An Overview of Steel Cleanliness From an Industry Perspective

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INTRODUCTION

The most common parameter that relates to steel cleanliness is non-metallic inclusions, especially their composition, size and distribution. All steel contains some level of non-metallic inclusions, however not all are equally harmful. Small inclusions (< 4 μm) evenly distributed throughout the steel typically do not pose a problem; however inclusions that agglomerate to form clusters detrimentally affect the steel quality and performance. The level of cleanliness required for a specific operation depends on the application of the steel and the customer's expectations.

Steelmaking practices are typically developed to minimize the harmful inclusions that lead to steel defects. The effect of steelmaking practices on steel cleanliness is typically determined by total oxygen measurements, automated inclusion analyses by SEM, inclusion extraction techniques, Optical Emission Spectroscopy (OES) with Pulse Discrimination Analysis (PDA) and optical inspection systems. This paper will focus on how these techniques (individually and combined) are applied in a steel production environment to assess steel cleanliness and to measure the effect of process variables on steel cleanliness.

BACKGROUND

The processing of heats at the ladle station or degasser has been one of the key focus areas for research and study for many years as it relates to clean steel. The belief then and still today is that clean steel practices start in the ladle. A heat with high cleanliness could potentially stay clean during casting and result in a clean steel product. However, a marginal heat from the ladle refining station has very little chance of resulting in a clean steel product. The residence time and technology in the tundish and caster at this stage has limited ability to clean up the steel. The effects of the following parameters on clean steel in the ladle have been investigated in a number of studies:

1. Tapping practices and tap oxygen levels.[1-3]
2. Ladle slag composition (basicity, Al_2O_3 levels and %FeO+%MnO levels).[2,4-6]
3. Slagline and sidewall ladle refractories.[7-9]
4. Steel and slag deoxidation practices.[2,4]
5. Different alloy additions and types, and the timing of alloy additions.[10]
6. Chemical and electrical heating.[2]

7. The location and number of stir plugs in the ladle.[11-14]
8. Different stir mechanisms (Ar gas stir vs. EMS stir) and practices (impact of stirring time and intensity) at different stages of the refining process.[11,12]
9. The evolution of inclusions in terms of composition, size and amount during the processing of heats at the ladle station or the degasser.[4,15,16]
10. Desulfurization and steel sulfur levels.[4]
11. Ca treatment in terms of amounts, types of Ca sources, and method of injection or addition.[16,17]

The effects of these parameters on cleanliness have been evaluated using analytical techniques such as total oxygen measurements,[13,17,24] Optical Emission Spectroscopy (OES) with Pulse Discrimination Analysis (PDA),[19-24] and especially automated SEM inclusion analyses.[2,3,10,25-27] In combination with these techniques, thermodynamic modeling using propriety and commercial software, as well as water and CFD modeling, have been important tools to develop ladle refining practices for clean steel. Kaushik et al[18] wrote an excellent review paper comparing the different technologies. Also, portable OES units have been useful to classify slivers in the final product, determine the root causes of the defects and apply the appropriate corrective measures to minimize their occurrence.[28]

Over the last decade there has been a greater realization that the caster and the mold are equally important in terms of steel cleanliness. While the process of casting cannot make a dirty heat clean, it can certainly make a clean heat dirty. All the clean steel efforts at the ladle station can be undone by unfavorable conditions at the caster. Reoxidation is likely the major culprit and could have devastating effects on cleanliness, especially on Ca-treated heats.

Most of the clean steel practices in the ladle attempt to minimize the amount and size of deoxidation and reoxidation inclusions. In some cases the solid alumina or spinel inclusions are modified to liquid inclusions using Ca. The small (<10 μm) and discrete inclusions typically don't affect steel internal quality or mechanical properties but they could have an effect on electrical properties.[29] However, the quality of steel suffers when these small inclusions (solid or partially liquid) agglomerate (clog) due to mechanical forces (restricted metal flow through a slidegate or stopper rod), or chemical changes (reoxidation from air ingress or the environment). In extreme cases this is manifested as gross defects or slivers that can be detected with optical inspection systems and visual inspections by operators. Smaller inclusion agglomerations or clusters (100 to 1000 μm) that periodically break off and end up in the cast product are very difficult to detect or measure, especially when they are embedded deeper into the slab. These small agglomerations can re-appear at the most unfortunate time; i.e., when the final steel product is formed. Other "upset conditions" at the caster, such as entrapped mold powder or entrained tundish slag, could also result in micro and macro defects (slivers).

Inclusions are categorized in two categories - endogenous and exogenous. The small inclusions that originate from the steel are typically called endogenous or micro inclusions. Entrapped lining refractory and slag are called exogenous or macro inclusions. However, agglomerated endogenous inclusions due to a clogging event could also be classified as exogenous inclusions. Due to the significant impact of casting processes on steel cleanliness, the following parameters have been studied:

1. Argon purging or vacuum systems at the steel transfer points (ladle to tundish, tundish to mold).[30]
2. Extensive water and CFD modeling of metal flow in the tundish.[31-33,81]
3. Refractory furniture and impact pad systems.[34,35]
4. Tundish refractory materials, tundish covers, and basic tundish slags to minimize sources of oxygen.[4,36,37,80]
5. Ladle bottom designs and slag detection systems.[35]
6. Argon purging systems in the tundish.[35,38]
7. Different stopper rod tip designs and metal flow devices around stopper rod.[35,37]
8. CFD modeling of metal delivery in the mold.[33,39-41]
9. Different SEN designs and SEN seating systems.[42-44]
10. The impact of casting speed and SEN submergence depth.[48]
11. New mold level sensing and control systems.[45]
12. Electromagnetic stirring systems in the mold to direct metal flow and minimize mold level turbulence.[45-48]

The table below shows the critical size of the inclusion agglomerations that can typically be tolerated for different steel qualities[19,38,79]. Some of the very high quality grades also require total oxygen levels to be < 10 ppm. Some of the tolerated inclusion size levels listed in this table is now being challenged by more stringent demands by the customers. It is especially the increased use of AHSS (Advanced High Strength Steels) in the automotive industry ("lighter-stronger") and higher quality requirements that drives the quest for cleaner steel.[52]

Table I. Critical inclusions sizes for different steel grades

Steel Products (Slabs)	**Critical Size (um)**
Cold rolled sheet	240
UOE-Pipe	200
ERW-Pipe	140
IF Steel	100
DI-Can	50
Steel Products (Blooms)	
Cold Forgings	100
Steel Cord	30
Ball Bearing	15

This paper will highlight some of the findings on clean steel by other researches and also present some of the results from Nucor's experiences. The theoretical aspects of inclusion modification with Ca will not be discussed in this paper since it is the subject of another paper and the topic is well published.

ANALYTICAL EQUIPMENT AND SAMPLE PREPARATION

An ASPEX PSEM Explorer with a 30 sq mm LE EDS Detector was used for the automated SEM inclusion analyses in this work. Six polished lollipop samples could be loaded at time as shown in Figure 1. A 5x10 mm area was typically analyzed for routine analysis. The instrument was operated in three modes:

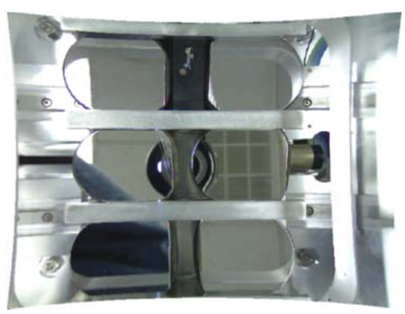


Figure 1. Sample holder and setup in the ASPEX SEM

- SD mode: Minimum inclusion size of 1.5 µm and step size of 1.2 µm for routine samples.
- HD mode: Minimum inclusion detection limit of 1 µm and a step size of 1 µm. This mode is used in special cases where solidification inclusions are very important or when the inclusion density in the steel is very low.
- Cluster mode: Minimum inclusion size of 10um, a larger area of sample to detect cluster formation.

In-house software was developed to create enhanced ternary plots that also allowed the selection and exclusion of foreign material and entrained ladle slag droplets from the analyses. Figure 2 show examples of foreign material (dust, dirt) detected on the surface of the sample. The two ternary plots most utilized for Al-killed steel are the Mg-Al-Ca diagram and the S-Al-Ca diagram (Figure 3). In both these plots MnS inclusions are excluded and they are plotted with the other sulfur containing inclusions on the S-Ca-Mn diagram (Figure 4a). The in-house software also generates density, volume and size distribution charts with the weighted inclusion composition for each sample (Figure 4b). Defects in steel products or any other SEM analysis on steel or refractory products were analyzed using a JEOL JSM-6490LV SEM with an EDAX detector.

