment using the same slag from H1 but with 1 kg of steel is done, and the evolution of oxide inclusion composition is compared to a FactSage simulation using the mass transfer coefficient measured for Al pick-up in experiment H1.

In the laboratory-scale experiments, mixing conditions depend on natural convection, as the graphite crucible shielded the magnetic field, avoiding direct induction heating and stirring of iron itself. Stirring was driven by heat loss on the melt surface and heating from the sides of the crucible. Using a heat balance, one can estimate the heat loss from the melt surface by radiation.

If radiative heat flux will control the heat loss, the heat input into steel is the same as the heat loss from the top to maintain melt temperature at steady state. Therefore:

$$q_{top}A_{top} = q_{side}A_{side} \quad (77)$$

Taking the melt temperature as 1600°C (1873.15 K) and insulating cap temperature as 1000°C (1273.15 K), crucible diameter is 5.71 centimeters and melt height 3 to 6 cm, liquid iron emissivity is 0.2, heat flux can be estimated.

$$q_{side} = \sigma\epsilon(1873^4 - 1273^4) * \frac{\left(\frac{\pi D^2}{4}\right)}{(\pi Dh)} \quad (78)$$

$$q(h = 3 \text{ cm}) = 52237 \text{ W/m}^2 \quad (79)$$

$$q(h = 6 \text{ cm}) = 26119 \text{ W/m}^2 \quad (80)$$

The estimations show that, for due to the increased lateral area for a deeper melt, the inward heat flux into the steel is lower, so the stirring is expected to be weaker as well.

Steady-state steel flow for the assumed heat transfer conditions was performed using COMSOL Multiphysics 5.2, using the Non-Isothermal Flow Heat Transfer module. The assumed boundary

conditions were a fixed temperature of 1873 K (1600°C) for the side wall, acting as the heat input from the sides, and heat loss by thermal radiation with emissivity of 0.2 for the top surface, with outside temperature of 1273 K (1000°C). The bottom of the crucible was considered insulated. A no-slip boundary condition was assumed for the sides and bottom, and zero shear stress was assumed at the top surface. The solutions were performed for the default-sized mesh, automatically generated by the software. In order to model non-isothermal, natural convection flow, the temperature dependence of density and viscosity of iron should be given. The values were linearized as the following [35]:

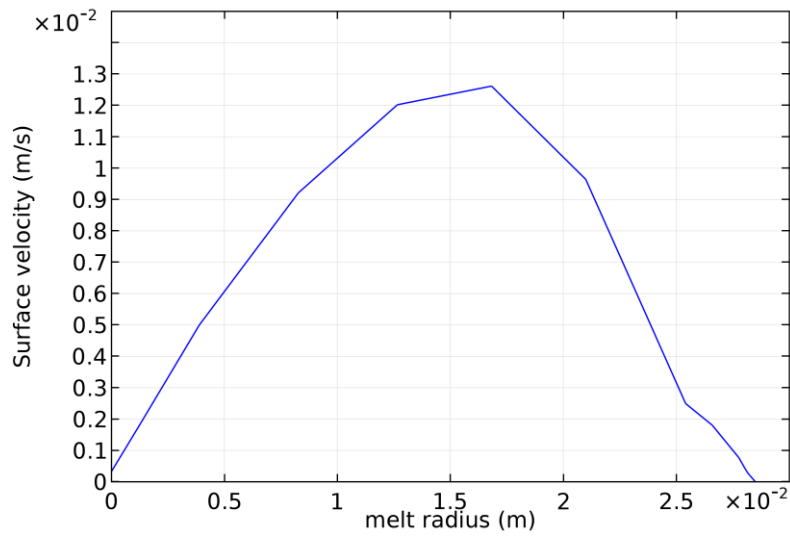
$$\rho_{steel} = 8300 - 0.836 * T \text{ (}^{\circ}\text{C)} \text{ [kg/m}^3\text{]} \quad (81)$$

$$\eta_{steel} = 21.24 - 0.0102 * T \text{ (}^{\circ}\text{C)} \text{ [mPa. s]} \quad (82)$$

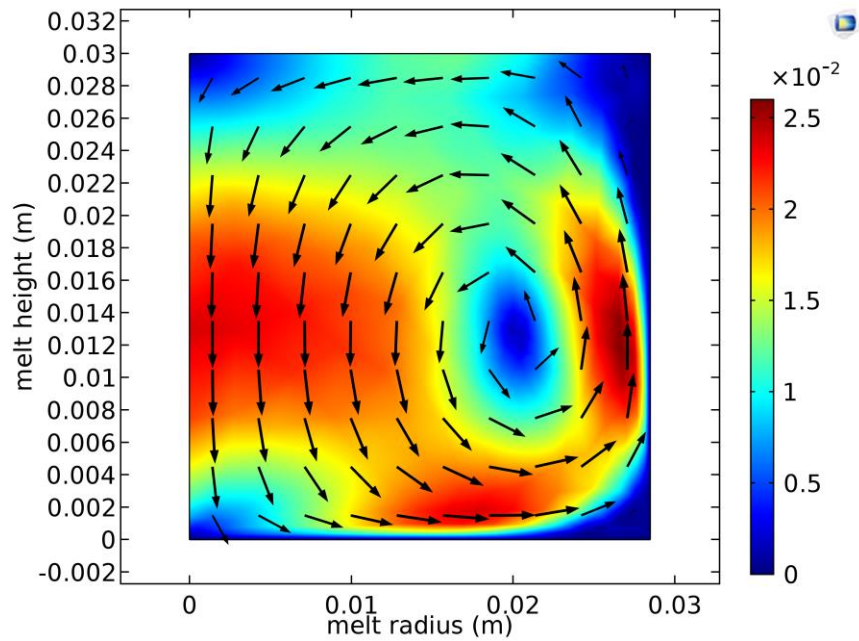
$$C_{p, steel} = 824 \left[\frac{\text{J}}{\text{kg. K}} \right] \quad (83)$$

$$k_{steel} = 35 \text{ [W/m. K]} \quad (84)$$

Figure 157 shows that a melt 3 cm deep will demonstrate dead zones at the crucible center (Figure 157b), and large temperature differences on the order of 40 K from the sides where the material is being heated to the center at the surface, where larger heat loss by radiation is expected (Figure 157c). The velocity at the surface is shown in Figure 157a, and the value can be used to estimate mass transfer using the Higbie model. For the 6 cm deep melt, temperature is more homogeneous (Figure 158c). The stirring profiles are similar, with slightly slower velocities on the edges (Figure 158b). The velocity magnitude at the top surface is similar for both cases, so there should not be an effect of melt depth on mass transfer coefficient (Figure 158a). The mass transfer coefficients for the maximum velocities are 4×10^{-5} m/s for the 0.6kg melt compared to 4.6×10^{-5} m/s for the 1kg. Although the mass transfer coefficient for the shallower melt is smaller, the rate constant for is 47% larger due to smaller steel volume. To test this, one induction furnace experiment was done using a melt depth of 6 cm (around 1 kg of steel), with 180g of slag with 47%CaO-35%Al₂O₃-10%MgO-8%SiO₂. Inclusion composition modeling using the same mass transfer coefficient of steel as calculated for a 600g melt yielded results that agreed with the experimental observations. The data points shown in Figure 159 are individual inclusions with composition analyzed manually by EDS using FEG-SEM Quanta 600. The experimental results did not show significant differences between the two mass transfer coefficients.

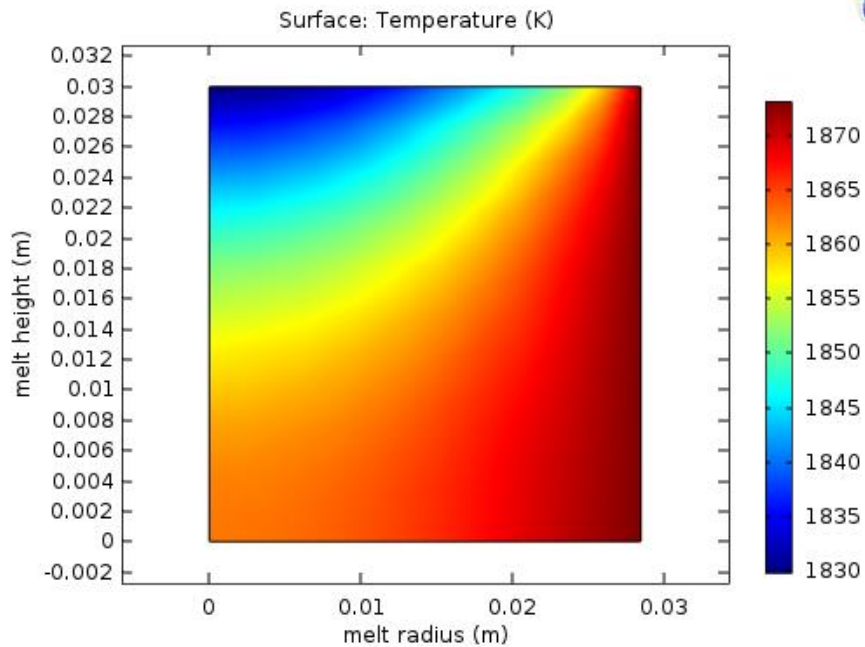


(a)



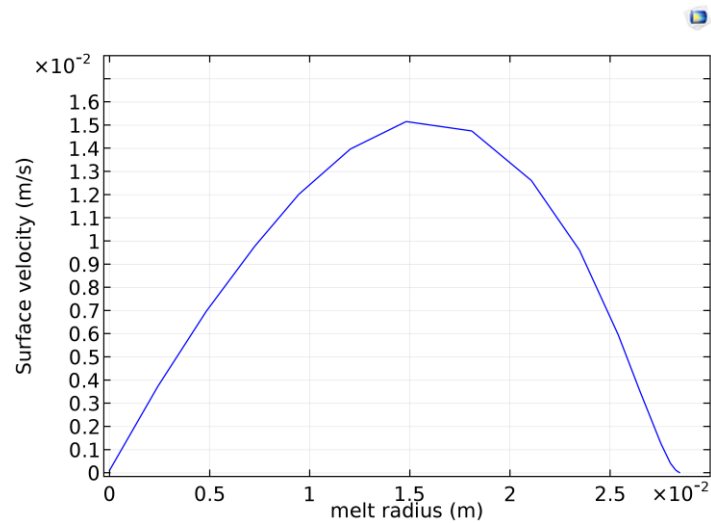
(b)

Figure 157 – COMSOL Multiphysics simulation results for 3 cm-deep melt flow behavior. (a) Plot of velocity magnitude along the radius at the top surface of steel melt. (b) Surface plot of velocity magnitude distribution in the melt. Arrows show the flow direction of the fluid. (c) Surface plot of temperature distribution in the melt.



