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Optical Emission Spectroscopy
Pulse Distribution Analysis on Steel Production Samples

Accuracy, sample variation, spread in different samples and steel grades/routes

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Abstract

This thesis work aimed to contribute to the development of online characterization techniques for non-metallic inclusions in steelmaking. The study focused on assessing the precision and accuracy of the optical emission spectroscopy pulse distribution analysis (OES/PDA) technique using as reference light optical microscope (LOM) and scanning electron microscope (SEM).

Steel samples were collected from three different routes at SSAB Oxelösund steel mill, including vacuum degassing with aluminium or silicon as deoxidizers, and a direct route using magnetic stirring.

The precision study compared the inclusion index obtained from each burn spot within the same sample. The precision study includes two parts, the first one compared the dispersion of a set of samples when testing four and eight burn spots, and the second part all the samples were tested to determine the overall dispersion using four burn spots. This study revealed that samples with eight burn spots exhibited higher dispersion and higher average inclusion index, indicating potentially higher inclusion content in the middle section of the sample. Overall, the precision of PDA/OES was found to be satisfactory, with the possibility of further improvement by eliminating outliers.

The particle size distribution (PSD) and volume fraction of inclusions obtained from OES/PDA and LOM was compared, and it was observed that OES/PDA yielded higher values in most samples, suggesting limited agreement between the two techniques.

Comparing the results of OES/PDA with scanning electron microscopy (SEM) for PSD and volume fraction of inclusions showed relatively better agreement, although accuracy could not be described as entirely accurate.

The comparison of the B-factor indicated that OES/PDA generally provided lower values than SEM. SEM was more effective in capturing additions during the steelmaking process, while OES/PDA exhibited lower sensitivity.

Finally, the comparison of inclusion chemical composition between OES/PDA and SEM indicated significant disagreement, emphasizing that OES/PDA should not be utilized for this purpose.

The limited gathered data from the seven sampled heats indicate that OES/PDA is a precise tool that need more development to be consider accurate to be consider as a monitor tool during secondary metallurgy.
Sammanfattning

Detta examensarbete syftade till att bidra till utvecklingen av online-karakteriseringstekniker för icke-metalliska inneslutningar i ståltillverkning. Studien fokuserade på att bedöma precisionen och noggrannheten hos OES/PDA-tekniken (Optical Emission Spectroscopy Pulse Distribution Analysis) med hjälp av ljusoptiskt mikroskop (LOM) och svepelektronmikroskop (SEM) som referens.

Stålprover samlades in från tre olika produktionsvägar vid SSAB Oxelösunds stålverk, inklusive vakuumavgasning med aluminium eller kisel som deoxidationsmedel, och en direkt produktionsväg med magnetisk omrörning.

Precisionsstudien omfattar två delar, den första jämförde spridningen av en uppsättning prover vid testning av 4 och 8 brännfläckar, och den andra delen testades alla prover för att bestämma den totala spridningen med 4 brännfläckar. Denna studie visade att prover med 8 brännfläckar uppvisade högre dispersion och högre genomsnittligt inkluderingsindex, vilket tyder på potentiellt högre inkluderingsinnehåll i den mellersta delen av provet. Precisionen för PDA/OES var överlag tillfredsställande, med möjlighet till ytterligare förbättringar genom att eliminera avvikande värden.

Partikelstorleksfördelningen (PSD) och volymfraktionen av inneslutningar som erhållits från OES/PDA och LOM jämfördes, och det observerades att OES/PDA gav högre värden i de flesta prover, vilket tyder på begränsad överensstämmelse mellan de två teknikerna.

Jämförelsen av resultaten från OES/PDA med svepelektronmikroskopii (SEM) för PSD och volymfraktion av inneslutningar visade relativt bra överensstämmelse, även om noggrannheten inte kunde beskrivas som bra.

Jämförelsen av B-faktorn visade att OES/PDA i allmänhet gav lägre värden än SEM. SEM var mer effektivt för att fånga upp tillskott under ståltillverkningsprocessen, medan OES/PDA uppvisade lägre känslighet.

Slutligen visade jämförelsen av den kemiska sammansättningen mellan OES/PDA och SEM på betydande oenighet, vilket understryker att OES/PDA inte bör användas för detta ändamål.

De begränsade data som samlats in från dem sju utvalda härdarna indikerar att OES/PDA är ett exakt verktyg som behöver utvecklas ytterligare för att anses vara korrekt som ett övervakningsverktyg under sekundärmetallurgi.
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1 Introduction

The production of steel is an important industrial process that has had a major impact on the development of modern society and has been an important source of income for many countries and their citizens. Steelmaking involves converting iron ore and other raw materials into steel through various process steps such as blast furnace, basic oxygen furnace, and electric arc furnace [1]. According to the World Steel Association, global steel production reached 1,832 million tons in 2022 (4.4 million tons produced in Sweden) [2]. To produce steel effectively, it is necessary to monitor and control a long list of process parameters to achieve optimal casting conditions and ensure the final product has the desired chemical composition and mechanical properties. The parameters that influence the steelmaking process include temperature, chemical composition, and the level of steel cleanliness [3]. The cleanliness of steel is determined by factors such as the numbers, size distribution, chemical composition, and morphological characteristics of non-metallic inclusions [4]. The correct control of inclusion is important to avoid problems such as clogging during casting [5], surface [6], and internal [7] defects in the cast product, and deterioration of the mechanical properties [8] of the final product. Unexpected material failure due to low inclusion control can not only have a major economic effect, but also be a threat to the lives of the people and the environment that interacts with it.

The methods for monitoring these process parameters can be classified into two categories based on the time taken to procure the results. The first category, known as "offline tools", require several hours to days to produce results. Because of this time constraint, the data generated cannot be employed for modifications during the heat production process. Nonetheless, these offline tools supply valuable and reliable information that can be used for subsequent process modifications or enhancements. The second category is the "online monitoring tools". These tools generate results within minutes, which makes it possible to adjust process parameters during the heat production process itself. This real-time data can be instrumental in making necessary amendments to optimize the production process [9]. Temperature is gauged utilizing disposable thermocouples, providing a reliable means of monitoring thermal variations during the process. The chemical composition, on the other hand, is determined by employing spectroscopic equipment on steel samples obtained during the process. This procedure allows for a precise chemical breakdown of the
samples. Further, the characteristics of inclusions can be inferred from the data procured during the chemical composition analysis. This process provides valuable insights into the non-metallic inclusions and their impact on the steel production process.

Online monitoring of temperature and chemical composition is not a challenge nowadays for most steel producers, but the online monitoring and control of non-metallic inclusions is a topic that is being investigated by steel plants and research groups [8]–[13]. There are two online tools that have been the topic of studies looking to develop fast characterization methods for non-metallic inclusion. These are laser-assisted plasma spectroscopy and optical emission spectroscopy pulse distribution analysis (OES/PDA) [9]. The second one, OES/PDA, provides information about inclusion size, inclusion size distribution, inclusion composition, insoluble part (B factor), and total oxygen content. To assess the accuracy of the OES/PDA, its results have been compared with offline characterization tools such as light optical microscope, scanning electron microscope, and electrolytic extraction [10]–[14], [16].

1.1 Aim and scope of the thesis

The proposed study aims to aid in developing of online characterization tools for non-metallic inclusions by evaluating the precision and accuracy of the OES/PDA for SSAB Oxelösund. Samples were collected from three different production routes during the secondary metallurgy process and at the initial stage of casting. To assess the precision of the OES/PDA, measurements were conducted four times per sample. The accuracy of the technique was evaluated by comparing the particle size distribution, B factor, and inclusion composition obtained from the OES/PDA with those obtained from Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM). The study provides valuable insights into the effectiveness of the OES/PDA in characterizing non-metallic inclusions.

1.2 Environmental and social aspects

Steel products are used across a diverse range of industries and applications, including but not limited to construction, shipbuilding, heavy machinery, pressure equipment, pipes, and other metal structures. As such, steel is constantly engaged in a dynamic interaction with both communities and the environment. It is therefore imperative that the steel utilized for these purposes adheres to specified requirements to prevent any unexpected material failure that could risk human life and the environment. This is especially critical in industries such as
automotive and construction, where the failure of a single component can result in catastrophic consequences. The production of steel requires meticulous monitoring and control throughout the entire process to ensure appropriate mechanical properties, chemical composition, and low non-metallic inclusion content. The attainment of low non-metallic inclusion content is particularly crucial, as it typically has an adverse impact on ductile fracture, fatigue, and corrosion behavior [8]
2 Literature Review

2.1 Steelmaking at SSAB Oxelösund

A simplified schematic of SSAB Oxelösund is presented in Figure 2-1. In the blast furnace, iron ore, limestone, coke, and oxygen-enriched air are supplied in a counter-current configuration (solid moving from top to bottom and air moving from bottom to top). In the blast furnace, the iron ore pellets are reduced by carbon monoxide in a series of reactions that transform magnetite ($\text{Fe}_3\text{O}_4$) and hematite ($\text{Fe}_2\text{O}_3$) into iron. The end products of this process are hot metal, slag, and combustion gases. The hot metal is transported to the steel mill (Stålverk) with torpedoes. In the torpedoes, the sulphur content in the hot metal is reduced by performing a desulphurization pre-treatment with calcium carbide. The next step in the production process is the Linz and Donawitz converter (LD-converter). The LD-converter, also known as basic oxygen furnace, is the last step before secondary metallurgy, and converts the incoming hot metal into low-carbon steel. The main reactions that the hot metal undergoes are the oxidation of carbon, silicon, manganese, and phosphorus [17]. After the LD-converter, there are two possible routes depending on the steel grade that is being produced: the direct route (dash line Figure 2-1) or the vacuum route (solid line Figure 2-1). The direct route is characterized by using the ladle furnace (LF) to adjust the temperature and composition. The vacuum route includes a vacuum tank degasser (VTD) that allows the production of exceptionally clean steel. The last step, continuous casting, is performed via tundishes, and the resulting steel slabs are sent to the integrated rolling mill or to the rolling mill in Borlänge.

