Inclusions Size Distributions After Calcium Treatment in Low Carbon Aluminum Killed Steels

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Abstract

This work addresses conflicting results shown in the literature regarding liquid inclusion agglomeration. It has been shown that liquid calcium aluminates do agglomerate and hence change in size over time. Under laboratory conditions, solid spinels and alumina inclusions were successfully modified into calcium aluminates. Those liquid inclusions exhibited a weak but statistically significant tendency to agglomerate. The main mechanisms by which liquid inclusions agglomerate is by Stokes collision and laminar fluid flow collisions when no external stirring is present. For industrial conditions, where the liquid steel is agitated via either argon bubbling or electromagnetic stirring, turbulent collisions appears be the dominant mechanism. Regarding flotation and removal of liquid calcium aluminates, similar flotation rates between liquid and solid inclusions were observed. This contradicts common sense in the industry that liquid inclusions, once formed, are more difficult to remove compared to their solid counterparts.

It was observed that, immediately following CaSi₂ injection, inclusions reduce their size by approximately two to three times, depending on the parent inclusion. Experimental data suggests that calcium aluminates consists of a new population of inclusions formed upon calcium addition. The presence of calcium in the liquid steel will destabilize alumina and MgO-alumina inclusions, which then dissolve into the melt. It is observed that solid spinels that remain in the steel after calcium treatment are slightly smaller than prior to Ca insertion.

When floating on top the steel, liquid inclusions will appear approximately twice as large then when embedded in liquid steel. Confirmation using theoretical calculations based on literature data and experimental evidence, comparing average size of inclusions using SEM analysis and confocal microscope measurements, is provided in this work.

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Chapter 1 - Introduction and background literature

This section consists of a review of secondary metallurgy and the main reactions of concern in this project. It also presents the current state of knowledge on particle size distribution as well as some mechanisms of inclusion agglomeration.

1.1 Overview of the secondary refining process in steelmaking

Secondary metallurgy is the general term for the branch of the steelmaking process taking place between the primary steelmaking reactor, whether a basic oxygen furnace (BOF) or an electric arc furnace (EAF), and the caster. It consists of all refining processes that take place in the ladle. This part of the process has been through many developments in the past years and several types of equipment were designed to better serve the purpose of secondary refining. The most abundant form of ladle refining is in a ladle metallurgy furnace (LMF). However, depending on the steel application a degassing stage is mandatory to achieve lower carbon and hydrogen levels. Ladle treatment is a key process to also manipulate inclusion composition and morphology, to ensure that inclusions are not detrimental to the product and/or the manufacturing process.

Steel cleanliness is the net result of inclusion formation and removal^[1] as well as control of dissolved impurities such as nitrogen, phosphorus and sulfur. To obtain a cleaner steel, secondary metallurgy plays an indispensable role in tailoring the inclusion population and morphology. In this context, most non-metallic inclusions have their genesis in steels during deoxidation when an alloying element is added to the liquid steel to remove the dissolved oxygen. The removal of the dissolved oxygen is necessary so the product can be castable, hot workable and have the desired mechanical properties^[2]. Several deoxidizers can be used to perform this treatment in steels, such as ferrosilicon, ferromanganese and/or silicomanganese in silicon-manganese killed steels, or aluminum in the case of aluminum killed steels, as examples. In low carbon aluminum killed steels (LCAK), Al₂O₃ is the most abundant inclusion formed due to the deoxidation reaction of aluminum with oxygen dissolved in the

liquid steel. The alumina formed in the bath is solid at steelmaking temperatures, which is typically around 1600°C. The rate of this deoxidation reaction is very fast and measured dissolved oxygen activities shortly after deoxidation agree well with equilibrium thermodynamic calculations ^[3], for equilibrium with alumina (deoxidation product). The alumina formation reaction is shown in equation 1. Figure 1 shows the relationship between dissolved Al and O calculated assuming $a_{Al_2O_3} = 1$ and calculating the equilibrium constant K_{eq} at 1600°C using FactSage 7.1.

$$2[Al] + 3[0] = (Al_2O_3) \quad K_{eq} = \frac{a_{Al_2O_3}}{h_{Al}^2 h_0^3}$$
 Equation 1

Note in Equation 1 that the species in square brackets [] are dissolved in the steel, while the species in parenthesis () are inclusions that can be floated out to the slag or remain in the bath.



Figure 1: dissolved O vs. [%Al] in steel at 1600°C^[4].

Aluminum oxide can also react with dissolved Mg originating from refractory or slag to form solid magnesia-alumina spinel inclusions. Dissolved aluminum can react with MgO and dissolve magnesium in the steel. Equations (2) and (3) illustrate these reactions mentioned involving. Magnesia-alumina spinel inclusions are expected to form in steels with low oxygen levels in contact with MgO refractories^[5].

$$4(Al_2O_3) + 3[Mg] \rightarrow 3(MgO.Al_2O_3) + 2[Al] \quad K_{eq} = \frac{a_{MgAl_2O_4}^3 h_{Al_2}^2}{a_{Al_2O_3}^4 h_{Mg}^3}$$
 Equation 2

$$2[Al] + 3(MgO) \rightarrow Al_2O_3 + 3[Mg] K_{eq} = \frac{h_{Mg}^3 \cdot a_{Al_2O_3}}{a_{MgO}^3 \cdot h_{Al}^2}$$
 Equation 3

Figure 2 shows the phase diagram of the $MgO - Al_2O_3$ system according to Jung et al.^[6]. As observed in practice, at 1600°C alumina and spinel inclusions will be solid. For casting purposes, that is not desirable.



Figure 2: MgO-Al₂O₃ phase diagram at 1 atm^[6].

For steelmakers, solid inclusions present in the steel can cause nozzle clogging during casting of the product due to accumulation of inclusions in the nozzles. To circumvent this issue, it is common practice in the steel industry to calcium treat the steel to form liquid or partially liquid calcium aluminates. These calcium aluminates are less likely to cause clogging issues and their formation is represented in equations 4 - 9.

Turkdogan ^[7] enumerated other advantages in modifying oxide and sulfide inclusion by calcium treatment. Some are: (i) improvement in castability due to nozzle blockage minimization; (ii) fewer

surface defects; (iii) improved steel machinability at high cutting speeds and prolonged carbide tool life; (iv) minimized susceptibility of steel to re-heat cracking, as in heat-affected zones of welds; (v) minimized susceptibility of high strength low-alloy line pipe steels to hydrogen induced cracking (HIC) in sour gas or sour oil environments ^[7].

Calcium can be introduced into the liquid bath in a variety of methods, but the most common is through wire feeding ^[3] of calcium or calcium silicide enveloped in an iron sheath. Regardless of the form in which calcium is added to liquid steel, the subsequent reactions taking place are the same, as follows ^[8]:

$Ca_{(l)} \rightarrow Ca_{(g)}$	Equation 4
$Ca_{(g)} \rightarrow [Ca]$	Equation 5
$[Ca] + [0] \rightarrow (Ca0)$	Equation 6
$[Ca] + [S] \rightarrow (CaS)$	Equation 7
$[Ca] + (x + \frac{1}{3})Al_2O_3 \rightarrow CaO. xAl_2O_3 + \frac{2}{3}[Al]$	Equation 8
$(CaO) + \frac{2}{3}[AI] + [S] \rightarrow (CaS) + \frac{1}{3}(Al_2O_3)$	Equation 9

Verma et al. ^[9] studied the early stages of the calcium reaction kinetics and found that initially CaS is the main reaction product (if the steel contains more than approximately 10 ppm S). The CaS was found to be attached to Al₂O₃/Spinel inclusions; subsequently sulfur diffuses out into the steel and liquid/partially liquid CaO.xAl₂O₃ is formed. In addition to reactions described in eq. (3-8), Verma et al. ^[9] proposed that the calcium sulfide will interact with alumina forming CaO.Al₂O₃ and dissolving back sulfur and aluminum into the liquid steel (the reverse of Equation 9). Figure 3 compiles images that illustrate the stages of the calcium reaction.



Figure 3: Inclusion morphologies after deoxidation and Ca treatment; in this case the deoxidation product was spinel. From ^[9].

As mentioned, the overall objective of calcium treating inclusions is to modify these into liquid particles. To do so, a restrict range of chemical composition is necessary to satisfy his condition when at temperature. Figure 4 shows the CaO-Al₂O₃ phase diagram: at 1600°C, calcium aluminates will only be fully liquid if the inclusion composition ranges from 38-58% (mass basis) ^[4].



Figure 4: CaO-Al₂O₃ phase diagram at 1 atm. From ^[4]

As shown in Figure 3, not only alumina but also spinel inclusions can be modified into calcium aluminates. The formation of calcium aluminate from a spinel inclusion is given by Equation 10^[9]:

$$MgAl_2O_4 + CaS \rightarrow CaAl_2O_4 + [Mg] + [S]$$
 Equation 10

The liquid window for MgO containing calcium aluminates is given in a MgO-CaO-Al₂O₃ (%at.) ternary diagram at 1550°C in Figure 5, in red. It shows not only the liquid region, which is very narrow, but also the 50% liquid boundary line, in blue. For practical purposes, the >50% liquid region is useful when analyzing the efficiency of a calcium treatment.



Figure 5: MgO-CaO-AlO_{1.5} ternary diagram at 1550°C (mole fractions), showing the fully liquid (red) and >50% liquid regions (blue). Calculated with FactSage 7.1.

1.2 Inclusion size and size distribution

In addition to chemical composition, the size distribution of non-metallic inclusions (NMIs) also plays an important role in steel casting and application performance. Although small (<1 μ m) well distributed inclusions throughout the solid steel can be useful in tailoring microstructure, NMIs are generally harmful to the quality of the final product, in addition to causing of problems during processing (like nozzle clogging). On the other hand, large inclusions (>20 μ m) can lead to catastrophic failures in the material due to their influence on toughness ^[10]. When studying and controlling nonmetallic phases present in steel, the distribution of sizes of such inclusions is an important component of steel cleanliness. Yin et al. ^[11] published the first paper discussing particle agglomeration of inclusions observed in a confocal scanning laser microscope (CSLM). They observed an interaction between alumina and alumina-rich solid inclusion particles. This phenomenon has its origin in the capillarity effect around alumina particles on the molten steel surface ^[11]. Agglomeration of inclusions at the steel-gas interface is inherent to observations in the confocal microscope, but capillarity-driven agglomeration would only occur in the industrial environment where an interface is available, e.g. steel/slag, steel/gas, and slag/gas. The clustering sequence found in that work was through (1) formation of intermediate aggregates (\sim 5µm) from smaller (1µm) particles. Those agglomerate (2) and form loosely-structured dendrites and finally (3) densify to more compact units by sintering.

In a second paper, the same authors observed different types of inclusions, both solid and liquid in molten steels. It was found that such capillarity attraction does not occur between liquid CaO-Al₂O₃-SiO₂ inclusions ^[12]. Another study carried out by Coletti et al. with similar setup observed the same lack of attraction ^[13]. Ohta et al. ^[14] studied the effect of dissolved oxygen and particle size distribution on particle coarsening for a series of deoxidation products. The authors' findings agreed with what was observed in the confocal microscope, i.e. liquid CaO-Al₂O₃ particles did not change their average size with time ^[14]. This contrasts with the results of Verma et al. ^[15], who found a shift of the liquid calcium aluminate size distribution to larger sizes in fully modified (tundish) steel samples, compared with unmodified or partially modified (solid) inclusions in preceding ladle samples.

Figure 6 illustrates the absence of interaction between liquid inclusions. It is worth noting that the inclusion diameters appear to be relatively large (up to $10\mu m$), with a distribution of sizes.



Figure 6: Absence of long-range interaction between liquid CaO-6%Al₂O₃ (<10%SiO₂) inclusion particles (A^o and B^o for instance) on HSLA steel melt surface at 1813K. Particle A^o is driven by surface flow in (a) to get very close to particle B^o in (b), but separates freely from B^o without being attracted in (c). From Ref. ^[12]

The size distribution of the inclusion population after deoxidation is the result of a combination of processes of nucleation, growth and removal ^[16]. The size distribution of inclusions in steels is often found to have a lognormal form ^[10] and the inclusion sizes in different steels can be distinguished by comparing the mean and standard deviation of the log-normal distribution. The lognormal distribution is related to a normal distribution and is derived as follows: If X is a normally distributed variable, with mean μ and variance σ^2 , then the variable $Y = e^X$ is said to have a lognormal distribution with parameters μ and σ^2 ^[17]. In other words, if Y is a variable that follows a lognormal distribution, then $X = \ln(Y)$ follows a normal distribution. Equation 11 shows the lognormal probability density function and Figure 7 depicts the shape of a lognormal curve with μ =0 and σ =1.

$$f(x) = \frac{1}{\sigma x \sqrt{2\pi}} \exp\left[-\frac{1}{2\sigma^2} (\ln x - \mu)^2\right]$$
 Equation 11



Figure 7: Lognormal probability density function of variable x, with $\mu=0$ and $\sigma=1$.

A lognormal distribution results from multiplicative random effects. This has been used as a justification for the applicability of the lognormal function to describe the distribution of sizes of recrystallized grains; the grains nucleate at random and grow at a rate that depends on their size ^[18]. The basic requirements for particle sizes to be log-normally distributed are that (a) the growth process for each particle can be considered to be the result of a very large number of growth impulses, and (b) each growth impulse comes from an independent source and has an effect which is dependent on the size at the time of action of the impulse ^[19]. Ohta et al. ^[14] have found the lognormal curve to represent the experimental data of inclusion sizes well.

The analysis of three-dimensional particle size distribution data from two-dimensional measurements is based on a discretization of the size distribution proposed by Saltikov^[20]. In this method, particlesize distribution is based on the principle that the distribution of random cross-sectional areas of any body depends only on its shape ^[20]. The PDF (population density function) (presented by Van Ende et al. ^[21,22]) can be useful to compare size distributions without an effect of bin size. The PDF function is described by Equation 12 where $n_V(L_{XY})$ is the number of particles per unit volume with a linear dimension (such as diameter) between L_X and L_y and $(L_X - L_Y)$ is the bin size. The idea of a density function is originally based on stereology concepts and more details about how the PDF function is derived can be found in ref.^[23].

$$PDF = \frac{n_V(L_{XY})}{(L_X - L_Y)}$$
 Equation 12

Compared to classic (and popular) histograms, this representation of the size distributions eliminates the arbitrariness caused by the choice of the number and the size of the bins defined by the user ^[16]. Therefore, this approach is more useful when comparing different samples or studies. Figure 8 shows one example of a same sample analyzed with different bin sizes. Even with an apparently different histogram, the density of sizes (PDF) was the same.



Figure 8 (a) to (c): Histogram and PDF representations of the size distribution of an identical data set using three different bin definitions. The three PDF's curves are superimposed in (d). From [1].

1.3 Mechanisms of Inclusion Nucleation, Agglomeration and Growth

After nucleation, there are several mechanisms by which inclusions may agglomerate and grow. This section discusses some of these in detail.

1.3.1 Homogeneous and Heterogenous nucleation

During deoxidation, heterogeneous nucleation can occur on pre-existent inclusions formed earlier in the process, on argon bubbles used to stir the system or on the refractory walls of the ladle/crucible ^[24]. Classical homogeneous nucleation theory indicates that the change of volumetric free energy of a system, e.g., Fe–Al–O, should overcome the barrier due to interfacial energy between nuclei in its parent phase (molten steel) in order to form oxide nuclei ^[25]; see Equation 13:

$$\Delta G = \frac{4\pi r^3}{3} \cdot \frac{\Delta G_m}{V_m} + 4\pi r^2 \sigma$$
 Equation 13

Where ΔG is the total free Gibbs energy change in the system, ΔG_m is the change in Gibbs free energy per mole due to the deoxidation reaction, V_m is the molar volume and σ is the surface energy of the deoxidation product in the steel, assuming a spherical particle.

The change in Gibbs free energy per mol, ΔG_m , is given by:

$$\Delta G_{\rm m} = -RT \ln \left(\frac{\kappa}{Q}\right)$$
 Equation 14

Where the ratio (*K*/*Q*) is the degree of supersaturation of the system, with *Q* the reaction quotient. The critical radius, r_c , and the critical Gibbs free energy, G_c , are found at $\frac{\partial \Delta G}{\partial r} = 0$. Therefore:

$$r_{\rm C} = \frac{2\sigma V_{\rm m}}{\text{RTln}\left(\frac{K}{Q}\right)}$$
Equation 15

$$\Delta G_{\rm C} = \frac{16\pi}{3} \cdot \frac{\sigma^3 V_{\rm m}^2}{\text{RTln}\left(\frac{K}{Q}\right)}$$
Equation 16

If $r > r_c$, nucleation occurs, and stable particles precipitate and start to grow. The critical size of nucleus decreases with increasing supersaturation and decreasing surface tension ^[26]. Figure 9 depicts the critical radius as a function of the degree of supersaturation as per Equation 15.

It is important to recognize that the interfacial energy between the steel and alumina, σ , depends on the oxygen content in the steel [27] and that will influence of the critical radius shown in Figure 9.

Nucleation can continue to occur until supersaturation is no longer present. At this point further nucleation could only occur if the temperature of the steel decreased, of when alloying elements are added to the steel or when oxygen is re-introduced into the steel during reoxidation events ^[28].



Figure 9: Critical radius vs. supersaturation for an Al₂O₃ particle at 1600°C. $\sigma = 1.5$ Nm⁻¹; V_m = 2.6×10^{-5} m³.mol⁻¹.