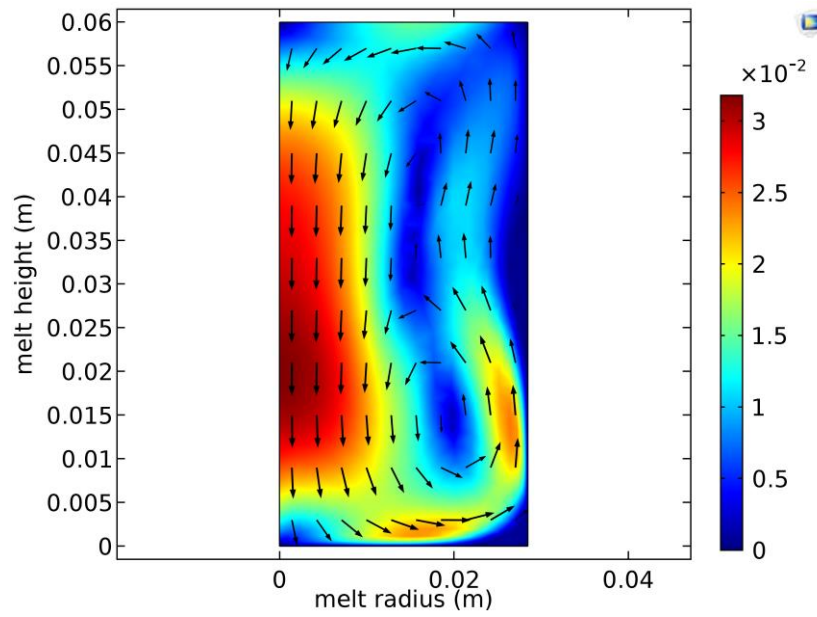
(c)

Figure 157 (cont.) - COMSOL Multiphysics simulation results for 3 cm-deep melt flow behavior. (a) Plot of velocity magnitude along the radius at the top surface of steel melt. (b) Surface plot of velocity magnitude distribution in the melt. Arrows show the flow direction of the fluid. (c) Surface plot of temperature distribution in the melt.

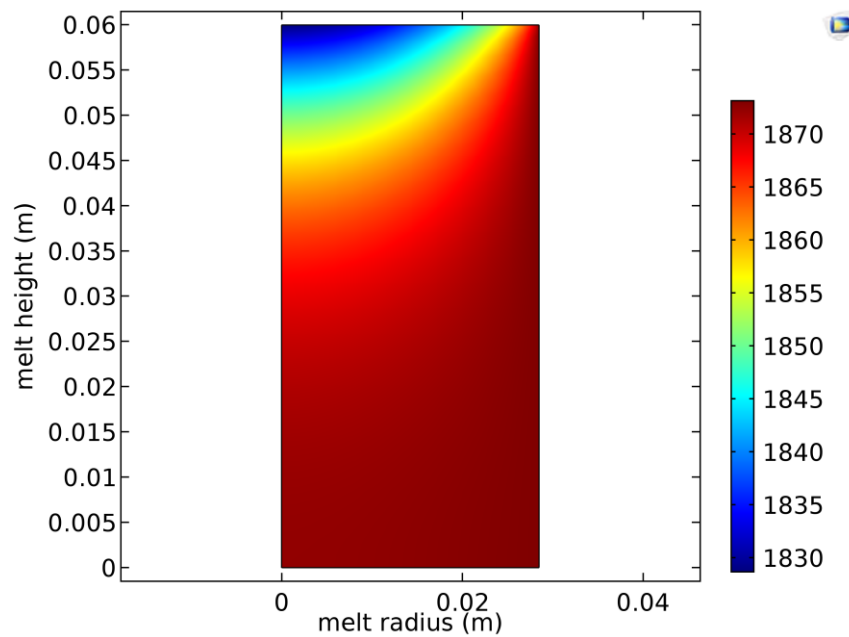


(a)

Figure 158 (cont.) – COMSOL Multiphysics simulation results for 6 cm-deep melt flow behavior. (a) Plot of velocity magnitude along the radius at the top surface of steel melt.



(b)



(c)

Figure 158 (cont.) – COMSOL Multiphysics simulation results for 6 cm-deep melt flow behavior. (a) Plot of velocity magnitude along the radius at the top surface of steel melt. (b) Surface plot of velocity magnitude distribution in the melt. Arrows show the flow direction of the fluid. (c) Surface plot of temperature distribution in the melt.

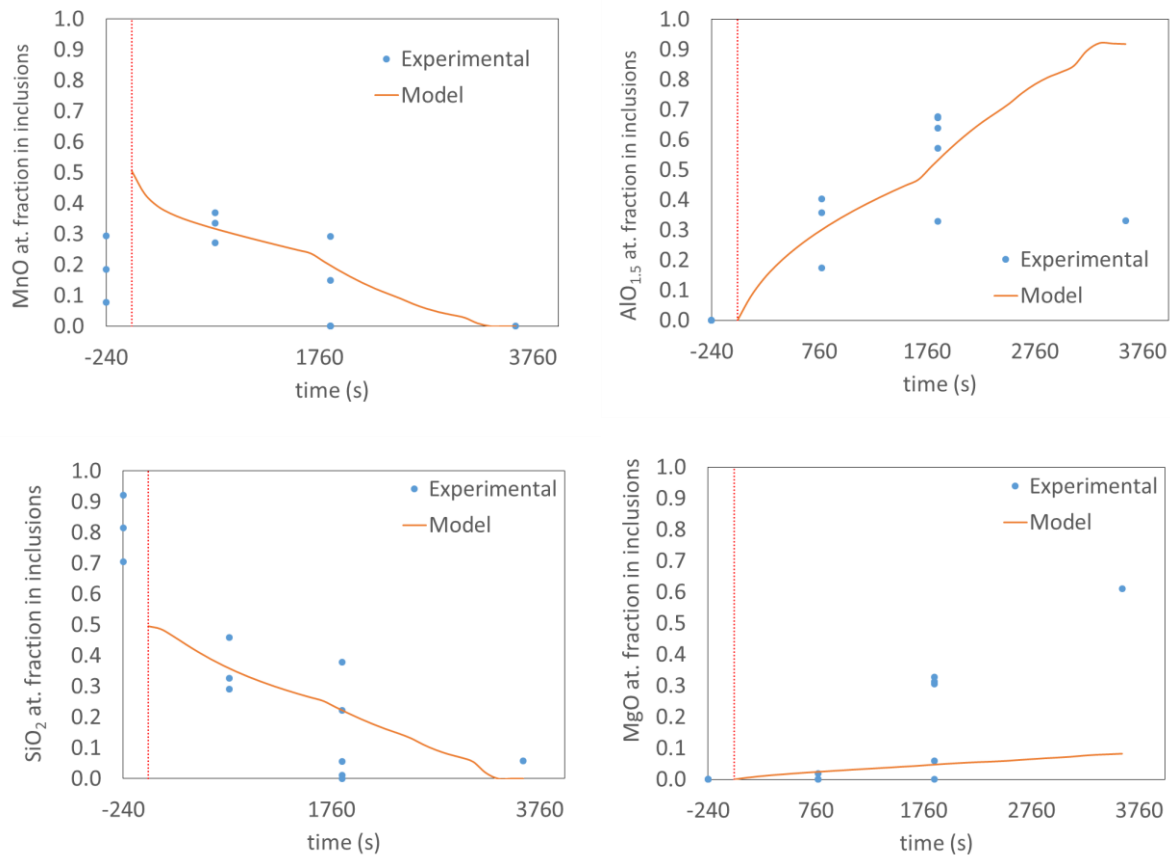


Figure 159 - Comparison between model and experimental results for the non-metallic inclusion composition evolution in a 1000g Si-Mn killed steel melt in contact with basic, Al₂O₃ containing slag. The data points represent the chemical composition of individual inclusions as measured using EDS with FEG SEM Quanta 600.

5.5. High-Temperature Confocal Laser Scanning Microscopy reoxidation on Mn-Si killed steels – gas-metal interactions

In this section, the objective was to selectively reoxidize the steel through the gas phase to precipitate out possible dissolved Mg and Ca in the form of oxide inclusions. For this, samples taken from the same Si-killed, degassed steel analyzed in Section 5.2 are used – those samples are expected to contain dissolved Mg and Ca according to the composition of their inclusions. If the oxygen partial pressure at the gas phase is controlled and the gas phase mass transfer coefficient is known, reoxidation of the steel sample at the CLSM can be controlled and the growth of

reoxidized Mg and Ca containing inclusions can be observed *in-situ* and *ex-situ*, if there is any. The experiments were done by switching the gettered, clean argon by ungettered argon for certain periods of time, and then the resulting oxidation products are analyzed. The experimental setup and results are described below.

5.5.1. Experimental Setup

In this experiment, samples were prepared from a ladle furnace lollipop sample taken at the end of degassing process of a Si-killed steel, which showed similar inclusion composition results (C_2S and MgO) as seen in Section 5.3.2. Pieces of 0.15g of this steel were placed in a MgO crucible, heated up to 1400°C in a 500 K/min heating rate, then to 1550°C in a 100 K/min rate under gettered Ar (less than 10^{-18} atm pO_2) inside the High-Temperature Confocal Laser Scanning Microscope (seen in Figure 160). The sample was held at 1550°C for 60 seconds, after which the protective Ar atmosphere was switched to oxidizing gas (ungettered Ar with 10^{-5} atm pO_2). One sample was not reoxidized, the second was reoxidized for 120 seconds and the third was reoxidized for 300 seconds. After reoxidation, the atmosphere was switched back to the ungettered Ar, which quickly recovered very low pO_2 levels. The samples were then cooled under the gettered Ar atmosphere at 100 K/min to 1300°C then the halogen lamp was shut down, effectively quenching the sample to room temperature. The inlet gas flowrate was fixed at $250 \text{ cm}^3/\text{min}$ and the absolute pressure inside the chamber was 110 kPa on average.