![Figure 2-1: Schematic production SSAB Oxelösund [18].](image)

2.2 Secondary Metallurgy

Secondary metallurgy is a group of processes implemented to transform the liquid steel from the converter into liquid steel with the correct temperature and
composition for continuous casting [19]. Secondary metallurgy has three main tasks [20]:

1. Adjust the alloying element to meet the steel grade specification
2. Adjust the temperature to ensure correct solidification during continuous casting

During secondary metallurgy, temperature drops due to heat loss by radiation, mainly from the top surface, and to keep the temperature within acceptable levels, graphite electrodes are used to generate an electric arc that heats the melt. Another source that contributes to increase the melt temperature are exothermic reactions between dissolved elements and deoxidizers.

3. Impurity removal

Impurities in steel originate from various sources, such as liquid iron (which typically contributes phosphorus (P) and sulphur(S)), scrap metal (adding P, S, and tramp elements), ambient air (introducing hydrogen (H), oxygen (O), and nitrogen(N), and refractory materials. Each specific steel grade has a critical concentration threshold for each of these elements, which must be adhered to before the steel reaches the continuous casting stage. Oxygen removal plays a key role in the production of high-quality steel. The equilibrium between carbon, oxygen, and carbon monoxide varies depending on the temperature and pressure of the system and can be derived from the chemical reaction between carbon-oxygen-carbon monoxide (equation (2.1) and (2.2) and their variation of the standard free energy of oxidation [19].

\[ C + O = CO(g) \]  
\[ K \propto \frac{1}{T}, \quad K = \frac{P_{CO}}{C_{o} \cdot C_{C}} \]

An increase in temperature decreases the equilibrium constant and increases the amount of dissolved carbon and oxygen in the melt. In the same line, an increase in the carbon monoxide partial pressure will increase the amount of dissolved carbon and oxygen in the melt. But if there is a decrease in temperature, which is the case during solidification, the system will tend to from carbon monoxide (gas outburst). The formation of carbon monoxide is undesirable during solidification; therefore, it is necessary to reduce the dissolved carbon or, preferably, the dissolved oxygen. Oxygen can be removed by adding elements that have a higher affinity for oxygen, which are called deoxidizers [19], [20].

The most common deoxidizer elements are aluminium, silicon (ferrosilicon), and manganese (ferromanganese). These deoxidizers are commonly added in
wire form, which is the SSAB case, but they can also be added in powder form. The general chemical equation (2.3) that describes the deoxidation process is:

\[ a \text{Me} + b \text{O} = Me_a O_b \]

Where ‘Me’ is the deoxidizer element, ‘a’ and ‘b’ are the stoichiometric coefficients. For aluminium, the oxide that is formed is alumina \( (Al_2O_3) \) and for silicon, it is silica \( (SiO_2) \). Once the deoxidizer element is dissolved in the steel melt, it reacts with the dissolved oxygen, leading to the nucleation, precipitation, and growth of the oxides [21]. This part is controlled by the diffusion of the elements. When the oxides have reached a large size, the growth rate will be controlled by the collisions in the turbulent flow [21]. Finally, the large oxide particles end up in the slag due to buoyancy effects, bubble attachment, and fluid transport [21].

Sulphur removal is another important task performed during secondary metallurgy due to the detrimental effect that it has on the mechanical properties. This element negatively affects toughness, ductility, workability, and weldability [22]. Sulphur removal is performed throughout the entire production line - starting from the blast furnace stage and continuing right through to the secondary metallurgy phase. Most of the sulphur is removed in the blast furnace; however, to obtain low sulphur contents, desulphurization in secondary metallurgy is necessary [23]. Desulphurization of the melt in secondary metallurgy is performed either by adding reagents containing elements with high affinity for sulphur, such as lime, magnesium, calcium silicide, or rare earth elements, or by having a slag with a high ability to remove sulphur from the melt [19]. The following chemical reactions (2.4 and 2.5) describe sulphur removal with reagents addition and removal by melt/slag interaction [19], [23].

\[ a \text{Me}_{\text{melt}} + b \text{S}_{\text{melt}} = Me_a S_{\text{slag}} \]

\[ \text{S}_{\text{melt}} + MeO_{\text{slag}} = MeS_{\text{slag}} + O_{\text{melt}} \]

The vacuum degassing route allows for the removal of certain problematic gases from the liquid steel. The main concerning gases are hydrogen and nitrogen, but it also helps to reduce further the oxygen and carbon content. The sources of hydrogen during steelmaking are air moisture and additives moisture, while the main nitrogen source is air.

Hydrogen poses two significant problems in the steelmaking process. Firstly, during the solidification or cooling stage, hydrogen gas molecules nucleate due to a decrease in solubility, resulting in an abrupt rise in pressure that leads to the formation of cracks, known as hydrogen flakes. Secondly, hydrogen being
an interstitial element, can increase yield strength but decreases ductility significantly, and this phenomenon is referred as hydrogen embrittlement [24]. Similar to hydrogen, nitrogen gas can nucleate and form subsurface pores during solidification or cooling. Moreover, unbounded nitrogen atoms can contribute to aging brittleness [24].

The vacuum treatment technology employed at the Oxelösund steel mill utilizes a vacuum tank system. This system involves placing the entire ladle inside a vacuum tank. To expedite the degassing reactions within this setting, argon gas is introduced to facilitate stirring.

2.3 Non-metallic Inclusions

Non-metallic inclusions (NMI) are phases that are formed during the steelmaking process from the combination of metallic elements (such as iron, aluminium, silicon, manganese) with non-metallic elements (such as oxygen, nitrogen, hydrogen, and sulphur) [25], [26]. NMI are considered essential in the task of producing clean steel, because their formation helps to remove non-desire elements and the proper removal of the inclusions affects both the process control and the mechanical properties [27]. Therefore, it is important to understand and study NMI, which can be categorized according to its origin, chemical composition, and morphology [26].

2.3.1 Endogenous and Exogenous Non-Metallic Inclusions

Endogenous inclusions are originated during the steelmaking process. These types of inclusions are deoxidation products or precipitates that form during cooling and solidification of the steel. The inclusions that come from the deoxidation process are the result of aluminium or silicon addition to the liquid steel that contains dissolved oxygen, then these two metallic elements react with the oxygen forming alumina ($\text{Al}_2\text{O}_3$) and silica ($\text{Si}_2\text{O}$). Ideally, all the newly formed inclusions are removed with the slag; Nevertheless, a fraction of these inclusions will remain in the liquid steel [20], [28]. Regarding precipitated inclusions, during the cooling and solidification process, dissolved elements such as oxygen, nitrogen, and sulphur increase their concentration in the liquid (segregation) while their solubility decreases with the temperature. The result is the precipitation of inclusions such as alumina, silica, nitrides, and sulphides [28].

Exogenous inclusions, as its name implies, are those inclusions appearing from external sources [26]. These external sources of inclusions are (1) the reoxidation of the melt by contact with air or an oxidizing slag and (2) the
interaction of the mechanical interaction of the melt with the refractory lining and the slag [20], [28], these sources are well represented in Figure 2-2. According to L. Zhang and B.G. Thomas [28], exogenous inclusions share the following common characteristics.

- Large size: up to several hundred micrometres.
- Compound composition or multiphase.
- Irregular shape.
- Fewer numbers compared with small inclusions.
- Significant negative impact in the steel properties due to their larger size.

![Figure 2-2: Schematic origin of formation of inclusions. A - Products of deoxidation and desulphurization; B - Reaction between slag and metal; C - Reoxidation due to contact with air; D - Reactions between slag and refractory; E - Reaction between melt and refractory [25].](image)

### 2.3.2 Morphology

The morphology of NMI is an important characteristic to investigate since it delivers information of their state of existence in the melt. This information can be used to investigate the formation and transformation of inclusions and their effects on the process and the mechanical properties of the final product [29].

NMI can be found in a wide range of morphologies, such as spheres/globular, elongated, polyhedral, dendrites, and clusters (See Figure 2-3) [30], [31].

![Figure 2-3: Illustration inclusion shapes [32].](image)
2.3.3 Chemical composition

Non-metallic inclusions can be classified depending on the non-metallic element that forms them. Non-metallic inclusions are classified as oxides, nitrides, sulphides, or compounds [33].