1.3.2 Ostwald Ripening

In supersaturated solid or liquid solutions, inhomogeneous structures change size over time. More specifically, particles smaller than a critical size tend to shrink while particles greater than the critical size tends to grow. This phenomenon - Ostwald Ripening - was first studied fundamentally by Lifshitz and Slyozov ^[29] as well as by Wagner ^[30]. These works became known as the Lifshitz-Slyozov-Wagner (LSW) theory. It predicts that the mean particle radius will increase from the initial size, r_0 , according to Equation 17:

$$r^3 - r_0^3 = \frac{8}{9} \cdot \frac{\sigma c_\infty V_m D}{RT} \cdot t$$
 Equation 17

In Equation 17, σ is the particle interfacial tension, c_{∞} is the solubility of the particle in substrate (steel), V_m the molar volume, D represents the diffusivity coefficient, R is the ideal gas constant and finally T is the temperature.

1.3.3 Collision

The literature describes different types of collision mechanisms related to inclusion clustering. Particle collisions that lead to agglomeration can occur by Brownian motion, turbulent motion, velocity gradients and Stokes collision ^[28].

The term "classic Brownian motion" describes the random movement of microscopic particles suspended in a liquid or a gas^[31]. The apparently random movement of suspended particles arise from the collision with atoms or molecules that form the fluid. This takes place in a stationary isothermal fluid.

Other collision mechanisms involving motion of the fluid can be used to describe inclusion motion in steel. If temperature or concentration gradients are present at the melt surface, for example, particle motion driven by surface tension gradients takes place by the so-called Marangoni effect. Yan et al. ^[32] observed a strong influence of the Marangoni effect on MnS particles reprecipitating in the steel as the temperature decreased in the Confocal Scanning Microscope. As MnS started to form and grow, a gradient in sulfur concentration caused the particles to move ^[32]. In fact, temperature and concentration gradients can cause inclusions to move by the Marangoni effect even on a millimeter length scale ^[33].

Immiscible particles with different densities, such as inclusions in steel, will have induced movement in the fluid. This particle movement is the balance between inertial and Archimedean fluid forces ^[34]. The terminal velocity of a falling (or rising – in the case of an inclusion) rigid sphere, also known as Stokes-motion is given by:

$$U = \frac{8}{9} (\rho_{\text{steel}} - \rho_{\text{inclusion}}) \frac{g D^2}{\mu}$$
 Equation 18

In Equation 18, the terms are: U: Stokes terminal velocity; ρ_i : density of a given medium i; *g*: gravity acceleration constant; *D*: particle diameter; μ : viscosity of steel.

Because particles of different sizes will have different velocities in the fluid, they might collide with one another and form a larger particle. In a static fluid, smaller particles will have much lower rising speed compared to larger particles, given the quadratic relationship between diameter and velocity. Figure 10 illustrates the different terminal velocities for different inclusion sizes, taking the density of steel as 7000kg/m³, inclusion density 3900kg/m³, steel viscosity $6.0 \times 10^{-3} Pa.s$ and gravity $9.81m/s^2$. Particles ranging from 0-2µm have a very low terminal speed. For this reason, large particles will tend to float whereas smaller particles will remain almost static in the steel.

Of course, any motion in the fluid (i.e. the liquid steel) will increase the chance of collisions between inclusions. For that reason, external stirring via argon bubbling or electromagnetic stirring (EMS) is commonly used in steelmaking practices around the world. In this case, turbulent motion in the fluid is the main cause of inclusion agglomeration.

In fact, all the mentioned mechanisms take place and contribute to inclusion size evolution during ladle refining. Ostwald ripening is the prevailing mechanism for growth at the initial stage immediately after nucleation. Brownian collision then predominates followed by turbulent coagulation in the case of efficient agitation. At later stages, inclusion growth is primarily attributed to the joint effort of both turbulent collisions and Stokes collisions ^[35]. Figure 11 summarizes the predominant mechanism in different stages and times for inclusion nucleation and growth.



Figure 10: Stokes terminal velocity vs. particle size (μm) for the steel-inclusion system.



Figure 11: Stages and times for inclusion nucleation and growth. From [36].

Chapter 2 - Motivation and Objectives of Current Work

Even though reactions involving calcium treatment of steels have been widely studied, no work has been done so far to explain fundamentally how these liquid/partially liquid calcium aluminates change size within liquid steel after Ca modification. Inconsistent conclusions on whether inclusions of this type agglomerate have been reported in literature. That is a clear indication that this gap must be addressed and is the main motivation for this project.

Additional questions emerged during this study and became objects of study. They are:

a) Explain why solid alumina/spinels inclusions are larger than the calcium aluminates that form from these solid inclusions by calcium treatment.

As it will be showed in the results section, liquid calcium aluminates are two to three times smaller than its parent inclusion prior modification. An attempt to explain this behavior is addressed in the coming sections.

b) The effect of Mg in calcium aluminates sizes.

Industrially, the presence of Mg/MgO in steel will cause the modification of Al_2O_3 inclusions to spinel (MgAl_2O_4). It has been previously shown that spinels are readily modified by calcium just like alumina. The chemical reaction is of course different, since one of the reactants are not equal. An investigation into whether the resulting size is different was undertaken in this work.

c) Flotation of liquid inclusions compared to solid alumina/spinels.

It is a common belief in industry that liquid inclusions are not removed from steel as fast as solid alumina. A direct comparison of flotation of fully modified calcium aluminates and solid alumina is provided in this work. d) The size distortion of inclusion by the lens shape effect, for inclusions at the surface of liquid steel.

Calcium aluminates are liquid at steelmaking temperatures. If so, they should have different diameters when suspended in the melt and when at the top surface in contact with gas and the melt. The ferrostatic pressure around an inclusion immersed in liquid Fe is constant in all directions and therefore the particle will be spherical. However, at the surface different interfacial tensions will act on the inclusion and it will assume a lens shape. This work aims to quantify this distortion, so their sizes can be comparable, for example when analyzing liquid inclusions in the confocal scanning laser microscope.

Chapter 3 - Hypotheses

The hypotheses tested in this work are:

1) Fully treated liquid calcium aluminates agglomerate and hence change in size over time.

2) Magnesium contributes to spinel inclusion breakup upon modification.

3) Removal of liquid calcium aluminate from liquid steel happens at the same rate as solid alumina.

4) Liquid calcium aluminates form a new population of inclusions after calcium treatment. Calcium aluminates are formed by aluminum and oxygen transport from alumina/spinels to CaO or CaS nuclei.

5) The size of solid and liquid calcium aluminates will increase at the same rate.

6) Liquid inclusions at the steel/inclusion/atmosphere interface will have a larger apparent diameter due to lens-shaped deformation.

Chapter 4 - Experimental Methods

This chapter describes all the experimental methods used in this document. In general, the approach was to perform experiments in an induction furnace, melting electrolytic iron, deoxidizing the melt with aluminum, and taking several samples before and after Ca treatment. These samples were then analyzed using automated feature analysis (AFA) using the ASPEX Explorer scanning electron microscope (SEM), which uses a tungsten filament as electron source. AFA provided both compositions and sizes of all inclusions in the steel. Some samples were analyzed in a field-emission gun SEM for better spatial resolution, or to compare the capabilities and the resolution of two different microscopes. Industrial samples taken from the ladle and tundish were used in this study to compare the findings of the induction furnace experiments to real steelmaking practice. For more detailed examination of inclusion morphologies after Ca treatment, some samples were electrolytically etched to selectively remove the iron and preserve inclusions. To test the last hypothesis, one previously calcium treated sample from induction furnace experiment was remelted in a confocal scanning laser microscope.

Each step and equipment mentioned above is described in detail in the following subsections.

4.1 Induction Furnace

Laboratory steel samples were obtained by melting electrolytic iron and alloying elements in two different induction furnaces. Each type of equipment is explained in detail, below:

4.1.1 10kW induction coil with fused quartz silica tube

The primary type of induction furnace used was a 10kW induction furnace. To maintain an inert atmosphere, the crucible is surrounded by a fused-quartz tube and closed with two water cooled caps, one at each end of the tube. This is shown in Figure 12, a photograph of the induction furnace shortly after one experiment. Argon flows in through the bottom lid (not shown in Figure 12) and the offgas exits the furnace through a hose connected to the top lid. This gas line is connected to the lab exhaust system.



Figure 12: 10kW induction furnace just after one experiment.

A schematic representation of the equipment inside the silica fused-quartz tube is provided in Figure 13. The water-cooled copper induction coil surrounds the fused-quartz tube, which encloses the experimental setup. At each end of the silica tube, a stainless steel cap seals the furnace and helps maintain the argon atmosphere. Through the upper steel cap, two alumina tubes pass as shown in the top part of Figure 13. One tube is used to contain the type B thermocouple to acquire temperature readings. The other one, a ³/₄" OD alumina tube, is used for alloying additions, as well as sampling the steel. Between the silica tube and the crucible, a graphite susceptor is used to better distribute the heat generated by the coil to the system. The graphite also serves as a temporary container in case of a crucible breakage. Finally, the oxide crucible is placed in the innermost part of the system. To make sure the steel melt is in the hot zone of the furnace, alumina bricks were used to position crucibles as needed.


Figure 13: Schematic representation of the induction furnace.

Argon flowed through an inlet in the bottom steel cap. The gas was 99.9999% Argon and residual oxygen was removed prior entering the furnace by using Cu getters placed upstream in the gas line. Additional details regarding the induction furnace setup are provided in the results chapters. Details such as reactant amounts used, and sampling times varied per experiment.

Silica sampling tubes of diameters ranging from 4 mm to 1 cm were used in various experiments. A pipette pump was placed at one end of the silica tube to aspirate the steel. After collecting the steel, all samples were cooled in water and then removed from the tube.

In general, 600 g of electrolytic iron was melted in every experiment; the oxygen content upon melting was around 400 ppm. For deoxidation, 0.5 g of aluminum shot was added, aiming at a dissolved aluminum content of approximately 0.04% and a total oxygen content (remaining in the steel after flotation of most of the alumina) of around 15-20ppm total oxygen before calcium treatment. In some cases, the sulfur concentration was increased by adding FeS. Aluminum deoxidation is a very exothermic reaction and usually a 10°C increase was observed after Al addition. Once the temperature

stabilized again at the target, calcium di-silicide previously wrapped in iron foil was added to the steel melt. To improve calcium yield, the iron-wrapped CaSi₂ was pushed into the melt with an alumina rod. In all experiments, the total time for calcium addition was less than two seconds. After calcium treatment, samples were collected at selected times.

4.2 Vacuum chamber 15kW induction Furnace

This experimental setup consists of a cubic 8ft³ stainless steel chamber responsible for maintaining the inert atmosphere. Inside the chamber, the coil is placed close to the center. In the case of experiments done in the vacuum chamber, the graphite susceptor and crucible were surrounded with alumina insulation to reduce radiative heat losses. An alumina lid covering the top of the susceptor was also used for the same purposes. A photograph of the chamber is illustrated in Figure 14, on the left. The front of the chamber is equipped with a viewing window. The right-hand side of Figure 13 contains a photograph taken at the chamber window during an experiment. The crucible configuration is very similar to Figure 13. The alumina insulation surrounds the graphite crucible, which holds the ceramic crucible. The tube shown on the top part of the setup is used to guide the aluminum and calcium disilicide into the melt. This tube is important for this furnace because the chamber is taller than the other furnace and additions fall into the melt by gravity. Therefore, it is important to assure that all additions will reach the melt and do not miss the crucible.

All experiments in the vacuum induction furnace followed the same routine as in the other induction furnace. Electrolytic iron, with or without added FeS, was brought to 1600°C. Afterwards, aluminum was added to deoxidize the steel and a sample was taken once the temperature was restabilized. Following this, calcium treatment was performed, and samples were taken at times specified in each experiment, as described in the following chapters.



Figure 14: Picture of the vacuum chamber of the induction furnace (left) and view through the window during an experiment (right).

4.3 Industrial Samples

Industrial samples considered in this document were taken as "lollipops" from the ladle or tundish. Ladle samples are denoted with the label 'L', and tundish samples with 'T'. Other relevant information like the steel composition and sampling times are provided in the results and discussion section.

4.4 Automated Feature Analysis

Automated inclusion analysis was performed using automated feature analysis (AFA) software of the FEI/ASPEX Explorer SEM. The main advantage of using this technique is the possibility to measure thousands of inclusions at the polished surface of a sample within a few hours. AFA is briefly described as follows ^[37]:

The AFA application searches for features in a user-specified region. The region can be defined by a circle, a polygon or a list of stage points. The region is specified by driving the stage to the outline of a sample, focusing, and storing a point. The stage coordinates and working distance are saved at each point.

- The user specified region is sub-divided by tiling it with square 'stage fields'. The size of the stage field is determined by the search magnification. The AFA application moves the stage to each tile either sequentially or in a randomized order.
- The area in a tile is searched by scanning the electron beam across the sample and measuring a secondary or back-scattered electron signal. Features are distinguished from background using a threshold criterion based on pixel intensity (brightness).
- When a feature is found, it is measured using a rotating chord algorithm which finds the center of the feature and draws 16 chords through the center at approximately 11° intervals. Several parameters are computed from the lengths of the cords including average, maximum and minimum diameters, orientation and centroid.
- If the feature passes user-defined morphological acceptance criteria, the feature is analyzed using the EDS detector.
- The beam is centered on the feature (or rastered across its surface) and an EDS spectrum is collected. After acquisition, the EDS spectrum is quantified, and the size and composition data are used to classify the feature according to user defined rules.

This process is repeated for each feature in the stage field and each stage field in the sample area unless some other early stop criterion is met (e.g. maximum number of features, or idle time).

To process several different samples from many different heats, a standardized method to run the AFA was required, since different SEM settings can yield different results for the same sample. A standardized method was developed in this work. Part of the optimization procedure involved testing the effect of accelerating voltage and spot size (beam focus) on resolution and backscattered image brightness. Spatial resolution was assessed by imaging inclusions with varying spot size and acceleration voltage, quantifying the minimum detectable feature size in the microscope. The procedure involved acquiring a backscattered electron line scan over an inclusion such as the one presented in Figure 15. The resolution, Δx , was considered as the linear distance corresponding to a brightness

change from 25% to 75% of the brightness difference (ΔB) between matrix and inclusion; the distance was measured on the line scan using the open-source software WebPlotDigitizer^[38]. The results for 10kV and 20kV accelerating voltages are shown in Figure 16(a) and (b), respectively.



Figure 15: Screenshot of one inclusion used to determine the resolution at given microscope setting. At left is a backscattered electron image and at right a line scan across the inclusion and steel matrix.

At 10kV, the spot size more strongly affects the minimum detectable feature than at 20kV. It means that, to detect smaller inclusions using 10kV, one should use a smaller spot size. The collateral effect is a longer analysis time, because of a lower beam current. However, at 20kV, the resolution does not seem to be too much affected by spot size (because of the inherently larger electron interaction volume), which means that at that acceleration voltage, a larger spot size could be used without loss of resolution. Because of the much larger electron interaction volume at 20 kV, small inclusions could be missed (electrons backscattered from the surrounding steel matrix would increase the backscattered electron yield, increasing the apparent brightness of the inclusion area). Note that "Spot size" is a generic term used by the instrument manufacturer referring to incident beam size; the spot-size numbers in Figures 16 and 17 are related to the beam size, but the exact relationship is not known. The general trends are that the beam current is larger for larger spot sizes, and also depends on accelerating voltage^[39].



Figure 16: Inclusion resolution vs. spot size at (a) 10kV and (b) 20kV

The lower beam current at 10 kV implies a lower rate of electron backscattering, which means that the brightness of the backscattered electron image is lower. Most of our analyses at 20kV using INCA¹ and ASPEX have used standard backscattered electron brightness levels of 170 for the steel matrix, and 40 for aluminum tape (similar in brightness to oxide inclusions), giving a steel-inclusion brightness difference of approximately 130. However, because of the lower backscattered image brightness at 10kV and smaller spot sizes, a brightness difference of 130 could not be reached. Figure 17 shows the maximum achievable difference in backscattered image brightness between the steel matrix and an inclusion, with the contrast control set to 100%. Larger spot sizes give more contrast between steel and inclusion (Figure 17), but poorer spatial resolution (Figure 16). A compromise between resolution and threshold for 10kV was to set the spot size to 40%. In that case the aluminum tape has a brightness level close to 110 and the steel matrix has a brightness level of 170; the threshold for detecting inclusions was set at 125. At 20kV, a brightness difference of at least 130 could be achieved over the whole spot size range with the contrast control set to less than 100%. Since the image resolution is little affected by the spot size at 20 kV, the choice of spot size is less critical. In general, for 20 kV a spot size of 33% was

¹ INCA is a SEM EDS analysis software developed by Oxford Instruments (www.oxinst.com). INCA Feature is the automated inclusion analysis software that was used on the FEI Quanta 600 microscope used in this work. Both names INCA and Quanta 600 are used interchangeably in this work referring to AFA using this equipment.

used, with the steel matrix set to a brightness level of 170, aluminum tape at 40, and the inclusion detection threshold set to 70. Table 1 contains a summary of all settings used at 10kV and 20kV.



