Coarsening Mechanisms of CaS Inclusions in Ca-Treated Steels

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Abstract: In this work, the coarsening mechanisms of CaS inclusions in liquid steel were investigated by analyzing inclusions in experimental and industrial samples. A detailed particle size distribution evolution was reported. The observed CaS coarsening rate was compared with the theoretical coarsening rate calculated by using the models proposed in the literature. For both experimental and industrial data, it was observed that the coarsening mechanisms varied during different stages of Ca treatment. It was found that in the early stage (after Ca addition) of experiments and during Ca addition under industrial conditions, the coarsening of CaS was governed by diffusion-controlled growth. As the Ca dissolved in steel diminished, the coarsening was governed by collision-dependent mechanisms. For experimental conditions, the growth of CaS was controlled by the Brownian collisions, while the coarsening by turbulent collisions was the dominant mechanism under industrial conditions.

Keywords: ladle metallurgy; inclusion modification; calcium treatment; inclusion size distribution; inclusion growth

1. Introduction

A few decades ago, calcium treatment was introduced to improve steel castability by modifying solid Al₂O₃ inclusions to liquid or semi-liquid calcium aluminates inclusions (CAₓ, C and A denote CaO and Al₂O₃, respectively). Inclusions with compositions similar to C₃A, C₁₂A₇, and CA are usually considered to be liquid or semi-liquid at steelmaking temperature, as opposed to solid CAₓ, that are CA₂ and CA₆. This is achieved by calcium reacting with oxygen in Al₂O₃ inclusions. It is important to note that calcium has a high affinity to sulfur, so CaS inclusions are a common product of the calcium treatment. The formation of CaS inclusions does have some advantages. For example, the presence of CaS as transient CaS can act as a source of Ca supply for the modification of oxide inclusions [1,2]. Moreover, precipitating S in the form of CaS suppresses the formation of MnS inclusions. However, an excess amount of stable CaS inclusions is usually considered detrimental, as they behave similarly to other solid inclusions [3–5], such as Al₂O₃. The impact of CaS inclusions on both the castability and the product quality is related to their size. The presence of larger CaS inclusions accelerates the clogging and deteriorates the product’s physical properties. To the best of the authors’ knowledge, despite being a well-known inclusion type, there is no research on the growth of CaS inclusions in steelmaking conditions.

The common coarsening mechanisms are diffusion-controlled growth, coarsening due to Ostwald ripening, Brownian motion, ascending velocity difference, and laminar and turbulent flows [6–9]. The diffusion-controlled growth mechanism is applicable to conditions where the rate of inclusion coarsening is limited by the mass transport of species in liquid steel. Ostwald ripening is a unique diffusion-related scenario driven by the concentration gradient at the interface associated with different inclusion sizes. As a result, some inclusions grow at the expense of smaller ones. Continuous irregular motion causes inclusions to move randomly in the liquid steel. Such motion independent of fluid flow is...
characterized as Brownian motion, leading to the collision and coalescence of inclusions. The coarsening of inclusions due to the ascending velocity of small inclusions is suggested to be proportional to the square of their radii [10], so the larger inclusions may encounter smaller ones during floatation, which then increases the inclusion size. Inclusions can also collide and coalesce when driven by laminar and turbulent flows.

Two approaches in the literature are applied to determine the growth mechanisms of inclusions. The first compares the change in the average diameter of inclusions detected using SEM with those predicted by various theoretical coarsening mechanisms. The one that gives the closest agreement is considered to be the predominant mechanism. This approach was used in the work of Suzuki et al. [7] to determine the coarsening mechanism of SiO$_2$ inclusions in continuous casting slabs and test Ingots. The mechanism was reported to be Ostwald ripening, as the theoretical prediction of Ostwald ripening had the best agreement with the observations. The same approach was also used by Ohta and Suito [6] for MgO, ZrO$_2$, Al$_2$O$_3$, CaO-Al$_2$O$_3$, and MnO-SiO$_2$ inclusions in laboratory studies. The observed size change slightly deviated from the theoretical prediction; hence, they concluded Ostwald ripening to be the predominant mechanism but suggested that the effect of Stokes motion cannot be neglected. Wang et al. [8] also studied the impact of steel and inclusion compositions on the growth of oxide inclusions in experimental conditions using a similar method. Again, the reported mechanism was Ostwald ripening, but only during the first 10 min after aluminum (Al) addition. The mechanisms for the latter part were not reported. Overall, the previous studies emphasized the importance of Ostwald ripening on the growth of many oxide inclusions. It was unclear why the primary diffusion-controlled growth was never discussed in those studies and only included the unique diffusion-related mechanism of Ostwald ripening. Further, the first approach is accessible, and relationships between the inputs and the predicted inclusion size are clearly defined. However, it is essential to note that the particle size distribution (PSD), which provides more detail about the coarsening process, cannot be obtained through this method.

The second method to predict the change in inclusion diameter is to utilize the population balance equations (PBEs). It calculates how a fixed number of monomers are distributed between clusters; hence, they become inclusions of different sizes. This approach was first suggested in the study of Smoluchowski [11] and allows one to calculate the PSD. Later, this approach was used by Zhang and Pluschkell [9] and Zhang and Lee [12] to study the coarsening rate of Al$_2$O$_3$ inclusions. Based solely on the PBE calculation, Zhang and Pluschkell [9] suggested that after the initial nucleation, Al$_2$O$_3$ grew by Ostwald ripening and then by Brownian motion and turbulent collision for inclusions with diameters smaller than 2 µm and larger than 4 µm, respectively. However, the calculated PSD was not validated against any experimental or industrial data. Such shortness was improved later in the work of Zhang and Lee [12], whose calculation of the PBE reached the same conclusion in terms of the coarsening mechanism of Al$_2$O$_3$, except Stokes motion was proposed to be also effective starting about 1 min after the initial nucleation. Moreover, the PSD predicted based on PBE was compared with the experimentally observed PSD. The predicted and the observed values for the PSD of Al$_2$O$_3$ inclusions were in agreement for the initial stage of the defined experimental conditions. Some studies [13,14] used only quantification of collision frequency in PBE to determine the controlling coarsening mechanism, and they did not predict the evolution of PSD. An example is the work of Yin et al. [13], who studied the formation and growth of TiN clusters. By comparing the collision volume of Brownian collision, turbulent collision, and Stokes collision, they showed that the effect of Brownian collision on TiN growth was less significant than the other two collision mechanisms. Another example is the modeling work by Rimbert et al. [14] on precipitation and agglomeration of aluminum titanates. Again, by calculating the collision volume, Brownian motion was found to govern the growth of small micron size inclusions, and the increase in inclusion size caused the dominant mechanism to shift to collision in the turbulent flow, then Stokes motion. Overall, the PBE-based studies usually found diffusion to be significant in the early stages and later aggregation, but depending on the
inclusion type and size, the significance of different collision-related mechanisms may differ. Compared to the first approach, all coarsening mechanisms can be considered simultaneously when applying the PBE, and their overall effects on the PSD can be studied. As the PBE is a more fundamental way of calculating the size change, it takes more calculation power and is less accessible [15]. Because diffusion-related growth mechanisms (Ostwald ripening and diffusion-controlled growth) depend primarily on the correct estimation of the number of monomers, applying the complete form of PBE, including both diffusion- and collision-related coarsening mechanisms to calculate the evolution of PSD of inclusions can be challenging.

The authors conducted laboratory-scale inclusion modification experiments at 1873 K using synthetic steel with compositions similar to a typical LCAK commercial product. Moreover, industrial samples were retrieved from the ladle after Ca addition and from tundish. The characteristics of inclusions were analyzed mainly using an automated SEM-EDS system called ASPEX. The present study focused on understanding the growth mechanism of the CaS inclusions in experimental and industrial conditions. This was done by comparing the observed and the predicted size change of CaS inclusions by different controlling mechanisms. The effect of coagulation on the evolution of CaS PSD was also calculated using PBE. The results were compared with the observed change in inclusion number density to reveal the critical coarsening mechanisms in industrial conditions.