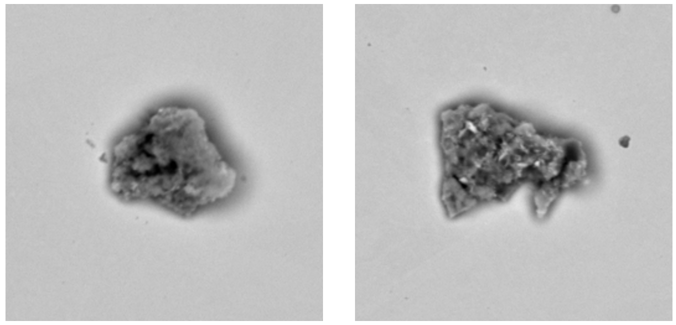


Figure 2. Examples of foreign material detected on the surface of the steel samples that are typically removed and excluded from the analyses

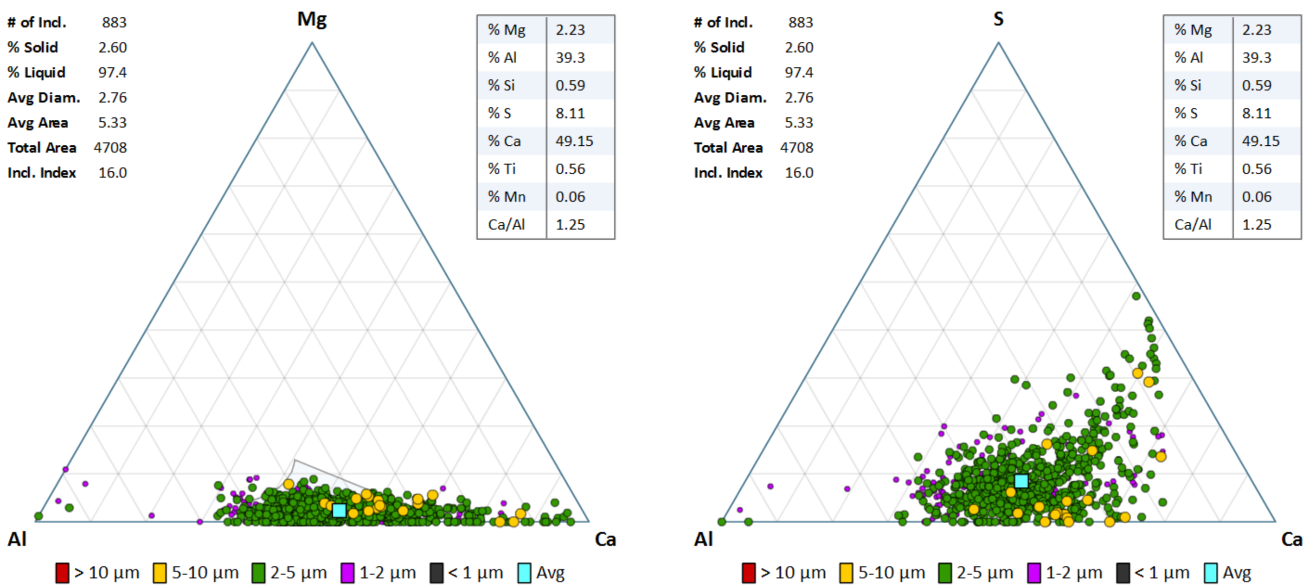


Figure 3. Examples of the two ternary SEM plots that are commonly used for inclusion evaluation.

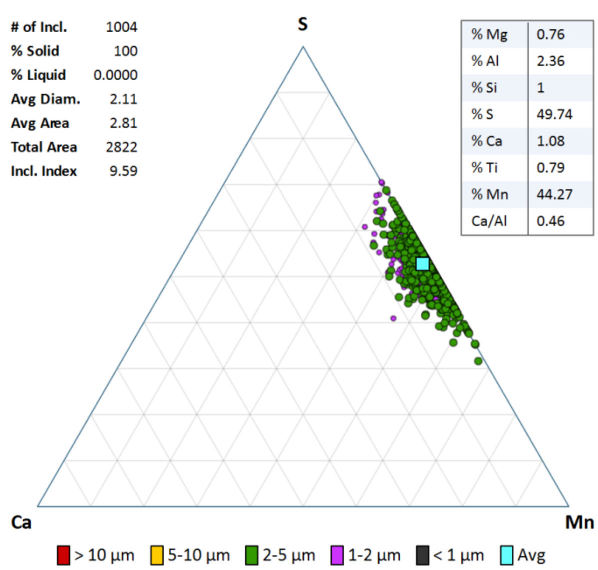


Figure 4a. S-Ca-Mn Ternary plot used for the display of sulfide inclusions. Oxide inclusions typically excluded

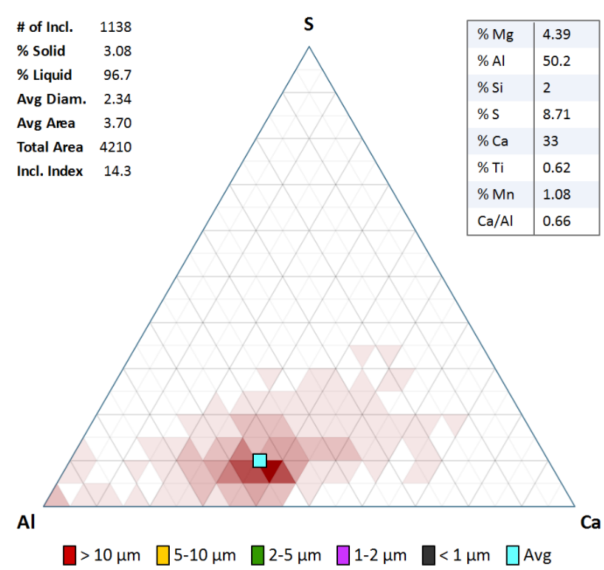


Figure 4b. Density plot of the inclusions in the S-Al-Ca diagram of Figure 3

A Thermo Scientific ARL 4460 metals analyzer equipped with the SparkDat option (Spark Digital Acquisition and Treatment) was used for the OES and PDA analysis (Pulse Discrimination Analysis) of select samples. Extensive trials were conducted with different sample preparation techniques which included milling of the samples and grinding with different media and grit sizes (the results from that study are beyond the scope of this paper). The best compromise in terms of sample preparation time and quality of results was the grinding of the samples. This also allows for the PDA analyses of strip samples, which were typically too thin for milling. A minimum of 4 burns were necessary for PDA analysis and often regrinding and more burns were required to get repeatable results. The best samples in terms of consistent repeatable results were strip samples, followed by tundish lollipop samples, followed by ladle lollipop samples.[52]

Steel sampling is typically done at the top of the ladle, which is unfortunately also the most reactive zone in the steel (slag/metal interactions, steel/atmosphere interactions, inclusion/slag interactions) so that representative sampling for inclusions is more of a challenge. A number of studies recommended the use of argon blowing devices to avoid slag entrapment.[23,24,53] A complete shutdown of the ladle gas stirring is also recommended for reliable samples, which is somewhat of a challenge in a high productivity shop. While the standard top of the ladle samples are good for SEM analyses since the results can be filtered for entrained slag, these samples are not that good for PDA analysis, since there is no ability to discriminate between inclusions and entrained slag in the results. Samples taken as deep as possible in the ladle and at the lowest possible stir, is in most cases a reasonable compromise.

An extensive comparative study of LECO total oxygen analysis versus PDA total oxygen analysis was also conducted and the results are shown in Figure 5. The total oxygen levels were measured using a LECO TC600 analyzer on filed TOS pins and punched strip samples. More total oxygen result comparisons are shown later in the paper. The PDA algorithms in the OXSAS software were extensively modified to match the type of steel grades produced and inclusions encountered in this study.

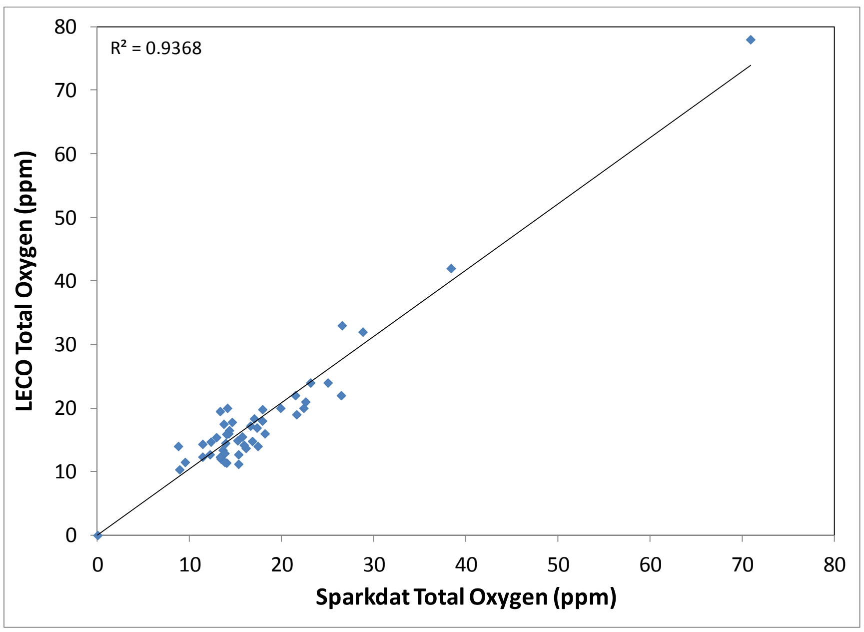


Figure 5. Comparison of Total Oxygen measurements (ppm) between LECO analysis and Thermo Sparkdat PDA analysis.

CLEAN STEEL PRACTICES AT THE LADLE REFINING STATION

The Role EAF/BOF Carryover Slag

Most steelmaking operations attempts to limit or control the amount of highly oxidized EAF or BOF slag (> 20% FeO) transferred to the ladle during taping. Since most of higher-end steel grades are Al-killed (reducing conditions) it is important to limit the amount of oxygen available from the slag to protect the Al in the steel and not cause Al reoxidation and further Al_2O_3 inclusion generation (Reaction 1).

$$2\ [Al] + 3\ (FeO) = Al_2O_3(incl) + 3\ [Fe] \quad (1)$$

(The [ ] denotes in solution in the steel and ( ) denotes in solution in the slag)

Some operations add slag deoxidants to lower the FeO levels in the ladle slag, while others only add flux materials to dilute the FeO levels in the slag to an acceptable range. For many operations a "white slag" practice is their mode of operation to make clean steel.