 Δ Brightness vs. Spot Size

Figure 17: Brightness difference between matrix and inclusion vs. Spot size at 10kV. – Contrast control set to 100%

Setting	ASPEX Explorer		Quanta 600	
			(INCA feature)	
Acceleration Voltage	10kV	20kV	10kV	
Steel matrix brightness level	170	170	170	
Aluminum tape brightness	110 40		40	
level				
Detection threshold	125	70	60	
Spot Size	40.5% 33%		4.0	
Working distance	(17 ±0.5) mm		(10 ± 0.1) mm	
Magnification	1200×		1200×	
Field Image Size (pixels)	512×512		1024 × 768	
Pixel size	0.33 µm		0.12µm	

Table 1: SEM settings used for AFA

In order to compare the results of measurements using 10kV and 20kV, a common area was analyzed in an industrial sample taken in the tundish; the distributions of inclusion sizes are shown in Figure 18. The results were treated as follows. A bin width was determined to discretize the size distribution; in the case shown in Figure 14, the bin width is 0.40µm. The x-axis is labeled according to the maximum size for each bin and the y-axis shows the total number of inclusions in that bin. It can be noted that counts of larger inclusions (>1 μ m) are approximately the same for the two voltages. However, for inclusions \leq 1 μ m the counts differ. At 20kV, the interaction volume of the electron beam is much larger than at 10kV. For that reason, smaller (or shallower) inclusions will appear much brighter and therefore will not be detected as effectively as at 10kV ^[40].



Size Distribution 10kV vs. 20kV

Figure 18: Distribution of inclusion sizes on a common area of a tundish steel sample analyzed at 10kV and 20kV using ASPEX. Scan area: 7.85mm².

Spatial resolution can also play an important role when analyzing small features. Figure 19 shows the measured size distribution for approximately the same area using two different microscopes. Quanta 600 (field emission gun SEM) has a measured resolution of 0.12μ m (for backscattered electron imaging at 10kV), approximately a third of that for the ASPEX Explorer, which is 0.33μ m (at 10kV acceleration voltage and 40% spot size). In Figure 19, the x-axis is similar to that in Figure 18 with a bin width of 0.15 μ m. A small increment was picked to show in detail how the microscopes behave in detecting smaller features. Based on the numbers of the smallest inclusions (the two bars at the left in Figure 19) it is possible to conclude that the Quanta 600 is capable to detect many more small features than the ASPEX Explorer. For inclusions up to 0.48 μ m, while ASPEX counted 47 inclusions, Quanta counted 2.6 times as many (123). For inclusions up to 0.63 μ m, this ratio decreases to 1.6 times (180 vs. 113).

For larger inclusions ASPEX and Quanta yielded similar counts. Small differences in the numbers of larger inclusions were probably caused by some offset between the areas analyzed.

This result confirms that, as the size of inclusions approaches the spatial resolution of the microscope, the smaller features go undetected and therefore smaller inclusions are undercounted. Undercounting would distort the size distribution, causing the distribution to appear lognormal even if it is not. (For the size distributions shown in Figure 19, the minimum detected feature size was set to be 0.33 μ m for both microscopes.)



Figure 19: Comparison of measured inclusion size distribution for a steel sample measured with a tungsten filament SEM (ASPEX) and an FEG SEM (Quanta 600) at 10kV. Scan area: 7.85mm².

4.5 Inclusion sorting and data treatment

When analyzing inclusions at 10kV, the software of the ASPEX Explorer does not include a calibration to calculate chemical composition (from EDX peak count rates), unlike measurements at 20kV. For that reason, for all analyses performed at the lower acceleration voltage, counts were converted to composition using the Merlet algorithm. The Merlet algorithm is a phi-rho-z correction method for quantitative microanalysis based on the X-ray distribution depth, atomic number and absorption correction. It is particularly useful for light elements and both high and low acceleration voltages, such as in 10kV^[41]. The calculation method presented in references ^[41,42] was implemented in a Excel Spreadsheet and the output data, the %Wt. of selected elements, were used in all remaining subsections.

4.6 Proportional symbol plot

As mentioned before, automated analysis is capable of analyzing thousands of inclusions in a short period of time. Representing such a large number of measurements in a single ternary diagram can be a hard task. Simply plotting each individual point might not show useful information as over-plotting might hide useful information. In this document, unless noted, all ternary diagrams are constructed using Proportional Symbol Plots, an in-house Python code that summarizes inclusions counts and area and plots these on a ternary diagram. Other methods of summarizing a large number of observations and avoiding over-plotting is used in the literature, such as contour plots or heatmaps, for instance. However, for this work, using proportional symbols to represent data was the preferred method of choice.

The software assigns 400 equal subdivisions of the relevant ternary composition diagram and computes the number of inclusions as well as the total area of inclusions with compositions in each subdivision. The counts and area are all then normalized based on a 0-1 scale.

Figure 20 shows an example of how assessing individual points might lead the observer to a different conclusion. On the left-hand side, each individual inclusion composition is plotted on an MgO – CaO – $AlO_{1.5}$ ternary diagram. The same ternary is shown Figure 20(b). Individual points show an apparent widely spread major population of calcium aluminates and a few alumina rich inclusions in the right-hand side of the graph in Figure 20(a). However, when all compositions are consolidated by proportional occurrence, the most common inclusions, represented by the largest triangle, is in fact at the alumina corner (Figure 20(b)).



Figure 20: (a) individual measurement and (b) proportional symbol plot of composition distribution, for inclusions in a tundish sample.

It is important to note that the composition was normalized by the three elements of interest in every ternary diagram e.g., in a Mg-Ca-Al, the composition was normalized for these three elements. Calcium from CaS was subtracted prior to normalization. In the case of the S-Ca-Al ternary, sulfur from MnS inclusions was subtracted from the total sulfur prior to normalization. All compositions are plotted as molar ratios.

The size distribution of liquid (or mostly liquid) inclusions is of particular interest in this work. For this reason, in many cases only inclusions that contain 50% liquid or more were considered in detail. The filtering process is illustrated in the ternary composition diagrams of Figure 21, showing all the measured compositions (a) and those remaining after filtering out all composition that lie outside the >50% liquid region (b). For this example (S-Ca-Al composition diagram), the 50% liquid line was drawn for inclusions containing 5% MgO.



Figure 21: Unfiltered data containing solid and liquid inclusions (a) and after selecting only the inclusions that lie inside the 50% liquid region (b)

4.7 Deep-etching experimental setup

Steel samples were electrolytically etched in some cases. The electrochemical cell consisted of a 6mm graphite rod as cathode and the steel sample as anode. Voltage and current were set to 10V and 0.2-0.4A, depending on the wetted area of steel, typically around 0.30cm². The solution contained 180ml of anhydrous methanol, 14.50ml (10%wt) of acetylacetone and 14.25g (10%wt) of tetramethylammonium chloride ((CH₃)₄NCl). It is important that the solvent, methanol, be as free of water as possible, since H_2O can dissolve CaS inclusions. Acetylacetone is used as a chelant to help dissolve iron cations. Tetramethylammonium chloride is a supporting electrolyte to carry the current. As anodic product, Fe³⁺ ions are released into solution and the typical red color of this ion dyes the solution immediately. After a 20-25min of dissolution, the piece of steel remaining in the anode was washed with methanol and coated with Pt before SEM analysis.

4.8 The Saltikov method, Population Density Function (PDF) and CSD Corrections

Measured sizes of inclusions in SEM are from a 2D planar section. To convert area based information into real 3D dimensions a method introduced by Saltikov ^[20] was tested in this work. The method is used to determine particle size distribution from random cross-sectional areas analyzing only its shape. It is well suited to spherical particles. The Saltikov method contains four assumptions in its calculations. They are: 1) the particles may be mono or poly-dispersed. 2) All particles must have the same shape and differ only in size from one another. 3) The shape of the particles must be such that a random plane intersects a particle only once. This third assumption might not be valid for Al_2O_3 clusters, since a random plane might intersect a dendrite like alumina inclusion more than once. And finally, 4) the particles are randomly oriented in space.

To include complex shaped forms, an adaptation of the Saltikov method was proposed by Higgins ^[23,43]. In general, both models correct the observed 2D diameter of a body (inclusion) based on the probability of that planar measurement approaching the true (3D) inclusion diameter. Figure 22 illustrates the probability that random intersections through a spherical particle correspond to the true diameter.



Figure 22: Distribution of diameters of random intersections through a sphere, normalized by true sphere diameter. From ^[23].

The model proposed by Higgins ^[23,43] take into account different particle shapes. The same author published a free software called CSD Corrections², which calculates the corrected 3D size of a particle from 2D information. The tests of 3D data conversion (presented below) were performed using CSD Corrections.

² http://www.uqac.ca/mhiggins/csdcorrections.html

However, in most of the analyses in this work, changes in inclusion sizes were based on the apparent (measured) 2D diameters, and not converted to 3D. The reason is illustrated by Figure 23, which contains histograms of the apparent 2D sizes of inclusions, the converted data using the Saltikov method and manual measurements of 55 inclusions after deep etching sample (Experiment 5.1, 3 minutes after calcium treatment; more detail presented later). The data used in CSD corrections to generate the calculated 3D sizes were the measured sizes of around one thousand inclusions. One advantage of the method used by Higgins over Saltikov is that particles sizes converted to 3D are independent of the number of bin sizes and/or number of bins per decade.

The Saltikov method assesses the probability that apparently small features are off-center sections through larger inclusions; as a result, the corrected size distribution shows fewer small inclusions. The 2D measurements slightly overestimate the proportion of small inclusions, as can be seen when comparing the two smallest size ranges in the diagram, for the "Saltikov" and "2D diameter" distributions. Similarly, the corrected (Saltikov) size distribution contains more inclusions that are larger than 1 µm in diameter. Despite these differences, the uncorrected and corrected size distributions are very similar and in general agreement with what was measured manually in the deep-etched sample. For that reason, the extra step in converting all 2D measurements to 3D was considered unnecessary. Lekakh et al. ^[44] investigated 2D vs. 3D sizes of spherical inclusions in Si-Mn killed steels and also concluded that, for spherical particles, 2D data is similar to what is seen in 3D.



Figure 23: Comparison between apparent (2D) inclusion size distribution, deep etched 3D measurements and corrected 3D sizes (based on the Saltikov method)

Although deep etched samples reveal in more detail the true sizes of the inclusions, it is biased by loss of inclusions from the dissolving steel surface (which would not affect all inclusion sizes and shape equally). These lost inclusions are exemplified in Figure 24, in which the circular depressions mark places where inclusions had been.



Figure 24: Micrograph of deep-etched sample, showing voids that previously contained inclusions.

Chapter 5 - Fully modified calcium aluminates

This section contains the result of experiments using the induction furnace where fully modified calcium aluminates were achieved. A comparison with industrial case is also provided.

5.1 Fully treated (liquid) calcium aluminates – low sulfur

This section discusses the results obtained by fully modifying spinel or alumina inclusions. Induction furnace experiments are listed in Table 2. In these experiments, different ideas were tested. Experiments 5.1 and 5.2 were design to test the initial hypothesis of this project, that is, to determine whether liquid calcium aluminates agglomerate or not. Experiment 5.2 served not only as a confirmation of what was seen in its previous counterpart, and also used an expanded sampling plan of calcium treated inclusions, including more samples taken after injecting CaSi₂. To assess the influence of magnesium on the size of inclusions after Ca treatment, experiment 5.3 used the same conditions of 5.2, but with an alumina crucible instead of MgO, to avoid formation of spinels. In experiment 5.3 more "cal-sil" was used. Given the low yield of calcium, other experiments between 5.2 and 5.3 (not reported here) using alumina crucible inclusions were usually undertreated. The SEM resolution for ASPEX Explorer and Quanta 600 in all AFA were 0.33µm and 0.15µm, respectively.

Experiment	Electrolytic	Al addition	CaSi ₂	Crucible
	Fe (g)	(g)	addition (g)	material
5.1		0.5	1.0	MgO
5.2	600	0.55	1.08	MgO
5.3	w/ 7ppm S	0.53	1.5	Al_2O_3

Table 2: Summary of induction furnace heats in Section 5.1

5.2 Experiments 5.1 and 5.2 (low sulfur, MgO crucible)

These two heats served to establish the baseline of all induction furnace experiments. In these heats an MgO crucible was used, with no extra sulfur added. These two experiments were used to answer the initial hypothesis that started this project:

Hypothesis 1: fully treated liquid calcium aluminates agglomerate and hence change in size over time.

The results of the two experiments are reported below. A comparison between experiments is provided at the end of this section.

In experiment 5.1, the times at which each sample was collected are listed in Table 3. Three samples were collected before Ca treatment and named A1, A2 and A3. In this case, "A" stands for aluminum-killed; the samples were taken 3min, 6min and 9min after aluminum deoxidation. Approximately eleven minutes after deoxidation, when temperature is restabilized at 1600°C, Ca treatment was executed as previously described (page 19). The steel was subsequently sampled at three, six and nine minutes after calcium modification. The calcium-treated samples are denoted with the letter "C", to distinguish them from non-treated samples.

Sample name	Time	Notes
_	(min)	
A1	3	
A2	6	After Al deoxidation
A3	9	
C1	3	
C2	6	After Ca treatment
C3	9	

Table 3: Sampling plan for Experiment 5.1

The effectiveness of calcium treatment was assessed in terms of the measured inclusion compositions plotted on Mg-Ca-Al and S-Ca-Al ternary diagrams. Ideally, all inclusions should fall in the liquid region. However, as shown earlier in Figure 5, the fully liquid region is too restricted and only a limited number of inclusions typically would fall in that area, and all inclusions within the 50% liquid boundary were considered for size analysis. Beyond providing more data, the region where the NMIs are mostly liquid is also considered good for casting applications ^[45]. All inclusions that fall within the 50% liquid line are referred as "liquid inclusions" for the purpose of this document.

Figure 25 show the Mg-Ca-Al composition diagram for the aluminum deoxidized samples. The ternary diagrams are overlapped showing in detail the increase of magnesium concentration as time progresses.



Figure 25: Mg-Ca-Al ternary diagrams for Al deoxidized samples in Experiment 5.1

The only source of Mg in these experiments is the MgO crucible. That indicates a crucible-steel reaction, where the melt dissolves magnesium from the crucible. Steel-crucible reactions in the same setup was extensively studied by Kumar et al.^[46]. The results observed in Experiment 5.1 agrees with his findings where magnesium-alumina spinel inclusions were formed by reaction of the steel and thin slag coating formed at the steel-crucible interface. A more detailed discussion of steel-crucible reactions in this thesis can be found in Section 7.4, on page 103.

Figure 26 (a-f) show the ternary diagrams for the calcium treated samples. Mg-Ca-Al diagrams are shown from (a-c) and the S-Ca-Al ternary diagrams from (d-f).



Figure 26(a-f): Mg-Ca-Al and S-Ca-Al ternary diagram for the Ca treated samples

It is observed in Figure 26(a-c) that, after Ca treatment, the inclusions had a higher Mg content than observed usually in well treated industrial samples. The average magnesium observed in samples of Figure 26 (a-c) was 15% Mg (%at.) versus 6-8%at. in the industrial samples (see page 55). Although a few small spinels are still present nine minutes after calcium treatment, the compositions of most of the inclusions fall within the 50% liquid boundary, indicating that the treatment was successful.

The total sulfur content of inclusions decreased slightly from samples C1 to C3. This decrease can be observed in the ternary diagrams in Figure 26 (d-f) as the biggest triangles are moving towards the Ca-Al line but also more clearly in Figure 28, where the average sulfur content (%at.) of inclusions is plotted in a bar chart. From Figure 28, the sulfur content starts at 3.6% and decreases to approximately 2% over a 6-minute interval. A thin slag-like layer on top of the steel puck was observed after the experiment. Probably that thin layer was enough to desulfurize the steel slightly and therefore decrease the sulfur concentration in inclusions.

Figure 27 shows a typical spinel inclusion observed in deoxidized sample A1 and a calcium aluminate from sample C3. The spinel is faceted, and its average size is around $2\mu m$. The calcium aluminate is globular, as expected for a liquid inclusion, with a few facets imitating a soccer ball. Note the decrease in size from before calcium treatment (spinel) to the calcium-treated (calcium aluminate) inclusion. Inclusion sizes and size distribution will be discussed in more detail later in this section.

By assessing the chemical compositions shown in the ternary diagrams and the morphology of the inclusions both before and after Ca addition it was concluded that the experiment was successful in modifying solid alumina/spinels into liquid/partially liquid calcium aluminates.



Figure 27: Typical spinel and liquid calcium aluminates found in samples A1 (left) and C3 (right). Note the sharp decrease in size



Figure 28: Average sulfur content of calcium treated inclusions (C1-C3)

After confirming successful calcium modification, the size distribution of the inclusions could be evaluated. Figure 29 shows multiple histograms of all samples. The results for specimens before Ca injection are in the left column and samples after calcium treatment are in the right-hand column. Experimental data is shown as blue bars while the fit of a lognormal distribution is presented as a continuous red line. In samples A1 and A2 the lognormal distribution (red line) does not exactly fit the experimental data: some bin sizes are under-represented while other sizes appear to be above the fitted distribution. For that reason, in both cases, the statistical test indicates the distribution not to be truly lognormal (P-value <0.05) even though the shape of the experimental distribution is similar to a lognormal distribution. In sample A3, the fit agrees better with experimental values and the data conforms to a lognormal density function (P-value=0.143). In Figure 29, "Loc" stands for location; this is the parameter μ of the distribution. "Scale" is the parameter σ of the lognormal distribution (see page 19).

It was expected that the average size of the spinel inclusions, the major inclusion type present in deoxidized samples, would increase with time due to agglomeration and at some extent to coarsening. However, from sample A1 to A2 the exact opposite was observed. As discussed later, it appears that sample A2 was affected by reoxidation. The counts of small inclusions (<1.8µm) increased. From sample A2 to A3 the frequency of features below 1.8µm decreased again.