2. Experimental Methodology

The high-temperature experimental setup is shown in Figure 1. In total, 0.3 g graphite rod, 6.5 g Mn, electrolytic Fe, and an appropriate amount of FeS depending on the targeted S content were placed inside an Al$_2$O$_3$ crucible at room temperature and then heated in the vertical tube furnace to 1873 K and held for 10 min to homogenize the melt. Throughout the experiment, 99.999% Ar gas was fed into the furnace at a rate of 0.5 L/min to maintain a protective atmosphere. After that, Al and Si were added to deoxidize the steel melt. The melt was homogenized for an additional 15 min after deoxidation. Thereafter, Ca was added. The Ca addition technique was adopted from Verma et al. [3]. A mixture of electrolytic Fe and Ca enclosed in a capsule of steel shim was guided to the crucible. It helped Ca to immerse into the melt and increased the recovery rate. The total mass of raw materials was approximately 500 g.

![Schematic diagram of the experimental setup.](image-url)
The present study used data from three laboratory experiments and four industrial heats. The compositions are summarized in Table 1. This study did not involve Heat 2 [2], which was studied in the authors' previous work due to a low number of CaS inclusions. The laboratory experiments are denoted in the form of “[S content (ppm)] [final Ca content (ppm)]”.

Table 1. Chemical composition of experimental and industrial samples (wt. pct.).

| Laboratory Experiments | Exp. # | C (wt. pct) | Si (wt. pct) | Al (wt. pct) | Mn (wt. pct) | S (ppm) | Ca (ppm) | O (ppm) |
|------------------------|--------|-------------|-------------|-------------|-------------|---------|----------|---------|
| 2035                   | 0.06   | 0.27        | 0.09        | 1.09        | 21          | 56–35   | 21–35    |
| 3035                   | 0.06   | 0.23        | 0.06        | 0.98        | 31          | 41–36   | n/a      |
| 2025                   | 0.05   | 0.26        | 0.03        | 0.91        | 22          | 40–25   | n/a      |

| Industrial Sample      | Heat # | C (wt. pct) | Si (wt. pct) | Al (wt. pct) | Mn (wt. pct) | S (ppm) | Ca (ppm) | O (ppm) |
|------------------------|--------|-------------|-------------|-------------|-------------|---------|----------|---------|
| 1                      | 0.05   | 0.23        | 0.03        | 1.14        | 28          | 44–32   | 20       |
| 3                      | 0.06   | 0.22        | 0.03        | 1.07        | 29          | 47–34   | 20       |
| 4                      | 0.05   | 0.22        | 0.03        | 1.13        | 18          | 40–30   | 20       |
| 5                      | 0.06   | 0.21        | 0.04        | 1.12        | 18          | 69–35   | 20       |

Pin-shaped samples with 0.005 m diameter and about 0.1 m length were taken at 1, 3, 5, 10, and 20 min after Ca addition and were cooled in air. Additional samples were taken at 30 and 40 min in Exp. 2025. The sample taken during the experiment are referred to as “pin samples”. The rest of the experimental steel was cooled inside the furnace at a rate of 10 K/min. Samples taken from the remaining steel are “bulk samples”. Lollipop samples were taken from ladle and tundish in 4 industrial heats. The lollipop samples are approximately 10 mm × 32 mm × 35 mm. A schematic diagram and the dimensions are shown in Figure 2.

Figure 2. Schematic diagram of the lollipop sample.

The surface of collected pin samples was cleaned, then the pin samples were sectioned for chemical analysis and inclusions analysis. Al, Si, Mn, and Ca contents of steel samples were measured using inductively coupled plasma optical emission spectrometry (ICP-OES). In Exp. 2035 and Exp. 3035 (see Table 1), an initial 0.03 wt. pct. Al content was achieved.
All concentrations have the unit of wt. pct. in this study unless specified. In Exp. 2025, no Al was added. The Mn, Si, and S contents were constant in an experiment, but Al increased from the initial concentration due to Ca-crucible reaction. The change was more significant in Exp. 2035 and Exp. 3035 because the initial Ca contents were higher. In Exp. 2035 and Exp. 3035, the initial Ca contents were 56 and 41 ppm, respectively, then decreased to 35 ppm in both experiments. In Exp. 2025, the Ca content reduced from 40 to 25 ppm. LECO™ CS744 carbon/sulfur analyzer was used to measure the S and C contents of steel samples. Total oxygen (T.O.) in Exp. 2035 were analyzed using a LECO™ ON736 oxygen/nitrogen analyzer. The measured concentrations were confirmed using pulse-height distribution analysis (spark OES-PDA).

A cross-section of every pin sample and a bulk sample was analyzed using an automated SEM-EDS system (ASPEX) to study the characteristics of inclusions. The automated SEM detects inclusion based on the contrast between the inclusions and the steel matrix. The SEM determines the geometric center of an inclusion, then 16 chords (diameters) are drawn, passing through the center. The average of all 16 chords is the average diameter of the inclusion. This should not be confused with the average diameter of multiple inclusions (average diameter for short), denoted as $d_{avg}$. Connecting the ends of all chords determines the shape, perimeter and area. The details are discussed in elsewhere [16]. The inclusions with the longest diameter ($d_{max}$) larger than 2 µm were detected. A detailed discussion on steel chemistry change and the methodology of inclusion analysis can be found in the authors’ previous publication [2] and will not be repeated here.

The detailed composition of the industrial samples can be found in Table 1. Sampling time slightly varies from heat to heat. Ladle samples L1 to L5 of Heat 1 were taken at 1848 K, and after 1, 2, 3, 4, and 5 min of the start of Ca addition. For the other three heats, only one sample (L5) was taken after Ca addition close to the end of ladle refining. Samples T1 and T2 were from tundish when about 30 and 80 t steel was cast from a 165-ton tundish at 1833 K. Lollipop samples were taken to conduct inclusion analysis. The samples were cut at 12 cm from the bottom. The intersecting surface of the lower part was cleaned and polished, then analyzed using the same automated SEM-EDS system, so the experimental and industrial inclusion data are comparable.

Based on inclusion compositions, the observed inclusions were classified into Ca-rich, liquid CA$_x$, solid CA$_x$, Al$_2$O$_3$, CaS, CaS-other, CaS-MnS, and MnS. Liquid CA$_x$ includes C$_3$A, C$_{12}$A$_7$, and CA inclusions, whereas solid CA$_x$ includes CA$_2$ and CA$_6$ inclusions. Ca-rich inclusions have higher CaO content than that in the liquid CA$_x$. CaS-other inclusions are those with compositions between CaS and CA$_x$. CaS-MnS inclusions have a significant fraction of both CaS and MnS phases; however, their fractions are not high enough to be considered as single-phase CaS or MnS. The CaS type inclusions still contain both CaS and MnS phases, but the CaS phase is more dominant. The term “CaS” refers to CaS type inclusions for simplicity unless otherwise specified.

3. Methods of Calculating Coarsening of CaS Inclusions

This study applied two methods described in the introduction section to determine the coarsening mechanism of CaS inclusions under laboratory and industrial conditions. Both calculation methods are explained in detail in this section.

The first method was to compare the evolution of the average diameter of CaS inclusions against the theoretical growth rate predicted by individual mechanisms. Mechanisms 1 to 5 listed below were considered in the present study.

1. Diffusion-controlled growth due to concentration gradient created by the Gibbs-Thomson effect (Ostwald ripening);
2. Diffusion-controlled growth;
3. Collision and coalescence due to the effect of Brownian motion;
4. Collision and coalescence due to ascending velocity difference (Stokes motion);
5. Collision and coalescence due to flow of the melt.
The second method, which was mainly used to study the coarsening of CaS inclusions under industrial conditions, was the population balance equation (PBE). Collision-related mechanisms 3 to 5 were considered. Mechanisms 1 and 2 were not used to calculate PBE because of the difficulty in estimating the number of CaS monomers that participate in the growth of CaS inclusions. The change in the volumetric number density of CaS inclusions calculated by PBE considering mechanisms 3 to 5 was compared with the observed number density change. The similarities between the two indicated the contribution of collision-related coarsening mechanisms.