The reoxidized samples were analyzed under FEG-SEM for imaging and energy dispersive X-ray (EDS) to observe the chemical composition of the resulting oxide products.

To understand the gas-metal relations inside the CLSM, the mass transfer coefficient of the gas phase was measured in separate experiments by the mass loss of a liquid manganese and different Fe-Mn alloy samples, whose Mn vapor pressure at high temperatures would make a mass loss by evaporation from a 0.2g droplet measurable in the range of 0.0001g. The mass loss rates were then compared to a simple first-order kinetics mass transfer model.

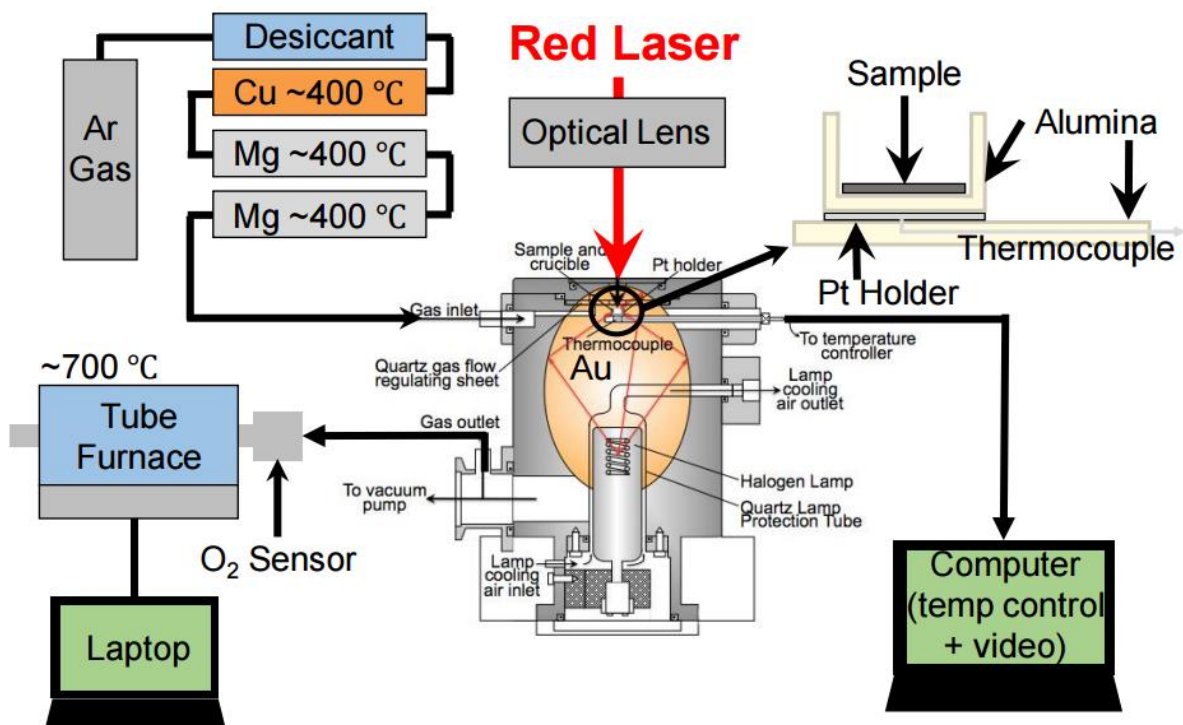


Figure 160 – Schematics of the High-Temperature Confocal Laser Scanning Microscopy (HT-CSLM) apparatus; off-gas oxygen partial pressure is analyzed at 700°C [126].

5.5.2. Results and Discussion

The experimental results shown in Figure 161 to Figure 165 show that there was reoxidation with increased ungettered Ar exposure time. However, with increasing reoxidation times, no Ca or Mg selective oxidation was observed. The first sample (Figure 161) showed the appearance of forsterite inclusions. A certain extent of reoxidation is expected when remelting a CSLM sample, due to atmospheric oxidation and at high solid-state temperatures, when the Ar oxygen partial pressure is not low enough to make the oxidation thermodynamically unstable.

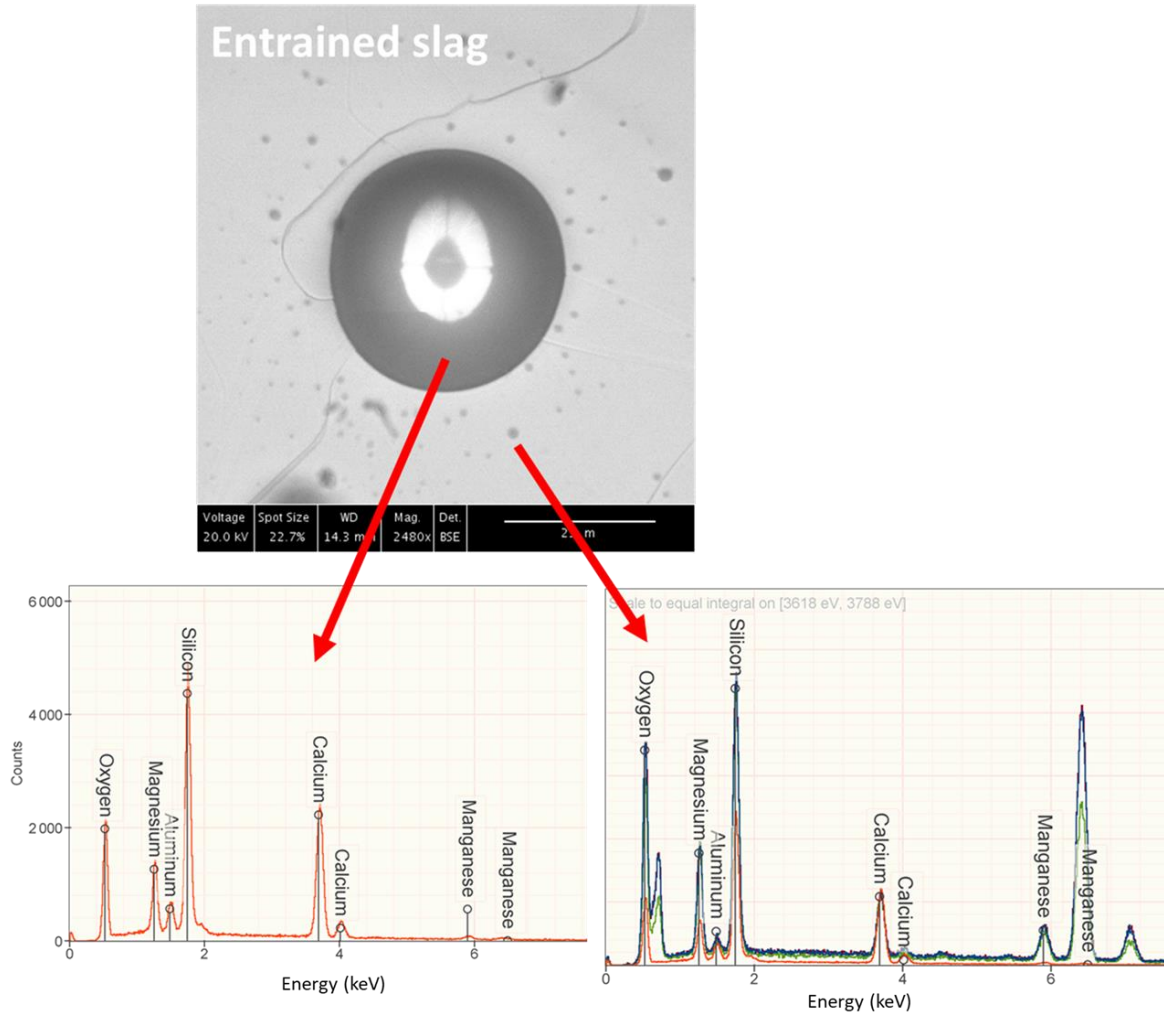


Figure 161 – Resulting agglomerated non-metallic inclusion after HT-CSLM observation with no gas-phase reoxidation. The non-metallic inclusion in the center shows slag-like composition (C_2S , MgO and residual Al_2O_3 , with almost no Mn). The satellite inclusions formed also show Ca, Mg, Al and a higher concentration of Mn.