It appears that reoxidation happened when sampling sample A2 based on the increased number of small inclusions observed in sample A2; in addition to the increase in the number of inclusions, the inclusion density and total oxygen (shown in Figure 30) also increase. To test whether the number of small inclusions is inherent to the sample and not a concentrated spot of small inclusions, Figure 31 shows the average diameter in each field of the SEM analysis. A field is denominated as a 0.5×0.5 mm subdivision of the area analyzed. Overall, Sample A2 contains smaller inclusions than A1 and A3, and not a concentrated "cloud" of inclusions. These factors lead to the conclusion that sample A2 suffered reoxidation when sampling and is probably not representative of the system in terms of inclusion size.

From sample A₂ to A₃, the area fraction decreased as did the inclusion number density. Also, the average size increased from A₂ to A₃. Besides that, from Figure 29 one can observe that proportionally there are more larger inclusions (say, over 1μ m) in A₃ than in sample A₂ indicating that the spinels agglomerated and floated up in the steel bath.



Figure 29: Histogram with lognormal fit for Experiment 5.1 samples. Location and Scale are parameters of the lognormal distribution. Continuous lines show fitted lognormal distributions.



Inclusion Density & Area Fraction Experiment 5.1

Figure 30: Inclusion density and area fraction (ppm) in all six samples of Experiment 5.1



Figure 31: Average diameter per field in samples before Ca. Each field represents a 0.5 X 0.5mm subdivision in the area analyzed.

As stated earlier, the property of lognormal distributions is that of a natural logarithm of a given observed distribution follows a normal distribution. Therefore, if one takes the natural log of the diameter of all inclusions, it should follow a normal probability function. The reason for using this mathematical property is that, once the data is described by the well-known Gaussian curve, statistics becomes much simpler and well-described. Using this property, the average diameters of inclusions are compared in Figure 32. The error bars are the calculated confidence interval for each sample individually using a 95% confidence level. A two-sample t-test confirms what can be seen graphically in Figure 32: calcium treated samples have significantly different mean sizes (relative to the spinels, and changed over time), for the confidence interval tested. For a difference $(\mu_1 - \mu_2) = 0$, the p-value is smaller 0.05 in all cases. This confirms that the means are significantly different.

The purple mark in Figure 32 show the simulated results for inclusion collision and growth. A detailed explanation of the steps consisting these simulations is provided in section 5.11. For Figure 32, the initial size distribution used was the lognormal parameters found in the fitted curve for sample 3 min after Ca on the top right histogram in Figure 29. The fitted curve in Figure 29 is the "true" size distribution and accounts small particles that can't be detected by the microscope. The number of particles per unit volume was then estimated to match the simulated volume fraction with the experimental measured area fraction in the SEM. Using then a hard cut-off at the microscope's resolution, the simulated distribution is plotted in Figure 32. One can observe that, simulated data under predicts what was observed experimentally. This suggests that more collision mechanisms could be in place besides the ones listed in Section 5.11.

In the aluminum deoxidized samples, the change in size is difficult to assess given the reoxidation in sample taken 6min after aluminum injection. After reoxidation, the sizes again increased as seen by comparing the average diameters between six and nine minutes after deoxidation.



Figure 32: Average sizes of inclusions from Experiment 5.1; bars show the confidence interval around the mean. Purple marks show simulated results for inclusion collision and growth.

Comparing samples from before and after calcium injection (i.e. 9min after Al and 3min after Ca), there is a decrease in average diameter of about 2.5 times. That is an indication that beyond forming transient CaS inclusions, more mechanisms are operating in the calcium treatment reaction. In fact, Chapter 6 of this work is fully dedicated to address why this size decrease happens. After calcium treatment, there is a small but significant change in size of calcium treated inclusions at early stages. A more pronounced change is observed from six to nine minutes after calcium. Judging by the samples taken, the agglomeration of liquid inclusions does clearly occur, and a longer sampling sequence was performed (Experiment 5.2) to clarify this trend.

One additional approach to confirm the trend of increasing diameter of calcium aluminates is to look in detail at large inclusions. Table 4 shows the incidence of inclusions larger than $1\mu m$, confirming the increasing prevalence of larger inclusions with time after calcium treatment.

Table 4: number density and percentage of inclusions greater than 1 micron.

Sample	A1	A2	A3	C1	C2	C3
Inclusion Density (#/mm ²)	48.4	58.3	37.4	16.4	16.3	24.8
Percentage	86.8%	69.9%	85.8%	14.1%	29.9%	55.7%

From the calcium treated samples, the number density decreased (from C2 to C3; Figure 30) while the percentage of inclusions over 1µm increased over time (Table 4), confirming that the liquid calcium aluminates agglomerated over time.

Experiment 5.2 used essentially the same conditions as its predecessor, but with a different sampling plan (Table 5). Calcium treatment was done approximately ten minutes after deoxidation, when temperature restabilized at 1600°C. To better characterize the decrease in size after Ca modification, a specimen was taken one minute after Ca treatment was taken.

Sample name	Time	OBS
_	(min)	
A1	5	After Al deoxidation
C1	1	
C3	3	
C6	6	After Ca treatment
C9	9	
C15	15	

Table 5: Sampling plan for Experiment 5.2

Figure 33 shows the ternary inclusion composition before Ca. The sample was taken five minutes after aluminum addition, when the system temperature had stabilized at 1600°C. As previously observed, after Al deoxidation, the crucible served as a source of Mg for the melt and the formation of spinel inclusions are also observed. Both number and area ternaries exhibit essentially the same information, for this reason, only the area-based diagram is shown.

One minute after calcium treatment, specimen C1 was collected; its Mg-Ca-Al and S-Ca-Al ternary diagrams are shown in Figure 34 (a-b) and (c-d) respectively. Comparing the inclusion density plot on the left-hand side and the area fraction on the right-hand side of Figure 34 (top), a larger number of calcium modified inclusions compared to spinel/alumina inclusions is present one minute after "Cal-Sil" injection, but with a similar inclusion area fraction to sample A1. The unmodified inclusions are larger in size. Also, a minor proportion of CaS was observed as shown in Figure 34 (bottom) where small triangles are present close to the Ca-S binary. Just 17 CaS 48

inclusions were detected out of a total of 900. All CaS observed ranged from 0.5 – $2.5 \mu m$ in

diameter with an average size of 1.12 μ m.



Figure 33: Ternary diagram of sample before calcium.

The sample taken 3 minutes after calcium treatment (Figure 35) contained fewer unmodified inclusions than after 1 minute. Out of a 2000+ population, only 76 inclusions lie outside the 50% liquid boundary.



Figure 34: Mg-Ca-Al (a-b) and S-Ca-Al (c-d) ternary plots of sample C1

In sample C6, there is an unexpected increase in inclusion area fraction (which is also shown in Figure 39(right)). Along with the observed peak in the area fraction, the inclusion number density also increases and there is a shift in the Ca/Al ratio. This might be taken to indicate that reoxidation happened before or when taking sample C6. However, given that the Ca/Al ratio only decreased from 1.03 to 0.73 (from C3 to C6), and the area fraction doubled, reoxidation alone could not be the cause of the area fraction increase. One other probable cause is that as inclusions were getting bigger, more inclusions were detected by the microscope.

In sample C9, 95.5% of the inclusions lie within the 50% liquid boundary line in the S-Ca-Al ternary diagram. That indicates that, after 9min virtually all alumina/spinel inclusions were successfully modified into liquid calcium aluminates.



Figure 35: Mg-Ca-Al (top) and S-Ca-Al (bottom) ternary diagrams of sample C3.



Figure 36: Mg-Ca-Al (top) and S-Ca-Al(bottom) ternary diagrams of sample C6



Figure 37: Mg-Ca-Al (top) and S-Ca-Al (bottom) ternary diagrams of sample C9

The ternary plots indicate that the treatment in Experiment 5.2 was successful and the sizes of inclusions can be compared using the same procedure applied in Experiment 5.1. In both experiments, inclusion diameters follow lognormal distributions. Figure 38 shows the histogram of all inclusions studied in Experiment 5.2. As shown in Figure 33, before calcium treatment the sample contained only solid alumina and spinels and their size distribution is shown in the top graph of Figure 38. For calcium treated samples (CX), the sizes plotted on the graph corresponds to all inclusions that fall within the 50% boundary line of the S-Ca-Al ternary diagram, i.e., solid inclusion sizes are excluded from the plot. Because the number of inclusions in each histogram varies significantly, plotting Figure 38 using the observed numbers would not show useful comparison. For this reason, the y-axis is shown as density.

Immediately after calcium injection, the lognormal distribution does not fit the data well. As time progresses, the system becomes more "lognormally oriented", as it was prior to calcium treatment. Although the lognormal fit is not good for some samples, the shape of all curves is roughly lognormal, and all samples were considered to follow this distribution for comparison of average inclusion sizes.



Figure 38: Histogram of inclusions diameters from Experiment 5.2.

After taking the natural logarithm of the diameters, the average and confidence interval of each specimen are shown in Figure 40. The layout showed in the interval plot for Experiment 5.2 is different from what was shown in Figure 32, on page 47. Instead of showing only the average size of liquid inclusions, the sizes of remaining solid inclusions for each sample are also shown in the grey circles. This will be useful in the discussion about the size decrease (see page 81). The black circles shown in the interval plot correspond to the liquid inclusions.



Figure 39: Inclusion density (left) and area fraction (right) of solid (grey) and liquid (black)



inclusions of Experiment 5.2.

Figure 40: Average sizes of liquid and solid inclusions, Experiment 5.2.

By direct observation of the results shown in Figure 40, it is possible to confirm that, over time, liquid inclusions do agglomerate and therefore change their average size, just like in Experiment 5.1. The same slow trend was consistently observed in these two experiments. Also, in accordance to what was observed previously, there is a sharp decrease in the average inclusion size immediately after calcium modification. The first initial measurement after treatment shows an average diameter 3.5 times smaller than prior to Ca injection. Figure 38 helps explaining this difference, since after Ca addition, inclusions over 1µm are a rare observation and most

measurements are concentrated in sub-micron range. As time progresses, >1 micron inclusions are more commonly observed, and the size distribution becomes "wider".

5.3 Remarks on Experiments 5.1 and 5.2; revisiting hypothesis one

To summarize the experimental results shown so far, both experiments were successful in modifying alumina and spinel inclusions into calcium aluminates. Reoxidation, when it happened, shifted the average size of inclusions due to formation of new small inclusions in the steel. This trend was clearly observed in samples taken between three and six minutes after aluminum deoxidation of Exp. 5.1, as well as comparing samples taken nine and fifteen minutes after calcium of Exp. 5.2.

The experimental results show clearly that experimental results agree with hypothesis number one. Liquid/partially liquid calcium aluminates do agglomerate and hence change in size. The tendency is weak, but statistically significant. Because this slow trend is difficult to observe under industrial conditions, where the time frame where the process happens is relatively short, it makes sense that steelmakers did not perceive it and therefore believed that calcium aluminate inclusions do not change their size over time.

Moreover, the conditions where liquid inclusions were observed in early confocal studies are not the same as in industry. In the latter, inclusions are surrounded by liquid steel and buoyancy forces act on the particles, causing them to move and therefore collide. In the CSLM, inclusions are at the surface of the melt and are not susceptible to agglomeration by Stokes motion. A more detailed discussion regarding liquid inclusions in bulk steel vs. on the melt surface is provided on Chapter 8.

5.4 Industrial Sample – 13ppm sulfur

The induction furnace is a more controlled environment when compared to industrial equipment, such as the ladle furnace, the vacuum degasser or even the tundish. In the laboratory experiments, the atmosphere is controlled with a relatively low oxygen partial pressure and no gas or (strong) electromagnetic stirring is present. For that reason, it is easier to assess any isolated agglomeration effect on inclusions. However, industrial scale processing should show the same phenomena if one could eliminate other process variables.

In the case of this reported industrial heat it is exactly what happened: due to a logistical issue in the plant, the steel remained in the ladle after calcium treatment long after it would normally have been sent to the caster. In fact, the ladle remained under gentle argon stirring for approximately one hour after CaSi₂ wire injection. The chemical analysis for the elements of interest are shown below in Table 6:

Table 6: Concentration of elements of interest for the industrial sample

%C	%Al	%Mn	%Si	%S
0.058	0.033	0.55	0.032	0.0013

Three ladle samples were collected and one in the tundish, at the end of casting. Ladle samples are indicated with the letter "L" whereas tundish sample names start with "T". All details regarding sampling procedures are given in Table 7.

Table 7: Sampling plan for the industrial sample

L3	L8	L9	T6
Before "Cal-Sil"	5min after Ca	60min after Ca	End of cast
wire injection			

In accordance to what was reported for Experiments 5.1 and 5.2, the ternary diagrams are shown, followed by the statistical analysis of inclusion size. Before calcium treatment, all inclusions are like in laboratory conditions, i.e. all inclusions are mostly spinels, as per Figure 41. However, sample L3 shows a distinct difference from laboratory samples in terms of size. A bimodal population of alumina + spinels inclusions is present in the system. This can be observed in the number-based diagram on Figure 41(a), in the left, showing a small number of spinels, yet the area-based diagram shown on the right(b) exhibits large triangles in the spinel corner of the diagram.


Figure 41: Industrial sample before Ca treatment (L3)

The bi-modal population of inclusions is shown in Figure 42, where the histograms of solid inclusions and only spinels are shown in separate graphs. Comparing the two graphs, one can easily observe that almost all inclusions larger than 6μ m are spinels.



Figure 42: Industrial sample before calcium treatment: Histogram of (a) all solid inclusions and (b) only spinel inclusions

At five minutes after treatment, most inclusions were modified. A few spinels and calcium sulfides could be detected in the AFA. Just like in Figure 33 on page 49, the number and area based ternary diagrams of sample L8 did not show any significant difference and only the area based plots are shown in Figure 43. In sample L9, most inclusions remained as calcium aluminates after 60min 57 (see Figure 43(c-d)). The steel was gently stirred for the whole hour and no other alloy addition

or vacuum treatment was performed. Sample T6 was collected at the end of casting.



Figure 43: Mg-Ca-Al (left) and S-Ca-Al (right) ternary diagram of samples 5min(a-b), 60min(c-d) after Ca and end of cast(e-f) of the industrial samples.

As it can be seen in Figure 44, there is small trend for liquid inclusions to agglomerate. On average, liquid inclusions have approximately the same size under industrial and laboratory conditions, when comparing Figure 44 and Figure 40. However, when looking in detail samples L8 and L9 in the SEM, an interesting detail is noted: there are significant more inclusions over 10 μ m in the industrial sample (after 60 minutes) compared with the laboratory samples.



Figure 44: Inclusions diameter interval plot of the Industrial Heat.

Figure 45 shows an x-ray map of one calcium aluminate inclusion with approximately 20µm diameter. Each element of interest (sulfur, magnesium, calcium and aluminum) is presented in the black and white images. The first micrograph in Figure 45 depicts the backscattered electron image and the "clustered" image represents all elements overlapped in one single image. Sulfur is represented in blue, magnesium in pink and calcium + aluminum in yellow. This is an example of a fully treated MgO-containing calcium aluminate found in sample taken one hour after calcium treatment. Inclusions in the industrial sample were mostly fully modified in this heat and remained fully modified until the tundish.



Figure 45: X-ray map of a calcium aluminate inclusion in the industrial sample, taken 60 minutes after calcium treatment



Figure 46: Violin plot (left) and scatter plot(right) of inclusion size for industrial heat Figure 29 and Figure 38 (pages 44 and 53) show the histograms of liquid inclusion diameters for laboratory experiments. In all cases, inclusions larger than $10\mu m$ were rarely observed. In the AFA data, no inclusion was larger than $10\mu m$. Figure 46 in the other hand indicates that inclusions

over 10µm were found in the industrial sample. This observation confirms that, given enough time, liquid calcium aluminates will agglomerate into large inclusions.

5.5 Experiment 5.3 (low sulfur, Al₂O₃ crucible)

Sections 5.2 and 5.4 covered full modification of spinel inclusions. The current section aims to assess inclusion size after fully modifying pure alumina inclusions. By modifying separately these two types of solid inclusions, the effect of magnesium on inclusion size distributions after calcium treatment can be assessed. Like previous sections, after assessing whether the experiment was successful in terms of Ca injection, a size distribution analysis is presented. The overall objective of this subchapter is to answer the following question:

Hypothesis 3: Magnesium contributes to spinel inclusion breakup upon modification

Table 8 shows the chemical analysis for the relevant elements in this experiment. One sample before, one after Ca injection and the block of steel remaining after the experiment were analyzed. After killing the steel, the only major element present in the melt is aluminum. For a %Al_{total} of 0.063%, it is estimated that the initial dissolved oxygen before deoxidation was approximately 300ppm in the melt when the experiment started. The analysis indicates a sulfur content of less than 20ppm.

Table 8: Chemical analysis of samples before and after Ca treatment, and bulk sample remaining after the experiment

Sample	C (%)	S (%)	Si (%)	S (%)	Al _{total} (%)	Ca (%)	N (%)
A2	0.028	<0.002	0.02	<0.002	0.063	0.0005	-
C3	0.04	<0.002	0.17	<0.002	0.071	0.0031	-
Steel "puck"	0.03	< 0.002	0.17	0.002	0.071	0.0021	0.0021

Figure 48 shows the relevant ternary diagrams for Experiment 5.3. All triangles are proportional to the area fraction of inclusions. Before calcium treatment, see Figure 48 (a) and (b), the Mg-Ca-Al ternaries show that no Mg was detected and therefore no spinels formed after deoxidation, as expected. Sample A2 showed almost twice the inclusion concentration compared to sample A1. Besides, the number of inclusions smaller than 2µm in sample A2 is much higher than sample A1, comparatively. The drop in size can be confirmed by inspecting the histograms of the samples before calcium treatment shown in Figure 47. The latter contains a narrowly-distributed lognormal shape with the clear majority of inclusions below 2µm.