Oxide NMI are primarily formed during the deoxidation process, but additional oxide inclusions can enter the melt due to reoxidation or slag emulsification in the melt. Examples of simple oxides inclusions are iron oxide (FeO), manganese oxide (MnO), chromium oxide (Cr$_2$O$_3$), alumina (Al$_2$O$_3$) and silica (Si$_2$O). Also, these simple oxides can form compounds e.g., FeO·Al$_2$O$_3$, FeO·SiO$_2$, FeO·Cr$_2$O$_3$ [25], [34].

Sulphides NMI are the result of desulphurization and can also be formed during casting when the dissolved sulphur reacts with metallic elements. Desulphurization of the melt is the transferring of dissolve sulphur in the melt to a slag with high basicity. Dissolve sulphur during casting can react with elements such as manganese forming manganese sulphide, which is a soft inclusion that gets deformed during hot rolling ending up with an elongated morphology [35]. Examples of sulphide NMI are iron sulphide (FeS), manganese sulphide (MnS), aluminium sulphide (Al$_2$S$_3$). Also, these simple sulphides can form compounds e.g., FeS·FeO, MnS·MnO.

2.4 Off-line Investigation Methods

Off-line investigation methods refer to characterization techniques that require extensive time ranging from several hours up to months to obtain results; therefore, these results cannot be used to take immediate decisions on the process [9], [10]. Examples of off-line investigations methods are light optical microscopy (LOM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and x-ray diffraction (XRD). These methods have been used to study steel cleanliness and are proven to provide reliable results that can be used as validation method for other analyses under development [10], [13], [29], [36]–[39]. In the following sections SEM and LOM methods are described in more details.

2.4.1 Scanning electron microscopy (SEM)

The scanning electron microscope is a type of instrument that uses a highly focused electron beam to generate magnified images of the sample. The imaging of the sample surface ranges from 10 to 100,000x magnification and its resolution is normally 1 to 10 nm [40], [41].
A typical scanning electron microscope consists of four main components: the
electron-optics column, the specimen chamber, the support system, and the
control and imaging system [41]. The electron-optics column is responsible for
producing and narrowing the electron beam that will hit the sample surface. The
specimen chamber holds the sample and the primary detectors in a vacuum for
the imaging and analysis, these detectors are for secondary electrons (SE) and
backscattered electrons (BEs). The support system may vary depending on the
capabilities of the specific SEM equipment, but it is common to have water lines
to cool sensitive components, gas lines to perform the purge during the venting
process and to produce the vacuum that is needed for the correct operation.
Lastly, the control and imaging system is used to control the electron beam, the
image formation, sample positioning, and the vacuum operation [41].

The study of NMI characterization using SEM can be done by 2D or 3D
methods. Both methods have advantages and disadvantages, and the method
to use depends on the purpose of the study and available resources [29].

Traditional inclusion analysis is done by preparing a smooth surface on the
steel sample (2D method). This smooth surface can be obtain by polishing the
sample surface or by cutting a cross section of the sample [41], [42].

Several studies have used SEM and/or SEM automated tools to study non-
metallic inclusions [43]–[48]. For example, Capurro et al. [43] developed a
measuring tool based on SEM to characterize non-metallic inclusions. At the
beginning of the study, previous SEM data was collected to tune the measuring
tool. This tool was then used to follow several heats in a real steel mill. The
inclusions evolution in terms of their density, size distribution, chemical
composition, and solid fraction was analysed from the LF all the way to
continuous casting using lollipop samples. The gathered data led to conclude
that

1. NMI were homogenous close to the surface of the lollipop samples,
2. a scanning area of 100 mm² will guarantee low result dispersion for
   inclusion density, and
3. the oxygen content derived from the inclusion population was in good
   agreement with other measuring methods.

Another study from Zinngrebe et al. [44] focused on studying the evolution of the
inclusions population during the secondary metallurgy process (Vacuum
degasser-Stirring Station-Continuous Casting) of a Ti-alloyed Al-killed steel. To
study the inclusion population evolution, the researchers used SEM together
with an automated inclusions analysis (AIA), and the sampling was performed
before, during and after each station. The inclusion related data that was collected with the SEM was presented in particle density functions plots (PDF). From the PDF plots two types of curve shapes were seen alone or in combination, lognormal and power law. The lognormal shape denotes active nucleation, which can be due to deoxidation or reoxidation. The power law shape denotes that there is no deoxidation or reoxidation for some time, this means that there is chemical equilibrium between solutes and inclusions and that the size distribution is controlled by the breakup/coalescence of particles.

Even if traditional SEM has been a strong method to study NMI, the real morphology and size is better to be studied with 3D methods. 3D methods have the advantage of studying inclusions after extracting them from the steel matrix which allows to investigate the real morphology and size [29], [36], [49]. The available extraction procedures can be categorized in most cases in chemical and electrolytic methods. Chemical extraction dissolves the steel matrix using acids or halogen solutions while electrolytic extraction dissolves the steel matrix with the use of a galvanic cell and a correct electrolyte [29], [50].

R. Ying et al. [51] applied an automated particle analysis (ASPEX) to study NMI in steel samples coming from continuous casting. This analysis has the capability of providing morphology, size, position, and inclusion composition. In addition to this analysis, the inclusions morphology was studied by chemical extraction at different times. Even if ASPEX was able to provide morphology result with decent resolution, the morphology study by CE gave substantially better resolution and three-dimensional morphology. From the CE results and thermodynamic calculations, one of the conclusions was that during casting most oxide inclusions were solid, which increases the risk of clogging during casting. One limitation of the study regarding the use of CE is that this method is not suitable to study inclusions that are dissolve by the acid e.g., CaS and MnS. The work by Y. Wang et al. [29] consisted on studying three type of steel and ferroalloys using traditional 2D investigation, 3D investigation after electrolytic extraction (EE), and 3D investigation on a metal surface after electrolytic extraction (MS). The samples were first polished and prepared for 2D SEM observations on a cross-section. After the 2D SEM observation the polished surface was dissolved by EE, and the undissolved inclusions were filtered to study morphology, size, composition, and number distribution. The remaining surface after EE was used to study the surface after EE. The results of the study were: dissolution rate of metal samples during EE, inclusion
morphology, inclusion composition, and inclusion size and numbers. From the results they concluded the following:

1. The 2D SEM investigation provides faster results compared to the 3D investigation methods at the price of lower accuracy to determine inclusion morphology, size, and number of inclusions.

2. The EE 3D investigation is good to determine accurately inclusion morphology and to detect small size spherical and elongated inclusions.

3. The MS 3D investigation is suitable when big inclusions are the aim of the study.

Similar to 2D SEM investigation, 3D investigation methods have disadvantages. These disadvantages are that these methods can possibly break clusters into individual particles, the inclusions can get damaged, and that it requires considerably longer time to perform.

2.4.2 Light optical microscopy (LOM)

The light optical microscope is the most common instrument to study microstructure of ceramics, composites, metals, minerals, and polymers. Light optical microscopes work with a magnification from 50X to 1000X [52].

Light optical microscopes work under the same principle, i.e. a light source emits visible light, and a set of lenses magnifies an image from the sample surface. There are several illumination methods, for example bright-field illumination, dark-field illumination, and polarized light. The bright-field illumination method is used to study non-metallic inclusions on as-polished samples [52].

The Swedish standard SS 111116 together with the use of a light optical microscope allows the assessment and reporting of quantity, morphology, size, and size distribution of non-metallic inclusions. This standard is primarily intended to be used to detect inclusions in plastic wrought metallic materials, but can be also used to detect non-metallic inclusions from steel samples coming from the steel mill [53].

Sjöqvist T. et al. [54] studied the microstructure of two ferromanganese alloys by electron microprobe and light optical microscope. The study used 6 samples coming from casted products. The electron microprobe determined the type of inclusions (oxide, sulphide, and complex), while the light optical microscope provided the amount and volume fraction of inclusions. The obtained results using the SS111116 method revealed the following: the most abundant inclusion size was D heavy, dendritic manganese oxides were the most common
inclusion, and the inclusion volume fractions follows an inverse relationship with carbon content.

Malmberg K. et al. [55] compared three different stirring treatments during the production of tool steel to elucidate which treatment removes non-metallic inclusions the best. The three stirring treatments were: (1) induction stirring using 650 [A] current for 20 minutes, (2) induction stirring using 650 [A] current for 10 minutes, and (3) a combination of induction stirring with 650 [A] current with argon gas stirring (flowrate 10-20 [L/min]). The steel samples were taken before and after each stirring treatment. The inclusion content was investigated using the Swedish standard SS 111116. Inclusions type DM, DH, and DP were analysed, and it was found that using a combination of induction and argon gas stirring is the most efficient way to decrease all inclusion types.

2.5 On-line Investigation Methods

On-line investigation methods refer to the characterization techniques that require short times (5-30 minutes) to obtain results; Therefore, these results are used to control and take decisions during production [9]. Examples of on-line investigations methods are total oxygen (TO), laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS), and optical emission spectroscopy coupled with pulse distribution analysis (OES/PDA) [9].

The methods TO and OES/PDA are actively used to monitor the chemical characterization of each heat at the steel mill in Oxelösund. Several samples are taken and analysed with these two methods from the LD to the tundish to ensure that the chemical composition follows the specification sheet.