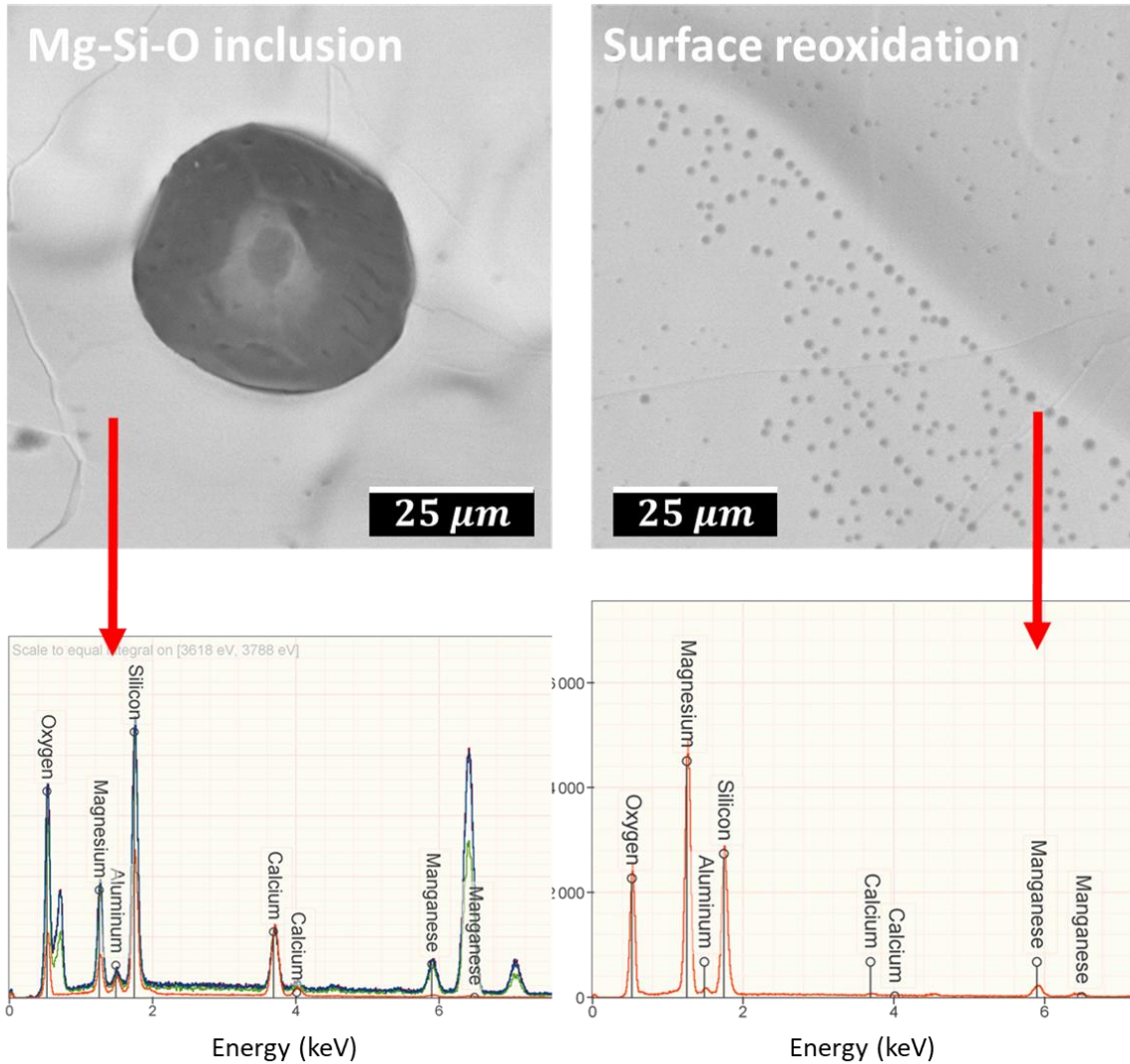


Figure 162 - Resulting agglomerated non-metallic inclusion after HT-CSLM observation with no gas-phase reoxidation. The image on the left shows the appearance of a forsterite inclusion, which might be a result of reoxidation. The result is consistent to the results of the experiment H8 (Section 5.3.6). Surface oxides (manganese silicates) appeared upon cooling (right).

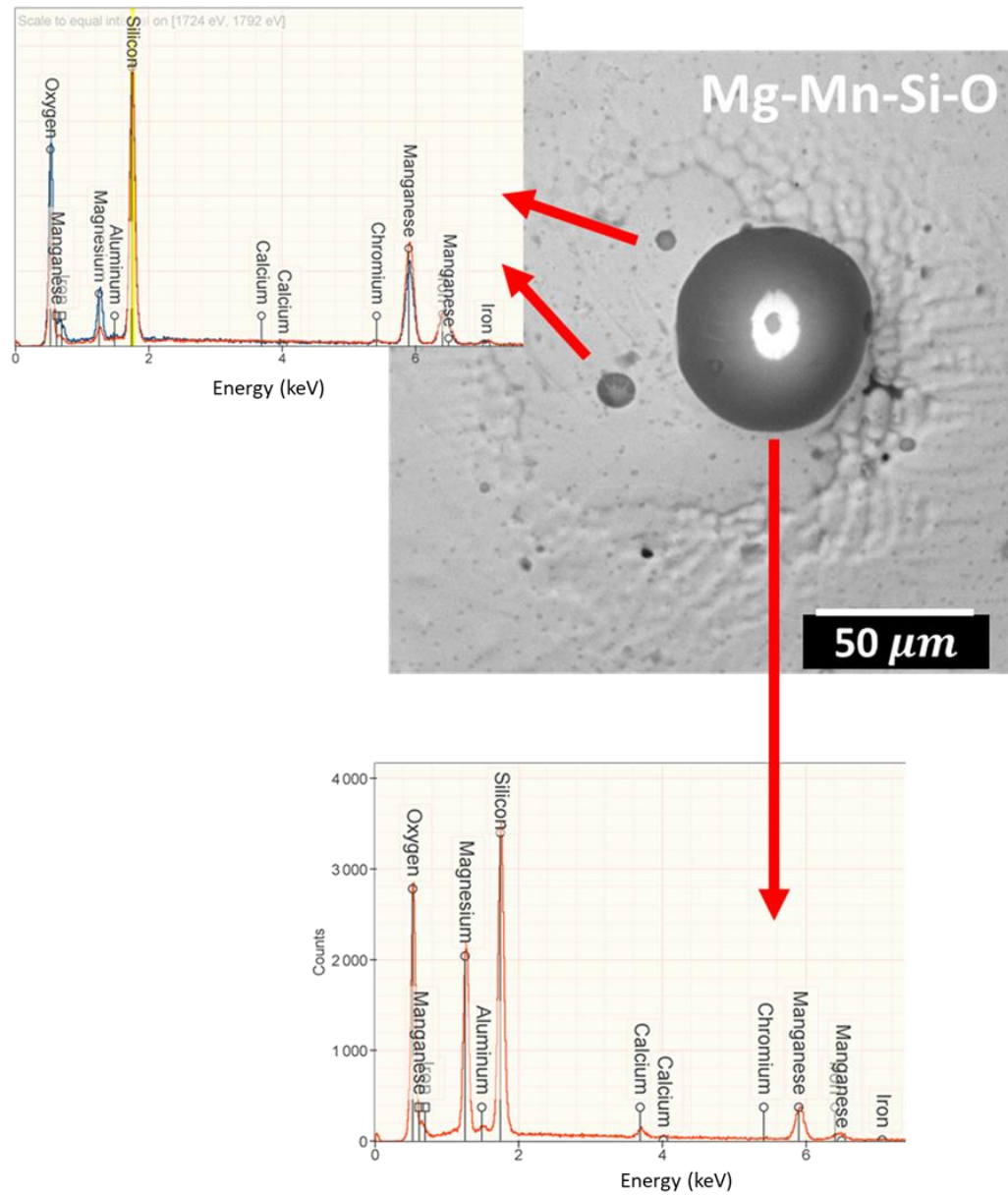


Figure 163 – Resulting inclusions after 120 seconds of reoxidation with their respective EDS analysis. Ca and Mg are diluted by Mn-silicates in the larger inclusion. The satellite inclusions are also depleted in Ca and Mg.

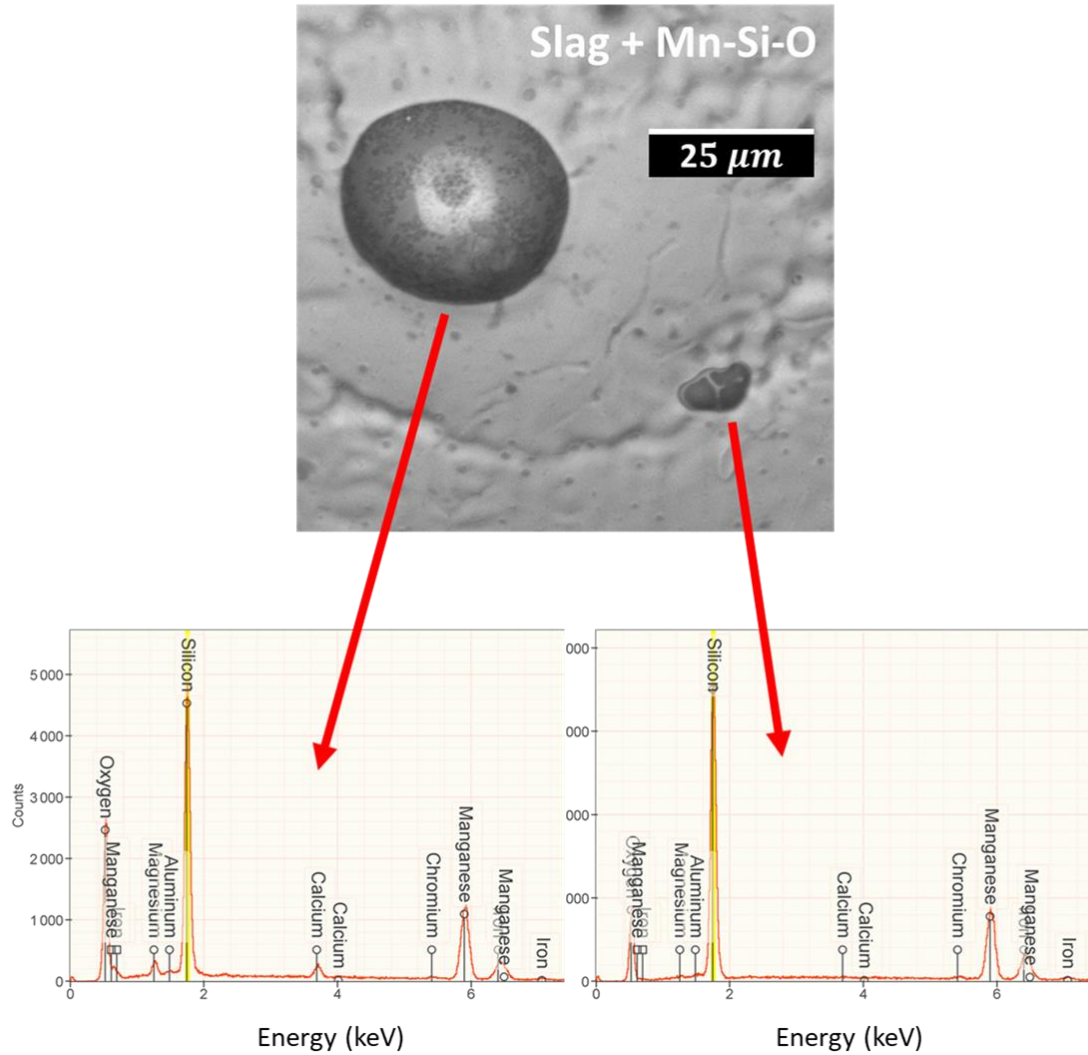


Figure 164 - Resulting inclusions after 120 seconds of reoxidation with their respective EDS analysis. Ca and Mg are further diluted by Mn-silicates in the larger inclusion, with an increasing Si:Mn peak ratio. The satellite inclusions are pure Mn-silicates.