Figure 47: Histogram of samples A1 and A2 (Before Ca)

Another practical method in determining whether the different average size observed in samples A1 and A2 comes from reoxidation is via Population Density Plots (PDF). Figure 49 shows a PDF vs. equivalent diameter in a log-log scale plot. The PDF of Sample A1 is a straight line, indicating size independent growth of inclusions, whereas in A2 the PDF has a parabolic-like shape. It will be discussed later that the reoxidation observed in sample A2 is due to sampling and not related to total oxygen content in the melt.



Figure 48(a-h): Experiment 5.3 Ternary Diagrams.



Population Density Function

Figure 49: PDF plot of inclusions in samples A1 and A2 (before Ca).

Figure 50 shows the average inclusion sizes of the samples collected during Experiment 5.2. As seen also in Experiment 5.1, samples showing reoxidation due to sampling, have a smaller average size compared to previous samples taken in the same experiment. In the case of experiment 5.3, not only the average size drops, but the area fraction almost doubles. Because of this undesired effect, sample A2 is not representative of the system. From sample A1 to C1 (that is, upon calcium treatment) the inclusions decrease in size, as seen in the other experiment using a MgO crucible (Experiment 5.2).



Figure 50: Interval plot of average diameters (a), Area fraction & inclusion density (b) - Exp. 5.3

From three to six minutes, the average size of liquid inclusions increased, as seen in Figure 50 (a). However, an increase in area fraction and inclusion density was also observed. (Figure 50 (b)). In addition to the inclusion content increase, a move towards the Al corner in the ternary diagram in Figure 48 [(d) \rightarrow (e)] indicates an increase in the aluminum content. This shift was likely due to dissolution of the alumina crucible, which can provide a constant supply of oxygen to the melt. In fact, a continuous growth in the molar ratio $\frac{Al}{Ca}$ is observed in this experiment. Figure 51 shows in detail this increase. In the boxplots shown in Figure 51, each boxplot represents the inclusions in one steel sample. The vertical lines in each symbol show the upper and bottom 25% of the data. The dark grey rectangles represent the intermediate 25% percentiles and the line in the middle of the rectangle is the average. The black box inside the rectangles are the confidence interval around the mean of each sample. The reference lines show the $\frac{Al}{Ca}$ for C₃A, CA and the theoretical C₁₂A₇ calcium aluminates.



Figure 51: Boxplot of Al/Ca ratio of calcium treated samples for Experiment 5.3. Dotted lines represent the composition of CA, C3A and the theoretical C12A7.

Although a continuous change in inclusion composition was observed, the composition remained in the desired region where inclusions are at least 50% liquid at 1600°C. Figure 52 is a SEM image of sample three minutes after calcium treatment electrolytically deep etched. All inclusions appear round and approximately 1 μ m diameter, which agrees with the 2D planar section analyzed in Aspex. The micrograph contains seven inclusions labeled (1-7) in the figure. The big globular feature appearing the in the top part of the figure is undissolved iron, and not an inclusion.



Figure 52: SEM image of sample taken three minutes post calcium in experiment 5.3 after deep etching. Numbers 1-7 indicates the actual inclusions. (The large irregularly shaped region at the top center is undissolved steel.)

5.6 Remarks and hypothesis revisited

Experiment 5.3 was conducted to test whether calcium treated alumina or magnesia-alumina spinel inclusions would have any difference in size after calcium. Successful experiments using alumina crucible to avoid spinel formation was carried out in experiment 5.3. Although some reoxidation was observed during experiment, inclusions remained mostly in the $CA+C_{12}A_7$ calcium aluminate range, which is liquid at 1600°C. An unexpected increase in inclusion area fraction was observed from three to six minutes after treatment. This increase will be discussed in detail in 5.7 and 5.10. Figure 53 shows that in all three experiments, spinels and alumina average size were almost identical. With this result, it can be concluded that magnesium had no significant role in liquid inclusion size changes after calcium treatment in Experiment 5.3. Therefore, hypothesis three has no experimental support and is refuted.



Figure 53: Interval plot of inclusion size for induction furnace experiments. Exp 5.1 & 5.2 treated spinels and 5.3 alumina.

5.7 Flotation of liquid inclusions

The objective of this chapter is to elaborate on the flotation and removal of liquid inclusions. It is common sense in the industry that liquid inclusions are more difficult to remove compare to solid alumina inclusions ^[47]. The main argument is the low contact angle of liquid inclusions at the steel-gas interface compared to solid alumina and/or spinels^[48]. In this chapter, the following hypothesis will be tested:

Hypothesis 3: Liquid calcium aluminates removal from liquid steel happens at the same rate of solid alumina.

Prediction of alumina inclusions removal was described by Schwerdtfeger^[49]. In that case, it is assumed that flotation of inclusions is governed by steel mass transfer. When the rate limiting step is steel mass transfer, the system can be described by fitting a first order parameter. Therefore, oxygen removal follows an exponential trend as shown in Equation 19.

$$[0]_{t} = ([0]_{initial} - [0]_{final}) \times \exp\left(-\frac{kAt}{v}\right) + [0]_{final}$$
Equation 19

Where k is the mass transfer coefficient of steel in contact with a surface area A, t is time and V is the volume of steel. The mass transfer coefficient varies according to the stirring rate. For the system used in this work, that is, with no external agitation, Kumar^[50]measured the effective mass transfer coefficient of alumina and spinel inclusions. The same $k = 4.5 \times 10^{-5}$ m/s was applied to Equation 19 in all experiments. Using the area and volume described by Piva et al.^[51] a value of $\frac{kA}{V} = 6.5 \times 10^{-4}$ s⁻¹ was used. That is, the time constant for inclusion flotation is expected to be approximately 26 minutes. The initial oxygen concentration ([O]_{initial}) is taken as the area fraction of inclusions before calcium treatment in each experiment.

5.8 Results and discussion

Figure 54 (a-c) depicts the experimental vs estimated area fraction using the approach described above. In all three cases, the decrease in total oxygen experimentally observed agrees broadly with what was predicted. Experimental points are specified by SEM used in the measurements, since, as it can be seen and will be discussed later, depending on which stage after Ca treatment the sample was taken, ASPEX Explorer did not detect most of inclusions, because the inclusions were small.

In Figure 54(a), the sample furthest from the calculated line is the one taken six minutes after deoxidation (at t=-5min). As discussed in previous sections, this sample suffered from reoxidation and the total oxygen is not representative of the system. The remaining samples agrees well with theoretical values, given the variation observed in these samples.



Figure 54: Area fraction vs. time after calcium treatment for experiments 5.1, 5.2 and 5.3. "ASPEX" and "Quanta 600" are the SEMs used in each analysis.

For Experiments 5.2 and 5.3, samples before calcium were analyzed more than once to evaluate analytical reliability. A more detailed discussion about reproducibility and repeatability of experiments 5.1-5.3 is provided in section 5.10. Figure 54(b) shows results from analysis of the sample before calcium was measured in completely different regions from the steel rod. Areas 1, 2 and three are shown in shades of orange in the plot. The average of these three measurements is shown as a black line. Results from ASPEX analysis are shown as white circles. For samples taken one and three minutes after Ca one can see that the ASPEX analyses under-analyzed the inclusion concentration. Quanta 600 gives better spatial resolution (see Figure 19 on page 29). For that reason, a repeat analysis of these samples was performed in this field emission gun microscope in order to better resolve small inclusions formed moments after calcium injection. Inclusions analyzed with the Quanta 600 are shown as black diamonds. Three minutes after treatment, the area fraction is within the expected range of observed values. That indicates that inclusions are mostly small, with sizes in the range between the resolution range of the ASPEX and Quanta 600 microscopes. However, one minute after calcium treatment, inclusions are so small that even the field emission gun SEM could not resolve all inclusions present in the melt at that time. This is concluded by comparing the difference in inclusions measured between one and three minutes on both SEMs. For samples taken three minutes after Ca, ASPEX was still not capable of resolving small inclusions whereas Quanta 600 detected many more features. When analyzing samples taken one minute after calcium, the results with both microscopes were similar. The same observation was seen in both experiments 5.2 and 5.3. The existence of such a large number of small (and in some cases undetectable) inclusions indicates that that the calcium oxide (or sulfide) nuclei formed upon injection are very small.

The same trend was observed in Experiment 5.3 (Figure 54(c)). This time not three but two measurements of the sample before calcium was done. Each analysis is depicted in a different shade of orange and the average in black. One and three minutes after calcium treatment, ASPEX did not detect all inclusions present in the system and therefore the inclusion concentration was under-analyzed. But - as for the other samples - when measured at a higher resolution, the area fraction does agree to what was calculated initially. As discussed previously, sample at t=-2min in Figure 54(c) had a significant amount of reoxidation, causing a higher than expected inclusion concentration.

5.9 Remarks regarding liquid inclusion flotation; revisiting hypothesis 3

Experimental data of fully treated calcium aluminates was plotted against an exponential fit for a mass transfer-controlled flotation in liquid steel. The mass transfer coefficient used was measured for solid alumina and magnesia-alumina spinel inclusions by Kumar^[50]. Because the experiments were carried out using exactly the same apparatus, a direct comparison could be used. Liquid calcium aluminates floated to the top surface of the liquid melt at the same rate as alumina inclusions as seen in Figure 54. That is, the hypothesis was consistent with the experimental observations.

This conclusion contrasts with what has been observed in industry. Pretorius et al. ^[45] studied removal of liquid and solid inclusions in the tundish using an argon diffuser. In their findings,

spinel inclusions were more efficiently removed compared to liquid calcium aluminates with the diffuser turned on. However, no data regarding how area fraction and size distribution of liquid inclusions changed with and without the diffuser was shown, but only alumina and spinel inclusions. Common sense in the steel industry that, once formed, liquid calcium aluminates are not as "easy" to remove compared to solid alumina. The main difference between industrial and laboratory conditions used in this study is the amount of external agitation. Even in the tundish, the steel should be more agitated than the melt in the crucible inside the induction furnace. This agitation could be one source to not only promote collision between inclusions, but also to disturb the liquid inclusion particles in suspension in liquid steel, causing the particles to break. Once liquid inclusions become smaller, they tend to stay in the melt.

5.10 Reliability of experimental results

This section discusses the repeatability and reproducibility (R&R) of current results. It is divided in three separate parts regarding R&R of the experiments itself, discussed in section 5.6.1, reproducibility of sampling in section 5.6.2 and reproducibility of the characterization method, i.e., regarding SEM settings in section 5.6.3.

5.10.1 Repeat experiments

Chapter 5 contains three repeated experiments. In all experiments, liquid calcium aluminates did agglomerate and showed similar trends. A summary of the three experiments is compiled in Figure 55, where data shown in Figure 40, Figure 32 and Figure 50.



Figure 55: Interval plot of inclusions size from experiments 5.1 to 5.3

As it can be seen, in all three cases, the inclusion sizes are similar, and show a similar increase in size during the experiment. It is shown that, given good experimental conditions are maintained, such as good furnace sealing, proper inert atmosphere and adequate calcium injection, results are reproducible with close agreement to one another.

5.10.2 Repeatability & Reproducibility within the sample

Figure 56 shows how composition varies for sample in experiment 5.2 before Ca. Three different parts of the steel rod taken as sample was analyzed. All diagrams show inclusions as spinel with small variations in Mg/Al ratio, which is expected. The average diameter for all inclusions in the three analyses was $2.1 \pm 0.2 \mu$ m, which compared with 1.9 μ m previously reported in Figure 40 is within experimental error. The range of area fraction (212-329) ppm was plotted as initial values in Figure 54(b). One can see that except for samples analyzed in ASPEX Explorer samples taken one and three minutes after Ca treatment, and samples taken one minute after calcium treatment on Quanta 600, the subsequent area fraction values are in the range of what is expected based on initial total oxygen before calcium treatment. As it will be discussed later, under-analysis shortly after injection is because inclusions are too small to be detected, even on Quanta 600.



Figure 56: Mg-Ca-Al of experiment 5.2 before Ca for reliability purposes

Similarly, in experiment 5.3 the same procedure was applied for the sample before calcium. All inclusions are alumina. Differences observed in total oxygen (199-305) also shown in Figure 54(c). Most SEM analyses of inclusion area fractions agree with predicted values, given the experimental variation. Disagreements with calculated values were observed in A2 (t=-8min) (which was affected by reoxidation) and in the analysis by ASPEX of samples taken one and three minutes after Ca (small inclusions). Regarding average diameter for sample A1, the value was $2.0 \pm 0.1 \mu m$.

5.10.3 Repeat of same sample with the same SEM.

This section concerns the analysis itself. Clearly, when switching SEMs, similar results in chemical composition were observed, but completely different results in terms of inclusions concentration and size distribution were achieved. These differences are quantified and discussed in previous sections. The question that this section tries to answer is different: Given one is using the same microscope, analyzing the same region and using the same settings, how different can the analysis be?

This analysis emerged from a user mistake: when setting a multiple analysis on ASPEX Explorer, the same area was selected three times for analysis A, B and C. The analyses were performed in immediate succession, one after another. Therefore, the microscope scanned the same region in the same sample while maintaining all settings. Although all settings were maintained, the emission current cannot be held constant. Given the nature of the tungsten filament, the emission current will decrease over time. Based on this variation, the matrix will appear darker as the emission current decreases and the number of detected inclusions might vary. This is what happened in the current analyses, summarized by Table 9. For later analyses, fewer features (including inclusions, pores, dirt, etc.) were detected. However, the number of actual inclusions, after filtering, was approximately constant between runs A and B and decreased more in run C.

Analysis	Α	В	C
Initial emission (µA)	21.1	20.7	20.7
Features detected before filtering	3591	3226	2390
Features considered as inclusions	753	775	611
after filtering	(20%)	(24%)	(26%)
Duration (h:mm)	5:36	5:39	4:22
Scanned Area (mm ²)		23.902	

Table 9: Initial emission current, features detected before and after filtering and scanned area for analyses A, B and C.

Because the number of inclusions varied in each run, so did the area of inclusions. This affects the area fraction of detected inclusions. For Analyses A and B the area fraction is approximately equal, but in Analysis C the steel appeared "cleaner" because of less inclusions being detected. Small variations were observed in the chemical analysis, as seen in Figure 57. The position of the largest triangle varies from sample to sample. However, the overall composition of inclusions remains equal for all three analyses. Runs A, B and C detected some alumina inclusions and a range of compositions from calcium aluminates to calcium rich CaS.



Figure 57: Ternary diagrams of Analyses A, B and C.

In terms of size, the average remained equal in all three cases. Figure 58 shows a violin plot of inclusions size (at left). A violin plot is a combined boxplot and density function in one figure. The inner black rectangle is a classical boxplot. The median is represented in the white circle inside

the rectangle that separates the 50% and 75% quartiles. Surrounding the boxplots are the density functions (mirrored) showing a clear shape lognormal shape. Only small differences between the density plots can be seen. In the right-hand side of Figure 58 is an interval plot which shows that the average size of inclusions is statistically identical. The error bars shown in the interval plot in Figure 58 are the confidence interval around the mean with 95% of confidence level.



Figure 58: Violin plot (left) and interval plot (right) of inclusions size for Analyses A, B and C

A Chi-square test was performed in data from analyses A, B and C to test whether they are equal. To perform this test, inclusion diameters were grouped in ten bins as shown in Table 10. The choice of bin number was based on the constraint that every bin should contain at least five observations ^[52]. In this case, the null hypothesis tested is that data from each analysis are not significantly different (i.e. columns are similar). The calculated values are $\chi^2 = 4.176$, which is below the critical value^[52]. P-value = 0.9997, which means that the null hypothesis is accepted. Therefore, diameters measured in analyses A, B and C are statistically identical.

In summary, it can be concluded that given the same instrument settings, both chemical analysis and size measurements of inclusions are reliable, as expected. Small variations were seen due to emission current decrease of the SEM. That is inherent of a tungsten filament and cannot be entirely avoided. Good practice when running multiple analyses is to wait for a stable emission current before running multiple samples in the SEM.

Bin range (µm)	Α	В	С
[0.25,0.75)	40	47	33
[0.75,1.25)	153	157	132
[1.25,1.75)	150	154	117
[1.75,2.25)	73	85	59
[2.25,2.75)	45	49	37
[2.75,3.25)	35	35	29
[3.25,3.75)	17	15	9
[3.75,4.25)	19	19	19
[4.25,4.75)	11	12	10
[4.75, D _{MAX})	19	22	13

Table 10: Bin values for discretized measured diameters in analyses A, B and C.

5.11 Mechanism of collision

According to Lindborg and Torsell^[36], the number of collisions per unit volume between two particles of size r_i and r_j , is given by:

$$N_{ij} = W_{ij}n_in_k$$
 Equation 20

In Equation 20, W_{ij} is the collision volume, $n_{i,j,k}$ is the number of particles per unit volume of a given size $r_{i,j,k}$. The collision volume (units of m^3/s) will be a function of the collision mechanism in which two particles collide. In fact, there is no single mechanism in collision of inclusions. Every mechanism acts at the same time to some extent, and the overall collision rate is assumed to be a summation of all of them^[53]. Although all mechanisms will contribute to inclusion collision, it is expected that one or some mechanism(s) will predominate for a given inclusion size. Table 11 shows the mathematical relations for different acting mechanisms in particle collision. The comments columns contain the constants used for calculations for the plots shown in Figure 60.