The methods LA-ICP-MS and OES/PDA can not only produce quick chemical composition results but also information regarding the inclusion content. Due to their potential significance in the production of clean steel, these two technologies have been the focus of several studies [10]–[15], [36], [56]–[58].

2.5.1 Optical Emission Spectroscopy – Pulse Distribution Analysis (OES/PDA)

Optical emission spectroscopy is a characterization method used for the quantitative determination of major and trace elements in numerous sample types [59]. The estimated analysis time ranges from 30 seconds to several hours depending on the sample preparation [59]. At SSAB sample preparation for OES is automated and allows to have results is less than 5 minutes.

The principle behind the OES equipment is illustrated in Figure 2-4 [12]. The following steps describe how this method operates. [12], [59].
1. The sample is exposed to a high-energy discharge of electric sparks that ablates material from the sample surface. The frequency of the electric sparks depends on the equipment.

2. The energy from the sparks excites the atoms in the ablated material resulting in changes in the energy of valance of the electrons in the outer shells. Each excited atom produces a specific emission spectrum when the elevated electrons go back to a stable level.

3. The light pulses contain the emission spectrum of all the elements present in the ablated material. This light is split by the diffraction grating, and the detection units measure the presence or absence for each element.

4. The gathered information is post-processed by a computer software that returns the results of the OES analysis.

![Figure 2-4: Schematic illustration of OES/PDA measurements [12].](image)

Pulse distribution analysis is based on the information that is gathered from the OES. The OES/PDA provides “pulsograms” (Figure 2-5), which display the intensity of each spark for each element. The intensity of each spark is directly proportional to the concentration of that element. The sparks that have an intensity higher than a certain number of standard deviations than the background intensity is considered to be inclusions. The standard deviation of each pulsogram is calculated by an iterative numerical method [12].
A study conducted at Outokumpu Stainless AB Avesta evaluated the NMIs characteristics in steel samples, the possibility to use OES/PDA as a control tool for their production, and a possible correlation between OES/PDA results with the slivers index of the final rolled product. The steel samples were taken during ladle treatment and from the tundish of 37 heats for two duplex stainless-steel grades. All the samples were tested using OES/PDA and samples from four heats were used for SEM analysis. The NMIs composition was compared between both techniques, and an expected difference was observed due to the statistical limitations with the OES/PDA method. The total oxide (alumina, calcium oxide, magnesium oxide) present in the ablated mass was calculated using the data from OES/PDA. The B factor calculated from the OES/PDA data was used to study the evolution of a specific element along the process. The main findings from this study describes the following.

1. OES/PDA could be used to compare the oxide content for the same process step and steel grade if more statistical data is gathered,

2. B factor value can used to follow the inclusion evolution and make metallurgical evaluations, and

3. A moderate correlation between the sliver index, the B factor value, and the number of inclusions larger than $4 \, \mu m$ [12].

A study conducted at SSAB special steels Oxelösund evaluated the characteristics of NMIs in steel samples taken along the production of two low-alloyed steel grades. The evaluation of NMIs characteristics was done using three analytical techniques: OES/PDA, SEM-INCA Feature, and Electrolytic extraction (EE) together with SEM. The average NMIs composition change along the process was performed by OES/PDA and SEM-INCA Feature. The EE + SEM technique evaluated the morphology, size, and composition of outer layer. The study concluded that the OES/PDA technique is suitable for the fast online evaluation of NMIs during steelmaking [10].
3 Experimental Method

3.1 Sampling

Three production routes were chosen to study the OES/PDA method. These routes are Al-deoxidized VTD (Vacuum Tank Degasser), Si-deoxidize VTD and direct route SU (Ladle Furnace). The total amount of steel samples is shown in Table 3-1. The designation of each steel sample was described in Table 3-2.

Table 3-1: Sample overview.

<table>
<thead>
<tr>
<th>Processing Route</th>
<th>Heat Number</th>
<th>Alternative name</th>
<th>Number of steel samples</th>
<th>Number of slag samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTD</td>
<td>59688</td>
<td>VTD 1</td>
<td>24</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>59689</td>
<td>VTD 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>59690</td>
<td>VTD 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VTD Si-deox</td>
<td>59789</td>
<td>1</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>59790</td>
<td>VTD Si-deox</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SU</td>
<td>60933</td>
<td>SU 1</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>60934</td>
<td>SU 2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The sampling process involves collecting both steel and slag samples at various production stages (Figure 3-1). Specifically, steel samples were taken on four occasions: thrice during secondary metallurgy and once at the onset of continuous casting. Concurrently, slag samples were collected during the secondary metallurgy phase. Figures 3-2 to 3-4 illustrate the sampling schematics for the three distinct routes. During "sampling 1" and "sampling 3", two steel samples were collected, while only a single steel sample was procured during "sampling 2" and casting. The additions of fluxing agents and/or alloying elements were described with a symbol “A”, The information mentioned in Table 3-3.
Figure 3-1: Steel sample (left), Slag sample (right).

Table 3-2: Samples name.

<table>
<thead>
<tr>
<th>VTD Al-deox Route</th>
<th>VTD Si-deox Route</th>
<th>SU Route</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTD (1,2,3) – 1.1</td>
<td>VTD Si-deox (1,2) – 1.1</td>
<td>SU (1,2) – 1.1</td>
</tr>
<tr>
<td>VTD (1,2,3) – 1.2</td>
<td>VTD Si-deox (1,2) – 1.2</td>
<td>SU (1,2) – 1.2</td>
</tr>
<tr>
<td>VTD (1,2,3) – 2</td>
<td>VTD Si-deox (1,2) – 2</td>
<td>SU (1,2) – 2</td>
</tr>
<tr>
<td>VTD (1,2,3) – 3.1</td>
<td>VTD Si-deox (1,2) – 3.1</td>
<td>SU (1,2) – 3.1</td>
</tr>
<tr>
<td>VTD (1,2,3) – 3.2</td>
<td>VTD Si-deox 1 – 3.2</td>
<td>SU (1,2) – 3.2</td>
</tr>
<tr>
<td>VTD (1,2,3) – CC1</td>
<td>VTD Si-deox (1,2) – CC</td>
<td>SU (1,2) – CC</td>
</tr>
<tr>
<td>VTD (1,2,3) – CC2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VTD (1,2,3) – CC3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-2: Schematic sampling during VTD Al-deoxidation.

Figure 3-3: Schematic sampling during VTD Si-deoxidation.
Table 3-3: Additions for each route.

<table>
<thead>
<tr>
<th>Route</th>
<th>VTD Al-deox</th>
<th>VTD Si-deox</th>
<th>SU</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Dolomite, Alumet, Burnt lime, Al-dabs</td>
<td>Dolomite, FeSi, Alumet, Burnt lime</td>
<td>Alumet, Burnt lime</td>
</tr>
<tr>
<td>A2</td>
<td>FeB, FeMn, FeNb, Al-dabs, FeTi</td>
<td>FeSi</td>
<td>FeB, FeNb</td>
</tr>
<tr>
<td>A3</td>
<td>Dolomite, FeMo, FeMn, FeCr, Al-dabs</td>
<td>FeMo, FeSi, FeMn, El mangan, uppkol, FeCr, FeV</td>
<td>Al-wire, C-wire, FeSi, FeMn</td>
</tr>
<tr>
<td>A4</td>
<td>Al-flip, C-wire</td>
<td>FeSi</td>
<td>FeTi, Al-wire, C-wire, CaFe</td>
</tr>
<tr>
<td>A5</td>
<td>CaSi</td>
<td>FeSi, FeMn, FeNb, C, FeCr, FeTi</td>
<td>-</td>
</tr>
<tr>
<td>A6</td>
<td>-</td>
<td>FeTi, C-trådb, CaSi</td>
<td>-</td>
</tr>
</tbody>
</table>

Each steel sample was subjected to OES/PDA, resulting in a total of 47 analyzed samples. Furthermore, 26 samples were examined using LOM, and 12 were inspected via SEM. In addition, slag samples were analysed for chemical composition with x-ray fluorescence (XRF).

3.2 OES/PDA analysis

3.2.1 Sample preparation

Samples for Optical Emission Spectroscopy/Particle Distribution Analysis (OES/PDA), often referred to as "lollipop" samples due to their characteristic appearance, require minimal preparation before testing. First, the "stem" was removed. Secondly, one of the faces of the steel sample was ground so a clean and flat surface was properly exposed for the analysis. The whole OES procedure, i.e. moving, grinding, and placing of the sample in OES equipment is performed by automatic robotic arms.
3.2.2 OES/PDA measurement device

All the steel samples were analysed using the Thermo Fisher ARL 8860 at SSAB chemistry laboratory facilities in Oxelösund. The ARL 8860 is a spark optical emission spectrometer, and the operational parameters are summarized in Table 3-4. According to the provided information from the laboratory, 79 [ng] of material is ablated per spark. All the data collected from the analysis was processed by SSAB internal OES/PDA software. In Figure 3-5 it can be seen a PDA sample that has been tested.