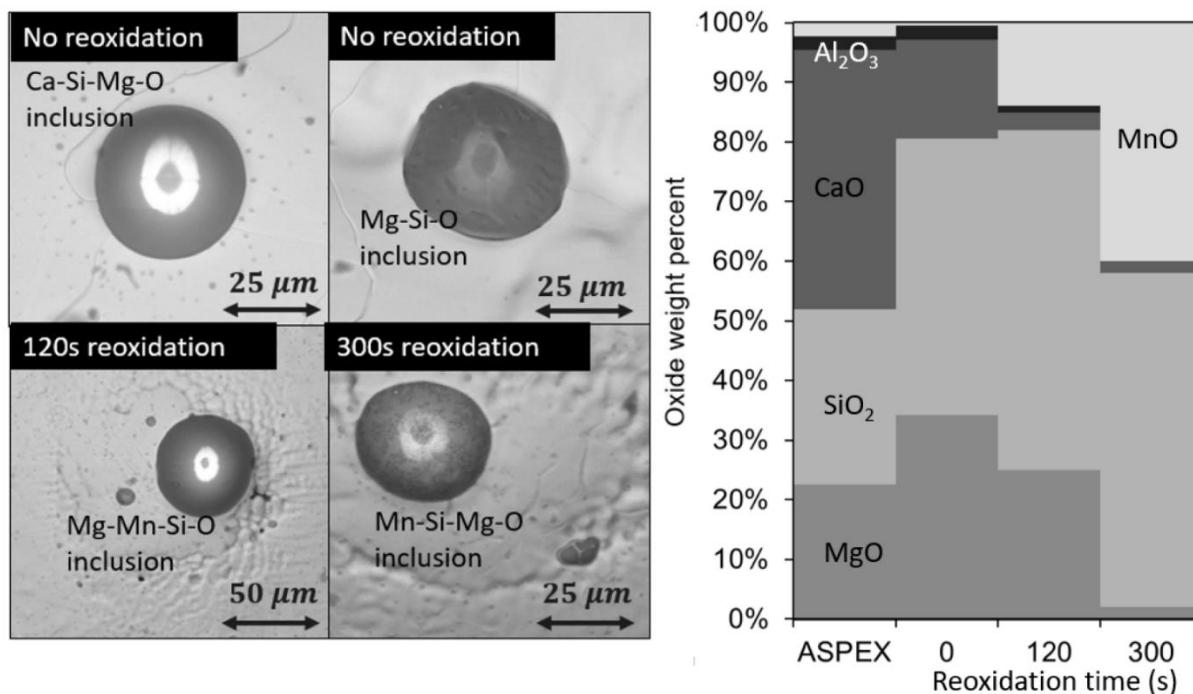


Figure 165 - Secondary electron images of non-metallic inclusion agglomerate located at the center of solidified HT-CSLM samples, for oxidation times as labeled. The overall chemical composition of the inclusions is given at right; the column marked "ASPEX" refers to inclusions present before reoxidation (measured by automated feature analysis).

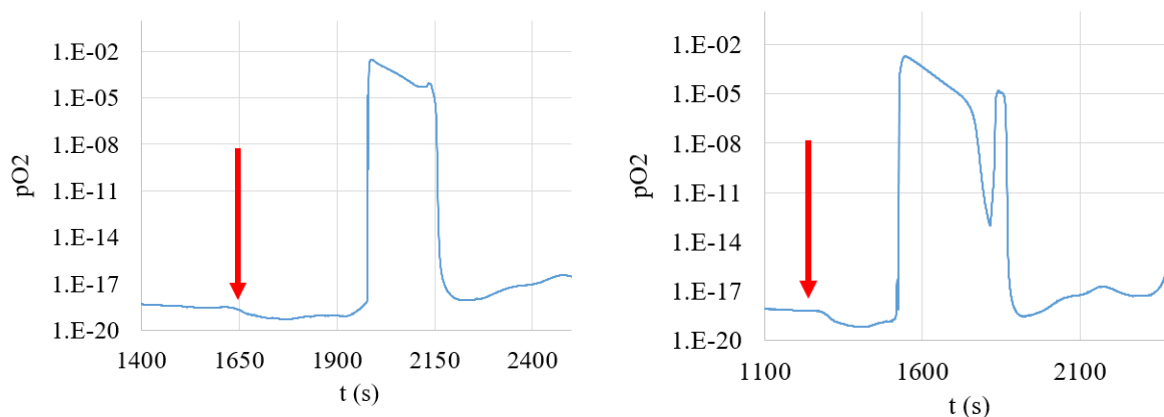


Figure 166 – Evolution of partial pressure of oxygen in the off-gas during experiment, showing increase in $p\text{O}_2$ during reoxidation. (a) 120 seconds of reoxidation, (b) 300 s of reoxidation. The red arrow marks the beginning of the experiment.

To understand the gas-phase kinetics for this system, a droplet of pure manganese (melting point of 1246°C) was put in an Al₂O₃ crucible of 8mm diameter and allowed to evaporate for a controlled amount of time (250 seconds and 375 seconds) at 1500°C. The initial and final sample masses were measured five times each using a precision balance with 0.0001 g resolution. The mass loss results are presented below in Figure 167.

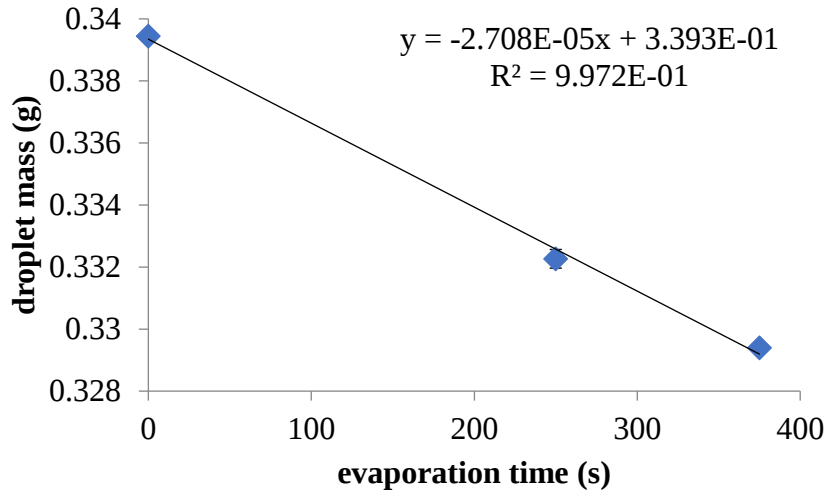


Figure 167 – Mass loss of pure Mn droplet in confocal microscope at 1500°C.

The final droplets had approximately hemispherical shapes. Assuming the density of Mn at the melting point being 5.95 g/cm³, the radius of the droplet is approximately 2.5 mm, so the assumed surface area is $4 \times 10^{-5} \text{ m}^2$. The mass loss was of $2.708 \times 10^{-5} \text{ g/s}$. Therefore, the molar flux of Mn can be written as:

$$\frac{1}{A} \frac{dN_{\text{Mn}}}{dt} = \left(\frac{1}{4 \times 10^{-5} \text{ m}^2} \right) \frac{(2.708 \times 10^{-5} \text{ g/s})}{(54.94 \frac{\text{g}}{\text{mol}})} = -1.255 \times 10^{-2} \text{ mol/m}^2\text{s} \quad (85)$$

The partial pressure of Mn at 1500°C (1773 K) is $2 \times 10^{-2} \text{ atm}$. Then, using the Langmuir expression in Eq. 86 [34,35] the effective vapor pressure at the interface can be calculated, and then a gas-phase mass transfer coefficient can be estimated by Eq. 87. p_{eff} is the effective vapor pressure at the surface, p_{vap} is the vapor pressure of metal at the experiment temperature, M_{Me} is the molar mass of the metal, p_{gas} the concentration of metal in the bulk gas (essentially zero), k_{gas} is the gas phase mass transfer coefficient and α is the sticking coefficient (taken to be 1).

$$\frac{1}{A} \frac{dN_{Me}}{dt} = \frac{\alpha(p_{vap} - p_{eff})}{\sqrt{2\pi M_{Me}RT}} \quad (86)$$

$$\frac{1}{A} \frac{dN_{Me}}{dt} = k_{gas} \frac{p_{gas} - p_{eff}}{RT} \quad (87)$$

Using the measured evaporation rates and the partial pressure of the system in Eq. 86, the difference between the effective pressure and the vapor pressure is estimated to be 8×10^{-6} atm. This difference is much smaller than the vapor pressure of Mn in the experiment, so evaporation should be controlled by gas-phase mass transfer.

Using Eq. 87, the k_{gas} value obtained is 5.3×10^{-2} m/s. This allows calculation of the Sherwood number (Eq. 88), in which k is the mass transfer coefficient, $d_{droplet}$ is the diameter of the droplet and D_{Mn-Ar} is the binary diffusivity of Mn vapor in Ar. Data on Mn-Ar diffusivity is provided by Grieveson and Turkdogan [127].

$$Sh = \frac{k d_{droplet}}{D_{Mn-Ar}} \quad (88)$$

The diffusivity of Mn in Ar was calculated for the film temperature, taking the average between the droplet temperature (1773 K) and room temperature, since the chamber is water cooled. Then, it is found that $D_{Mn-Ar}(1085 \text{ K}) = 1.368 \times 10^{-4} \text{ m}^2/\text{s}$. The resulting Sherwood number is 1.9, which demonstrates that the transport of Mn through the Ar phase is very close to static diffusion for which $Sh = 2$. Using this Sherwood number, the gas phase mass transfer coefficient can be expanded to other evaporating species in the melt.