For the Brownian collision volume, k_0 is the Boltzmann constant, T is the absolute temperature and μ_{Fe} is the viscosity of iron at 1600°C. In the Stokes motion collision volume, g is the gravity acceleration, ρ_i is the density of steel/inclusion. The turbulent collision volume, α is the coagulation coefficient and ϵ is the dissipation rate of turbulent kinetic energy. A typical ladle have a dissipation rate of the order of $1 \times 10^{-2} \text{m}^2/\text{s}^3$ [26,53]. The dissipation rate in the induction furnace is estimated to be three orders of magnitude lower than an industrial ladle, that $\epsilon_{furnace} = 1 \times 10^{-5} \text{m}^2/\text{s}^3$, according to COMSOL simulations conducted by Piva^[56], given there is no external agitation to the melt. The collision due to laminar flow of the fluid, $\frac{du}{dx}$ is the velocity gradient of the liquid steel. The value of velocity gradient was estimated based on the COMSOL simulations shown in Figure 59. A rough initial guess number was calculated dividing the variation in velocity magnitude by the distance between the top and the center of the melt at x=0 in Figure 59.

Table 11: General formula and parameters used in calculations for different collisionmechanisms. From [54].

Mechanism	General formula (W _{ij})	Comments
Brownian collision	$\frac{2k_0T}{3\mu_{r_0}}\left(\frac{1}{r_i}+\frac{1}{r_i}\right)(r_i+r_j)$	$k_0 = 1.38 \times 10^{-23} kgm^2 s^{-2} K^{-1}$
	orre (-1 - j)	$T = 1823$ K, $\mu_{Fe} = 0.005$ Pa. s
Stokes motion	$\frac{2\pi g(\rho_{Fe} - \rho_{inclusion})}{9\mu_{Fe}} (r_i^3 + r_j^3) r_i - r_j $	$g = 9.81 m. s^{-2};$
		$ \rho_{Fe} = 7000 \text{kg}. \text{ m}^{-3}; $
		$\rho_{inclusion} = 2900 \text{kg}. \text{m}^{-3};$
		$\mu_{Fe}=0.005 Pa.s$
Turbulent collision	$1.3\pi^{\frac{1}{2}}\alpha(r_i + r_i)^3$	$\epsilon_{\text{ladle}} = 0.01 \text{m}^2/\text{s}^3; \ \alpha = 0.3;^{[55]}$
	$\sqrt{\nu_{\rm Fe}}$	$\epsilon_{\rm furnace} = 1 \times 10^{-5} \frac{{\rm m}^2}{{\rm s}^3};$
		$\nu_{Fe}=\mu_{Fe}/\rho_{Fe}$
Collision due to	$\frac{4}{3}(r_i + r_j)^3 \frac{du}{dx}$	$\frac{\mathrm{d}u}{\mathrm{d}x} = 2\mathrm{s}^{-1[56]}$
fluid laminar flow	J UX	



Figure 59: Surface plot of velocity magnitude of the melt in m. s⁻¹. Arrows indicate direction of the flow. Courtesy of Stephano Piva^[56].

Using a particle size of 1, 5 or $10\mu m$ the collision volume was calculated and shown in Figure 60. For an industrial ladle, where stirring is almost always present, turbulence is the dominant mechanism of collision between inclusions (shown in red in Figure 60). For a large 10um particle with a higher Stokes velocity (Figure 60 right), Stokes collision is comparable to turbulent flow whenever the difference in particle size is large. As the size of the "*j*" particle approximates $10\mu m$, the collision rate goes to zero. This is because Stokes collision will be effective when particles have different terminal velocities. In the case of the induction furnace, the red line in all charts can be neglected, since no external agitation is present. In the case of a 10um particle in the induction furnace, Stokes collision volume and laminar flow collisions are the two main mechanisms. This is also true for mid-ranged 5 microns sized particles. For 5-10um particles, Brownian collision is in most cases orders of magnitude lower than the other two mechanisms.



Figure 60: Collision volume for a 1, 5 and 10µm inclusion through different collision mechanisms. For a small 1µm particle, the collision volume between small inclusions ($j \le 1µm$) is dominated by Brownian collision, when no external agitation is present. As particle size increases ($j \ge 1µm$), first laminar collisions and then Stokes collision becomes the dominant mechanism in the case of the induction furnace. In the industrial case, turbulence one more time will be more significant than the other types of agglomeration mechanism.

Therefore, it can be concluded that, specifically in the induction furnace experiments done in this work, liquid inclusions will coalesce via Stokes collision and due to laminar flow, predominantly. The variation of a finite number of particles (n_{ij}) of a given particle size (r_{ij}) can be discretized as shown by Smoluchowski^[57]:

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} W_{ij} n_i n_j - n_k \sum_{i=1}^{\infty} W_{ij} n_i$$
Equation 21

The first term in Equation 21 calculates the variation of "i" particles colliding with "j" particles to form a cluster with "k" particles. The second term is the depletion term^[58]- removal of *k*-sized inclusions by collisions with other inclusions. With Equation 21, one can estimate the number of particles colliding and coalescing each time step and calculate, for a given time, an estimate size distribution of inclusions, based on an initial population. Results of simulated inclusions sizes are shown in section 5.2, on page 37 and in section 7.5, on page 110.

The simulation will be very sensitive to the initial particle distribution and the number of particles per unit volume. For the simulations provided in this work, 600 particles were simulated each time, with three simulations ran in every sample simulated. The initial size distribution was used either as the experimental observed size distribution at a given time, or, at early stages after calcium treatment the regression estimating a "true" lognormal curve was used (as shown previously in Figure 32). The volume fraction calculated in the output of the simulation was used to match the area fraction of inclusions and check whether the collision rate was good to describe the observed size change. The width of the purple bar represents the range where the average size of inclusions at a given time varied in the three simulations.

Chapter 6 - Inclusion size decrease after Ca injection

As seen in section 5.2, immediately after Ca treatment inclusions were smaller than the untreated alumina or magnesia-alumina spinels prior to injection. Two possible explanations are that new (smaller) inclusions precipitated from dissolved species such as Ca, Al and O, or new calcium aluminates formed from the fragmentation of former spinel inclusions. In this section, the following hypothesis drives the discussion:

Hypothesis 4: Liquid calcium aluminates consists of a new population of inclusions. Calcium aluminates are formed by aluminum and oxygen transport from alumina/spinels.

Even shortly after calcium treatment, solid inclusions were rarely observed. As expected (based on the rapid mass transfer around micron-sized inclusions), calcium treatment happens very fast in liquid steel. Figure 61 illustrates the remaining solid inclusions found in experiment 5.1 three minutes after calcium treatment. In this experiment, that was the only sample containing enough data for statistical analysis. The area fraction of inclusions shown in Figure 61 corresponds only to 0.7ppm, whereas before calcium treatment, the area fraction of solid inclusions corresponded to 117ppm (see Figure 30 on page 44).



Figure 61: Mg-Ca-Al ternary diagram of solid inclusions in sample C1 (Experiment 5.1).

In experiment 5.1, only sample C1 (3min after Ca) contained a sufficient number of solid inclusions for statistical analysis. For that reason, only the result of C1 is shown below in Figure 62, which contains the probability plot of the solid inclusions in sample C1. One can see that, although the number of observations is low (N=20), the data follows a lognormal distribution, since the P-value is greater than 0.05.



Figure 62: Probability plot for a lognormal fit of solid inclusions in experiment 5.1 three minutes after Ca.

The mean size of solid inclusions in this sample is $0.49\mu m$. It indicates that the remaining solid spinels are smaller than before calcium treatment. This trend was confirmed with experiment 5.3, where the same composition filter was applied to classify solid inclusions. The filter was simply taking all inclusions with aluminum content (after normalization) greater than 0.75. Figure 63 depicts the inclusions considered in the size analysis of solid inclusions.



Figure 63: Mg-Ca-Al ternary diagrams of solid inclusions for experiment 5.2 one (left) and three (right) minutes after Ca.

The interval plot in Figure 40 on page 54 shows clearly that, as modification of inclusions by calcium occurs, the remaining alumina/spinels gradually become smaller. The tolerance around the mean in sample C3 is large, since the sample size is relatively small. Only 77 inclusions were alumina or spinels, as indicated on the legend of Figure 63 (right).

To understand better what could be happening thermodynamically, equilibrium scenarios using composition before and after calcium treatment were simulated using FactSage 7.2. FTMisc and FTOxid databases were used in these simulations. Before calcium, 600g of Fe was equilibrated with 0.5g Al and 0.24g O (400ppm). For this condition, the dissolved oxygen in equilibrium at 1600°C is 4.6ppm. Adding 0.15g of Ca to the system, the equilibrium products are CA + CA2 inclusions and the dissolved oxygen in steel is 3.4ppm. This small decrease could potentially destabilize the alumina/spinel inclusions, that would dissolve to reestablish equilibrium conditions. Simulations conducted by Kumar^[50] concluded that modification of CaS by precipitating alumina (by reaction of dissolved oxygen + dissolved aluminum with CaS) is expected to happen faster than modification of alumina by transfer of Ca (dissolved from CaS), due to low calcium solubility in steel. It is important to notice that these simulations showed that the volume of pure alumina inclusions would decrease in the melt. This finding agrees with what

has been seen experimentally in this work i.e. solid inclusions becoming smaller shortly after calcium treatment.

The encounter of dissolved aluminum and oxygen with calcium-containing (CaO or CaS-rich) nuclei therefore would form a new (and smaller in diameter) population of liquid calcium aluminates. Initially, inclusions in this population are so small in size that the inclusions could not be detected readily using backscattered electron imaging.

Experimental results (for inclusion concentrations and sizes) were mostly obtained by imaging of polished samples by backscattered electron imaging. That is why one minute after Ca modification, the measured area fraction is always smaller than what was expected, as seen in Figure 54 on page 69. In experiments 5.2(b) and 5.3(c), using Quanta 600, the area fraction was within the expected range three minutes after injection, but not when analyzing with ASPEX (with slightly coarser spatial resolution).

To test the idea that shortly after calcium treatment, a large number of small inclusions - below the instrument detection limit - are created, the sample taken one minute after Ca in experiment 5.2 was deep etched and an SEM image is shown in Figure 64. As the micrograph below shows, for every inclusion detected by the microscope, many more are being missed. The small inclusions observed most likely does not come from solidification inclusions. Two reasons support this idea: 1) The area fraction before and after Ca treatment are not very different. That is, total oxygen in both cases remained constant; 2) Long after calcium treatment, such small inclusions were not observed after deep etching the sample (see Figure 65). In Figure 64, the right-hand micrograph contains two circles with symbols "A" and "Q" written over it. This symbol puts in perspective what ASPEX's and Quanta's spatial resolution would be at 1200x magnification.



Figure 64: Micrograph of deep etched sample one minute after Ca in Experiment 5.2. Circles below symbols "A" and "Q" represent ASPEX's and Quanta's spatial resolution, respectively.



Figure 65: Micrograph of deep etched sample thirteen minutes after Ca in experiment 5.3. The presence of small undetected inclusions during AFA was not observed.

6.1 Remarks of chapter 6; revisiting hypothesis 4

In conclusion to this chapter, it was seen experimentally that the few solid inclusions present in the melt after calcium treatment were smaller than the inclusions that were present before calcium treatment. This is ascribed to the calcium treatment mechanism: When CaO/CaS and later calcium aluminates form, the dissolved oxygen activity decreases, destabilizing alumina inclusions and causing them to dissolve. This idea was further studied and simulated by other CISR researchers, who concluded in their simulations that alumina will be unstable and shrink rapidly in liquid steel when CaS is added. That would form a new population of small modified calcium aluminates, largely undetectable by standard SEM analysis used in this work. After deep etching the steel, these sub-micron inclusions were abundantly observed. These observations support hypothesis four: liquid calcium aluminates consist of new population of inclusions, separate and distinct from the unmodified alumina and spinel inclusions.

In summary, formation of new population of calcium treated inclusions happens according to the following steps:

- Upon calcium addition a large number of small calcium containing (CaO and/or CaS) nuclei form in the melt;
- Calcium addition reduces the activity of dissolved oxygen;
- The new level of dissolved oxygen disturbs the alumina/spinel equilibrium. For that reason, aluminum and oxygen are dissolved in the melt;
- Aluminum and oxygen are transported to the Ca-containing nuclei more efficiently than transport of dissolved calcium, given low calcium solubility levels in liquid Fe;
- Liquid inclusions are formed by reaction of Ca(O/S) with dissolved aluminum and oxygen.

Chapter 7 - Under-modified Inclusions

This chapter discusses observations of inclusion sizes in cases when calcium treatment did not completely modify Al_2O_3 or $MgAl_2O_4$ inclusions and the product is also mostly solid. The experimental procedure regarding induction furnace setup and SEM settings is described in each relevant section. The underlying idea in this chapter is to compare the size increase of solid inclusions with that of liquid inclusions, as discussed in Chapter 5. The hypothesis tested in this chapter is:

Hypothesis 5: The size of solid and liquid calcium aluminates will increase at the same rate.

The basis of this hypothesis is that growth of inclusions is limited by collision rate and not attachment of inclusions. Therefore, no observable difference between agglomeration of fully or partially modified inclusions should be observed.

Results for all induction furnace experiments will be presented and discussed in the following sections. Hypothesis five will be revisited in the conclusion of this chapter.

Different induction furnaces were used in experiments reported in this chapter. Table 12 summarizes all materials added to the melt as well as the type of induction furnace that was used in each experiment. FeS, when added, was mixed in the crucible with the electrolytic iron prior melting. Aluminum deoxidation and calcium treatment followed the method described previously in Section 4.1 on page 19. Deoxidation and calcium treatment were performed with a seven to tenminute intervals between each other. During this interval, one sample was taken to characterize the inclusions before calcium treatment.

Experiment	Electrolytic	FeS addition	Al addition	CaSi ₂	Crucible	Equipment
	Fe (g)	(g)	(g)	addition (g)	material	
7.1		-	0.5	1.0	MgO	Fused
						quartz ind.
						Furnace
7.2	600	-	0.55	1.08	Al_2O_3	Vacuum
						chamber
7.3	w/ /ppin s	0.17	0.6	2.0	Al_2O_3	Vacuum
						chamber
7.4		0.12	0.51	1.5	Al_2O_3	Fused
						quartz ind.
						Furnace

7.1 Experiment 7.1 (MgO crucible, low sulfur)

Experiment 7.1 was conducted in the same induction furnace setup as all experiments in chapter

5. The sampling plan of experiment 7.1 is described in Table 13.

Sample	Time after Ca		
	(min)		
A1	-2		
Со	0.5		
C2	2		
C4	4		
C7	7		
C10	10		
C13	13		

Table 13: Sampling plan for experiment 7.1

The analysis method is the same as in Chapter 5. That is, inclusions were analyzed in terms of composition and size before and after Ca. For this chapter, only an interval plot with all inclusions sizes for all experiments is provided. Detailed histograms are provided in the appendix.

7.1.1 Chemical composition of inclusions

All inclusions after calcium treatment appeared largely outside the 50% liquid line. Figure 66 contains two ternary diagrams of the sample taken before calcium treatment. On the left-hand side, there is the usual Mg-Ca-Al diagram. Even though the experiment was carried out using a

MgO crucible, no spinel inclusions were formed. That contrasts with previous observations in experiments 5.1 and 5.2. where the crucible provided magnesium to the melt and spinel inclusions were formed. Section 7.4 contains a detailed explanation of why this variation occurs between experiments.



Figure 66: Mg-Ca-Al (a) and Si-Ca-Al (b) ternary diagrams for sample before Ca in Experiment 7.1.

A Si-Ca-Al ternary diagram is shown in Figure 66(b). Unexpected silica-containing inclusions were observed in several samples during these experiments. The origin of this silica in the inclusion must be from the reaction of the liquid steel and the sampler, during the short period of contact time and before it solidifies. Silicon originated from CaSi₂ is present as dissolved Si and would not oxidize with this level of dissolved aluminum. Using the steel "puck" chemical analysis of experiment 7.2 (where the same silica formation was observed) as input in FactSage, calculations indicate a very low equilibrium silica activity (approximately $a_{SiO_2} = 0.0004$). Therefore, any silica observed must have come into contact with to the melt as silica. If the silica tube were to react with the sample in the interior of the tube, it would also react with the exterior in contact with steel. Given the dissolved aluminum concentration and the melt, if SiO₂ comes into contact with the melt, the following reaction is expected to occur:

$$4[AI] + 3(SiO_2) = 2(AI_2O_3) + 3[Si]$$
 Equation 22

Mullite may also form as an intermediate phase. Therefore, the silica sampler is a potential source of reoxidation in all experiments. Silica-containing inclusions were not observed in all samples 89 nor in all experiments. But when it was observed, these exogenous inclusions apparently readily reacted with the steel, and was a source of inconsistencies in area fraction when comparing predicted versus experimental results, as seen in some samples in Chapter 5. Silica-containing inclusions were mostly found near the edges of the samples, as depicted in Figure 67. However, as the sample solidifies, the inclusions can be pushed toward the center by the solidification front (see Figure 67(right)).



Figure 67: Backscattered electron image of sample before Ca treatment in experiment 7.1, with EDX spectra of selected inclusions.