EAFs typically tap higher sulfur levels (> 0.02% S) than BOFs and require extensive desulfurization. This is achieved by vigorous stirring with basic, highly fluid and well deoxidized slags (%FeO + %MnO levels < 1%). These ladle slags are typically deoxidized with Al-based products or CaC_2. During the process of slag deoxidation and desulfurization significant Mg pickup from the slag occurs so that the inclusions change from alumina (Al_2O_3) to spinels ($MgAl_2O_4$).[2,10,15] Figure 6 shows the change in inclusion composition just after deoxidation with Al (Figure 6a) from alumina to spinel inclusions after desulfurization (Figure 6b). Trials were conducted where only CaC_2 or Al-based deoxidation products (high purity with low/no Mg) were used to kill the slag, but in both cases the final inclusions were spinels.

Since the slag is almost completely deoxidized in these operations, the potential of P reversion or Si reversion for Si-restricted grades, further limits the amount of tolerable carryover slag. These reversion reactions can also form Alumina inclusions as shown by the equations below:

$$2\ [Al] + 3\ (SiO_2) = Al_2O_3(incl) + 3\ [Si] \quad (2)$$

$$10\ [Al] + 3\ (P_2O_5) = 5Al_2O_3(incl) + 6\ [P] \quad (3)$$

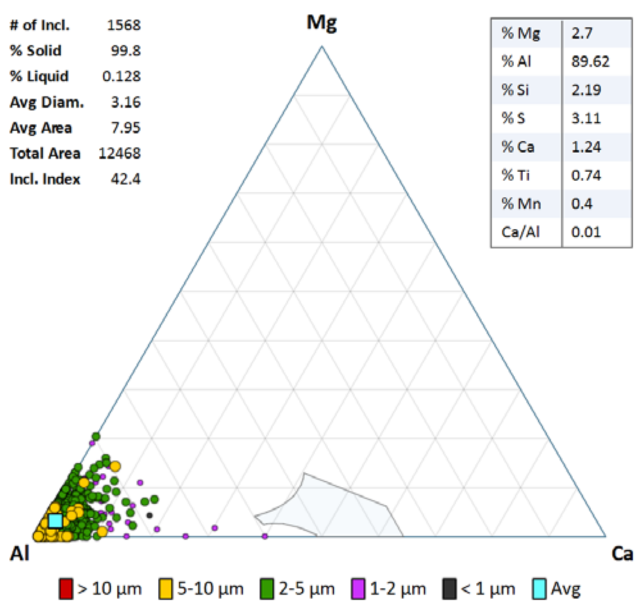


Figure 6a. Inclusion distribution just after Al-deoxidation of the steel.

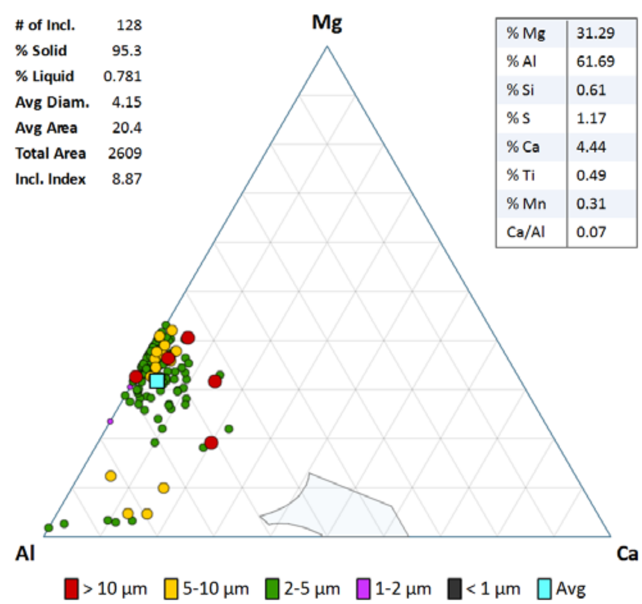


Figure 6b. Inclusion composition after desulfurization

Not all ladle refining operations require deoxidized slags. Some operations and grades (BOF and IF steel) require fairly oxidized slags to minimize Mg pickup. A detailed study by Story et al[2] using SEM inclusion data and slab surface inspection data, showed that when the FeO levels in the ladle slag dropped below 2% a significantly higher area fraction of alumina inclusions were observed. These low FeO slags also promoted higher area fractions of spinel inclusions, which can promote clogging. They concluded from their work that FeO levels between 8 and 15% FeO were optimal in terms of sliver diversion index and area fraction of Al_2O_3 inclusions for a specific operation. Figure 7a shows a gradual decrease in sliver index as the FeO level of the slag increases, and Figure 7b shows a significant increase Al_2O_3 inclusions when the FeO level in the slag is greater than 20% from their work.

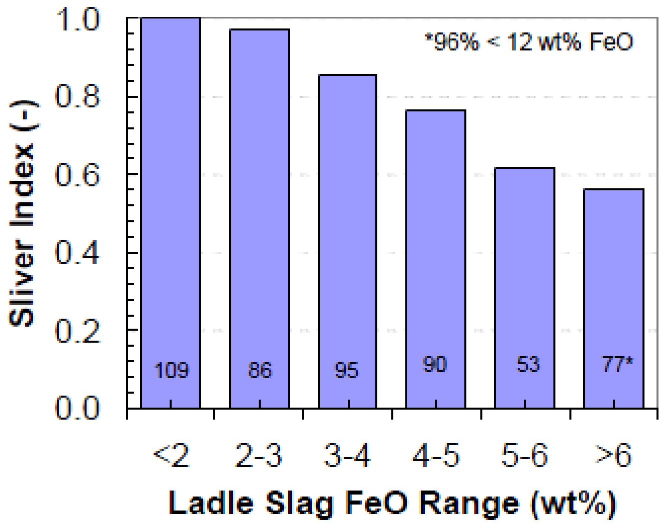


Figure 7a. Relationship between ladle slag FeO and frequency of sliver indications[2]

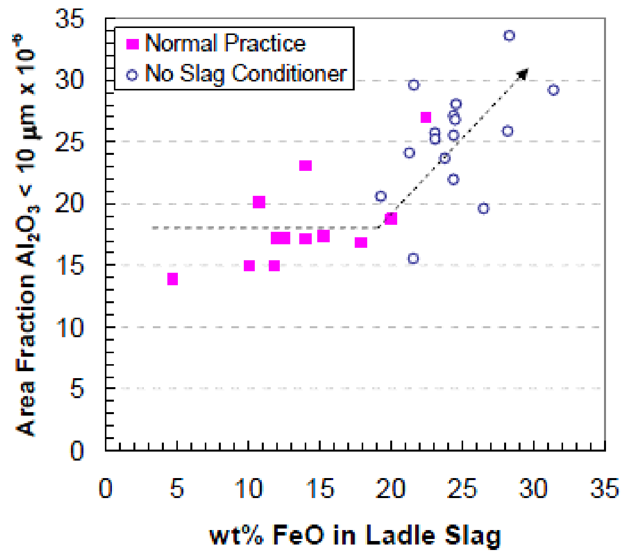


Figure 7b. Effect of ladle slag FeO on area fraction of Al_2O_3 inclusions < 10 um[2]

Figure 8, taken from the paper by Mendez et al[4] shows the effect of Slag FeO+MnO levels on the MgO content of the inclusions.

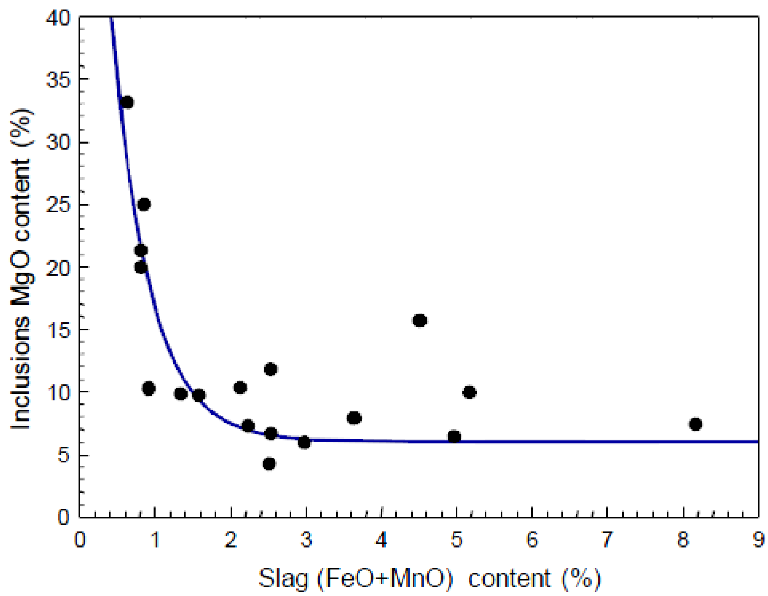


Figure 8. The effect of ladle slag (FeO+MnO) content on inclusions MgO content[4]

The Effect of Ladle Slag Composition on Inclusion Composition

Since all of Nucor's operations are EAF based, extensive steel desulfurization is a requirement for all flat products. The target slags are typically close-to or just CaO-saturated in order to maximize the S partition ratio. The MgO levels in slag are kept as low as possible to minimize the amount of Mg pickup in the steel during slag deoxidation and desulfurization. At elevated MgO levels in the slag (contamination) it was found that it is possible to form a significant amount of MgO inclusions in addition to the typical spinel inclusions. In this case, Figure 9a shows the inclusions in the steel before Ca treatment and Figure 9b the inclusions after treatment. Note that the spinel inclusions are modified by the Ca but the MgO inclusions are not. This mixture of solid and liquid inclusions from the ladle refining station results in clogging at the caster (stopper rod rise).