Table 3-4: Operational parameters OES.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Burn Spots</td>
<td>4</td>
</tr>
<tr>
<td>Integration Spark Frequency [Hz]</td>
<td>430</td>
</tr>
<tr>
<td>Integration Duration [s]</td>
<td>7.9</td>
</tr>
<tr>
<td>Spark Number</td>
<td>3397 (430 x 7.9)</td>
</tr>
</tbody>
</table>

Figure 3-5: Example PDA tested sample.

3.2.3 PDA method

The calculation procedure that is performed by the OES/PDA software was provided by the person in charge of the equipment at the chemistry laboratory. The following steps describe this procedure.

1. The first 500 sparks were removed from the analysis since it contained irrelevant information related with the surface preparation and/or contaminants.
2. All the sparks with low iron signals, less than 30%, were removed.
3. Normalization of matrix elements content to iron.
4. The high peaks due to inclusions increase the average and standard deviation significantly. For this reason, it was necessary to iterate this calculation, and remove the peaks with more than 3σ. Three iterations were performed before continuing.
5. Sparks with higher intensity than 3σ were selected (5σ for silicon)
6. The spark intensity was used to calculate the concentration of the elements
7. The intensity (or background intensity) coming from the matrix was subtracted
8. The known ablated mass was multiplied by the concentration of each element to obtain the mass of each element
9. Mass of inclusions was calculated using stoichiometry
10. Using inclusion density, the inclusions volume (size) assuming spherical shape was calculated. The weight and volume percentage were calculated.

3.3 Light optical microscope investigation

3.3.1 Sample preparation

The first step in sample preparation for the LOM investigation was cutting and mounting of the already tested PDA samples. The result can be seen in Figure 3-6.

![Figure 3-6: PDA samples cut and mounted.](image)

The second step was grinding, and it was performed by the grinding and polishing equipment Struers Tegramin-30. This equipment allows to grind up to six samples at the same time with minor user interaction reducing user error. The samples were grinded using a MD-Piano 120 grinding disk and cooled with water. All samples were grinded twice.

The third and last step in sample preparation was polishing, and it was performed by the same equipment. Samples were polished three times with three different disks. Each polishing lasts four minutes except for the last one, which lasts two minutes and twenty seconds. All the information regarding disks, lubricant, spray, and spray application time is summarize in Table 3-5.
### Table 3-5: Polishing parameters.

<table>
<thead>
<tr>
<th>Polishing Disk</th>
<th>First</th>
<th>Second</th>
<th>Third</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD-Allegro</td>
<td>MD-Dac</td>
<td>MD-Nap</td>
<td></td>
</tr>
<tr>
<td>Cooling media</td>
<td>DP-Lubricant-Blue</td>
<td>DP-Lubricant-Blue</td>
<td>DP-Lubricant-Blue</td>
</tr>
<tr>
<td>Spray</td>
<td>DP-Spray P 9(\mu)m</td>
<td>DP-Spray P 3(\mu)m</td>
<td>DP-Spray P 1(\mu)m</td>
</tr>
<tr>
<td>Time</td>
<td>4:00, 3:00, 1:00</td>
<td>4:00, 3:00, 1:00</td>
<td>2:20, 2:00, 1:00</td>
</tr>
</tbody>
</table>

#### 3.3.2 LOM investigation method

The Swedish standard SS 111116:2019 together with the microscope Olympus GX51 were used to quantitative investigate the inclusions content in each sample. The investigation procedure is the following:

1. The calibration was performed using a stage micrometer at 200X magnification
2. The field of view was set to 800 [\(\mu\)m] in diameter using the stage micrometer
3. The sample was marked at \(\frac{1}{4}\) of its width (See Figure 3-7). This point corresponds to the first field of view that was observed
4. The number of inclusions was counted, and the inclusion size was measured. The content of the field of view was registered according to the standard SS 111116
5. The movement to the next field was done following the pattern shown in Figure 3-7
6. The reading was repeated 100 times

![Figure 3-7: LOM investigation procedure](image)
3.4 Scanning electron microscope investigation

3.4.1 Sample preparation

The sample preparation for SEM is the same that was performed for LOM.

3.4.2 SEM Investigation method

The standard ASTM E2142 method 3 was used to as a guideline for the measurements.

Table 3-6 shows the parameters that were used for the SEM measurements of features.

<table>
<thead>
<tr>
<th>Run Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of analysed fields</td>
</tr>
<tr>
<td>Field Area [μm²]</td>
</tr>
<tr>
<td>Total analysed area [μm²]</td>
</tr>
<tr>
<td>Image width</td>
</tr>
<tr>
<td>Detector</td>
</tr>
<tr>
<td>Perform second pass</td>
</tr>
<tr>
<td>First pass dwell time [μs]</td>
</tr>
<tr>
<td>Second pass dwell time [μs]</td>
</tr>
<tr>
<td>Magnification</td>
</tr>
<tr>
<td>Exclude features smaller than</td>
</tr>
<tr>
<td>Detection mode</td>
</tr>
</tbody>
</table>

3.5 Precision study methodology

The precision study was done by comparing the "inclusion index" of each burn spot within a same sample. The inclusion index was calculated using the formula (3.1) [16]. The particle size distribution given by the PDA internal software was divided into 8 sections, which are: >0, >1.4, >2, >2.8, > 4, >5.7, >8, and >13.

\[
Inclusion\ Index = \sum_{i=1}^{8} (\text{Number of inclusions}_i \cdot \text{Inclusion diamater}_i)
\]

The average and standard deviation is calculated for each sample and the percentage of the standard deviation in relation to the average is also calculated to compare the dispersion between samples. There is not a general rule that indicates when a standard deviation value is low or high, it dependent on the interpretation of the data set. The data set was divided according to three
standard deviation “levels”. The “low” standard deviation values were considered below 10%, “mid” between 10% and 20%, and “high” over 20%.

3.6 Accuracy study methodology

3.6.1 Planar particle size distribution to volumetric particle size distribution calculation

The particle size distribution given by OES/PDA is volumetric while the particle size distributions given by LOM and SEM are planar. Therefore, these planar particle size distributions were transformed to a volumetric distribution using the mean diameter method [60], [61]. The mean diameter of spherical particles can be calculated with equation (3.2):

\[
\bar{d}_v = \frac{\pi}{2} \cdot \bar{d}_{A(H)} = \frac{\pi}{2} \cdot \frac{n}{\sum_{i=1}^{n} \left( \frac{1}{d_{Ai}} \right)}
\]

(3.2)

Where \( \bar{d}_{A(H)} \) is the harmonic mean diameter of the particle section, \( n \) is the number of particles, and \( d_{Ai} \) is the diameter of the \( i \)th particle in the polished section [60], [61]. Then, the number of particles per unit volume is calculated using equation (3.3) [60], [61]:

\[
N_v = \frac{N_A}{d_v}
\]

(3.3)

3.7 B factor calculation

The B factor is a quantitative way to measure the inclusion content in a sample. The B factor measures the mass fraction of an element that is in the form of inclusions [62]. The B factor is calculated with the following formula (3.4) [62].

\[
B_i = \left( \frac{0.5}{A} \right) \cdot \sum_{j=1}^{N} a_j \cdot c_j^i
\]

(3.4)

“A” is the total analysed area, \( a_j \) is the area associated with the inclusion \( j \), \( c_j^i \) is the mass fraction of the element \( i \) in the inclusion \( j \), \( N \) is the number of inclusions, and 0.5 is a density factor between the inclusions and the steel [62].
4 Results and discussion

In this section the main results are discussed. Additional results that are not needed to understand this document (i.e. extensive tables with chemical composition readings, and extra particle size distribution plots) are presented in the Appendix.

4.1 Precision study

As mentioned in section 3.2.2 each sample was read 4 times (i.e. 4 burn spots), but the samples from VTD 1 underwent an extra 4 reading after gridding a second time. Therefore, samples VTD1 1.1 to CC3 (Figure 4-1 (a) and (b)) have 8 reading and the rest of the samples have 4 reading (Figure 4-1 (c) and (d), Figure 4-2, and Figure 4-3).

Figure 4-1: Inclusion index VTD route. (a) first heat 1.1 to 3.1, (b) first heat 3.2 to CC3, (c) second heat, (d) third heat.
From these plots mixed results can be seen. Some samples show a low variation while other show significant outliers, e.g. the samples VTD 1 CC3 and VTD 1 Si-deox CC seem to have a low dispersion while the samples VTD Si-deox 1.2 and SU 1 3.1 seem to have a high dispersion. To not rely only on eye perception, the average inclusion index, and its respective standard deviation (SD), is presented for each sample from Table 4-1 to Table 4-7.