The significant rates of metals evaporation due to the high surface-to-volume ratio is expected to have a strong influence on gas-phase reoxidation behavior. According to the classic paper by Turkdogan, Grieveson and Darken [128] on the enhanced vaporization of metals in the presence of oxidizing atmospheres, the opposite fluxes of metal and oxygen will form a fume, and depending on the stoichiometry of the oxide and evaporation rates, the distance from the oxide film to the droplet can change (fume boundary layer δ in Figure 168). The gas phase boundary layer Δ can be calculated from the diffusivity of Mn in Ar and the measured mass transfer coefficient (Eq. 89).

$$k = \frac{D_{\text{Mn-Ar}}}{\Delta} \quad (89)$$

Since $k = 0.053 \text{ m/s}$ and $D = 1.37 \times 10^{-4} \text{ m}^2/\text{s}$, the gas phase mass transfer boundary layer thickness is $\Delta = 2.6 \times 10^{-3} \text{ m}$.

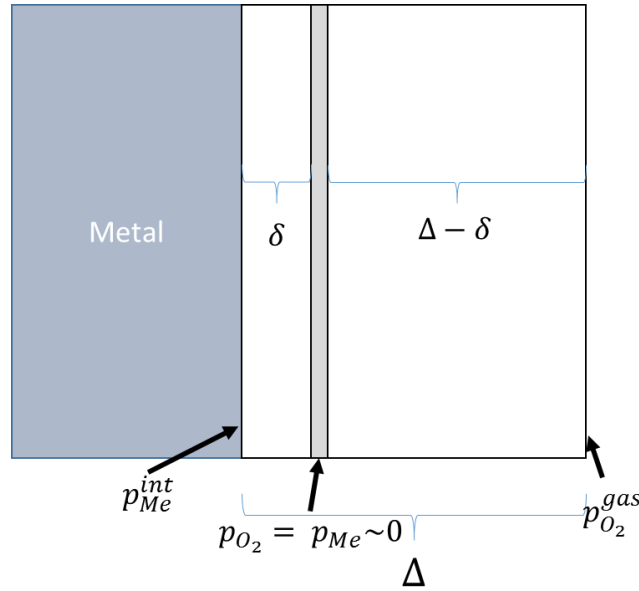


Figure 168 – Schematics of enhanced diffusion-limited metal vaporization by oxidizing atmospheres. The boundary conditions for this problem assumes that the pressure at the metal surface is its vapor pressure, the partial pressure of oxygen at Δ away of the interface and both p_{O_2} and the metal partial pressure is zero due to the chemical reaction.

The countercurrent fluxes of metal and oxygen are given by the following equations, where p^* are the partial pressures of metal and oxygen gas in equilibrium with the gas fume phase (taken to be zero):

$$J_{\text{Me}} = \frac{D_{\text{Me}}}{\delta} \frac{p_{\text{Me}} - p_{\text{Me}}^*}{RT} \quad (90)$$

$$J_{\text{O}_2} = \frac{D_{\text{O}_2}}{\Delta - \delta} \frac{p_{\text{O}_2} - p_{\text{O}_2}^*}{RT} \quad (91)$$

Since the oxide being formed at the boundary layer (at 735°C) at low p_{O_2} must be Mn_3O_4 (Figure 169), it can be written:

$$J_{\text{Mn}} = \frac{2}{3} J_{\text{O}_2} \quad (92)$$

For the oxidizing conditions ($p_{\text{O}_2} = 10^{-5}$ atm), we can calculate the size of the fume boundary layer δ , knowing the value of $D_{\text{O}_2-\text{Ar}}$, which is calculated to be 1.64×10^{-4} m²/s for Ar at 735°C.

$$\delta = \frac{\left(\frac{3}{2} \frac{D_{\text{Mn}} p_{\text{Mn}}}{D_{\text{O}_2} p_{\text{O}_2}} \right)}{\left(1 + \frac{3}{2} \frac{D_{\text{Mn}} p_{\text{Mn}}}{D_{\text{O}_2} p_{\text{O}_2}} \right)} \Delta \quad (93)$$

$$\delta = 6 \times 10^{-3} \text{ m} \quad (94)$$

The fume boundary layer thickness is very similar to the gas phase mass transfer boundary layer thickness – therefore, very little reoxidation should be expected, due to the gettering of O₂ by Mn vapors.

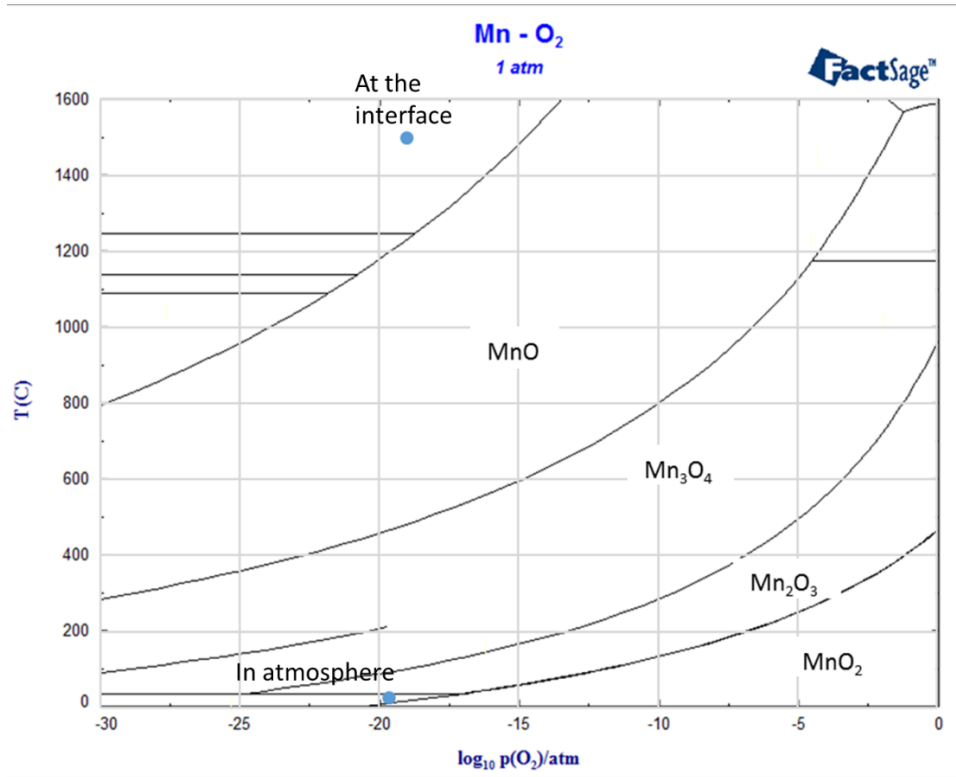


Figure 169 – Predominance diagram of Mn-O₂ system. For log(pO₂) around -20, Mn metal is stable at 1500°C and Mn₂O₃ at room temperature.

When the same steel-slag conditions from Section 5.3.6 are applied, the Mg vapor pressure in steel is calculated by FactSage 7.0 (FTmisc + FToxid) to be 9.5×10^{-3} atm. Assuming that the

diffusivity of Mg in Ar will not be very different from Mn or O₂, the mass transfer coefficient is given by $k_{Mg} = 5.3 \times 10^{-2}$ m/s, thus the Mg loss rate would be 6×10^{-6} g Mg/s. For a 0.15g sample, that means a loss of 40 ppm Mg/s. The loss of Mg might increase the solubility of oxygen in the steel, thus reoxidizing it.

Along with volatile metals, gaseous species such as CO and SiO might have a significant partial pressure. For a Si-Mn killed steel with 50 ppm of total oxygen, $p_{SiO} = 1.36 \times 10^{-4}$ atm at 1600°C; for a steel with 0.05%C-0.05%Al and 30 ppm total oxygen, $p_{CO} = 5.6 \times 10^{-3}$ atm at 1600°C as calculated by FactSage 7.0. Thus, the evaporation rates should be comparable to the ones calculated for Mg, and the steel might be *deoxidized* through the gas phase.

More work must be done to assess other rate-limiting steps such as the steel-inclusion reactions to fully understand the phenomena and critically assess the results of HT-CSLM experiments in which volatile species are involved, such as Mn, Ca and Mg.

6. Conclusions – Revisiting the hypotheses

1.

- a. A one-parameter liquid-liquid kinetic model using FactSage can successfully predict final inclusion composition in Si-Mn killed steel processing.*

The hypothesis is confirmed for experimental induction furnace conditions. The one-parameter model accurately predicts the evolution of inclusion chemical composition, with better accuracy when slag mass transfer is not limiting so the inclusion removal is also steel mass transfer-limited. The work was not sufficient to confirm the hypothesis for the analyzed industrial heats due to uncertainties in Ca thermodynamics and other possible sources of Ca in steel processing.

- b. The Si-SiO₂ reaction pair controls p_{O_2} at the steel-slag interface and thus the reduction of more stable oxides such as MgO and Al₂O₃ to steel.*

Yes. The lower the silica activity, the lower the oxygen potential at the steel-slag interface, thus more Al and Mg are expected to be reduced. This hypothesis was also confirmed. In Section 5.3.3, high SiO₂ activity lowered the equilibrium Al content in steel, while in Section 5.3.6 the high basicity and low SiO₂ promoted significant reduction of MgO, to the point that reoxidation yielded forsterite inclusions. The same effect is observed in the industrial samples observed in Section 5.2. Also, reoxidation through slag phase (as MnO) is controlled by slag mass transfer up to 5%MnO and does not affect Al and Mg pick-up if Si activity is still high enough. Also, in the industrial samples, it is seen that Mg pick-up is observed even after reoxidation of steel.

2. *Slag emulsification and ferroalloy impurities are more likely to be responsible for Ca pick-up in inclusions than reduction of CaO from slag.*

Partially. In none of the induction furnace experiments was there significant evidence of dissolved Ca, although Ca-containing non-metallic inclusions are observed in industrial ladle treatment. However, strong desulfurization or deoxidation might promote slag breakup, and experiments of

Ca-containing ferroalloys demonstrated that the Ca yield is high when added as a ferroalloy impurity. Literature review also showed that even slags with very low basicity (not very reducing) can yield a significant concentration of CaO-containing inclusions due to vigorous stirring. In samples taken after degassing of Si-killed steels, since there are many circulations of steel and the slag is very deoxidizing, the CaO and MgO observed in inclusions may originate from steel-slag reactions.