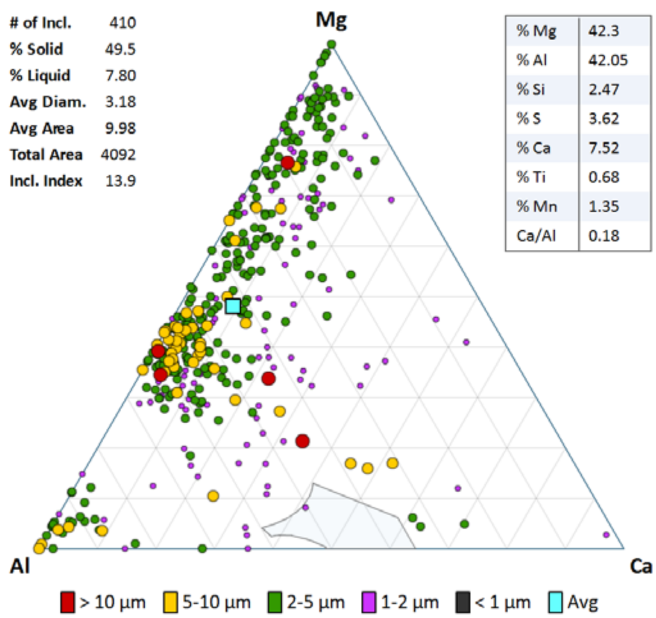


Figure 9a. MgO and spinel inclusions before Ca treatment

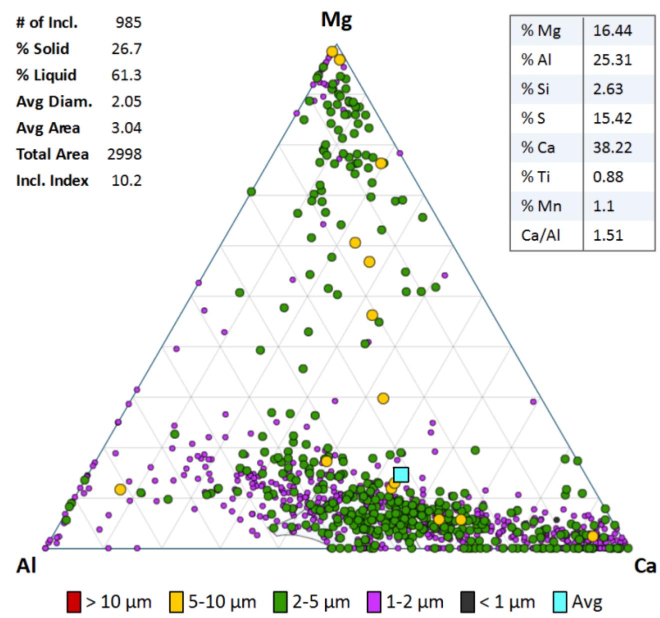


Figure 9b. MgO and liquid inclusions after Ca treatment

Tracking Inclusions Throughout The Ladle Refining Process

SEM analyses of ladle lollipop samples have been an effective tool to track the inclusion evolution throughout the ladle refining process.[16] A number of recent papers have shown the benefits of this technology because it shows the effects of certain ladle refining events on cleanliness.[56] Figure 10 show the change in inclusion composition for a heat that was tracked from initial steel deoxidation, through desulfurization, before and after Ca treatment, at the caster, and in the final strip. The L7 sample was taken directly after Ca treatment and the L8 sample was taken at the LMF after a 5 minute post Ca argon rinse.

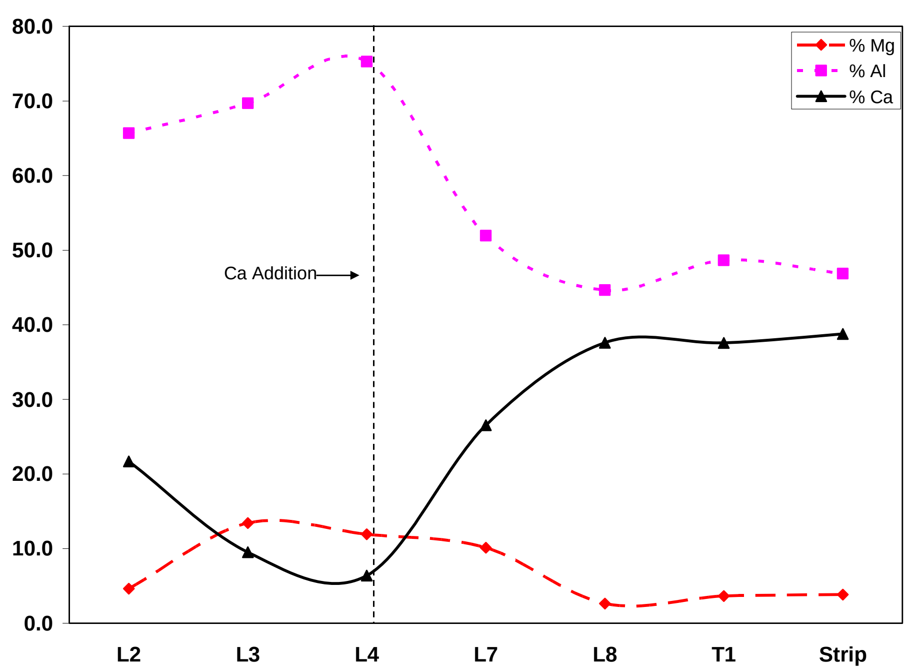


Figure 10. Change in inclusion composition (%) from steel deoxidation to final strip.

The following figure (Figure 11) from a recent study by Yang et al[57,58] shows the changes in the number and fraction of inclusions at the ladle refining station and the RH degasser.

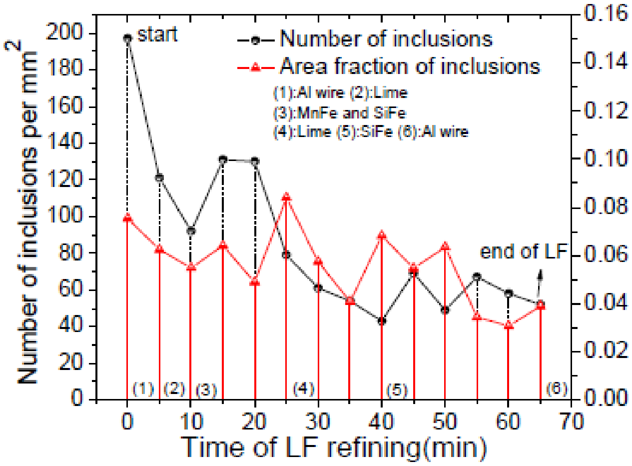


Figure 11a. Number and area fraction of inclusions during LF refining[57]

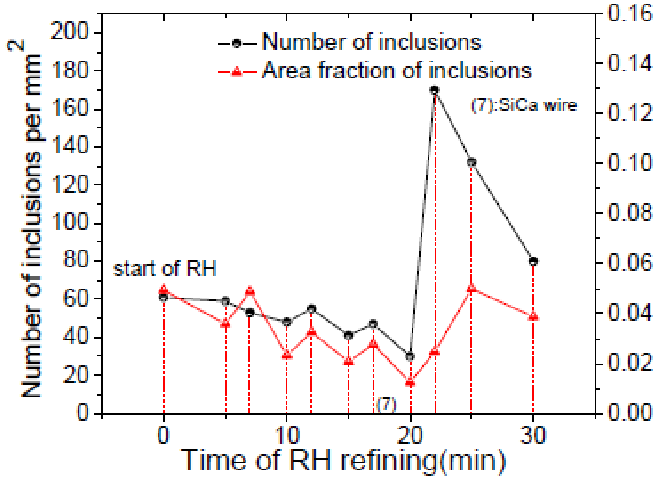


Figure 11b. Number and area fraction of inclusions during RH refining[57]

Another detailed study by Mendez et al[4] show the evolution of inclusion density during the refining process (Figure 12) and the change of the inclusion MgO content as a function of time for different analyzed heats.

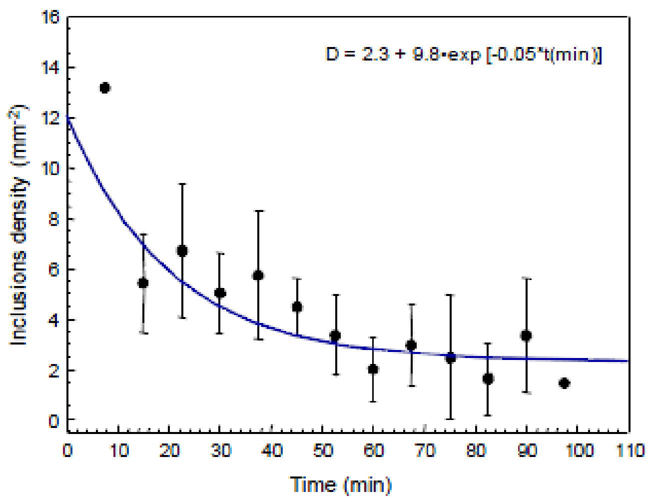


Figure 12a. Evolution of inclusion density along the process[4]

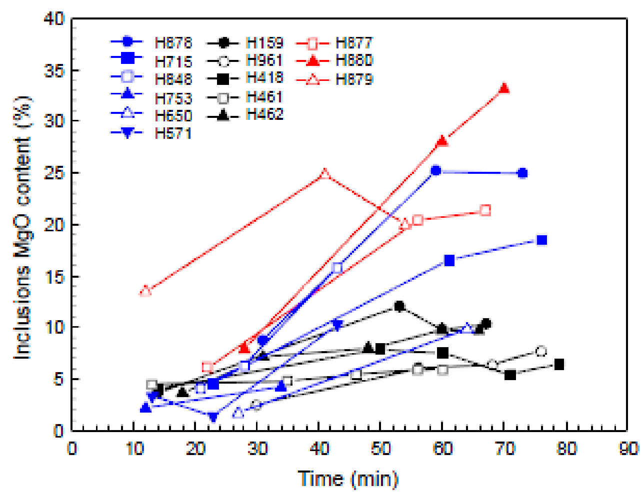


Figure 12b. Change of inclusions MgO content as a function of time for the different analyzed heats[4]

By taking multiple samples throughout the heat, the following effects could be investigated:

- Slag deoxidant type (CaC_2 versus Al) on inclusion evolution.
- Gas stir time and stir rate on steel cleanliness before and after Ca treatment.
- Stirring type on the inclusions (EMS versus gas stirring).
- Various ladle refining practices such as alloying, arcing, and desulfurization, on the inclusion types and distribution, their modification with Ca, and overall steel cleanliness.