**Table 4-1: Precision study. Average and standard deviation VTD1.**

<table>
<thead>
<tr>
<th>Stage</th>
<th>1.1</th>
<th>1.2</th>
<th>2</th>
<th>3.1</th>
<th>3.2</th>
<th>CC1</th>
<th>CC2</th>
<th>CC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>15870</td>
<td>16939</td>
<td>21610</td>
<td>15228</td>
<td>18641</td>
<td>22049</td>
<td>20049</td>
<td>21525</td>
</tr>
<tr>
<td>SD</td>
<td>3265</td>
<td>2324</td>
<td>3989</td>
<td>1415</td>
<td>7305</td>
<td>1684</td>
<td>1079</td>
<td>1042</td>
</tr>
<tr>
<td>SD, %</td>
<td>20.6</td>
<td>13.7</td>
<td>18.5</td>
<td>9.3</td>
<td>39.2</td>
<td>7.6</td>
<td>5.4</td>
<td>4.8</td>
</tr>
</tbody>
</table>

**Table 4-2: Precision study. Average and standard deviation VTD2.**

<table>
<thead>
<tr>
<th>Stage</th>
<th>1.1</th>
<th>1.2</th>
<th>2</th>
<th>3.1</th>
<th>3.2</th>
<th>CC1</th>
<th>CC2</th>
<th>CC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>17708</td>
<td>18542</td>
<td>19259</td>
<td>12543</td>
<td>14523</td>
<td>25465</td>
<td>25365</td>
<td>27518</td>
</tr>
<tr>
<td>SD</td>
<td>3548</td>
<td>3461</td>
<td>1437</td>
<td>719</td>
<td>1582</td>
<td>2699</td>
<td>1357</td>
<td>1119</td>
</tr>
<tr>
<td>SD, %</td>
<td>20.0</td>
<td>18.7</td>
<td>7.5</td>
<td>5.7</td>
<td>10.9</td>
<td>10.6</td>
<td>5.3</td>
<td>4.1</td>
</tr>
</tbody>
</table>
The first objective was to analyze the effect of sampling four burn spots versus eight burn spots in the precision. The average and standard deviation with four burn pots for VTD 1 samples is presented in Table 4-8. By comparing both cases, in all samples the standard deviation with eight measures is higher.
than with four measurements. Additionally, the average value is also higher in all samples with eight measurements. It is important to mention that the four extra measurements were done after grinding the surface that contained the initial four measurements. C. Capurro et al. [43] compared the inclusion density depending on the depth using SEM and the results indicated that the depth does not affect the inclusion density. This result might indicate that the number of inclusions could not be homogeneous across the lollipop sample.

Table 4-8: Precision study. Average and standard deviation VTD1, 4 burn spots.

<table>
<thead>
<tr>
<th>Stage</th>
<th>1.1</th>
<th>1.2</th>
<th>2</th>
<th>3.1</th>
<th>3.2</th>
<th>CC1</th>
<th>CC2</th>
<th>CC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>15648</td>
<td>16349</td>
<td>20278</td>
<td>15174</td>
<td>14755</td>
<td>20841</td>
<td>19886</td>
<td>20607</td>
</tr>
<tr>
<td>SD</td>
<td>2780</td>
<td>1699</td>
<td>4679</td>
<td>784</td>
<td>1257</td>
<td>1087</td>
<td>955</td>
<td>494</td>
</tr>
<tr>
<td>SD, %</td>
<td>17.8</td>
<td>10.4</td>
<td>23.1</td>
<td>5.2</td>
<td>8.5</td>
<td>5.2</td>
<td>4.8</td>
<td>2.4</td>
</tr>
</tbody>
</table>

The second objective was to analyze the precision between different processing routes. The percentage of samples that have low standard deviation is 46% for VTD, 45% for VTD Si-deox, and 33% for SU. The percentage of samples that have mid standard deviation was 37% for VTD, 18% for VTD Si-deox, and 50% for SU. The percentage of samples that have high standard deviation is 17% for VTD, 36% for VTD Si-deox, and 17% for SU. If only the first sample from continuous casting is considered for all VTD heats these percentages will be 27, 50, and 22 for low, mid, and high standard deviation respectively, which is similar to the SU results.

Finally, it can be concluded that the routes VTD and SU have a higher precision compared to the VTD Si-deox route. The precision can be further improved if the outliers present in samples VTD1 – 2, VTD1 - 3.2, VTD Si-deox1 – 1.2, VTD Si-deox2 – 3.1, and SU1 – 3.1 are removed from the data set.

4.2 Accuracy study

The results from LOM and SEM were compared with the results from OES/PDA to assess the accuracy of the method. The particle size distribution from OES/PDA was compared with LOM and SEM. The B factor, and inclusion composition obtained from OES/PDA were compared with LOM and SEM.

4.2.1 Particle size distribution OES/PDA and LOM

The particle size distribution of six samples (two samples per route) is presented from Figure 4-4 to Figure 4-6. The six particle size distribution plots that were selected out of the 28 total are the ones with the best and worst
agreement between both techniques. All the other particles size distribution plots can be found in the appendix A.2.

Figure 4-4: PSD LOM VTD route. (a) Best agreement, (b) Worst agreement.

Figure 4-5: PSD LOM VTD Si-deox route. (a) Best agreement, (b) Worst agreement.

Figure 4-6: PSD LOM SU route. (a) Best agreement, (b) Worst agreement.

To facilitate the comparison between OES/PDA with LOM, the volume fraction of inclusions was calculated for each sample using equation (4.1) [61].

(4.1) \[
f_V = \frac{n}{6} \sum_{i=1}^{n} \left( \bar{d}_{vi} \right)^3 \cdot N_{vi}
\]

The volume fraction is calculated for each size division in the particle size distribution and summed to obtain the volume fraction of inclusion from that
sample. The results are displayed in Figure 4-7, and the line going across the plot is $x = y$.

Figure 4-7: Volume fraction OES/PDA vs LOM. (a) VTD route, (b) VTD Si-deox route, (c) SU route.
Additionally, the ratio between OES/PDA and LOM volume fraction is presented in Table 4-9, 4-10, and 4-11 for each route.

**Table 4-9: Ratio volume fraction PDA/LOM, VTD route.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio PDA/LOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTD 1 - 1.1</td>
<td>11.4</td>
</tr>
<tr>
<td>VTD 1 - 1.2</td>
<td>20.9</td>
</tr>
<tr>
<td>VTD 1 - 2</td>
<td>6.6</td>
</tr>
<tr>
<td>VTD 1 - 3.1</td>
<td>53.7</td>
</tr>
<tr>
<td>VTD 1 - 3.2</td>
<td>15.7</td>
</tr>
<tr>
<td>VTD 1 - CC1</td>
<td>12.3</td>
</tr>
<tr>
<td>VTD 1 - CC2</td>
<td>2.5</td>
</tr>
<tr>
<td>VTD 1 - CC3</td>
<td>8.2</td>
</tr>
<tr>
<td>VTD 2 - 1.1</td>
<td>105.0</td>
</tr>
<tr>
<td>VTD 2 - 2</td>
<td>257.2</td>
</tr>
<tr>
<td>VTD 2 - 3.2</td>
<td>115.5</td>
</tr>
</tbody>
</table>

**Table 4-10: Ratio volume fraction PDA/LOM, VTD Si-deox route.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio PDA/LOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTD Si-deox 1 - 1.1</td>
<td>16.6</td>
</tr>
<tr>
<td>VTD Si-deox 1 - 1.2</td>
<td>33.0</td>
</tr>
<tr>
<td>VTD Si-deox 1 - 2</td>
<td>13.0</td>
</tr>
<tr>
<td>VTD Si-deox 1 - 3.1</td>
<td>0.9</td>
</tr>
<tr>
<td>VTD Si-deox 1 - 3.2</td>
<td>2.9</td>
</tr>
<tr>
<td>VTD Si-deox 1 - CC</td>
<td>1.0</td>
</tr>
<tr>
<td>VTD Si-deox 2 - 1.1</td>
<td>7.2</td>
</tr>
<tr>
<td>VTD Si-deox 2 - 1.2</td>
<td>5.4</td>
</tr>
<tr>
<td>VTD Si-deox 2 - 2</td>
<td>111.9</td>
</tr>
<tr>
<td>VTD Si-deox 2 - 3.1</td>
<td>115.8</td>
</tr>
<tr>
<td>VTD Si-deox 2 - CC</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**Table 4-11: Ratio volume fraction PDA/LOM, SU route.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio PDA/LOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU 1 - 1.1</td>
<td>172.6</td>
</tr>
<tr>
<td>SU 1 - 1.2</td>
<td>86.9</td>
</tr>
<tr>
<td>SU 1 - 2</td>
<td>13.6</td>
</tr>
<tr>
<td>SU 1 - 3.1</td>
<td>31.8</td>
</tr>
<tr>
<td>SU 1 - 3.2</td>
<td>56.7</td>
</tr>
<tr>
<td>SU 1 - CC</td>
<td>6.7</td>
</tr>
</tbody>
</table>

These results indicate that OES/PDA tend to overestimate the number of inclusions for all samples except for VTD Si-deox1 – 3.1, and VTD Si-deox1 – CC.

**4.2.2 Particle size distribution OES/PDA and SEM**

The particle size distribution obtained from SEM includes oxide and sulphide non-metallic inclusions. Therefore, for each sample the particle size distribution
was plotted for the total number, for the oxides, and for the sulphides. The particle size distribution that are presented in Figure 4-8, Figure 4-9, and Figure 4-10 are the ones with the best and worst agreement between both techniques for each route. All the other particles size distribution plots can be found in the appendix A.2.