3.1. Determination of the Rate-Controlling Component

To calculate the coarsening rate of inclusion due to Ostwald ripening, the first step is to determine the rate-controlling component. Equation (1) [6–8] is the expression of change in average radius, \( r \), from initial radius, \( r_0 \), during the time, \( t \), at temperature, \( T \). In Equation (1), the second term is the coarsening rate. \( \gamma \) is the interfacial tension between steel and CaS type inclusion, \( MV_i \) is the molar volume per mole of component \( i \) in a compound, \( D_i \) is the diffusion coefficient of component \( i \), and \( C_{(i),b} \) and \( C_{(i)} \) are the concentrations of component \( i \) in the bulk melt and in inclusion, respectively. CaS type inclusions studied are considered as non-stoichiometric CaS-CA\(_x\)-MnS complexes, so among Ca, Al, O, and S, the one that gives the lowest coarsening rate is the controlling component.

\[
r^3 = r_0^3 + \frac{4}{9} \frac{2\gamma MV_i D_i C_{(i),b}}{RT (C_{(i)} - C_{(i),b})} t
\]

The diffusion coefficients of Ca, Al, O, and S in steel at 1873 K used in calculations were obtained from the literature [17,18]. The diffusion coefficient of Ca at 1873 K was 3.0 \( \times \) 10\(^{-9} \) m\(^2\)/s, and those for S and O were 4.3 \( \times \) 10\(^{-9} \) and 3.1 \( \times \) 10\(^{-9} \) m\(^2\)/s, respectively. The diffusion coefficient of Al in liquid iron equaled 3.5 \( \times \) 10\(^{-9} \) m\(^2\)/s. The steel-CaS interfacial tension was assumed to be 0.6 N/m, which is similar to MnS and other sulfides such as FeS and Cu\(_2\)S [19], as the exact value was never reported in the literature. The interfacial tension of liquid CA\(_x\) with a weight percentage of CaO between 35 and 55 pct. can be found in the literature [20]. For CA\(_x\) with CaO lower than 35 wt. pct., the interfacial tension was assumed to increase linearly to 2 N/m, which was the reported interfacial tension of Al\(_2\)O\(_3\) [21–25]. The values used for density, \( \rho \), of C\(_{12}\)A\(_7\), CA, CA\(_2\) and CA\(_6\) were 2690, 2560, 2920 and 3790 kg/m\(^3\), respectively [8,26]. A value of 2602 kg/m\(^3\) was used for CaS. The ratio between inclusion density and the molar mass can be used to calculate \( MV_i \). Moreover, the inclusion densities were used to calculate \( C_{(i)} \), the concentration of component \( i \) in inclusions.

The mass fractions of dissolved Ca, Al, O, and S in steel were assumed to be 0.2 ppm, 0.04 wt. pct., 3 ppm, and 20 ppm, respectively. The conversion from mass fractions to mass concentration of component \( i \), \( C_{(i),b} \), used the temperature–density correlation proposed by A.F. Crawley [27].

One can notice that in Table 2 the calculated coarsening rates of C\(_{12}\)A\(_7\), CA, and CaS inclusions are consistently the lowest when Ca was considered as the rate-controlling element. This indicates that Ca is most likely the rate-controlling component. The calculated coarsening rates of CA\(_2\) and CA\(_6\), assuming that Ca is the rate-controlling element, are comparable and higher than those calculated for O, respectively. This suggests that the latter is the rate-controlling component. However, by noticing that CaS type inclusions only contained less than 10 wt. pct. of CA\(_x\) phase with a composition close to CA\(_2\) and CA\(_6\) during solidification (CaS composition evolution is included in a later section), Ca being the rate-controlling component as suggested in Table 2 is a more appropriate assumption. When the fraction of CA\(_x\) phase was higher, which only occurred in Exp. 2035, the modification extent of the CA\(_x\) phases was equal to or higher than CA phase. In that case, the rate-controlling component was Ca. Therefore, Ca was used as the rate-controlling
component in the present work when calculating the CaS diameter change controlled by Ostwald ripening.

Table 2. The comparison of calculated coarsening rate (m/s) of different CA$_x$ and CaS to determine the rate-controlling component, namely, Ca, Al, O, and S.

|          | Ca  | Al  | O   | S   |
|----------|-----|-----|-----|-----|
| C$_{12}$A$_7$ | 3.52 $\times$ 10$^{-19}$ | 1.79 $\times$ 10$^{-15}$ | 4.99 $\times$ 10$^{-18}$ |       |
| CA       | 6.93 $\times$ 10$^{-18}$ | 1.20 $\times$ 10$^{-14}$ | 4.65 $\times$ 10$^{-17}$ |       |
| CA$_2$   | 1.02 $\times$ 10$^{-17}$ | 9.97 $\times$ 10$^{-15}$ | 2.25 $\times$ 10$^{-17}$ |       |
| CA$_6$   | 4.15 $\times$ 10$^{-17}$ | 1.24 $\times$ 10$^{-15}$ | 1.24 $\times$ 10$^{-17}$ |       |
| CaS      | 1.38 $\times$ 10$^{-18}$ |               | 4.95 $\times$ 10$^{-16}$ |       |

3.2. Coarsening Due to Ostwald Ripening

As Ca was determined to be the rate-controlling component, Equation (2) was used to calculate the change in the average radius of CaS inclusions due to Ostwald ripening. The theories of Ostwald ripening had already been discussed in numerous studies [28–30]; hence, they will not be discussed here.

$$ r^3 = r_0^3 + \frac{4}{9} \frac{2\gamma MV_{Ca} D_{Ca} C_{[Ca],b}}{RT (C_{[Ca]} - C_{[Ca],b})} t $$

When calculating the coarsening rate of CaS type inclusions, their average composition from each sample were used to estimate $\gamma$, $MV_{Ca}$ and $C_{[Ca]}$. In the work of Wang et al. [8], the interfacial tension of CA$_x$ was calculated using Equation (3), where $x_i$ represents the molar fraction. The similar approach was used to calculate the interfacial tension of non-stoichiometric CaS-CA$_x$-MnS complexes, i.e., CaS type inclusions, through Equation (4). The approach of predicting the molar volume of slag was used to estimate the molar volume of inclusions. In Equation (5), $x_{Ca}$ is the molar fraction of Ca and $MV$ denotes molar volume. The molar volumes of CaO, Al$_2$O$_3$, CaS and MnS can be found in the literature [20,26]. Similarly, the method of estimating the density of slag [20] was applied to calculate the density of inclusion $\rho_P$ in Equation (6). Calculating $\rho_P$ allows one to obtain $C_{[Ca]}$ based on the mass fraction of CaO and CaS of the average composition of CaS type inclusions.

$$ \gamma_{CA_x} = x_{CaO} \gamma_{CaO} + x_{Al_2O_3} \gamma_{Al_2O_3} $$

$$ \gamma_{CaS-CA_x-MnS} = x_{CaS} \gamma_{CaS} + x_{CA_x} \gamma_{CA_x} + x_{MnS} \gamma_{MnS} $$

$$ MV_{Ca} = \frac{x_{CaO} \cdot MV_{CaO} + x_{Al_2O_3} \cdot MV_{Al_2O_3} + x_{CaS} \cdot MV_{CaS} + x_{MnS} \cdot MV_{MnS}}{x_{Ca}} $$

$$ \rho_P = \frac{x_{CaO} \cdot MV_{CaO} + x_{Al_2O_3} \cdot MV_{Al_2O_3} + x_{CaS} \cdot MV_{CaS} + x_{MnS} \cdot MV_{MnS}}{x_{CaO} \cdot MV_{CaO} + x_{Al_2O_3} \cdot MV_{Al_2O_3} + x_{CaS} \cdot MV_{CaS} + x_{MnS} \cdot MV_{MnS}} $$