3. Pressure does not influence the desulfurization of Si-Mn killed steels.

Yes. The experiment H8 (Section 5.3.6) demonstrated that very low S can be achieved for Si-killed steels given CaO saturation, low SiO₂ activity and enough solubility of CaS.

4. Calcium pick-up from ferroalloys is more efficient than via Ca-alloy wires. The mechanism of Ca pick-up involves the local reduction of excess dissolved oxygen, creating a new population of inclusions that will grow to be the definitive population of inclusions for that steel.

Yes. The Ca yield in the experiments shown in 5.4.10 of around 25% for Al-killed and 40% for Si-killed steels. Most inclusions that formed after Ca addition are small enough to be undetectable by ASPEX, indicating the formation of a completely new population of inclusions upon Ca treatment.

5. The chemical composition for secondary (solidification) inclusions in Si-Mn killed steels is significantly different than the primary population due to the consumption of Ca, Mg and Al as the liquid locally cools, precipitating more oxidized, Mn and Si-rich phases. Local cooling rate will affect their size, making the inclusions otherwise invisible appear to the SEM/EDS-based automated feature analysis.

Yes. The hypothesis is confirmed in Section 5.3.2, where both experimental results and Scheil solidification simulation using FactSage confirms that there is an effect of solidification in the apparent size of the non-metallic inclusions, and that for these Si-killed steels the secondary

inclusion population was mostly more oxidized phases, rich in Mn, Si. The formation of those can be explained by the consumption of Ca, Mg and Al during the initial stages of cooling and solidification.

6. Evaporation effects influence liquid metal observations in CSLM.

Yes. Evaporation certainly changes the chemical composition of steel on relatively short timescales, and the apparent reoxidation observed was more likely due to the evaporation of species such as Mg and Ca, causing O to redissolve and recombine with Mn and Si upon solidification.

7. Suggestions for Future Work

- Experimental and modeling studies on the behavior of slag emulsification during ladle treatment, especially during degassing to estimate minimum inclusion size obtainable.
- Induction furnace experiments with impeller stirring to increase mass transfer coefficient and observe Ca, Mg and Al pick-up from slag.
- Analysis of ladle furnace samples for typical Si-killed steel processing, to test the hypothesis of the one parameter kinetic model for industrial scale.
- Analyzing the effect of Ca as an impurity of ferroalloys in sulfur-containing steels, to test the effect of CaS on the inclusion-inclusion kinetics as an intermediate phase during Ca-treatment of steels.
- Study different possible sources of Ca into steelmaking practice, such as slag particles in other types of ferroalloys, refractory impurities or ladle glaze,

8. References

1. P. Kaushik, J. Lehmann, and M. Nadif, *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **43**, 710 (2012).
2. E. T. Turkdogan, *Fundamentals of Steelmaking* (The University Press, Cambridge, UK, 1996).
3. G. Bernard, P. V. Riboud, and G. Urbain, *Rev. Métallurgie - CIT* **78**, 421 (1981).
4. D.-H. Woo, Y.-B. Kang, and H.-G. Lee, *Metall. Mater. Trans. B* **33**, 915 (2002).
5. T. Malkiewicz and S. Rudnik, *J. Iron Steel Inst.* **33** (1963).
6. P. Nolli, *Metall. Mater. Trans.* **39B**, 56 (2008).
7. D. G. Edelman, P. C. Campbell, C. R. Killmore, K. R. Carpenter, H. R. Kaul, J. G. Williams, and W. N. Blejde, *Iron Steel Technol.* **6**, 47 (2009).
8. D. Roy, P. C. Pistorius, and R. J. Fruehan, *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **44**, 1086 (2013).
9. M. Allibert, H. Gaye, I. Geiseler, D. Janke, B. J. Keene, D. Kirner, M. Kowalski, J. Lehmann, K. C. Mills, D. Neuschültz, R. Parra, C. Saint-Jours, P. J. Spencer, M. Susa, M. Tmar, and E. Woermann, *Slag Atlas*, 2nd ed. (Verlag Stahleisen GmbH, Düsseldorf, 1995).
10. L. Zhang, C. Guo, W. Yang, Y. Ren, and H. Ling, *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **49**, 1 (2017).
11. D. Ladutkin, E. Korte, M. Bleymehl, C. Bruch, and K.-G. Doppler, *Bear. Steel Technol.* 11th Vol. Adv. Steel Technol. Roll. Bear. 48 (2017).
12. H. M. Piolet and D. Bhattacharya, *Metall. Trans. B* **15**, 547 (1984).
13. M. A. Van Ende, Y. M. Kim, M. K. Cho, J. Choi, and I. H. Jung, *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **42**, 477 (2011).
14. C. Pistorius, in *CISR Meet. - Fall 2014* (2014), pp. 1–17.
15. A. Harada, N. Maruoka, H. Shibata, and S. Kitamura, *ISIJ Int.* **53**, 2110 (2013).

16. G. K. Sigworth and J. F. Elliott, *Met. Sci.* **8**, 298 (1974).
17. I.-H. Jung, S. a. Decterov, and A. D. Pelton, *Metall. Mater. Trans. B* **35**, 493 (2004).
18. J. A. E. H. Shin, Y. Chung, and J. O. O. H. Park, *Metall. Mater. Trans. B* (1873).
19. S. Chen, M. Jiang, X. He, and X. Wang, *Int. J. Miner. Metall. Mater.* **19**, 490 (2012).
20. E. B. Pretorius, H. G. Oltmann, and B. T. Scharf, *AISTech 2013 Proc.* 993 (2013).
21. K. Wang, M. I. N. Jiang, X. Wang, Y. Wang, and H. Zhao, *Metall. Mater. Trans. B* **47**, 282 (2016).
22. K. E. Swartz, L. C. Hibbeler, B. P. Joyce, and B. G. Thomas, *AISTech - Iron Steel Technol. Conf. Proc.* 1865 (2014).
23. N. Tripathi, *Formation of Oxide-Inclusions by Ladle Glaze and a Preliminary Examination on the Possibility of Inclusion Separation by Bubble Flotation* (2003).
24. D. J. Sosinski and I. D. Sommerville, *Metall. Mater. Trans.* **17B**, 351 (1986).
25. J. Carlos, S. Pires, and A. Garcia, **7**, 517 (2004).
26. C. Pires and M. Fernandes, *Mater. Charact.* **51**, 301 (2004).
27. Y. Ren, L. Zhang, W. E. N. Fang, S. Shao, and J. U. N. Yang, *Metall. Mater. Trans. B* **47B**, 1024 (2016).
28. S. P. T. Piva, D. Kumar, and P. C. Pistorius, *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **48**, 37 (2017).
29. H. Gaye and J. Lehmann, in *VII Int. Conf. Molten Slags Fluxes Salts* (The South African Institute of Mining and Metallurgy, Cape Town, 2004), pp. 619–624.
30. H. Gaye, L. D. Lucas, M. Olette, and P. V. Riboud, *Can. Metall. Q.* **23**, 179 (1984).
31. L. Zhang, Y. Li, Q. Wang, and C. Yan, *Ironmak. Steelmak.* **42**, 705 (2015).
32. G. Irons, A. Senguttuvan, and K. Krishnapisharody, *ISIJ Int.* **55**, 1 (2015).
33. I.-H. Jung, *AISTech 2010 Iron Steel Technol. Conf. May 3, 2010 - May 6, 2010 I*, 1211 (2010).

34. N. J. Themelis, *Transport and Chemical Rate Phenomena* (Gordon and Breach Science Publishers, SA, Yverdon, 1995).
35. R. I. L. Guthrie, *Engineering in Process Metallurgy*, 2nd Editio (Oxford University Press, New York, 1992).
36. E. T. Turkdogan and R. J. Fruehan, in *Making, Shap. Treat. Steel Steelmak. Refin. Vol.*, 11th ed. (The AISE Steel Foundation, Pittsburgh, PA, 1999), pp. 37–160.
37. K. Beskow, J. Jia, C. H. P. Lupis, and D. Sichen, *Ironmak. Steelmak.* **29**, 427 (2002).
38. P. Dayal, K. Beskow, J. Bjorkvall, and D. Sichen, *Ironmak. Steelmak.* **33**, 454 (2006).
39. Y. Chung and A. W. Cramb, *Philos. Trans. R. Soc. A* 981 (1998).
40. S.-H. Kim and R. J. Fruehan, *Metall. Trans. B* **18**, 673 (1987).
41. L. Zhang and F. Oeters, *Steel Res.* **70**, 128 (1999).
42. C. Dannert, H. Koechner, U. Strack-thor, P. Valentin, C. Bruch, D. Sichen, L. Holappa, S. Louhenkilpi, and P. Väyrynen, *Improvement of Ladle Stirring To Minimise Slag Emulsification and Reoxidation During Alloying and Rinsing (STIMPROVE)* (Brussels, Belgium, 2012).
43. C. A. Abel, *Physical and Chemical Modeling of Continuous Steelmaking*, Carnegie Mellon University, 1991.
44. S. Asai, I. Muchi, and M. Kawachi, in *Foundry Process. - Their Chem. Phys.*, edited by S. Katz and C. F. Landefeld (Plenum Press, New York, NY, 1988), pp. 261–289.
45. J. Mietz, S. Schneider, and F. Oeters, *Steel Res.* **62**, 10 (1991).
46. P. Valentin, C. Bruch, and J. Gaule, *Steel Res. Int.* **80**, (2009).
47. Y. Chung and a. W. Cramb, *Metall. Mater. Trans. B* **31**, 957 (2000).
48. P. Dayal, K. Beskow, J. Bjorkvall, and D. Sichen, *Ironmak. Steelmak.* **33**, (2006).
49. D. Sichen and J. F. White, in *Proc. 10th Int. Conf. Molten Slags, Fluxes Salts* (2016), pp. 535–546.
50. G. J. W. Kor, T. Timken, and C. Retired, *Making, Shap. Treat. Steel* 11th Ed. 661 (1998).