Figure 4-8: PSD SEM VTD route. (a)-(c) Best agreement, (d)-(f) Worst agreement.
Figure 4-9: PSD SEM VTD Si-deox route. (a)-(c) Best agreement, (d)-(f) Worst agreement.
The total volume fraction, oxides volume fraction, and sulphides volume fraction was calculated for each route. The results are plotted in Figure 4-11, and the line going across the plot is $x = y$. 
Figure 4-11: Volume fraction OES/PDA vs SEM. (a) VTD route, (b) VTD Si-deox route, (c) VTD Si-deox route zoom, (d) SU route.

Additionally, the ratio between OES/PDA and SEM volume fraction is presented in Table 4-12, Table 4-13, and Table 4-14 for each set of non-metallic inclusions.

### Table 4-12: Ratio volume fraction PDA/LOM, total inclusions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio PDA/SEM</th>
<th>Sample</th>
<th>Ratio PDA/SEM</th>
<th>Sample</th>
<th>Ratio PDA/SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTD 1 - 1.1</td>
<td>0.51</td>
<td>VTD Si-deox 1 - 1.1</td>
<td>0.38</td>
<td>SU 1 - 1.1</td>
<td>0.83</td>
</tr>
<tr>
<td>VTD 1 - 2</td>
<td>1.02</td>
<td>VTD Si-deox 1 - 2</td>
<td>0.80</td>
<td>SU 1 - 2</td>
<td>0.38</td>
</tr>
<tr>
<td>VTD 1 - 3.1</td>
<td>0.95</td>
<td>VTD Si-deox 1 - 3.1</td>
<td>0.02</td>
<td>SU 1 - 3.1</td>
<td>0.88</td>
</tr>
<tr>
<td>VTD 1 - CC1</td>
<td>0.17</td>
<td>VTD Si-deox 1 - CC</td>
<td>0.01</td>
<td>SU 1 - CC</td>
<td>0.16</td>
</tr>
</tbody>
</table>

### Table 4-13: Ratio volume fraction PDA/LOM, oxides inclusions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio PDA/SEM</th>
<th>Sample</th>
<th>Ratio PDA/SEM</th>
<th>Sample</th>
<th>Ratio PDA/SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTD 1 - 1.1</td>
<td>0.72</td>
<td>VTD Si-deox 1 - 1.1</td>
<td>0.38</td>
<td>SU 1 - 1.1</td>
<td>0.84</td>
</tr>
<tr>
<td>VTD 1 - 2</td>
<td>1.52</td>
<td>VTD Si-deox 1 - 2</td>
<td>0.80</td>
<td>SU 1 - 2</td>
<td>0.38</td>
</tr>
<tr>
<td>VTD 1 - 3.1</td>
<td>1.13</td>
<td>VTD Si-deox 1 - 3.1</td>
<td>0.03</td>
<td>SU 1 - 3.1</td>
<td>0.92</td>
</tr>
<tr>
<td>VTD 1 - CC1</td>
<td>0.18</td>
<td>VTD Si-deox 1 - CC</td>
<td>0.01</td>
<td>SU 1 - CC</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Table 4-14: Ratio volume fraction PDA/LOM, sulphides inclusions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio PDA/SEM</th>
<th>Sample</th>
<th>Ratio PDA/SEM</th>
<th>Sample</th>
<th>Ratio PDA/SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTD 1 - 1.1</td>
<td>0.0001</td>
<td>VTD Si-deox 1 - 1.1</td>
<td>34.87</td>
<td>SU 1 - 1.1</td>
<td>2.25</td>
</tr>
<tr>
<td>VTD 1 - 2</td>
<td>0.72</td>
<td>VTD Si-deox 1 - 2</td>
<td>0</td>
<td>SU 1 - 2</td>
<td>0/0</td>
</tr>
<tr>
<td>VTD 1 - 3.1</td>
<td>0/0</td>
<td>VTD Si-deox 1 - 3.1</td>
<td>0</td>
<td>SU 1 - 3.1</td>
<td>1.51</td>
</tr>
<tr>
<td>VTD 1 - CC1</td>
<td>0</td>
<td>VTD Si-deox 1 - CC</td>
<td>0.03</td>
<td>SU 1 - CC</td>
<td>0/0</td>
</tr>
</tbody>
</table>

Overall, these findings show better agreement when compared to the results obtained through LOM investigation. When considering all types of inclusions, the ratio of PDA/SEM tends to consistently underestimate the number of inclusions in comparison to SEM. Specifically, among the samples analysed, seven samples show a low value, indicating underestimation, while five samples demonstrate good agreement between the two methods. Similar trends are observed when analysing only oxide inclusions. In this case, eight samples underestimate the number of inclusions, while 4 samples show good agreement. On the other hand, when examining sulphide inclusions, the results are mixed. Three samples overestimate the number of inclusions, while six samples underestimate them. This underestimation can potentially be attributed to the predominance of MnS type sulphide inclusions. Given that Mn is a primary alloying element in these steel grades, constituting approximately 1%, its high content may complicate the detection of inclusions through OES/PDA methods.

The only instances where both techniques reached perfect agreement were in the samples where no inclusions were detected by either method.

4.2.3 B factor

The B factor was calculated for the elements that are relevant for the respective route, e.g. the B factor for silicon was only calculated for the VTD Si-deox route and not for the other two routes. The B factor of Al, Ca, and Mg was calculated for the VTD route (Figure 4-12), the B factor for Al, Ca, Mg, and Si was calculated for the VTD Si-deox route (Figure 4-13), and the B factor for Al, Ca, and Mg was calculated for the SU route (Figure 4-14).
The B factor obtained from OES/PDA for VTD route tend to be lower that the B factor calculated from SEM. However, the evolution of the B factor has certain similarity between both techniques. For aluminium, both techniques show a decrease of the $B_{Al}$ as the process progresses which is expected as aluminium inclusions form, grow and buoy toward the slag. The increase in $B_{Al}$ toward the end of the process can be explain by reoxidation and dissolution of the slag into the melt. For calcium, both techniques detect the addition of CaSi during calcium treatment, and the main difference is that SEM detected a higher increase. For magnesium, both techniques detect the addition of dolomite after the stage 1.1 and the continue decrease of this element.
The $B_{Al}$ evolution during VTD Si-deox route was almost identical except for the reading in stage 1.1. The presence of alumina inclusions in stage 1.1 should be low since the addition of alumet is done between stage 1.1 and 2, this means that the OES/PDA reading is significantly overestimating the number of aluminium inclusions. The $B_{Mg}$ increase after the addition of dolomite and subsequent decrease after vacuum treatment is correctly detected by SEM, but OES/PDA has almost no reaction to this process addition. The $B_{Ca}$ follows a similar evolution to the VTD route, and in the same way OES/PDA has a lower response. The results for VTD Si-deox additionally include the $B_{Si}$ since is the primary deoxidizer for this route. The $B_{Si}$ evolution between both techniques is significantly different. The evolution detected by SEM is reactive to the addition of FeSi and CaSi during the process, while the reading from OES/PDA has the complete opposite behaviour. The reason for OES/PDA to not detect silicon inclusions is due its algorithm. As mentioned in section 3.2.3 an inclusion is considered when the intensity peak is higher than three standard deviations, but for silicon the intensity peak must be five times higher. The reason behind this criterion is because the sensitivity for Si is worse than the other elements, thus, to be sure that the peak represent a real inclusion and not only a background reading the standard deviation criteria is set to five. This means that OES/PDA
is not a suitable tool for the detection of silicon inclusion, i.e. not suitable for steels that use silicon as deoxidizer agent.

The $B_{Al}$ for SU coincide in both cases in stage 3.1, but it is underestimated by OES/PDA in all the other stages. Regarding calcium, the addition of CaFe was performed just a minute before the sampling in stage 3.1, this means that the Ca reading should not be high for stage 3.1. The higher B-factor detected by OES/PDA during stage 3.1 may be attributed to the possibility that one of the burn spots coincidentally hit an area with a significant concentration of calcium. During the SU route, there was no addition of magnesium, then it is expected for the $B_{Mg}$ to decrease as the process progresses. The decrease of the $B_{Mg}$ was correctly detected by the SEM, however, the OES/PDA first detected an increase follow by a decrease.

The evidence suggests that the OES/PDA generally yields lower B factor results and is less sensitive detecting changes made during the process. The B-factor for aluminium showed the best agreement and further testing might indicate that OES/PDA could be used to monitor this element. Additionally, the presence of impurities can significantly impact its results.
4.2.4 Inclusion composition

The chemical composition of inclusions is an important characteristic to study. The composition of the detected features was investigated using SEM and compared with the composition reading from OES/PDA. The SEM reports provide these results for Ca-Al-S (VTD and SU route) and Ca-Al-Si (Si-deox route), and the PDA software allows the user to choose the elements to display. The Figure 4-15, Figure 4-16, and Figure 4-17 show the inclusion composition for the VTD route, VTD Si-deox route, and SU route, respectively.
Figure 4-15: Inclusion composition comparison VTD route. (a) 1.1, (c) 2, (e) 3.1, (g) CC1 SEM results. (b) 1.1, (d) 2, (f) 3.1, (h) CC1 OES/PDA results.
Figure 4-16: Inclusion composition comparison VTD Si-deox route. (a) 1.1, (c) 2, (e) 3.1, (g) CC1 SEM results. (b) 1.1, (d) 2, (f) 3.1, (h) CC1 OES/PDA results.
Figure 4-17: Inclusion composition comparison SU route. (a) 1.1, (c) 2, (e) 3.1, (g) CC1 SEM results. (b) 1.1, (d) 2, (f) 3.1, (h) CC1 OES/PDA results.