The concentration of dissolved Ca in the bulk melt was proposed to be 0.2 ppm during the industrial Ca injection process in the literature [31]. In the present study, Ca addition was conducted once in each experiment. Because of the volatile nature of Ca, the $C_{[Ca],b}$ was assumed to decrease from 0.2 ppm to equilibrium $C_{[Ca],eq}$ following Equation (7) [32] starting at 1 min after Ca addition. The values of $C_{[Ca],eq}$ were calculated using FactSage 7.2 based on the steel chemistries. $k_{Ca}$ is the mass transfer coefficient of Ca in steel, which was suggested to be in the range of 2.35 $\times$ 10$^{-4}$ to 3.53 $\times$ 10$^{-4}$ m/s in a previous study with a similar experimental approach as the present study [32]. An average value of
2.94 × 10⁻⁴ m/s was used here. The term \( A \) in Equation (7) is the steel-Ar interfacial area per unit volume of steel calculated based on the geometry of the crucibles.

\[
\ln \left( \frac{C_{[\text{Ca}],b} - C_{[\text{Ca}],eq}}{C_{[\text{Ca}],0} - C_{[\text{Ca}],eq}} \right) = -k_{\text{Ca}} A \frac{t}{V}
\]

(7)

The diameter change of CaS inclusions was assumed to be neglectable after the solidification was completed. The solidus temperature was estimated to be 1773 K for all experiments using Equation (8) [33], and the estimated value was confirmed with FactSage calculation. So, with a 10 K/min cooling rate, the temperature decrease from 1873 to 1773 K was considered to be 10 min.

\[
T_{\text{sol}}(K) = 1809 - 344[\%C] - 183.5[\%S] - 124.5[\%P] - 6.8[\%Mn] - 12.3[\%Si] - 4.1[\%Al] - 1.4[\%Cr] - 4.3[\%Ni]
\]

(8)

3.3. Coarsening Due to Ca Diffusion

It was suggested in the literature that when the coarsening of inclusion is controlled by diffusion, the movement of the steel-inclusion interface can be expressed using Equation (9) [34]. \( C_{[\text{Ca}],i} \) is the concentration of Ca at the steel-inclusion interface. Its values were calculated using a simplification of the method adapted by Tabatabaei et al. [35]. Assuming the CAx at the surface of CaS type inclusions was insignificant, the calculation started with the mass balance at the interface, as given by Equation (10), where \( n_i \) denotes the transfer of component \( i \) through the boundary layer.

\[
r^2 = r_0^2 + 2D_{\text{Ca}} C_{[\text{Ca}],b} - C_{[\text{Ca}],i} t
\]

(9)

\[
n_{\text{Ca}} = n_S
\]

(10)

Then, at any \( r \) exists

\[
4\pi r^2 k_{m,\text{Ca}} \left( X_{[\text{Ca}],i} - X_{[\text{Ca}],b} \right) = 4\pi r^2 k_{m,S} \left( X_{[S],i} - X_{[S],b} \right)
\]

(11)

\( X_{[i],i} \) is the molar concentration of component \( i \) in steel. The mass transfer coefficient, \( k_{m,i} \) was suggested to follow the expression as Equation (12) [35]

\[
Sh = \frac{k_{m,i}d}{D_i}
\]

(12)

where \( d \) is the diameter of inclusion. Sherwood number, \( Sh \), can be assumed to have a constant value of 2 for small inclusions in liquid steel with low viscosity [36]. Substituting Equation (12) into Equation (11) gives

\[
D_{\text{Ca}} \left( X_{[\text{Ca}],i} - X_{[\text{Ca}],b} \right) = D_S \left( X_{[S],i} - X_{[S],b} \right)
\]

(13)

When modeling the modification of CAx inclusions, the concentration of O dissolved in steel was assumed to be at the level after Al deoxidation and before Ca addition. In other words, calcium would only affect the local steel chemistry at the early stage [35]. Using a similar assumption, the dissolved S content was considered to decrease linearly with time from a measured T.S concentration to the calculated equilibrium dissolved S concentration. Combining all the aforementioned assumptions with the concentration of other steel constituents allow one to determine \( X_{[\text{Ca}],b} \) and \( X_{[S],b} \). It is common to consider that equilibrium is maintained at the steel-inclusion interface [37–40]. With the
assumption that CA$_x$ phases were insignificant at the surface of CaS type inclusions, the only equilibrium established on the CaS surface was Reaction (14).

\[
[Ca] + [S] = \text{CaS} \tag{14}
\]

and must satisfy

\[
K_{eq} = \frac{a_{\text{CaS}}}{(h_{\text{Ca}}w_{[\text{Ca}],i})(h_{\text{S}}w_{[\text{S}],i})} = \frac{1}{(h_{\text{Ca}}X_{\text{CaS},i,MW_{\text{Ca}}})(h_{\text{S}}X_{\text{CaS},i,MW_{\text{S}}})} \tag{15}
\]

where $h_i$ is the activity coefficient and $\rho_{\text{steel}}$ is the density of steel. Equilibrium constant, $K_{eq}$, was calculated based on the standard Gibbs Energy through Equation (16), which is the summation of $\Delta G^\circ$ of related reactions from the literature [41,42]. $K_{eq}$ at 1873 K calculated using Equation (16) was confirmed to be similar to $K_{eq}$ proposed in the literature [43–45].

\[
\Delta G^\circ = -692158 + 205.33T \text{ J/mol} \tag{16}
\]

Equation (13) was solved in conjunction with Equation (15) to obtain $C_{[\text{S}],i}$ and $C_{[\text{Ca}],i}$. The latter was substituted into Equation (9) to calculate the average diameter of CaS type inclusions with time.

### 3.4. Coarsening Due to the Brownian Motion

The inclusions collide and coalesce due to their random motion. In that case, the change of volumetric inclusion number, $N_{V,i}$, can be calculated as suggested in Equation (17) [6,11,46]. $N_{V,0}$, $k_B$ and $\eta$ are the initial volumetric inclusion number density, Boltzmann constant and steel viscosity, respectively. Equation (18) expresses the conversion from inclusion volume fraction, $f$, to $N_{V,i}$. Equation (18) can be rearranged to write $N_{V}$ as a function of $f$ and $r$, and $N_{V,0}$ as a function of $f_0$ and $r_0$. Substituting $N_{V,0}$ and $N_{V}$ in Equation (17) gives Equation (19). The volume fraction was calculated by first converting the planar size distribution given by ASPEX to volumetric size distribution through the Schwartz–Saltykov method. The detailed procedure is available elsewhere [47]. Then, the total volume of CaS inclusions per unit volume of steel was estimated. The effect of temperature on steel viscosity, $\mu$, was reported in the literature [48]. It covers the temperature from 1783 to 1853 K; therefore, the relation with temperature was extrapolated to 1773 and 1873 K.

\[
N_{V,i} = \frac{N_{V,0}}{1 + \frac{8k_BTN_{V,0}}{3\mu}t} \tag{17}
\]

\[
f = \frac{4}{3}\pi r^3 N_{V} \tag{18}
\]

\[
r^3 = \left(\frac{f}{f_0}\right)^3 + \frac{2k_B T f}{\pi \mu} t \tag{19}
\]

### 3.5. Coarsening Due to Ascending Velocity Difference

Stoke’s law predicts that larger inclusions ascend faster than the small ones. This causes relative motion between inclusions of different sizes, leading to collision and coalescence. The inclusion radius change due to ascending velocity difference can be expressed using Equation (20) [7]. Term $g$ is the gravitational acceleration taken as 9.8 m/s$^2$.

\[
r = r_0 \left[1 - \frac{g f (\rho_{Fe} - \rho_P) r_0 t}{18 \mu}\right]^{-1} \tag{20}
\]

### 3.6. Coarsening Due to the Melt Flow

Inclusions can also be brought to collide and coalesce due to melt flow. In the laboratory experiments, the melt had no controlled stirring. Ca was added during the early
stage of an experiment and was rapidly consumed. During the dissolution of Ca, the Ca gas bubbles formed continuously but only for a limited time. Therefore, its contribution to stirring the melt was not taken into account for the coarsening of CaS inclusions in the analysis.