The Effect of Ladle Stirring

It is well documented that stirring is essential to clean the steel and that medium to soft stirring is the most beneficial to float the inclusions.[67,73] It has also been reported that solid inclusions are easier to remove than liquid inclusions because they coalesce due to Brownian motion and Stokes collision, and they float out to the slag during bath turbulence due to stirring. The total oxygen content (PDA) tracked for three heats at the ladle station shows the effect of ladle process time and stir time on cleanliness in Figure 13. Similar results were shown earlier in Figures 11 and 12a.

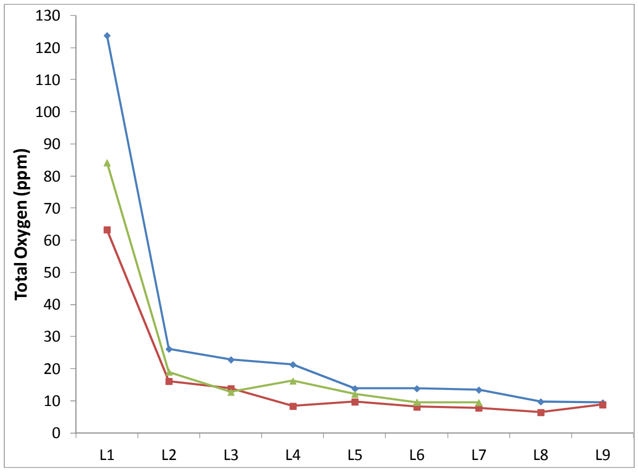


Figure 13. The effect of stir time on the cleanliness of the steel as determined by PDA total oxygen analyses

Unfortunately not all types of stirring are equal and extended stirring on some grades cause problems. A study by Karoly et al[1] has found that Ar stirring via a top lance is significantly worse for reoxidation than argon stirring though the bottom plugs. Kaushik et al[51] also showed that extensive stirring at the ladle refining station on Si-bearing grades, resulted in significant Ca-pickup from the slag and formation of CaS inclusions in the steel (unwanted in their case), which had a detrimental effect on the steelmaking process and the final product. Wang et al[59] in an attempt to minimize B-type oxide stringer inclusions did extensive trials with different practices. Their results show that increasing the stirring time in the RH degasser when the inclusions were still solid had the biggest impact on steel cleanliness and eliminating B-type inclusions. Increasing the RH degassing time by 15 minutes resulted in a decrease in the total number of inclusions by 40% and a decrease in the number of larger inclusions (> 10 um) from 16 to 2. This allowed for much more effective Ca treatment to form only CaO-CaS inclusions.

Alexis[11,12] did extensive modeling of the effect of ladle shape, number of plugs and type of stirring on temperature equilibration, alloy mixing, and slag-metal interactions. Their work showed that ladle configuration and the location and number of stir plugs could have an impact on cleanliness.

The Effect of Alloy Additions on Inclusion Formation

This paper focus mainly on inclusions that form from deoxidation, reoxidation and Ca modification. However, these are not the only inclusions in the steel that can lead to defects. A number of papers has shown that some of the inter-metallic species in the alloys can survive the ladle refining process and appear as defects in the final product.[10,54,55] Ti-rich and Nb-rich particles in the steel products are closely related to the phases in the ferro-titanium and ferro-niobium alloys added to the steel. It is especially the higher alloyed HSLA steels that are receiving more attention since a large amount of alloys are added and some alloys could be added fairly late in the process. The SEM micrographs in Figure 14 show some of the "non-equilibrium" inclusions encountered in these grades. A sufficient past alloy stir addition is required to clean up the steel for these grades.

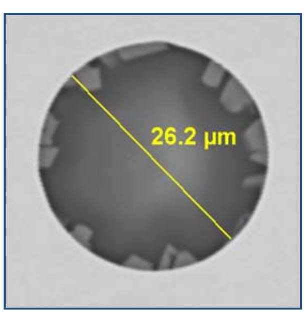


Figure 14a. Non-equilibrium inclusions (Mn-Si-Al oxide with Ti-rich oxides at the inclusion/steel interface)

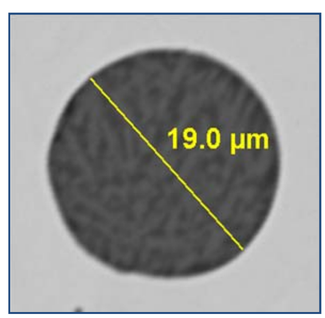


Figure 14b. Non-equilibrium inclusions (Mn-Si-Al-Ti oxide)

A recent paper by Tiekink et al[55] showed that the ferro-alloys typically added to steel contain significant amounts of oxygen, which could result in reoxidation when large amounts of these alloys are added late in the process. Table II shows the total oxygen values for some alloys as published in their paper.

Table II. Total oxygen values of some ferro alloys[55]

Alloy	Total Oxygen (ppm)
HC FeMn	930
MC FeMn	1,800
FeMnN	23,300
FeNb	4,700
FeB	720
FeP	680
FeTi "Standard"	7,400
FeTi powder (In wire)	16,000
Sponge Ti	650

During desulfurization trials at a Nucor plant where slag samples were taken at regular intervals, it was noted that the %MnO level of the slag increased from 0.5% to 2.5% after the addition of about 800 lbs of MCFeMn to the steel. This required a further addition of slag deoxidants to kill the slag in order to complete desulfurization of the steel. The addition of a slag deoxidant with the bulk ferro-alloys addition is now a standard practice on most grades.

The Effect of Si and FeSi Additions on Inclusion Modification

During the SEM evaluation of multiple samples from different grades, the following trend was observed: A significant Ca-enrichment and modification of the inclusions occurred for Si-bearing grades.[51,59] The Ca pickup is enhanced by very low S levels, very basic slags, and long process times. While this phenomenon is sometimes observed to a limited extent for Si-restricted grades after very long processing times, it is more common for Si-bearing grades. Current thermodynamic programs do not predict a significant difference in Ca solubility in the steel for Si-bearing or Si-restricted steel. However, the inclusion data suggest that significant transfer of Ca from the slag to the metal occurs for Si-bearing steel and this may be related to faster desulfurization and lower sulfur levels.[49] The Si in these grades is typically added as SiMn (does not contain Ca). Note that FeSi with significant Ca content can also affect inclusions. Figure 15a shows the typical inclusions for a Si-restricted heat after desulfurization to levels < 0.005% S. Figure 15b shows the inclusions for a Si-bearing grade at very low sulfur levels.

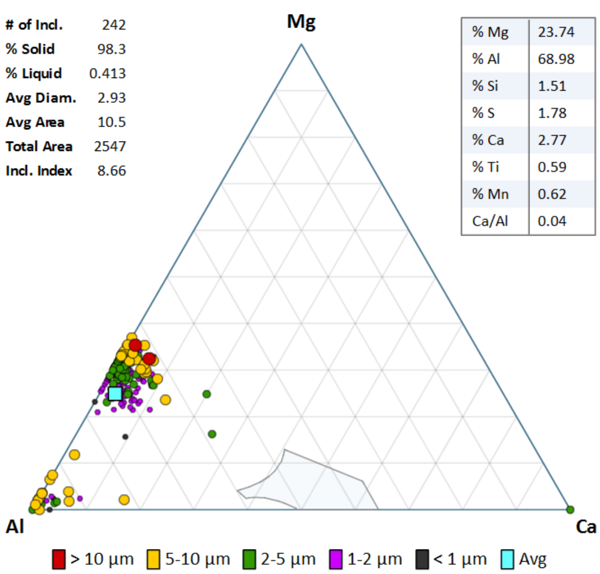


Figure 15a. Inclusions after desulfurization for a Si-restricted grade (% Si < 0.03)

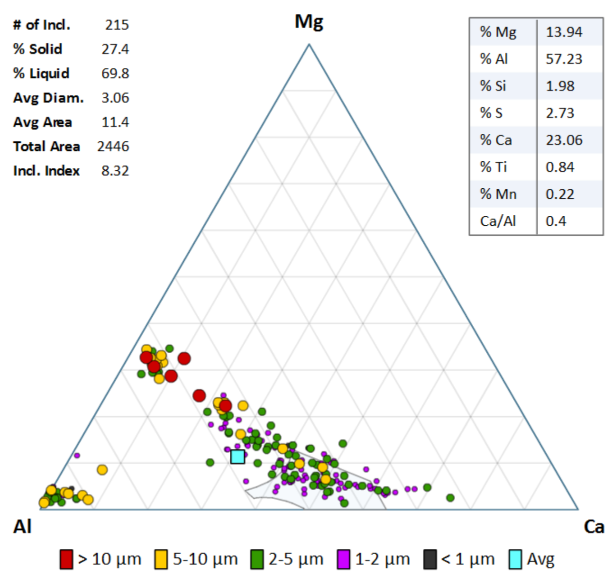


Figure 15b. Inclusions after desulfurization for a Si-bearing grade (% Si = 0.23) where SiMn was added

The evaluation of SEM results of other studies shows similar trends.[51,59] Table III shows the change in average inclusion composition as a function of time and sulfur content before Ca treatment (chemistry 0.23% C, 0.80% Mn, 0.20% Si and 0.03% Al). The Si was added in the form of SiMn and was already present in the L2 sample.