It can be seen that the agreement of OES/PDA with SEM is rather low in all samples, particularly for samples from Si-deox route due to the difficulty that
OES/PDA has detecting inclusions containing silicon. A big difference between both techniques is that SEM can label each individual inclusion to its corresponding chemistry while OES/PDA classifies inclusions in groups. The groups can contain multiple elements or single element inclusions. Janis D. et al. [12] found similar disagreement in ternary diagrams between SEM and OES/PDA and suggested that both techniques should not be compared since the results show a substantial difference regarding the inclusion composition.
5 Conclusions

The purpose of this thesis was to contribute to the investigation of the on-line characterization technique OES/PDA, which has the potential to enhance the control of steelmaking by providing information about the inclusion population. Steel samples were collected from three routes during the secondary metallurgy process: at the initial stage, in the middle, at the end of the process, and in the tundish at the beginning of continuous casting. These routes included vacuum degassing with aluminium as a deoxidizer, vacuum degassing with silicon as a deoxidizer, and a direct route utilizing magnetic stirring.

To assess the precision of OES/PDA, the study compared all the burn spots within the same sample. The particle size distribution (PSD) and volume fraction of inclusions obtained through OES/PDA were compared with the results obtained from light optical microscopy (LOM) and scanning electron microscopy (SEM). The B-factor and inclusion composition provided by OES/PDA were also compared with SEM. The outcomes of each comparison are as follows:

1) The precision study included two main aspects. Firstly, it examined the average and standard deviation of samples tested four times compared to those tested eight times. The additional four samples were obtained by grinding the surface containing the initial four burn spots. The findings revealed that samples with eight burn spots exhibited a greater dispersion and average, indicating the possibility of higher inclusion content in the middle section of the sample.

The second part of the precision study demonstrated that, overall, OES/PDA exhibited good precision. However, it was observed that the precision could be further enhanced by eliminating outliers.

2) When comparing the particle size distribution (PSD) and volume fraction of inclusions obtained from OES/PDA and LOM, it was found that OES/PDA yielded significantly higher values in 26 out of 28 samples. Only 2 samples exhibited good agreement between the two techniques. These results suggest that the comparison between OES/PDA and LOM may not be suitable.

3) When comparing the PSD and volume fraction of inclusions between OES/PDA and SEM, a relatively better agreement was observed compared to the comparison with LOM. However, it is important to note that the agreement between the two techniques cannot be described as entirely accurate.
In terms of the total number of inclusions, including oxides and sulphides, seven samples exhibited lower values when measured by OES/PDA compared to SEM. On the other hand, five samples showed good agreement between the two techniques. Analysing specifically the number of oxide inclusions, eight samples displayed lower values when measured by OES/PDA, while four samples showed good agreement. Regarding sulphide inclusions, six samples indicated lower values with OES/PDA, three samples displayed higher values, and three samples showed good agreement. It is worth noting that the instances of good agreement in this particular comparison were only observed when both techniques did not detect any sulphide inclusions.

4) The comparison of the B-factor between OES/PDA and SEM revealed that, in most cases, OES/PDA yielded lower values than SEM. The additions made during the steelmaking process were better reflected by SEM, while OES/PDA demonstrated less sensitivity to these additions. Nevertheless, a reasonable agreement was observed when comparing the B-factor for aluminium, indicating that further testing could determine whether OES/PDA can be utilized to monitor this particular element effectively.

On the other hand, the worst agreement was found when comparing the B-factor for silicon. This can be attributed to the stricter threshold that silicon peaks must surpass to be considered as inclusions (requiring five standard deviations compared to three standard deviations for other elements). As a result, OES/PDA cannot provide an accurate B-factor reading, especially for heats that employ silicon as a deoxidizer agent.

5) The final comparison focused on the chemical composition of the inclusions. The findings revealed a significant disagreement between OES/PDA and SEM in this aspect. The high level of disagreement indicates that OES/PDA should not be employed for determining the inclusion chemical composition.
6 Future work

It is advisable to subject all samples to SEM analysis, although this can be a time-consuming task for both the personnel at the microscopy laboratory and the individual responsible for analysing the resulting data. It is recommended to conduct a sampling campaign with a greater number of routes/steel grades and a larger sample size to ensure the statistical significance of the results. Furthermore, the utilization of electrolytic extraction in conjunction with SEM can provide supplementary information that cannot be obtained through 2D investigations.
7 Acknowledgments

I would like to thank my two supervisors Mats Söder (SSAB) and Björn Glaser (KTH) for the guidance and support. Also, I would like to highlight all the extra support that Mats Söder gave during these five months, such as taking me for tours around the steel mill, for introducing me to other colleges, for explaining me the theory behind steel production, and for helping me to analyse the results. Additionally, I want to thank Pär Jönsson (KTH) and Andrey Karasev (KTH) for providing me with relevant literature for my study.

Furthermore, I want to show my gratitude to Monica Jäger (SSAB) for helping me to understand OES/PDA, for letting me visit the chemistry laboratory, and for taking care of running the test.

Finally, I want to acknowledge the microscopy team for letting me use their facilities and specially to Jenny Bogne (SSAB) for teaching me how to read samples using LOM.
8 References


Appendix

Appendix A.1

The chemical composition for each sample presented in Table A-1, Table A-2, and Table A-3.

Table A-1: Chemical composition VTD route, wt.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>Al</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTD1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
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<td>0.297</td>
<td>1.183</td>
<td>0.007</td>
<td>0.0042</td>
<td>0.125</td>
<td>0.065</td>
<td>0.278</td>
<td>0.011</td>
<td>0.027</td>
<td>0.0004</td>
</tr>
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<td>1.2</td>
<td>0.126</td>
<td>0.301</td>
<td>1.186</td>
<td>0.007</td>
<td>0.0042</td>
<td>0.125</td>
<td>0.065</td>
<td>0.28</td>
<td>0.011</td>
<td>0.028</td>
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</tr>
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<td>0.0034</td>
<td>0.131</td>
<td>0.065</td>
<td>0.281</td>
<td>0.012</td>
<td>0.064</td>
<td>0.0002</td>
</tr>
<tr>
<td>3.1</td>
<td>0.154</td>
<td>0.306</td>
<td>1.309</td>
<td>0.008</td>
<td>0.0007</td>
<td>0.148</td>
<td>0.065</td>
<td>0.304</td>
<td>0.013</td>
<td>0.053</td>
<td>0.0002</td>
</tr>
<tr>
<td>3.2</td>
<td>0.155</td>
<td>0.309</td>
<td>1.315</td>
<td>0.008</td>
<td>0.0008</td>
<td>0.149</td>
<td>0.065</td>
<td>0.305</td>
<td>0.013</td>
<td>0.054</td>
<td>0.0002</td>
</tr>
<tr>
<td>CC1</td>
<td>0.159</td>
<td>0.319</td>
<td>1.316</td>
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<td>0.0008</td>
<td>0.15</td>
<td>0.066</td>
<td>0.306</td>
<td>0.013</td>
<td>0.048</td>
<td>0.0002</td>
</tr>
<tr>
<td>CC2</td>
<td>0.157</td>
<td>0.32</td>
<td>1.318</td>
<td>0.008</td>
<td>0.0007</td>
<td>0.15</td>
<td>0.066</td>
<td>0.306</td>
<td>0.013</td>
<td>0.05</td>
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<tr>
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<td>0.322</td>
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<td>0.0008</td>
<td>0.15</td>
<td>0.066</td>
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<td>0.05</td>
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<td>0.0048</td>
<td>0.119</td>
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<td>0.013</td>
<td>0.0004</td>
</tr>
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<td>1.188</td>
<td>0.007</td>
<td>0.0049</td>
<td>0.118</td>
<td>0.084</td>
<td>0.287</td>
<td>0.014</td>
<td>0.014</td>
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<td>0.125</td>
<td>0.084</td>
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### Table A-2: Chemical composition VTD Si-deox route, wt%.

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<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
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### Table A-3: Chemical composition SU route, wt%.

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<th>S</th>
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Figure 0-1: PSD plots OES/PDA vs LOM.

PSD vs LOM - SU 1 (1:2)

PSD vs LOM - SU 1 (2)

PSD vs LOM - SU 1 (5:1)

PSD vs LOM - SU 1 (2:5)

PSD vs LOM - SU 1 (2)

PSD vs LOM - SU 1 (1:1) Unipolar

PSD vs LOM - SU 1 (2:1) Unipolar

PSD vs LOM - SU 1 (2:3) Unipolar

PSD vs LOM - SU 1 (1:2) Unipolar

PSD vs LOM - SU 1 (2:5) Unipolar

PSD vs LOM - SU 1 (2:3) Unipolar

PSD vs LOM - SU 1 (1:2) Unipolar

PSD vs LOM - SU 1 (2:5) Unipolar

PSD vs LOM - SU 1 (2:3) Unipolar

PSD vs LOM - SU 1 (1:2) Unipolar
Figure 0-2: PSD plots OES/PDA vs SEM.