3.7. Coarsening Due to the Multiple Mechanisms Predicted by Population Balance Equation (PBE)

Smoluchowski [11] formulated the particle coagulation kinetics through PBE. A general form, Equation (21), expresses the rate of change of the volumetric number density of CaS inclusions in group $k$, $\frac{dN_{V,k}}{dt}$. The volumetric population density of inclusions with size $k$, $N_{V,k}$, can increase due to the coalescence of a pair of inclusions from group $i$ and group $j$, which is the first term of Equation (21). The second term is the expression of inclusions becoming too large to remain in group $k$ after coalescing with another inclusion of sufficiently large size. The number densities of CaS inclusions in group $i$ and $j$ are represented by $N_{V,i}$ and $N_{V,j}$, respectively. $\beta^C$ is the collision frequency function that quantifies the collective effects of Brownian motion, $\beta^B$, Stokes motion, $\beta^S$, as well as the turbulent flow, $\beta^T$, and laminar flow, $\beta^G$, on the growth of CaS inclusions. The detailed expressions are shown as Equations (22)–(26) [12]. $\epsilon$ is the energy dissipation rate that quantifies the stirring power, and was also suggested to be correlated to $\alpha$, the coagulation coefficient [49]. $\frac{du}{dy}$ is the velocity gradient in the laminar shear zones, which are usually near the walls [12].

$$\frac{dN_{V,k}}{dt} = \frac{1}{2} \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij}^C N_{V,j} N_{V,i} - \sum_{i=1}^{k} \beta_{ik}^C N_{V,j} N_{V,k}$$

(21)

$$\beta^B = \frac{2k_BT}{3} \left( \frac{1}{r_i} + \frac{1}{r_j} \right)$$

(22)

$$\beta^S = \frac{2\pi \gamma (\rho_{\text{steel}} - \rho_{\text{CaS}})}{\mu} \left| r_i - r_j \right| \left( r_i + r_j \right)^3$$

(23)

$$\beta^T = 1.3 \pi^{0.5} \alpha \sqrt{\frac{\mu_{\text{steel}}}{\mu}} \left( r_i + r_j \right)^3$$

(24)

$$\beta^G = \frac{4}{3} \left( r_i + r_j \right)^3 \frac{du}{dy}$$

(25)

$$\beta^C = \beta^B + \beta^S + \beta^T + \beta^G$$

(26)

In a later section, the combined contribution of relevant collision-related coarsening mechanisms on the evolution of PSD of CaS inclusions calculated using the PBE will be discussed. The particle-size-grouping (PSG) method introduced in the work of Nakaoka et al. [50] was used to simplify the calculation of PBE. This method was confirmed to give approximation close to the exact solution and had been used extensively in previous studies [51–53].

4. Results

4.1. CaS Growth in Experimental Conditions

Figure 3 shows the evolution of the area fraction (AF) of all inclusion types from the three laboratory experiments. The details of the evolution of inclusion types were discussed in the authors’ previous publication [2]. The value for the AF of CaS inclusions increased continuously over time in Exp. 2035 and 3035. By the end of the 20-min experiment, the values for AF of CaS were 44 and 22 ppm in Exp. 2035 and 3035, respectively. The authors suggested that CaS inclusions were stable at 1873 K [2], so these inclusions were reaction products. In Exp. 2025, in comparison, CaS was thermodynamically stable in the first 10 min after Ca addition, but the AF values were low at around 2 ppm. The AF of CaS increased to 6 ppm in the 20-min sample, followed by a slight decrease in the 40-min sample, but high CaS AF was again observed in the bulk sample to be 12 ppm. Some CaS-CAx...
complexes, classified as CaS-other inclusions, were also found in these experiments. SEM images and EDS mappings of typical CaS inclusions are shown in Figure 4 to provide some insight about their shape and structures. One can easily notice that the CaS inclusions were close to spherical. Therefore, in both methods of determining the coarsening mechanisms, CaS inclusions were assumed to be spherical for simplicity.

**Figure 3.** Evolution of area fraction (AF) of inclusions in (a) Exp. 2035, (b) Exp. 3035, and (c) Exp. 2025.

**Figure 4.** SEM-EDS elemental maps of CaS inclusion in (a) 1-min sample of Exp. 2035, (b) 3-min sample of Exp. 2035 and (c) 20-min sample of Exp. 3035.
The evolutions of the average diameter and the composition of CaS type inclusions are shown in Figure 5. The CaS type inclusions in samples taken in Exp. 2035 were composed of initially 27 wt. pct. CaO. The fraction of CaO phase decreased to 3 wt. pct when the experiment was close to the end. Because Ca mainly reacted with O in the early stage (Figure 3a), CaS type inclusions (whose number was small) contained approximately 10 wt. pct. MnS. As more CaS formed as Exp. 2035 proceeded, less S was available to react with Mn, so MnS content in CaS decreased. Some concentration of Al₂O₃ phase was also found in the CaS type inclusions. CaS fraction increased from 58 wt. pct. to 88 wt. pct. during the 20 min experiment. In Exp. 3035, on the contrary, the fraction of CaO phase never exceeded 4 wt. pct. and the maximum MnS phase fraction was at 8 wt. pct. because CaS inclusions were formed directly [2] through Ca and S reaction. As a result, the fractions of CaS were constantly above 82 wt. pct. The distribution of phases within CaS inclusions from Exp. 2025 were similar to that of Exp. 2035 in the early stages. The fraction of CaO phase can be higher than 25 wt. pct. during the first 10 min after Ca addition. That was because Al was not added before Ca addition; hence, a significant portion of Ca added reduced Al₂O₃ from the crucible and became a vital oxygen bearer. However, starting at 10 min, the fraction of the CaS phase was constantly higher than 75 wt. pct.

Figure 5. Average diameters and compositions of CaS type inclusions in (a) Exp. 2035, (b) Exp. 3035, and (c) Exp. 2025.

Both the average diameters and the standard deviations of the CaS inclusions are included in Figure 5. In Exp. 2035, at least 150 CaS inclusions were analyzed in each sample by ASPEX, except for the first sample, in which the number of inclusions was 41. The average diameter of CaS inclusions was initially 0.8 μm, then gradually increased to about 2.1 μm within 20 min after Ca addition at 1873 K, then slightly increased further.
to 2.4 μm in the bulk sample. The standard deviation for the average diameter values increased marginally from about 0.3 to 0.4 μm. In Exp. 3035, 26 CaS inclusions were detected in the first sample. The number of CaS in later samples varied from 60 to 628. CaS average diameter increased from 1.2 to 1.7 μm, and increased by another 0.5 μm during solidification to end with 2.2 μm average diameter in the final bulk sample. Because of the relatively smaller number of CaS inclusions analyzed, especially in the first sample, the standard deviation fluctuated in Exp. 3035. The number of CaS inclusions detected in Exp. 2025 was lower than in Exp. 2035 and Exp. 3035 because of the relatively lower Ca content and S content. In most samples of Exp. 2025, the number of detected CaS can be as low as 10, such as in the 1-min sample. The number gradually increased to about 50 in the 20, 30, and 40-min samples. In bulk, a total of 104 CaS inclusions were analyzed by ASPEX. During the first 20 min of Exp. 2025, the average diameter of CaS increased from 1 to 2.1 μm. Thereafter, generally it did not change until the last bulk sample, which was found to be 2.6 μm. Notice that a decrease in standard deviation from 0.8 to 0.5 μm occurred at 20 min.

The detailed evolution of CaS particle size distributions (PSD) of the three experiments is shown in Figure 6. The x-axis and the y-axis are shown in logarithmic form for better visualization. The increase in the average diameter and the planer number density (Nₐ) of CaS inclusions from Exp. 2035 were apparent during the first 5 min after Ca addition. The CaS showed a log-normal distribution starting at 3 min, indicated by the iconic parabolic shape [54–56]. One can notice that the left side of the 1, 3, and 5-min PSD curves overlapped. This trend means a consistent "supply" of newly formed small inclusions. High-temperature phenomena including inclusion formation were rarely reported to be limited by the chemical reaction rate [7,12,35,57,58], so the formation of new, small inclusions would largely depend on the rate of mass transport in the early stage of the experiment. As the experiment proceeded, the PSD curve shifted rightward while keeping a similar shape from 5 min to 20 min after Ca addition, indicating the disappearance of smaller inclusions. This was considered the result of collision and coalescence.