Table III. Change in average inclusion composition as function of time and %S in the steel

Sample #	% S in Steel	Ave % Mg in Incl	Ave % Al in Incl	Ave % Ca in Incl	Ca/Al Ratio
L1	0.0414	2.0	91.6	1.3	0.01
L2	0.0222	4.9	68.9	7.4	0.11
L3	0.0148	10.0	59.9	10.3	0.17
L4	0.0102	14.4	56.5	12.1	0.21
L5	0.0024	23.4	58.1	11.7	0.20
L6	0.0015	24.7	54.2	14.5	0.27
L7	0.0010	18.6	48.3	26.1	0.54
L8	0.0008	13.5	46.6	33.8	0.73

Figure 16a shows the change in average inclusion composition for the different samples and Figure 16b shows the actual inclusions for the L8 sample. The solid Al_2O_3 and Spinel inclusions in this Si-bearing steel were almost completely modified to liquid inclusions by the slag even before Ca wire was added.

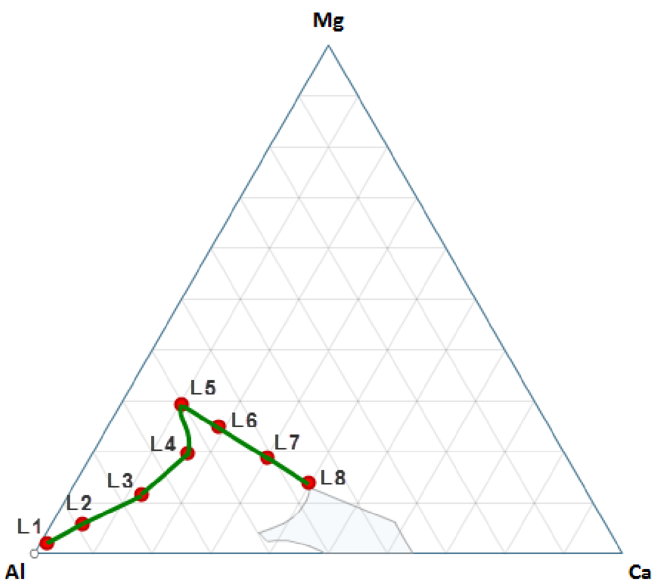


Figure 16a. Inclusion evolution as function of time and desulfurization

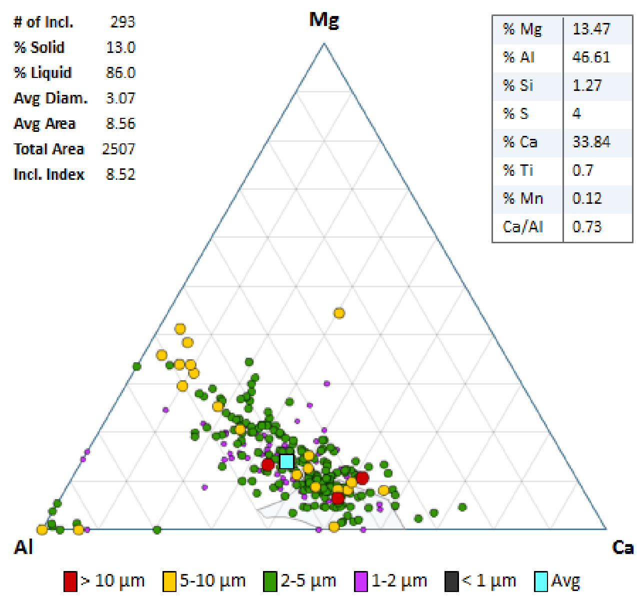


Figure 16b. The inclusion distribution for sample L8

It is well known that FeSi can contain significant amounts of Ca (0.1 to > 2%) and when FeSi containing Ca is added late in a heat, a significant amount of inclusion modification can occur.[60,61] Story et al[27] reported extensive clogging in low-carbon Si-containing ERW linepipe grades produced at U.S. Steel's Edgar Thomson Plant. These grades were not calcium-treated and contained Si levels in the range of 0.15 to 0.25. The heats that showed the most severe clogging, contained spinel inclusions (long LMF-arc and argon stir) and solid Calcium aluminates. The Ca in these inclusions originated from the FeSi that was added late in the LMF process. The FeSi added early with the first batch of fluxes and alloys did not generate solid Calcium aluminate inclusions. Analysis of the FeSi used at the LMF confirmed that it a contained significant amount of Ca (1.07%). The addition of FeSi at tap or using high purity FeSi (0.024% Ca) resulted in the vast majority of inclusions to being Al_2O_3, which did not represent an unusual clogging problem.

The experience at Nucor Berkeley was the opposite; extensive stopper rod wear was observed on the Si-bearing grades, which resulted in early termination of the caster sequence. The initial SEM investigation of the tundish samples showed the inclusions to be extensively over modified and a subsequent study of the ladle samples showed the inclusions to be over modified even before Ca was added. After some investigation it was determined that FeSi was the alloy that contained significant amounts of Ca (1.8% Ca) and caused the modification of the inclusions. Samples of all the alloys used at the LMF were analyzed for Ca content but FeSi was the major culprit with the other alloys typically containing < 0.1% Ca.

The Use of OES-PDA as An Inclusion Analysis Tool

A technology that has received significant attention the past few years is Optical Emission Spectroscopy (OES) with Pulse Discrimination Analysis (PDA) to rapidly analyze inclusions in steel. A number of OES suppliers have the technology available. In this study the PDA SparkDat option from Thermo Scientific was used. The theoretical aspects of the technology have already been covered in a number of publications and will not be discussed in this paper. It is important to note that the technology as described in this paper is only applicable to Al-killed steel and has shown promise to measure the following in lollipop or product samples:

- Total oxygen content of the steel.
- The amount, type and size of different inclusions based on predefined rules.
- The composition of the inclusions.
- The direct measurement of the amount of CaS inclusions.
- The indirect measurement of MnS inclusions.

Total oxygen measurements

Total oxygen measurements of steel samples using inert gas fusion has been the "gold standard" for steel cleanliness for many years. While the technology has proven itself it never became widely adopted as an in-line process tool because of the preparation time and the stringent sample preparation requirements. Some operations measure the total oxygen content every heat[63] but it is more commonly applied as a research or quality control tool after the heat has been processed. Any technology that can measure total oxygen, without too much effort in "real time" during the process and on product samples, is of great interest to steelmakers. It appears that OES-PDA, might be such an alternative. Figure 5 shows a comparison between LECO total oxygen measurements and Sparkdat PDA total oxygen measurements. Figure 17 is another comparison of the Total Oxygen (ppm) results of the two technologies on the first six bars of a startup heat.

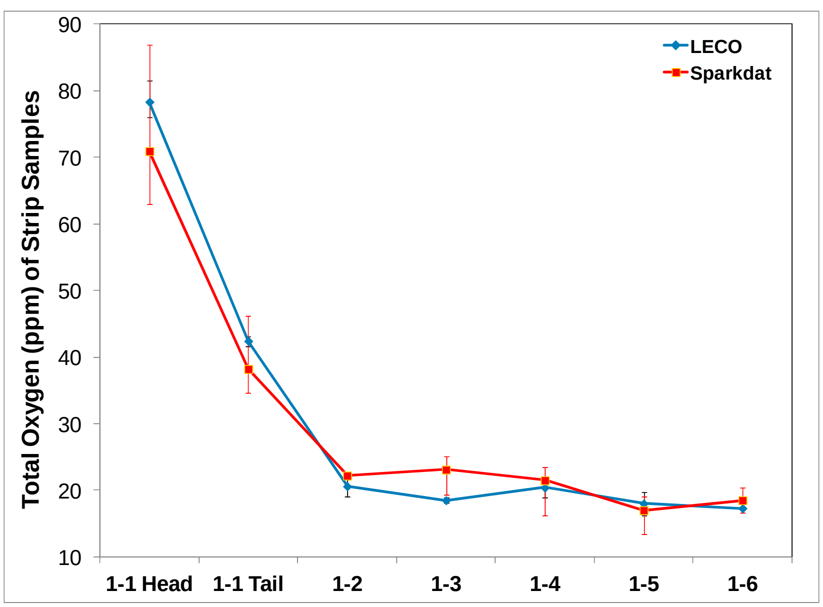


Figure 17. Total Oxygen comparison of LECO versus Sparkdat on the first six bars of a sequence heat

Figure 18a shows the total oxygen results of strip samples of multiple coils in a casting sequence. During this particular total oxygen trial, pin and lollipop samples were also taken in the tundish at periodic intervals. The pin and lollipop samples were taken within seconds in order to represent the same steel composition. The pin samples were analyzed on a LECO TC600 and the lollipop samples were prepared and analyzed on the Thermo 4460. The results (Figure 18b) of these samples show significant deviation in the tundish pin samples. The LECO total oxygen results of the pin samples were consistently higher than the SparkDat total oxygen measurements of the lollipop samples. When the Sparkdat tundish lollipop results were compared to the equivalent time-line Sparkdat strip sample, the total oxygen values were within 1 to 2 ppm of each other. The cause for the higher total oxygen measurements of the pin samples is not clear (sampling artifact or tundish slag/metal interactions).