51. J. Clift, in *Bubbles, Drops Part.* (1978), pp. 30–45.
52. A. Ishii, M. Tate, T. Ebisawa, and K. Kawakami, *ISS Iron Steelmak.* **35** (1983).
53. H. P. Liermann and J. Ganguly, *Geochim. Cosmochim. Acta* **66**, 2903 (2002).
54. D. Kumar, *Development of a Reliable Kinetic Model for Ladle Refining of Steel*, Carnegie Mellon University, 2018.
55. L. Zhang, *JOM* **65**, 1138 (2013).
56. J. Ishida, K. Yamaguchi, S. Sugiura, K. Yamano, S. Hayakawa, and N. Demukai, *Denki-Seiko* **52**, 2 (1981).
57. K. Schwerdtfeger, *Arch. Eisenhüttenwes.* **54**, 87 (1983).
58. L. Zhang and B. G. Thomas, *ISIJ Int.* **43**, 271 (2003).
59. W. Tiekink, R. Boom, a. Overbosch, R. Kooter, and S. Sridhar, *Ironmak. Steelmak.* **37**, 488 (2010).
60. G. Yuasa, S. Sugiura, M. Fujine, and N. Demukai, in *Electr. Furn. Conf. Proc.* (Kansas City, MO, 1982), pp. 7–10.
61. M. Valdez, G. S. Shannon, and S. Sridhar, *ISIJ Int.* **46**, 450 (2006).
62. M. Valdez, K. Prapakorn, A. W. Cramb, and S. Seetharamand, *Steel Res.* **72**, 291 (2001).
63. P. Yan, B. A. Webler, P. C. Pistorious, and R. J. Fruehan, *Metall. Mater. Trans. B* **46B**, 2414 (2015).
64. P. Misra, V. Chevrier, S. Sridhar, and a. W. Cramb, *Metall. Mater. Trans. B* **31**, 1135 (2000).
65. B. H. Reis, W. V. Bielefeldt, and A. C. F. Vilela, *J. Mater. Res. Technol.* **3**, 179 (2014).
66. U. Lindborg and K. Torssell, *Trans. Metall. Soc. AIME* **242**, 94 (1968).
67. C. Zener, *J. Appl. Phys.* **20**, 950 (1949).
68. H. Goto, K. Miyazawa, S. Ogibayashi, and K. Yamaguchi, *ISIJ Int.* **34**, 414 (1994).
69. Y.-M. Won and B. G. Thomas, *Metall. Mater. Trans. A* **32**, 1755 (2001).

70. J. Lehmann, P. Rocabois, and H. Gaye, *J. Non. Cryst. Solids* **282**, 61 (2001).
71. G. Wilde and J. H. Perepezko, *Mater. Sci. Eng. A* **283**, 25 (2000).
72. A. M. Zubko, V. V. Lobanov, and V. V. Nikonova, *Sov. Phys. Crystallog.* **18**, 239 (1973).
73. M. K. Surappa and P. K. Rohatgi, *J. Mater. Sci.* **16**, 562 (1981).
74. M. El-Bealy and B. G. Thomas, *Metall. Mater. Trans. B* **27**, 689 (1996).
75. E. Haug, H. J. Thevik, and M. Asbjorn, *Int. J. Heat Mass Transf.* **38**, 1553 (1995).
76. C. Garlick, M. Griffiths, P. Whitehouse, and C. Gore, *Ironmaking Steelmak.* **29**, 140 (2002).
77. Y. Kang, I. Jung, S. Decterov, A. Pelton, and H. Lee, *ISIJ Int.* **44**, 975 (2004).
78. V. Thapliyal, *Inclusion Engineering in Mn-Si De-Oxidized Steel for Thin-Strip Casting*, Missouri University of Science and Technology, 2015.
79. I.-H. Jung, Y.-B. Kang, S. a. Decterov, and A. D. Pelton, *Metall. Mater. Trans. B* **35**, 259 (2004).
80. J. S. Park and J. H. Park, *Metall. Mater. Trans. B* **45**, 953 (2013).
81. H. Mu, *Reduction of CaO and MgO by Al in Steel and Inclusion Modification*, Carnegie Mellon University, 2016.
82. Y. Sundberg, *Scand. J. Metall.* **7**, 81 (1978).
83. R. I. L. Guthrie and S. A. Argyropoulos, in *65th Steelmak. Conf. Proceedings, Iron Steel Soc.* (1982), pp. 156–167.
84. S. A. Argyropoulos, *Dissolution of High Melting Point Additions In Liquid Steel*, McGill University, 1981.
85. V. Thapliyal, A. Kumar, D. G. C. Robertson, J. D. Smith, A. Kumar, D. G. C. Robertson, J. D. S. Transient, V. Thapliyal, A. Kumar, D. G. C. Robertson, and J. D. Smith, **9233**, (2016).
86. D. S. Webber, K. D. Peaslee, V. L. Richards, and M. Hall, *ICS Proc.* 2005 **1**, 741 (2005).
87. *ASTM A100-07: Standard Specification for Ferrosilicon* (West Conshohocken, PA, 2018).

88. O. Wijk and V. Brabie, *ISIJ Int.* **36**, S132 (1996).
89. S. R. Story and R. I. Asfahani, *Iron Steel Technol.* **10**, 85 (2013).
90. E. B. Pretorius, US 7,785,393 B2 (2010).
91. M. M. Pande, M. Guo, X. Guo, D. Geysen, S. Devisscher, B. Blanpain, and P. Wollants, *Ironmak. Steelmak.* **37**, 502 (2010).
92. Y. Bi, Three Dimensional Determinations of Inclusions in Ferroalloys and Steel Samples, Royal Institute of Technology (KTH), 2014.
93. P. Yan, L. Pandelaers, M. Guo, and B. Blanpain, **54**, 1209 (2014).
94. P. Yan, M. Guo, and B. Blanpain, (2013).
95. M.-A. Van Ende, M. Guo, J. Proost, B. Blanpain, and P. Wollants, *ISIJ Int.* **51**, 27 (2011).
96. S. K. Choudhary, *Mater. Manuf. Process.* **27**, 925 (2012).
97. S. K. Choudhary, S. Chandra, and A. Ghosh, *Metall. Mater. Trans. B* **36**, 59 (2005).
98. a. D. Prasad and S. R. Sankaranarayanan, *J. Min. Metall. Sect. B Metall.* **48**, 37 (2012).
99. P. Yan, M. Guo, S. Huang, J. Van Dyck, and B. Blanpain, *Metall. Mater. Trans. B* **44**, 1105 (2013).
100. M. Kivio and L. Holappa, *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **43**, 233 (2012).
101. G. Eriksson and E. Königsberger, *Pure Appl. Chem.* **80**, 1293 (2008).
102. A. Harada, N. Maruoka, H. Shibata, and S. Kitamura, *ISIJ Int.* **53**, 2110 (2013).
103. D. Panda, N. Ross, G. McQuillis, and J. Jenkins, US 2012/0180601 A1 (2012).
104. C. Choi, S. Jo, S. Kim, K. Lee, and J. Kim, *Metall. Mater. Trans. B* **35B**, 115 (2004).
105. M. Uo, E. Sakurai, F. Tsukihashi, and N. Sano, *Steel Res.* 496 (1989).
106. D. Tang, M. E. Ferreira, and P. C. Pistorius, *Microsc. Microanal.* **23**, 1082 (2017).
107. A. Ishii, M. Tate, T. Ebisawa, and K. Kawakami, *Iron Steelmak.* 35 (1983).

108. H. Tozawa, Y. Kato, K. Sorimachi, and T. Nakanishi, *ISIJ Int.* **39**, 426 (1999).
109. H. Lei and J. He, *J. Mater. Sci. Technol.* **28**, 642 (2012).
110. P. Rocabois, J. Lehmann, H. Gaye, and M. Wintz, *J. Cryst. Growth* **198–199**, 838 (1999).
111. O. P. Cure, 4,037,478 (1977).
112. H. Liao, S. Yang, J. Li, and J. Feng, *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **48**, 3101 (2017).
113. J. M. Cabrera-Marrero, V. Carreno-Galindo, R. D. Morales, and F. Chavez-Alcala, *ISIJ Int.* **38**, 812 (1998).
114. ESI ProCast - Casting Simulation Suite. URL: https://www.esi-group.com/sites/default/files/resource/brochure_flyer/1530/casting_brochure_0.pdf. Accessed in June 26th, 2018.
115. O. Ericsson, *An Experimental Study of a Liquid Steel Sampling Process*, KTH - Royal Institute of Technology, 2010.
116. C. Merlet, in *Int. Congr. X-Ray Opt. Microanal.* (1992), pp. 123–126.
117. C. Merlet, *Mikrochim. Acta* **114–115**, 363 (1994).
118. M. A. Van Ende, M. Guo, P. T. Jones, B. Blanpain, and P. Wollants, *Ceram. Int.* **35**, 2203 (2009).
119. J. H. Park, *Calphad Comput. Coupling Phase Diagrams Thermochem.* **31**, 149 (2007).
120. G. J. W. Kor and P. C. Glaws, in *Making, Shap. Treat. Steel 11th Ed.* (AISE Steel Foundation, Pittsburgh, PA, 1998), pp. 661–713.
121. N. Verma, *Modification of Spinel Inclusions by Calcium in Liquid Steel*, Carnegie Mellon University, 2011.
122. D. Roy, *Effect of Silicon on the Desulfurization of Al-Killed Steels*, Carnegie Mellon University, 2012.
123. C. P. Manning and R. J. Fruehan, **44**, 37 (2013).

124. V. Raghavan, Phase Diagrams Ternary Iron Alloy. Indian Inst. Met. **6A**, 549 (1992).
125. M. D. Higgins, Am. Mineral. **85**, 1105 (2000).
126. M. Story and B. Webler, *High Temperature Oxidation of Advanced High Strength Steel: Investigating the Effect of Decarburization and Grain Size* (Pittsburgh, 2016).
127. P. Grieveson and E. T. Turkdogan, J. Phys. Chem. **68**, 1547 (1964).
128. E. T. Turkdogan, P. Grieveson, L. S. Darken, and C. U. Edgar, J. Am. Chem. Soc. **67**, 1647 (1963).