![Figure 6](image-url)
During the first 5 min of the Exp. 3035, the PSD curve barely changed. That was potentially related to lower Ca supply in Exp. 3035 than that of Exp. 2035. In Exp. 3035, the total Ca content was initially 42 ppm and remained stable. Then, the dissolved Ca concentrations were likely lower in Exp. 3035. This would affect the growth rate of CaS inclusions when mass transport was the controlling mechanism. However, as the CaS inclusions grew over time, they became detectable. And with the collision occurring at the same time, inclusions coalesced, and the rightward shift of the PSD curve became apparent, as seen from the 10-min PSD curve in Figure 6d. The following steps of the Exp. 3035 at 1873 K were similar to the later stages of Exp. 2035.

Similarly, CaS inclusions in Exp. 2025 started with a relatively high number of submicron inclusions. The PSD remained almost unchanged in the first 3 min after Ca addition. Then, until 10 min, the PSD curve shifted rightward, with the peak moved from \( d_{\text{avg}} \) equals 0.8 to 1.3 \( \mu \text{m} \). Because of the presence of submicron size inclusions, the growth of CaS inclusions was still mainly relevant to mass transport. A sudden change in the shape of PSD was observed at 20 min after Ca addition, where small CaS inclusions disappeared, and \( N_A \) of inclusions larger than 2 \( \mu \text{m} \) drastically increased compared to the previous sample. This can be considered to signify the coarsening through collision and coalescence.

During solidification, the PSD curve evidently broadened and deviated from the symmetrical shape seen in the last pin sample in all experiments. In Exp. 2035, the \( N_A \) of CaS inclusions with a diameter larger than 3.25 \( \mu \text{m} \) \( (\log(d_{\text{avg}}) > 0.51) \) shown as the right side of the PSD evidently increased, while the left side of the PSD peak remained practically unchanged. A similar trend can also be observed in Exp. 2025 in Figure 6f. In Exp. 3035, the entire PSD shifted further to the right during solidification, and the width of the curve increased. These observations were correctly reflected by the change of average diameter and standard deviation shown in Figure 5, which were potentially due to the precipitation of CaS phase and MnS phase on CaS type inclusions.

4.2. CaS Growth in Industrial Conditions

The coarsening behaviors of CaS inclusions in samples taken from ladle and tundish during steel-refining processes are evaluated in this section. For this purpose, lollipop samples from four industrial heats were studied. The evolution of the average diameter of CaS type inclusions with respect to sample number is shown in Figure 7. In Figure 7, small offsets are introduced on the x-axis to improve readability.
Figure 7. Evolution of the average diameters of CaS type inclusions in samples taken from (a) Heats 1 and 3–30 ppm S and 35 ppm T.Ca and (b) Heats 4 and 5–20 ppm S and 35 ppm T.Ca.

Figure 7 suggests that once the CaS type inclusions were observed, their average diameters were already at around 2 μm regardless of heat chemistries. In Exp. 2035 and Exp. 3035, it took about 20 min for the average diameter of CaS to increase to slightly above 2 μm. This was longer than the roughly 5-min Ca addition in industrial conditions, meaning that some differences exist between the coarsening of CaS in the two conditions. Comparing the first tundish sample (T1) with the ladle sample after Ca addition (L5), the increase in CaS average diameter is apparent. In Heat 1 and Heat 5, the difference between T1 and L5 was 0.6 and 0.9 μm, respectively. For Heat 3 and Heat 4, the difference was higher at 1.6 μm.

The evolution of the PSD of CaS inclusions in Heat 1 is shown in Figure 8 for a more detailed discussion. It is worth mentioning that Figure 8 is based on the ASPEX analysis, including inclusions with \(d_{\text{max}}\) (longest diameter of a non-spherical inclusion) larger than 0.5 μm. This will be referred to as 0.5 μm analysis for simplicity. All other plots and related discussions are based on the ASPEX analysis, including inclusions with \(d_{\text{max}}\) > 2 μm. The ASPEX processing time drastically increased when decreasing the \(d_{\text{max}}\) threshold from 2 to 0.5 μm, so the 0.5 μm analysis was only performed on samples of Heat 1.

Figure 8. The evolution of particle size distribution for CaS type inclusions in Heat 1 including inclusions with \(d_{\text{max}}\) > 0.5 μm (a) ladle samples and (b) tundish samples.

Figure 8a includes the PSD of CaS inclusions from all the ladle samples in Heat 1. One can see that the PSD shares a very similar pattern in all five ladle samples. Small CaS inclusions formed immediately after Ca addition, showing the parabolic shape associated with the typical log-normal distribution. During the Ca addition from L1 to L5, the number
density ($N_A$) of all sizes increased. This caused the PSD curves to remain similar in all ladle samples, with the peak at around log($d_{avg}$) equal to 0. This is reflected in Figure 7 by a stable average CaS inclusion diameter. The change in the PSD of CaS inclusions from ladle to tundish was very apparent in Figure 8b. The PSD of tundish samples compared to the PSD of ladle samples appeared much broadened and shifted rightward. This is reflected in Figure 7a by the increased average diameter and standard deviation in T1 compared to L5. At 33 min after Ca addition, the $N_A$ of inclusions with log($d_{avg}$) < 0.24 decreased by at least one order of magnitude, while the $N_A$ of inclusions with log($d_{avg}$) > 0.24 slightly increased.

5. Discussion

The evolution of PSD in all three experiments suggests that the diameter change of CaS inclusions was related to mass transport in the early stage and later depended on coagulation. To better understand the inclusion coarsening kinetics, the present work compares the change of average diameter of CaS inclusions observed through the experiments with models explained in the previous section.

5.1. Coarsening Mechanisms of CaS Inclusions under Experimental Conditions

The diameter change calculated using the methods explained in the previous sections was plotted and compared with the observed average diameters of CaS inclusions in Exp. 2035, Exp. 3035 and Exp. 2025 in Figure 9. For modeling calculations, the initial diameter of CaS inclusions was set to be 0.01 µm in all conditions. The final diameter predicted from lowest to highest are through the mechanisms of Stokes motion, Ostwald ripening, diffusion-controlled growth, and Brownian motion for all three experiments. The diameter changes due to Ostwald ripening and Stokes motion are insignificant, with less than 0.2 µm regardless of experimental conditions, which clearly underpredict the CaS inclusions diameter change. The diffusion-controlled growth shows a rapid increase in the first 5 min but then decreases. The predicted diameter decrease is much more apparent in Exp. 3035 than the other two experiments. The Brownian motion predicts the most significant change among the four mechanisms included in Figure 9. The CaS inclusion diameters are expected to increase by 2.0, 1.9, and 1.3 µm in Exp. 2035, Exp. 3035 and Exp. 2025, respectively.

The authors noticed that the diffusion-controlled growth agrees with the experimental results in the first 5 min after Ca addition when assuming the initial dissolved Ca concentration being 0.1 ppm for Exp. 2035 and 0.15 ppm for Exp. 3035 and Exp. 2025. After that, the rate of growth controlled by Brownian motion is very similar to the experimentally observed growth rate. In fact, if considering the dominant CaS coarsening mechanism changed from Ca diffusion to Brownian motion at 5 min after Ca addition, one can obtain Figure 10. The solid lines in Figure 10 are the theoretical change due to diffusion already shown in Figure 9. The dashed lines were calculated by simply taking the average diameter calculated for diffusion-controlled growth at 5 min as the initial diameter and calculating the diameter change considering Brownian motion thereafter. A reasonable agreement between the experimental results and the models can be achieved by considering the transition between coarsening mechanisms. The diameter change in Exp. 3035 was over-predicted by the model for Brownian motion. Equation (19) shows that the radius change is related to the ratio of the new-to-old volume fraction $\frac{f}{f_0}$. If not, all $f_0$ participated in the formation of new CaS inclusions, for example, when some formed CaS-other inclusions, $\frac{f}{f_0}$ would be over-predicted; hence, so would $r$. Diffusion-controlled CaS formation/dissolution predicts a major decrease in the average diameter of CaS inclusions in Exp. 2035 and Exp. 2025 and some decrease in Exp. 3035 (Figure 9 black lines). In reality, diffusion-controlled growth and coarsening through Brownian collision must have occurred simultaneously. Overprediction was observed in Figure 10 because the diameter decrease due to diffusion was not incorporated in the calculation of dashed lines shown in Figure 10.
Figure 9. Comparison of the average diameters of CaS type inclusions in samples taken in (a) Exp. 2035, (b) Exp. 3035, and (c) Exp. 2025, and predicted using different coarsening mechanisms.