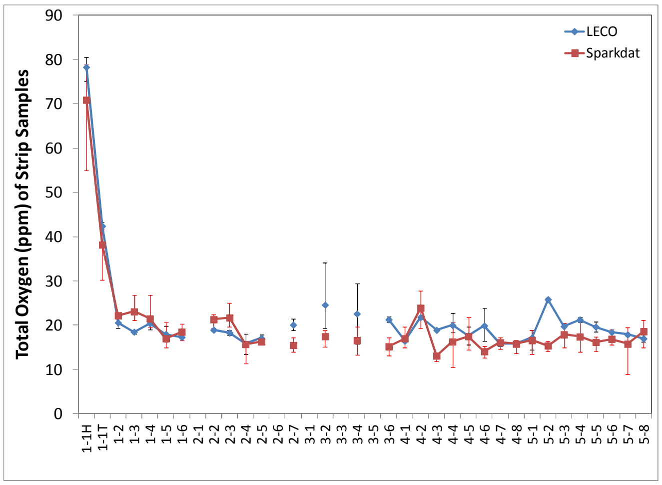


Figure 18a. Total oxygen measurements on strip samples (LECO and PDA) of a casting sequence

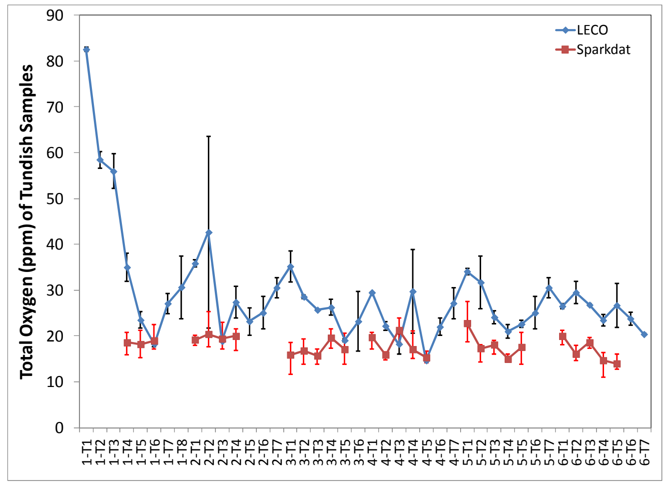


Figure 18b. Total oxygen on tundish pin samples (LECO) and lollipop samples (PDA) of the same casting sequence

Figure 19 shows the total oxygen results obtained by using different OES PDA equipment and LECO. A number lollipop and strip samples from random heats were submitted to Bruker for analyses on their Q8 Magellan Spectrometer and the results were surprisingly close and consistent as shown by Figure 19.

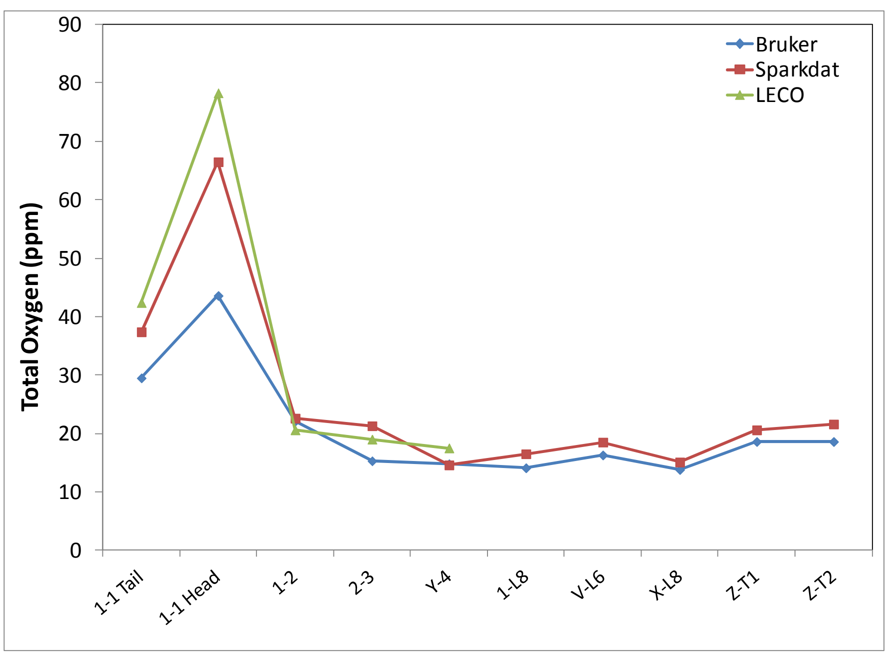


Figure 19. Comparison of total oxygen results using LECO and different OES-PDA technologies (Thermo and Bruker)

Inclusion type, amount and size as determined by OES-PDA

PDA inclusion analyses typically evaluate inclusion peaks on the various elemental channels and then classify the inclusions based on the presence or absence of coinciding peaks of element combinations. For example:

- Alumina Inclusions – Al peaks but no Ca, Mg or S coinciding peaks
- Al_2O_3-CaO inclusions – Al peaks coinciding with Ca only, not Mg or S
- Al_2O_3-CaO-MgO inclusions – Al peaks coinciding with Ca and Mg but not S

The following Sparkdat Inclusion classes were considered:

- Al_2O_3 Inclusions (A)
- MgO-Al_2O_3 Inclusions (MA)
- MgO-Al_2O_3-CaO Inclusions (MAC)
- CaO-Al_2O_3 Inclusions (CA)
- Al_2O_3-CaO-MgO-CaS Inclusions (ACMCaS)
- Al_2O_3-CaO-CaS Inclusions (ACCaS)
- CaS inclusions (CaS)
- MnS inclusions (MnS)

Figure 20 shows the ternary plot of the SEM results of a sample before Ca treatment and the corresponding SparkDat inclusion classification results.

The Sparkdat Inclusion Index = (# of inclusions) x (average size)

Note that inclusions classified by SEM as spinels can contain trace Ca and these same inclusions would be detected by PDA with a coinciding Ca peak and classified as MgO-Al_2O_3-CaO (MAC) inclusions. In principle it should be possible to improve classification of spinels by tweaking the Sparkdat formulas to include some level of Ca; however, this was not done for this study.

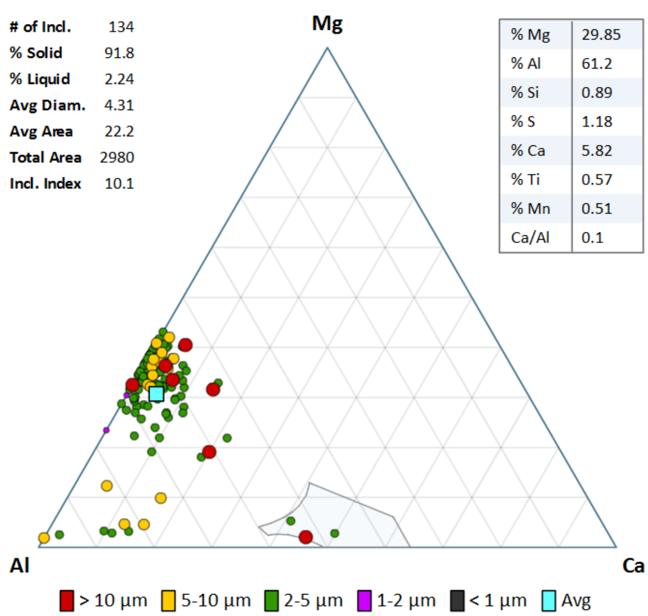


Figure 20a. SEM Inclusion results of a ladle sample before Ca treatment

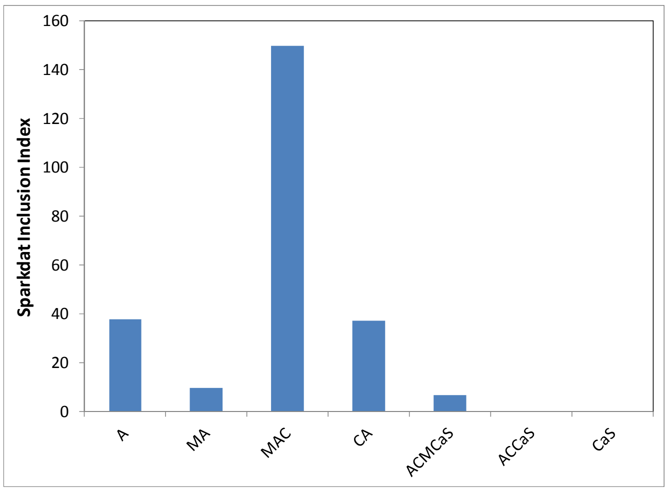
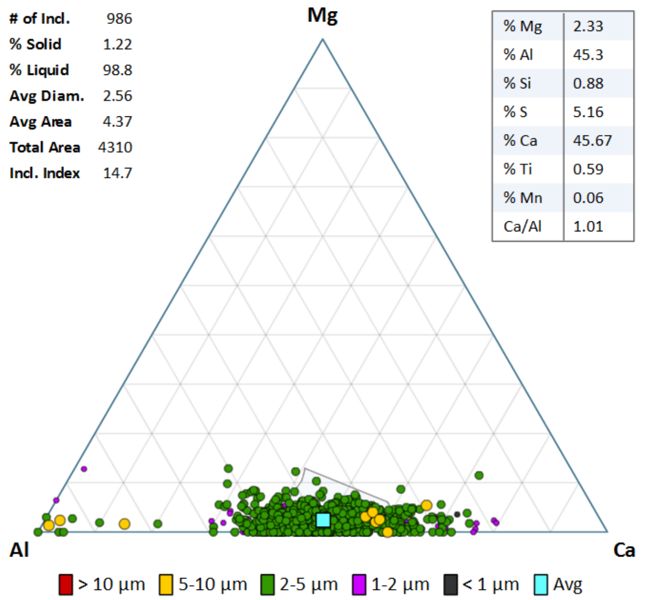


Figure 20b. Sparkdat Inclusion results of a ladle sample before Ca treatment

Figure 21 shows the ternary plot of the SEM results of a sample After Ca treatment and the corresponding SparkDat inclusion classification results. The "Before" and "After" Ca SparkDat results as summarized in Figure 22 and it shows the shift from the Al_2O_3 and spinel inclusions to the Ca-Aluminate inclusions.