Compositions of inclusions in selected calcium treated samples are shown in Figure 68. Looking at the Si-Ca-Al ternaries shown on the right-hand side of Figure 68, one can see that in this experiment contamination by the silica tube was a recurring issue. Given the short time of contact between the steel melt and the silica tube, the sampler should be stable and not interact with the liquid. Because of the repeated reoxidation, the Ca/Al ratio moved towards the Al corner on the Mg-Ca-Al ternaries shown on Figure 68 (left). Calcium treated inclusions observed in Experiment 7.1 did not fall inside the 50% liquid line and were under-modified. The persistent formation of new inclusions means that it cannot be used to study inclusion growth.

Figure 69 shows the area fraction for experiment 7.1. As seen before, shortly after calcium treatment, the area fraction is apparently small due to spatial resolution limits of the SEM. As time progresses, the area fraction constantly increases beyond what was expected for a given flotation constant. That is again another indication of how the exogenous silica particles affected Experiment 7.1.

An interval plot of all inclusion sizes of this section is provided along with a discussion in section 7.5, on page 110. Histograms of all undertreated inclusions for experiments in this chapter are provided in the appendix.



Figure 68: Mg-Ca-Al (left) and Si-Ca-Al plots of inclusions in selected calcium treated samples in Experiment 7.1


Figure 69: Area Fraction and Inclusion Density of inclusions for Experiment 7.1. Calculated values are for a first order flotation rate of $6.5 \times 10^4 s^{-1}$.

7.2 Experiment 7.2 (Alumina crucible, low sulfur)

Table 14 show the chemical analysis for the steel of Experiment 7.2. The composition was measured using Optical Emission Spectroscopy (OES) at a CISR industrial member plant. The sulfur content of this experiment is shown as <20ppm, which is the limit of detection of the equipment. Originally, this experiment was intended to be in high sulfur. The electrolytic iron was labeled as containing 40ppm S. The iron might have been mislabeled, or calcium treatment contributed do desulfurization, or a combination of both of these occurred. For that reason, the original idea of calcium treating a high sulfur steel was not achieved and no CaS inclusions were observed after calcium treatment.

%С	%S	%Si	%Al	%Ca	%N
0.015	< 0.002	0.12	0.017	0.0002	0.0045

Table 14: Chemical analysis (%Wt.) of the steel block after Experiment 7.2.

The ternary diagrams assess the chemistry of inclusions before and after Ca treatment as well as treatment effectiveness. Figure 70 (left) shows that before Ca treatment, all inclusions were alumina, as expected.



Figure 70: Mg-Ca-Al ternaries of sample A1 and C1, before and 1 min after Ca injection, respectively.

One minute after treatment (Figure 70 (right)), most inclusions are on the Al_2O_3 -rich side of the $CaO - Al_2O_3$ join, indicating incomplete Ca treatment. One possible reason for the unsuccessful treatment compared to previous experiments is the method of addition. Instead of pushing the iron-wrapped $CaSi_2$ with an alumina rod to insure it reaches the bottom of the melt, the addition was made by letting the wrap fall under gravity. The terminal velocity when the $CaSi_2$ contacted the melt apparently was not fast enough to overcome the drag force of the liquid steel. If this were the case, most of the calcium would have evaporated near the surface of the steel, leading to a partial modification of alumina.

Figure 71 contains the bottom right of the ternary diagrams for samples C3 (3 min after Ca), C6 (6 min after Ca) and C11 (eleven minutes).



Figure 71: Mg-Ca-Al diagrams of samples 3min (C3), 6min (C6) and 11min (C11) after Ca treatment.

From Figure 71(a), whereas a majority of calcium aluminates were observed in sample C1, these represented the minority of inclusions in sample C3. A shift towards the aluminum corner in the ternary diagram is observed from samples C3 – C11. As inclusions floats to the surface, the total oxygen content is expected to decrease. However, the area fraction fluctuated and showed no defined trend.

As the experiment progressed, more alumina was observed. As seen in Figure 72, most inclusions were close to the Al corner of the diagram after the longer times.



Figure 72: Mg-Ca-Al diagrams of samples 16 min (C16), 25 min (C25) and 30 min (C30) after Ca treatment.



Figure 73: Boxplot of Ca/Al ratio for Experiment 7.2

Figure 73 shows the boxplot of the Ca/Al ratio of inclusions in the samples shown. The horizontal broken lines indicate the Ca/Al ratios of different calcium aluminates. Although at three minutes after treatment a reasonable proportion of inclusions were calcium aluminates, the average inclusion composition rapidly reverted to the alumina line. At 16 and 25 minutes, all inclusions were essentially alumina, except for a few Ca-containing inclusions, as also illustrated in Figure 72 (a) and (b). For comparison, results from a previous experiment where alumina inclusions were successfully modified is shown in Figure 51, on page 65. Experiment 5.3, discussed in the previous chapters, was performed in the induction furnace that uses a fused-quartz enclosure, under similar conditions as Experiment 7.2 (i.e. low sulfur content, alumina crucible). The two main differences were the induction furnace used and the Ca addition method. While in Experiment 5.3, the iron wrap was pushed into the melt with an alumina rod, in exp. 7.2 calcium was added by letting it fall by gravity.

In Experiment 5.3, inclusions gradually became richer in aluminum, however the tendency was weaker and even fifteen minutes after calcium treatment, most of the inclusions were still in the liquid window at 1600°C. One possible cause of increased alumina content is reoxidation. However, when reoxidation is present, formation of new small inclusions is observed, as seen in Experiment 5.1. The increase in area fraction from sample A1-A2 in Experiment 5.1 was approximately 17%. As total oxygen content increased, the average size of inclusions decreased, as more sub-micron inclusions was present. In Experiment 7.2, the area fraction increase was more abrupt. From sample C11 to C16, for example, the increase was 32%. The worst case in area fraction increase is from samples C3 to C6 where the total oxygen increased 4.4 times. In both apparent reoxidation events in Experiment 7.2, the average size of inclusion increased. The larger jump in area fraction, coupled with the opposite trends in inclusion size suggests that the cause of reoxidation might be different in each experiment. While in Experiment 5.1 new small inclusion are formed as the melt is exposed to oxygen, in Experiment 7.2 reoxidation may have been caused by exogenous silica particles in the melt, as discussed for experiment 7.1.

Another possible source of oxygen enrichment is through constant supply of alumina from the crucible (by erosion). However, from examining the crucible wall by SEM, this seems unlikely. Figure 74 show SEM micrographs of the alumina crucible above the melt (left) and below (right). Above the melt, the structure of the crucible remains granular and dense. Below the melt, the crucible surface appears to be smoother. By inspecting the EDS spectrum in both locations (Figure 75), one can see a higher Ca peak where the crucible had been in contact with the liquid steel. In fact, during Ca treatment, calcium would also have reacted with the crucible walls, forming a layer of solid calcium aluminate. No significant signs of erosion were observed in the parts of the crucible that had been in contact with steel. Figure 75 shows the presence of Si in the part of the crucible that had been in contact with steel. In fact, a significant number of inclusions also exhibited Si content, especially near the edge of the samples, indicating that the sampler was as a source of reoxidation in the system.



Figure 74: Crucible wall above (left) and below (right) the melt line.



Figure 75: EDX Spectrum of crucible wall in two different locations: below (green line) and above (grey line) the melt.

7.3 Experiment 7.3 (Alumina crucible, high sulfur)

The chemical composition of the steel, listing the elements of interest, is presented in Table 15. The analysis was done by Optical Emission Spectroscopy (OES) on the steel puck that remained in the crucible after the experiment. Figure 76 shows the planned and actual sulfur and aluminum concentrations. As seen in Figure 76, the planned and analyzed concentrations of both elements are similar and within the region where CaS activity is below unity in contact with liquid calcium aluminate. Therefore, under these conditions, any CaS formed as a transient phase should transform into calcium aluminates over time. The amount of CaSi₂ added for this experiment was approximately double what was usually employed in previous successful experiments.

Table 15: Chemical composition of steel puck after Experiment 7.3.

Heat No.	C	Mn	S	Si	Al	Ca	Ν
HEAT #11	0.029	0.006	0.009	0.201	0.050	0.0008	0.0068



Figure 76: Sulfur and aluminum levels planned and analyzed for Experiment 7.3. Isothermal lines indicate stability region of CaS.

However, the ternary diagrams indicate that the pure alumina inclusions that formed after deoxidation (see Figure 77 top left) stayed as alumina plus small CaS particles (likely solidification products) at times one and three minutes after treatment and finally became under-treated calcium aluminates six minutes after calcium addition (Figure 77 bottom right). This was unexpected since the amount of "Cal-Sil" used was almost double what is usually added in successful experiments. The excess Ca was used since previous attempts to fully modify inclusions into liquid calcium aluminates in higher sulfur melts were not successful. In all cases, inclusions were usually under-treated. This indicates that the method of adding Ca must be improved to promote higher yield. Simply increasing the amount of calcium added is probably not enough to succeed in this case.

As the experiment progressed, samples at nine, twelve, thirteen and fifteen minutes were taken. Sample C9, i.e. 9min after Ca, showed the same silica pickup as seen in previous experiments in this section. The chemical analysis in Table 15 shows 0.201% total silicon in the steel. Assuming 100% yield of silicon from CaSi₂, there is a 5% excess silicon over what was added initially to perform calcium treatment. In terms of mass, this represents 0.053g of extra silicon added to the steel. Considering 5% is above the standard error in an OES analysis, this mass balance supports that extra silicon is being added during the experiment as silica tube debris.



Figure 77: Ternary diagrams of inclusion composition before (a) Ca treatment and one (b), three(c) and six(d) minutes after.

The reoxidation observed in sample C9 translated in a shift to Ca/Al ratio from the sample taken six minutes (C6) and thirteen minutes (C13) after Ca. The same enrichment in aluminum content was observed between samples C13 and C15. The overall assessment of this experiment is that, chemically, alumina inclusions were undertreated and gradually moved back to calcium containing alumina inclusions. Besides reoxidation given by the sampling method, eventual failures in guaranteeing proper sealing in the chamber can be a source of reoxidation. One indication that it could be happening is the high level of nitrogen in the puck after experiment. The nitrogen level in Experiment 7.3 is more than five times higher than Experiment 7.4. A continuous intake of air inside the melt will certainly increase the total oxygen to some extent.



Figure 78: Calcium to aluminum ratio of inclusions in Heat 11.

Another method to summarize how reoxidation affected this experiment is presented in Figure 78. A boxplot of calcium to aluminum ratio shows how rich in aluminum inclusions became as the experiment carried away. One and three minutes after treatment, inclusions are still two populations of alumina and calcium rich inclusions, therefore the boxplot shows a very broad ratio. At six minutes, where inclusions are mostly under-treated calcium aluminates, one sees from Figure 77 that most inclusions fall in the CaO. Al_2O_3 (CA) + Ca Al_4O_7 (CA₂) region. With the reoxidation event observed in sample C9, inclusions shifted into CA₂ + CA₆ inclusions. This drastic shift might be a sampling effect, since the undertreated calcium aluminates are again present in sample C13 (i.e. 13min after Ca), even though inclusions in sample C13 are slightly richer in Al

compared to sample C6. Finally, in sample C15, inclusions show again aluminum enrichment with most of inclusions between $CaAl_{12}O_{37} + Al_2O_3$ region.



Figure 79: S-Ca-Al (a, d, e) and Si-Ca-Al (b, c) ternary diagrams of inclusion compositions 9min after calcium treatment.

Even with the shift in inclusion composition, from sample C6-C15 the total oxygen remained approximately constant, as seen in Figure 80.



Figure 80: Calculated and measured area fraction for inclusions in Experiment 7.3. White dots represent measurements done using ASPEX Explorer. Calculated lines are from a first order flotation parameter of $6.5 \times 10^{-4} s^{-1}$.

In summary for Experiment 7.3, full calcium treatment for moderately high sulfur levels could not be performed in the system. The method of calcium addition was not enough to prevent calcium loss and successfully modify inclusions. In addition to the poor calcium addition, reoxidation by the silica tube was observed in sample C9. Excess silicon was confirmed with the steel chemical analysis and the retroactive mass balance, showing that more silicon that what was added via CaSi₂ was present in the puck after the experiment. As inclusions gradually modified into alumina again, inclusions rapidly agglomerated.

Moreover, excess nitrogen was also seen in the chemical analysis. That clearly shows that the sealing from the experimental setup was not sufficient to enforce an inert atmosphere. For that reason, experiments performed after experiment 7.4 were done using the previous setup, that is, the fused quartz tube induction heating setup.

7.4 Experiment 7.4 (MgO crucible, high S)

Because of the lack of proper sealing in the vacuum chamber, Experiment 7.4 was carried in the same format as 7.3 but using the 10kW induction furnace where the system is sealed by a capped fused quartz tube. Detailed materials used in experiment 7.4 are mentioned in Table 12, on page 88. Calcium treated samples were taken 1, 3, 6, 9, 12, 15 and 20 minutes after injection and named respectively C1, C3, C6, C9, C12, C15 and C20.

In addition to using the fused quartz tube to maintain the inert atmosphere, Experiment 7.4 was performed using an MgO crucible instead of alumina. Table 16 shows the chemical composition of the steel puck after Experiment 7.4. Whereas in Experiment 7.3, 2.0g of CaSi₂ was added, Exp. 7.4 used 1.50g. Even with less total calcium added, this steel from experiment contained 15ppm of Ca in the puck, while the steel from experiment 7.3 contained almost half this calcium concentration, indicating that the Ca yield was better. In the fused-quartz furnace experiments, calcium was added by pushing the iron wrapped CaSi₂ with an alumina rod, while in the vacuum chamber it falls by gravity.

The nitrogen levels are approximately five times lower in the steel after experiment 7.4 compared to its predecessor, as previously indicated on Table 15. It indicates that the latter setup was more effective in promoting an inert atmosphere than using the vacuum chamber. According to Figure 81, sulfur and aluminum levels were appropriately planned and executed to ensure that CaS reacted with oxides to convert these into liquid inclusions. In Experiment 7.4, the aluminum level was slightly higher than what was observed in Experiment 7.3 (Figure 76). The difference might be to eventual fluctuations in total oxygen dissolved in the melt before aluminum deoxidation. In all calculations, it was assumed that the initial oxygen concentration was 400ppm at the onset of the experiment, before deoxidation.

Table 16: Chemical composition of steel puck after Experiment 7.4

Heat No.	С	Mn	S	Si	Al	Ca	Ν
HEAT #12	0.032	0.006	0.005	0.139	0.057	0.0015	0.0013



Figure 81: Sulfur and aluminum levels planned and analyzed for Experiment 7.4.

Before calcium injection, inclusions were predominantly alumina (see Figure 82). No significant magnesium pick-up was observed in sample A1. In previous experiments, more pronounced magnesium pick-up and subsequently spinel formation was observed.



Figure 82: Mg-Ca-Al ternary diagram of sample before Ca treatment (A1) for Experiment 7.4.

As concluded by Kumar ^[50], Mg dissolution from the crucible will vary depending on whether a slag layer is present between liquid steel and crucible wall. The slag layer might form depending on the level of oxide impurity (i.e. SiO₂, CaO or Al₂O₃) present in the crucible before use. The presence of those components is strongly dependent on product variation from the crucible supplier and was found to vary between batches. Figure 83 shows two cross section micrographs of the MgO crucible used in Experiment 7.4. The region was analyzed just above the melt line after 105

the experiment. The microstructure at the outside wall, on the left-hand side of Figure 83, is largely single-phase, with direct contact between MgO grains, and no slag-like entrapment between grains. However, from the inner wall to depth of over 200µm, a second phase penetrated between the grains; this had a slag-like (calcium aluminate) composition (see the right-hand side of Figure 83).



Figure 83: Cross section of crucible wall above the melt. Left micrograph is the outside wall edge and right micrograph is the inside wall.

The penetrating slag phase between the shown grains is evident when looking at the line above melt facing the inner wall of the crucible, on the left-hand side of Figure 84. Just above the melt, MgO grains were surrounded by a calcium aluminate wetting the grain boundaries. The droplets seen in the MgO grains are Pt droplets from the coating deposition. As seen, excess platinum was deposited on the surface of this crucible but this did not interfere with the analysis.

Below the melt, shown on the right-hand side of Figure 84, The MgO crucible wall was covered by spinel precipitates seen in some grains and also as the plate-like features seen more abundantly in the top left corner of the SEM image.



Figure 84: Crucible wall below melt line after Heat 12. Spinel inclusions on top of MgO grain were present.

Since no slag layer was initially formed before calcium treatment, spinel inclusions formed on the crucible wall remained attached, poor Mg transfer to the steel occurred, and the alumina inclusions did not transform to spinels. This is similar to what Deepoo Kumar^[50] previously reported for high-purity (slag-free) MgO crucibles

After calcium treatment, it appears that the calcium aluminate slag layer that formed detached spinel particles from the crucible wall. That is in part why spinel inclusions were observed after Ca treatment, as seen in Figure 85. Also, the presence of MgO-saturated liquid calcium aluminate (with low Al_2O_3 activity) on the crucible wall promotes Mg dissolution into the Al-killed steel, as previously shown by Deepoo Kumar ^[50].



Figure 85(a-l): Ternary diagrams of calcium treated inclusions for Experiment 7.4.