Figure 10. Comparison of the average diameters of CaS type inclusions in samples taken from (a) Exp. 2035, (b) Exp. 3035, and (c) Exp. 2025, and predicted based on diffusion-controlled growth followed by Brownian motion.
The authors are aware that the theoretical growth shown in Figure 10 cannot accurately predict the diameter of CaS inclusions in the course of experiments. However, the focus of the present study is not to establish a model that calculates the CaS diameter change but to determine the coarsening mechanisms. Figures 9 and 10 do show that none of the four coarsening mechanisms considered can independently explain the growth of CaS observed in Exp. 2035, Exp. 3035 and Exp. 2025. A transition of the controlling coarsening mechanism is clear in the experiments. The diameter change of CaS inclusions was initially governed by the diffusion and later related to Brownian-motion-driven collisions.

5.2. Cause of Change in Coarsening Mechanisms

The authors further analyzed the cause of the change in the dominating coarsening mechanism. The change in the driving force over experimental time was calculated for the diffusion-controlled growth mechanism, as shown in Figure 11. According to Equation (7), the Ca concentration in metal bulk, \( C_{[\text{Ca}],b} \), decreased over time; therefore, the driving force rapidly reduced. In other words, the influence of Ca diffusion on the size change of CaS inclusions became insignificant. The coarsening of CaS inclusions stopped after 5 min from Ca addition (Figure 9). Later, the driving force in Exp. 2035 and Exp. 2025 was negative while that of Exp. 3035 remained much closer to 0. The variation in driving force is related to the difference in sulfur content. With a higher \( C_{[\text{S)],i} \) given by the lower S levels, \( C_{[\text{Ca}],i} \) to maintain Equilibrium (14) in Exp. 2035 and Exp. 2025 were higher than that of Exp. 3035. So, the concentration differences, \( C_{[\text{Ca}],b} - C_{[\text{Ca}],i} \), from Equation (9) were slightly negative starting from 10 min after Ca addition; hence, negative slopes were seen in Figure 9a,c. The lower \( C_{[\text{Ca}],i} \) in Exp. 3035 was able to maintain \( C_{[\text{Ca}],b} - C_{[\text{Ca}],i} \) much closer to 0 before Exp. 3035 ended, so the theoretical diameter change due to diffusion is less apparent in Figure 9b. Further, for all experimental conditions, the importance of Brownian motion on the coarsening of CaS inclusions increased over time. This is due to the fact that Brownian motion largely depends on the volume fraction of inclusions of interest. The volume fraction of CaS inclusions increased with time as shown in Figure 12 for all three experiments. The Brownian motion eventually became the dominant coarsening mechanism at 5 min after Ca addition.

![Figure 11. Change of driving force for Ca diffusion in Exp. 2035, Exp 3035, and Exp. 2025.](image-url)
The significance of Brownian motion over the Stokes motion can be explained by the difference in frequency of collision. The change in collision frequency function, $\beta$, of inclusion pairs with a diameter $d_i$ and $d_j$ is shown in Figure 13. Figure 13a–d correspond to $d_i$ equal to 0.5, 1, 2, and 3 $\mu$m, respectively. These values cover the diameter range of CaS type inclusions shown in Figure 5a. The range of $d_j$ was set from 0 to 4 $\mu$m in all four plots. The temperature was set to 1873 K and the viscosity was equal to $2.3 \times 10^{-3}$ kg/(m·s). The values for steel density and CaS density were 6975 and 2650 kg/m$^3$, respectively. Even though the densities were estimated, the authors confirmed that slight density change opposes minor change on the orders of magnitudes of $\beta$ values; hence, it has no impact on the findings.

In Figure 13, the frequency function of Brownian motion, $\beta^B$, remains stable at the same order of magnitude, i.e., around $-17$ to $-16$ m$^3$/s, for all four $d_i$. The values are slightly higher at lower $d_i$, but decrease to a stable level as $d_i$ increases. In comparison, when $d_i < 2$ $\mu$m, $\beta^S$ values are generally lower than that of $\beta^B$ until $d_i$ increases to higher than approximately 2.5 $\mu$m. That is partially due to the presence of the dip at $d_j$ equals to $d_i$. The reason being inclusions of similar sizes show no relative motion while ascending; hence, they cannot coalesce during flotation. The $\beta^S$ are higher than $\beta^B$ in Figure 13d across almost the entire $d_j$ range. Based on Figures 5 and 13, it can be inferred that the frequency of inclusions to collide is higher due to Brownian motion than due to Stokes motion in almost the entire size range of CaS type inclusions observed in the experimental conditions. As a result, the prediction given by the Brownian motion model is relatively more in agreement with the experimental data, as seen in Figure 9. The collision frequency due to Stokes motions is higher when an inclusion in an inclusion pair is close to 3 $\mu$m. Still, according to Figures 5 and 6, inclusions of such diameters are a small portion of the entire CaS population in the experiments, and they are mainly found close to the end of experiments. With the limited available time for further collision, the effect of Stokes motion is understandably low.
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Figure 12. Variation in the volume fraction of CaS inclusions over time in Exp. 2035, Exp. 3035, and Exp. 2025.

The significance of Brownian motion over the Stokes motion can be explained by the difference in frequency of collision. The change in collision frequency function, $\beta$, of inclusion pairs with a diameter $d_i$ and $d_j$ is shown in Figure 13. Figure 13a–d correspond to $d_i$ equal to 0.5, 1, 2, and 3 μm, respectively. These values cover the diameter range of CaS type inclusions shown in Figure 5a. The range of $d_j$ was set from 0 to 4 μm in all four plots. The temperature was set to 1873 K and the viscosity was equal to $2.3 \times 10^{-3}$ kg/(m·s). The values for steel density and CaS density were 6975 and 2650 kg/m³, respectively. Even though the densities were estimated, the authors confirmed that slight density change opposes minor change on the orders of magnitudes of $\beta$ values; hence, it has no impact on the findings.

(a)  
(b)  
(c)  
(d)  

Figure 13. Comparison of collision frequency function of Brownian motion and Stokes motion for an inclusion of diameter $d_i$ (a) 0.5 μm, (b) 1 μm, (c) 2 μm, (d) 3 μm and varied $d_j$.

The analysis of three experimental results strongly suggests that the coarsening of CaS inclusions would be governed by the diffusion-controlled growth mechanism in laboratory conditions when Ca supply is sufficient for a limited time. After Ca evaporates, CaS inclusions may either stop growing or start to dissociate. Because of that, the growth will depend more on the Brownian collision. These findings are in line with the general trend, i.e., diffusion to collision transition reported in the previous studies [12,59], and should also be applicable to industrial conditions where the growth of CaS inclusions is not interfered by the steel flow. At the current stage, a mathematical model incorporating all coarsening mechanisms has not been established yet to predict the evolution of PSD of CaS inclusions. It will be the focus of a later study.

5.3. Coarsening Mechanisms of CaS Inclusions under Industrial Conditions

To determine the coarsening mechanism of CaS inclusions under industrial conditions, the effects of collision-related mechanisms on the rate of CaS volumetric population density were calculated using Equations (21)–(26).