Solid inclusions were also under-treated in this experiment. As shown by Figure 85 (a) and (b), inclusions three minutes after calcium treatment appeared as solid spinels + MgO-containing solid calcium aluminates together with CaS. Comparing Figure 85 (b, d, h, j, l) i.e., the S-Al-Ca ternary diagrams, one can see a slow progression where calcium sulfides and spinels gradually become calcium aluminates as the triangles. It seems at first that inclusions remained at the same composition throughout the experiment and therefore they were not treated at all, remaining as CaS + spinels. To clarify whether inclusions remained the same, a manual SEM analysis was done. Two example micrographs are depicted in Figure 86. One minute after calcium treatment, inclusions typically were CaS together with spinels, as shown in Figure 86(a). 20 minutes after, the last sample taken in this experiment appeared usually as spinel/calcium containing inclusions surrounded by a CaS ring. That is, the observed CaS likely formed during solidification.

In previous experiments, where virtually no sulfur was present, solid spinel/alumina were readily modified and usually samples taken at the three-minute mark were already fully modified. The high-sulfur experiments indicate that inclusions might take longer to modify when sulfur is present.



Figure 86: Backscattered Electron Image of a complex inclusion 1min(a) and 20min(b) after calcium treatment.

Figure 87 shows the expected and experimental area fraction over time for experiment 7.4 (calculated assuming first-order flotation kinetics). All experimental measurements were performed using ASPEX Explorer. Particularly for experiment 7.4, a small difference was observed in the flotation rate constant compared to fully modified inclusions. In this experiment, inclusions seem to float twice as fast. A rate constant of 1.5×10^{-3} s⁻¹ fitted the results better. While this might indicate that solid inclusion will float faster, this would need to be tested with more experiments with under-modified inclusions and is suggested as future work.



Figure 87: Area fraction (ppm) of inclusions in samples taken during Experiment 7.4. Lines show expected inclusion flotation behavior, with different rate constants.

7.5 Size analysis of inclusions for experiments 7.1-7.4

Figure 88 shows an interval plot for Experiment 7.4. Reoxidation observed in Experiments 7.1-7.3 promoted by reaction with silica-containing exogenous inclusions, combined with inappropriate furnace sealing had an undesirable impact on the results. Therefore, any size distribution and size change analyses using these experiments would be distorted. Instead, results from an experiment performed by Kumar^[50] where pure alumina inclusions were sampled every minute for five minutes after aluminum addition are also shown in Figure 88. The idea is to compare how solid calcium aluminates agglomeration compares to solid alumina. In addition to experimental data, a simulated trend of inclusion size growth is also plotted in Figure 88. For the simulation of the solid aluminates shown on Figure 88, 200 inclusions following at t=0 a lognormal distribution with $\ln(\mu) = 0.33$ and $\ln(\sigma) = 0.288$ was used. The initial number of particles per unit volume (n_V) was set to 15000/mm². Similarly, in the alumina inclusions, an initial size distribution of $\ln(\mu) = 1.015$ and $\ln(\sigma) = 0.534$ with $n_V = 20000/mm^2$ was used as input data. These numbers are the fitted lognormal parameters for each sample, with the number density chosen to match the measured area (volume) fraction of inclusions. The calculation procedure was previously described in section 5.11. The initial distribution was simulated three times for each experiment. The range of simulation results is plotted over experimental observation a using a blue shade. The alumina inclusions were larger than solid calcium aluminates for all times considered. However, at one minute after deoxidation, these were already larger than solid calcium aluminates. In a five-minute sampling interval, the alumina inclusions grew by 1µm, which is the same growth observed in solid calcium aluminates. Because the inclusions grew by the same amount, no direct conclusion comparing alumina to solid calcium aluminates could be done. However, because the simulation shows similar growth for both alumina and solid calcium aluminates, it could be the case that both type of inclusion will grow at same rate. It should be noted that the simulations assumed that growth is collision-limited. Agreement between the simulated and measured inclusion sizes indicates that the attachment efficiency of alumina and solid calcium aluminates is similar.



Figure 88: Inclusion sizes of experiment 7.4 (solid calcium aluminates), Kumar's experiment (alumina) and simulated growth trend.

7.5.1 Comparison between fully modified and partially modified inclusion sizes, revisiting hypothesis five.

Figure 89 depicts the average inclusion size (with confidence interval) for the experiments grouped by outcome. Undertreated inclusions are shown in green, and fully treated inclusions are shown in red. Pure alumina inclusions are shown in purple.

A comparison between pure alumina inclusions and calcium aluminates was already done in previous section. With regards to growth of calcium aluminates, the differences between fully treated and partially treated inclusions are mostly indistinguishable. This supports hypothesis five, that is, solid and liquid calcium aluminates increase in size at the same rate. It is tempting to conclude that solid calcium aluminates are slightly larger than liquid ones, since all green circles lie above the red ones in Figure 89. However, this difference is small, and more work would be necessary to test whether this apparent difference is real.



Figure 89: Interval plot of inclusion sizes from all induction furnace experiments.

Chapter 8 - Considerations about lens shape effect and distortion of apparent inclusion size

This chapter discusses changes in inclusion morphology, more specifically liquid calcium aluminates when analyzed using a SEM *versus in-situ* observation by CSLM and how comparable the observed sizes are. The shape of a liquid inclusion on top of the steel melt in contact with Fe and the atmosphere was estimated using literature data. Calculations are then compared with experimental results.

This chapter provides a review of the CSLM and presents the theoretical calculations to estimate the degree of deformation of a liquid inclusion at the surface of the steel melt. The governing hypothesis of this chapter is:

Hypothesis 6: Liquid inclusions at the steel/inclusion/atmosphere interface will have a larger apparent diameter due to lens-shaped deformation

A brief introduction about confocal microscopy, theoretical calculations and experimental approach used to test hypothesis six is provided in the following sections.

8.1 Confocal Scanning Laser Microscopy

The Confocal Scanning Laser Microscope (CSLM), also referred to in some cases in the literature as High Temperature Confocal Scanning Laser Microscope (HT-CSLM) is an advanced optical microscope that allowed scientists to perform direct *in situ* high temperature observations of various phenomena, such as solidification of Fe-C alloys, precipitation of MnS in Fe-Ni alloys ^[59], inclusion agglomeration ^{[11][12]}, crystallization of mold fluxes^[60], CCT and TTT curves of Fe-O slags ^[61] and oxidation events ^[62]. The equipment consists of a gold-coated ellipsoidal chamber. Gold is used because of its high reflectivity and low absorptivity of the IR wavelength spectrum ^[63]. This is important, since the source of energy to increase the temperature in the system is a 1.5kW halogen lamp at one focal point of the chamber. Heat is transferred to the other focal point, where the specimen is placed. Figure 90 contains an illustrative representation of the CSLM chamber.



Figure 90: Schematic representation of the CSLM chamber

To avoid oxidation of the melt, the chamber is evacuated and backfilled with ultra-purity argon (99.9999%). To remove any remainder oxygen from the argon, Mg and Cu getters at 350°C are used in the upstream gas line to collect the oxygen through formation of the respective oxides. To measure the partial pressure of oxygen inside the chamber, the off-gas is measured with an oxygen probe. Oxygen pressure readings are taken at 700°C.

Another source of oxygen to the melt is any FeO layer on the surface of sample. To run the experiments, the oxygen partial pressure must be low enough to make Fe the only stable phase.

Figure 91 shows the equilibrium phase diagram of the system $Fe - O_2$ for oxygen partial pressure ranging from 1 to 1×10^{-30} atm. The graph indicates that the oxygen content should be always kept low (below 10^{-8} atm) to avoid any iron oxide formation before melting and to remove any containing oxides in the surface.



Figure 91: Fe - O₂ equilibrium phase diagram. From FactSage 7.2

To resolve the images, a He-Ne red laser is directed at the sample surface. The light in the focal plane can pass back through the microscope optics and be captured by the video system. Out-offocus images appear darker in CSLM micrographs. The video system captures seven frames per second and stores the images on a computer for future video rendering.

The temperature is measured by a type R thermocouple placed underneath the Al_2O_3 crucible. The thermocouple also acts as sample holder. Usually, temperature readings are approximately 30°C different from the actual metal temperature given the distance and various thermal resistances between the thermocouple and the melt; the difference is measured by melting pure samples with known melting points.

8.2 Theoretical calculations

When a liquid inclusion is embedded in the melt, ferrostatic pressure is constant everywhere at the inclusion surface. For that reason, the inclusion would have a spherical shape. However, when in the steel surface, the inclusion will assume a lens shape. Figure 92 shows schematically the inclusion shape when in contact with both liquid metal and gaseous atmosphere.



Figure 92: Schematic representation of an inclusion floating on the steel-argon interface.

For the following calculations, the lens shape was approximated as two spherical caps, as illustrated schematically by Figure 92. The balance between surface tension of the steel atmosphere, the inclusion-atmosphere interface and the inclusion-steel interface is given by Young's law, illustrated in eq. 1-3 below.

 $S = \gamma_{M} - (\gamma_{ML} + \gamma_{L})$ Equation 23 $S = -\frac{1}{2}\gamma \theta_{E}^{2}$ Equation 24^[64] $\frac{1}{\gamma} = \frac{1}{\gamma_{M}} + \frac{1}{\gamma_{ML}}$ Equation 25

Where S is the spreading coefficient, γ_i is the surface tension at a given interface and θ_E is the angle between γ_M and γ_{ML} vectors, and $\theta_E = \alpha + \beta$ (see Figure 92).

To estimate how the apparent diameter of a floating inclusion will differ from that of a fully immersed inclusion, it is assumed that the total volume of the liquid inclusion will not change i.e. the volume of the two spherical caps (that make up the lens shape) will be equal to the volume of the spherical embedded inclusion. For a spherical cap with base circle of radius a, the volume is given by:

$$V_{cap} = \frac{1}{3}\pi h(3R - h)$$
 Equation 26

Where R is the radius of the full sphere that originated the cap, as illustrated in Figure 93.

The radius of the base circle (a) is given by:

$$a = \sqrt{h(2R - h)}$$
 Equation 27

The radius of the original sphere (R) is given by:



Figure 93: Spherical cap and its variables of interest.

In the two spherical caps shown in Figure 92, the base circle is common, and the heights are different. By combining Equations 26 and 27, Equation 28 follows:

$$a = h_1 \left(\frac{2}{1 - \sin(90^\circ - \theta_\alpha)}\right)^{\frac{1}{2}} = h_2 \left(\frac{2}{1 - \sin(90^\circ - \theta_\beta)}\right)^{\frac{1}{2}}$$
 Equation 29

With the equation mentioned above, the original radius is removed from the calculations and the unknowns are the height (h_n) and the contact angles (θ_n) of a given spherical cap. The inclusion diameter (2*a*) was measured experimentally in the CSLM. The contact angle of each spherical cap

can be calculated according to Olette^[65] by balancing the forces between surface tensions given in Figure 92, as follows:

$$\gamma_{\rm M} = \gamma_{\rm L} \cos(\alpha) + \gamma_{\rm ML} \cos(\beta)$$
 Equation 30

Where
$$\alpha + \beta = \theta_E = \sqrt{-\frac{2S}{\gamma}} [64, 65]$$
.

A list of all variables used to perform the calculations and estimate the volume of the coupled spherical cap is given in Table 17. For the steel/air interface, Turkdogan^[2] provided data for surface tension of steel with different sulfur contents. The calcium aluminate surface tension with argon is estimated using data provided by Wegener ^[66]. Finally, the steel/inclusion interfacial energy was estimated to be in the range 1.25-1.4N/m according to what was reported by Park et al. ^[67]. Results show that, for a surface tension of 1.4N/m between steel and the inclusion, the contact angle (θ_E) is 57°. This result is within the range of 54-65° contact angle of a CaO-Al₂O₃ oxide in contact with argon and liquid steel reported by O'Malley ^[28].

Table 17: surface tensions and calculated contact angles for the inclusion-steel-Ar system

$\gamma^{[67],[64]}$	S ^[64,67]	θ_{E}	α	β	γ _M ^[2]
N/m	m/N	0	0	0	N/m
0.42	-0.2	57	36	21	1.8

Knowing the contact angle of each individual spherical cap and the apparent diameter, one can use Equation 28 to calculate the height (h_n) of each cap and therefore use Equation 25 to calculate the volume of the particle. Considering that liquid calcium aluminates do not agglomerate in the steel-argon interface^[11–13], it is assumed that the inclusion volume is conserved when it emerges from the melt to the top surface. Therefore, by using the lens volume, the original size of the particle can be calculated.

8.3 Experimental Methods

The experimental temperature vs. time curve for CSLM experiments in this work is illustrated in Figure 94. Initially, the chamber was conditioned using a $5\%H_2 - 95\%N_2$ atmosphere. A tenminute plateau at 880°C was used to have enough time to reduce any amounts of FeO present in the sample. Two minutes before increasing the temperature from 880°C, the atmosphere was purged and switched to high purity Ar.



Figure 94: Planned Temperature vs. time curve for CSLM experiments

Frames captured by the computer in the confocal microscope were analyzed after experiment using ImageJ. Based on a user defined threshold, inclusions can be separated from the matrix and the area of each measured. The area of each inclusion was converted to a diameter and their sizes compared to the sizes of inclusions inside the steel, previously analyzed using ASPEX Explorer. The sample chosen for this comparison was sample from experiment 5.2, three minutes after calcium treatment (C3).

8.4 Results and discussion

Figure 95(a) exemplifies an inclusion that was a liquid calcium aluminate (when at temperature) within the steel. Since the ferrostatic pressure is constant over the inclusion surface, the inclusion exhibits a spherical shape. The morphology of the inclusion in this sample, taken 6 min after Ca

treatment, was revealed after deep etching part of the sample. The inclusions shown in Figure 95(b) are from an *in-situ* observation of the same sample in Figure 95(a) upon remelting in the confocal scanning laser microscope (CSLM). Figure 95 (c) is a large liquid droplet found floating on the steel "puck" remaining on the crucible after a different experiment. One can observe a shallower angle of the floating inclusion compared to the immersed one.



(a) in steel

(b) on steel - CSLM

(c) on steel - SEM

Figure 95: Calcium aluminates (a) in the steel melt, (b) liquid at temperature floating on steel/argon interface, (c) on steel after experiment.

Inclusions do appear larger in the CSLM as can be seen comparing the histograms in Figure 96(a) and (b). Proportionally, there are more inclusions larger than 2μ m in the CSLM (b) than in the SEM analysis (a) (see Figure 96). Figure 96(c) shows the probability plot of inclusion sizes for the CSLM experiment. Given p-value = 0.094, inclusions measured in the CSLM follow roughly a lognormal distribution. Based on lognormally distributed data, the average sizes of inclusions were calculated and shown in Figure 96(d). The average size of inclusions in both equipment is compared in Figure 96(d). On average, inclusions on the melt surface appeared approximately twice as large as a submerged calcium aluminate of equal volume. This experimental result confirms what was estimated using literature data.



Figure 96: (a) Histogram of SEM inclusion sizes, (b) histogram of CSLM inclusion sizes, (c) Probability plot of CSLM inclusion sizes, (d) calculated vs. experimental average sizes for an inclusion observed in SEM vs. CSLM.

8.5 Remarks of chapter 8; revisiting hypothesis 6

As seen on Figure 96(d), theoretical calculations agree well with measured values. Inclusions floating on top of the steel melt are approximately twice as large compared to sunk inclusions. Therefore, it can be concluded that hypothesis six is supported by the experimental values and the lens shape effect would change the apparent diameter of inclusions.

Chapter 9 - Conclusions

This work has presented experimental evidence showing that liquid calcium aluminates do agglomerate and hence change in size over time. Under laboratory conditions, solid spinels and alumina inclusions were successfully modified into calcium aluminates. Those liquid inclusions exhibited a weak but statistically significant tendency to agglomerate. The main mechanisms by which liquid inclusions agglomerate are Stokes collision and collisions due to fluid laminar flow when no external stirring is present. Calculations showed that collisions due to turbulence is the dominant mechanism under industrial conditions. Regarding flotation and removal of liquid calcium aluminates, this work observed comparable flotation rates between liquid and solid inclusions. This contradicts common sense in the industry that liquid inclusions, once formed, are more difficult to remove compared to their solid counterparts.

It was observed that, after CaSi₂ injection, inclusion diameters decrease by a factor of two to three, depending on the parent inclusion. What experimental evidence suggests is the following sequence:

- Upon calcium addition a large number of small calcium containing (CaO/CaS) nuclei form in the melt;
- Calcium addition reduces the activity of dissolved oxygen;
- The new level of dissolved oxygen disturbs the alumina/spinel equilibrium. For that reason, aluminum and oxygen are dissolved in the melt;
- Aluminum and oxygen are transported to the CaO/CaS nuclei more efficiently than transport of dissolved calcium to the solid alumina or spinel inclusions, given low calcium solubility levels in liquid Fe;
- Liquid inclusion is formed by reaction of Ca(O/S) with dissolved aluminum and oxygen.

It was also seen that agglomeration of partially solid, solid and liquid inclusions is very similar to one another. This is because collision of particles happens mostly because of fluid flow conditions and inclusions growth is apparently not limited by particle attachment. The modelled growth by collisions agrees well with experimental observations for pure alumina and partially treated calcium aluminates.

When floating on top the steel, the diameter of liquid inclusions will appear to be approximately twice as large as when submerged in liquid steel. This was confirmed both using theoretical calculations, using literature data, and experimentally, comparing average size of inclusions using SEM analysis and confocal microscope measurements.

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Appendix



Histograms shown in log10 scale to depict lognormal \rightarrow normal conversion graphically.

Figure 97: Histogram of inclusion sizes for Experiment 7.1.


Figure 98: Histograms of inclusion size for Experiment 7.2



Figure 99: Histogram of Inclusion size of Experiment 7.3 samples



Figure 100: Histogram of Inclusion size of Experiment 7.4 samples.