The collision-related coarsening mechanisms in industrial conditions include Brownian motion, Stokes motion, and laminar and turbulent flows. For Equations (22) and (23), a constant viscosity of $2.55 \times 10^{-3}$ kg/(m·s) was used. The energy dissipation rate, $\varepsilon$, varies with operation conditions and locations in ladle and tundish. The exact values were not measured during the sampling of industrial heats available for this study. However, it was reported that when gas was injected at a rate of 8.4 m³/hr, the velocity gradient varied from 0.7 to 3.5 s⁻¹, and the energy dissipation rate was from 0.001 to 0.007 m²/s³ close
to the top of the ladle, where samples were taken [60]. Similar values were also reported in other studies [61,62]. With a similarly low Ar flow rate used in Heat 1, the velocity gradient, $\frac{du}{dy}$, of 2 s$^{-1}$ was used to calculate $\beta^C$, and $\beta^T$ was calculated using $\varepsilon$ equals $1 \times 10^{-3}$ m$^2$/s$^3$. The values of coagulation coefficient, $\alpha$, were estimated using the data reported for the steel-$\text{Al}_2\text{O}_3$ system by Taniguchi et al. [49], as data of the steel-CaS system were not available in the literature. The calculation was conducted for both the ladle and tundish samples of Heat 1. The data of 0.5 μm analysis was used as the input to calculate the rate of change $\frac{dN_V}{dt}$ due to collisions using PBE and compared with the apparent rate of change $\frac{\Delta N_V}{\Delta t}$. The values for $\frac{\Delta N_V}{\Delta t}$ were calculated through dividing the $N_V$ difference between the two samples by elapsed time between them. The comparisons are shown in Figure 14.

Figure 14. Comparison of the observed rate of change of CaS population density and the calculated rate of change of population density due to collision in the ladle at (a) 1 min and 2 min, (b) 3 min, and (c) 4 min after Ca addition, and (d) in tundish at 33 min after Ca addition.

Figure 14a shows that in the first three minutes after Ca injection started, the $\frac{\Delta N_V}{\Delta t}$ are evidently positive for inclusions lower than 2 μm. This is already shown in Figure 8. However, the calculated $\frac{dN_V}{dt}$ appears to be effectively a straight line, suggesting at the time that the combined effects of Brownian motion, Stokes motion, and laminar and turbulent flow cannot explain the growth of CaS inclusions. Considering that the actual PSD changes (red marks in Figure 14) are the results of growth by diffusion and coalescence, the authors suggest that during the first three minutes of Heat 1, the diffusion control would be the dominant mechanism for CaS inclusions growth. A similar explanation could be offered for the inclusion growth from 3 min to 4 min after Ca injection started, as shown in Figure 14b. The only exception is that the PBE predicted the PSD change due to collision to become slightly more noticeable compared to the earlier stages but is still lower than $\frac{\Delta N_V}{\Delta t}$. However, at the very end of Ca addition, similarities between $\frac{\Delta N_V}{\Delta t}$ and $\frac{dN_V}{dt}$ can be spotted. Starting from $d_{\text{avg}}$ equals 1.5 μm or higher (log($d_{\text{avg}}$) > 0.18), the observed and PBE predicted
number density change are generally the same in Figure 14c. The effect of diffusion was still significant, as disagreement can be found for the rate of change of inclusions smaller than 1.5 μm (log(d_{avg}) < 0.18). The peak of $\frac{\Delta N_v}{d t}$ in Figure 14c is not as apparent as that is in Figure 14a,b because of the negative $\frac{d N_v}{d t}$. The phenomenon in Figure 14c suggests that the effect of coalescence became comparable with diffusion only at the very end of the Ca injection process. No sample was taken from the ladle later than 5 min after Ca injection started, but based on the trend shown from Figure 14a–c, the similarity between curves of $\frac{\Delta N_v}{d t}$ and $\frac{d N_v}{d t}$ is highly likely to further increase.

In the tundish, the values of $\frac{\Delta N_v}{d t}$ drastically decreased compared to those for samples from the ladle. The change was less than 500 cm$^{-3}$s$^{-1}$ in all size groups, with the maximum value seen for inclusions with d_{avg} between 2 and 2.5 μm. This is again very different from the calculated $\frac{d N_v}{d t}$ due to collision and coalescence. This finding suggests that diffusion was still an important mechanism for CaS inclusions' growth in the tundish.

Overall, Figure 14 suggests that the growth of CaS inclusions in Heat 1 depended dominantly on diffusion-controlled growth at the early stage because the size of inclusions was small during this time. As the volume fraction of inclusions increased, the effect of collision and coalescence became comparable. There was a constant supply of Ca during injection [31], so CaS grew by Ca diffusion throughout the ladle-refining process. During the tundish treatment, even though the Ca injection stopped, the decreased temperature must reduce the extent of modification of CA and the solubility of Ca. Both prevented the dissolved Ca concentration from dropping; hence, CaS inclusions could continue growing through diffusion. The authors suggest that a similar route also occurred for Heats 3 to Heat 5. However, analyses provided in Figure 14 cannot be generated for those heats because only one sample was taken from the ladle, and the 0.5 μm analysis was not conducted.

The contribution of different collision-related coarsening mechanisms, i.e., Brownian motion, Stokes motion, and laminar and turbulent flow, can be quantified using the $\beta$ values. The comparisons are shown in Figure 15. $d_i$ and $d_j$ in Figure 15 include the range of CaS inclusions seen in the industrial samples.

![Figure 15](image-url)

**Figure 15.** Comparison of collision frequency function for Brownian motion, Stokes motion, and laminar and turbulent flow for an inclusion with a diameter $d_i$ of (a) 2 μm, (b) 3 μm, (c) 4 μm and varied $d_j$.

Figure 15 shows that the values for $\beta^T$ can reach up to $-14$ order of magnitude when one assumes the energy dissipation rate of $1 \times 10^{-3}$ m$^2$/s$^3$. The values for $\beta^T$ are always higher than those of $\beta^B$, $\beta^S$ and $\beta^G$. The values of $\beta^B$ and $\beta^G$ are about one order of
magnitude less regardless of the inclusion sizes. The values for $\beta^S$ can reach close to those for $\beta^T$ for some combinations of $d_i$ and $d_j$. For example, when $d_i$ and $d_j$ are equal to 2 $\mu$m and 5 $\mu$m, the values for $\beta^T$ and $\beta^S$ are $2.04 \times 10^{-15}$ and $7.6 \times 10^{-16}$ m$^3$/s, respectively (Figure 15a). In such a scenario, both mechanisms are responsible for the coarsening of CaS inclusions, while in other cases, the contribution of turbulent flow was dominant over the other three mechanisms. The significance of turbulent flow had also been reported in previous theoretical studies [60,63].

Overall, this study suggests that the coarsening mechanisms of CaS type inclusions followed the same route in experimental and industrial conditions. When there is sufficient Ca available at the early stage, diffusion-controlled growth is particularly critical. After more CaS inclusions formed, the increased collision volume and in some cases decreased dissolved Ca concentration made the coarsening process depend on collision-related coarsening mechanisms. As in the laboratory conditions, the dominant mechanism later becomes Brownian motion with the absence of flow. When the system is stirred like the industrial conditions, the turbulent flow will influence the coarsening process.

6. Conclusions

The coarsening mechanisms of CaS inclusions under experimental and industrial conditions were studied in this work. The findings are summarized as follows:

1. Under the experimental conditions, the coarsening rate of CaS inclusions is initially controlled by the Ca diffusion. As experiments proceed, the rate of diffusion-controlled growth decreases with the rate of Ca transport due to the decrease in Ca concentration in steel. During the same time, the volume fraction of CaS inclusions increases, and the Brownian motion becomes a controlling coarsening mechanism.

2. Determining the coarsening mechanisms based on the similarities between the observed and the calculated diameters of inclusions has the limitation of not incorporating the effect of each mechanism when the growth of inclusions depends on multiple mechanisms for an extended time. Hence, such a method may be only appropriate if there is limited or no mechanism change or the transition time is short, as seen in some experiments.

3. The increasing importance of the collision-dependent coarsening mechanism also occurs in industrial conditions. Because of the stirring effects in ladle and tundish, the turbulent flow becomes responsible for the CaS size change sometime after Ca injection starts. Because of the stable Ca supply during Ca injection and the decrease in the modification extent of CA$_{x}$, the diffusion-controlled growth remains important during both ladle and tundish treatments.

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