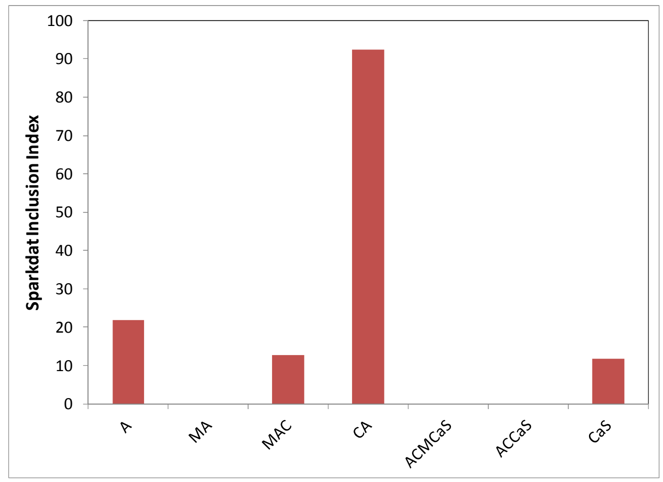


Figure 21a. SEM Inclusion results of a ladle sample after Ca treatment

Figure 21b. Sparkdat Inclusion results of a ladle sample after Ca treatment

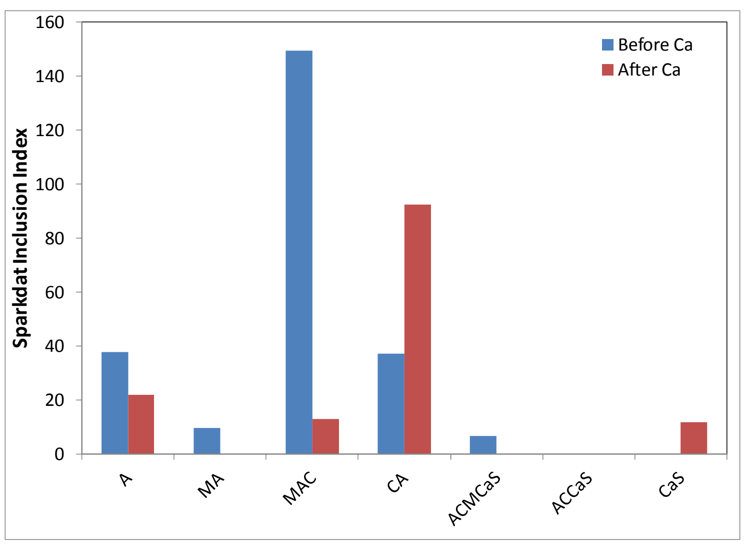


Figure 22. Sparkdat Inclusion results of ladle samples before and after Ca treatment

Determining the composition of the inclusions

Classifying the inclusions based on coinciding peaks is useful for comparative purposes but it is not that useful from a composition perspective. For instance a Calcium Aluminate (CA) could have a wide range of Ca/Al ratios and still be classified the same. Some Ca-aluminate inclusions may be liquid while others may be solid, so it is important to know the inclusion composition. The average Ca/Al ratio of the inclusions is of special interest to the steelmaker as it is related to effective Ca treatment and the amount of liquid inclusions. The ternary SEM plots and the 100% and 50% liquid overlays are good visual tools to determine the extent of modification. The 100% liquid overlay indicates that inclusions with Ca/Al ratios > 0.8 and < 1.7 will be completely liquid. Since the OES-PDA technology actually measures the undissolved Ca and

Al in the steel originating from inclusions, it should be possible to relate that to the inclusion Ca/Al ratio as determined by the SEM.

Figure 23a plots the SEM Ca/Al ratio of the series of samples listed in Table V and Figure 16a against a Sparkdat Ca/Al ratio. The Sparkdat Ca/Al ratio is related to the undissolved Ca and Al fractions in the steel and the coinciding peaks of the two elements. Please note that the two ratios are not numerically equivalent but they are related as shown by Figure 23a. Figure 23b shows the same relationship for a large number of samples (lollipop and strip) that was analyzed on the SEM and the Spectrometer. The correlation between these results in combination of the other PDA data now allows for a reasonable prediction of inclusion composition prediction at any stage of the process using a Spectrometer.

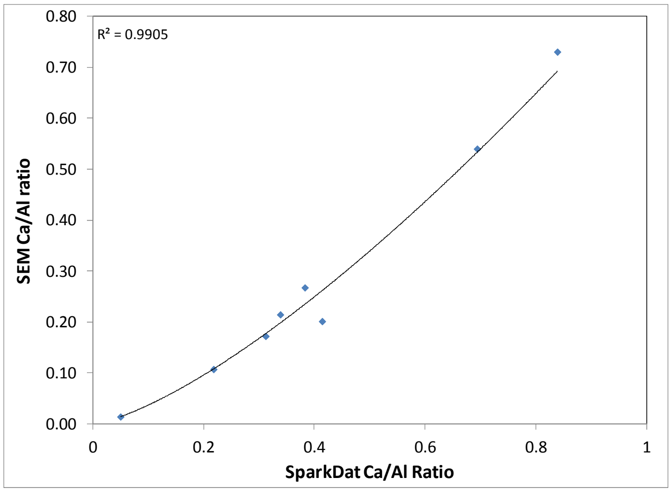


Figure 23a. The relation between the SEM Ca/Al ratio and the Sparkdat Ca/Al ratio for series sequential ladle samples

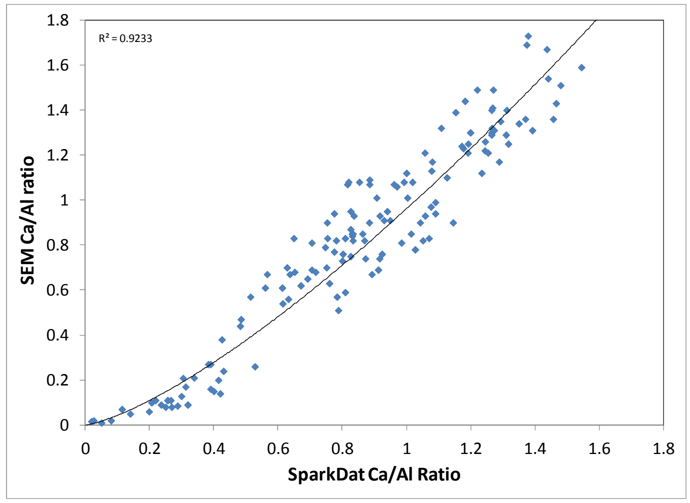


Figure 23b. The relation between the SEM Ca/Al ratio and the Sparkdat Ca/Al ratio for large number of samples

Figure 24a shows the SEM Ca/Al ratio versus Sparkdat Ca/Al ratio for a number of strip samples from a short caster sequence. The red lines on the graph indicate the heat transitions. A comparison of the Ca/Al ratio for different OES-PDA technologies is shown in Figure 24b. Although different PDA formulas were used to the calculated the ratios and result in different numerical values, the results show consistent trends.

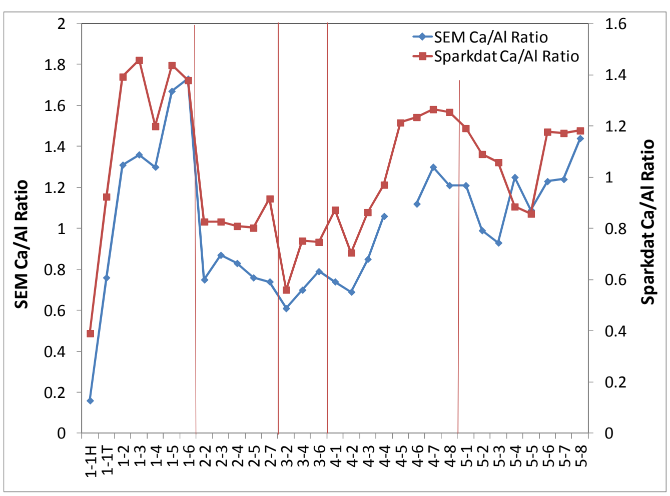


Figure 24a. SEM Ca/Al ratio inclusion ratio versus SparkDat Ca/Al inclusion ratio for a series of strip samples from a caster sequence

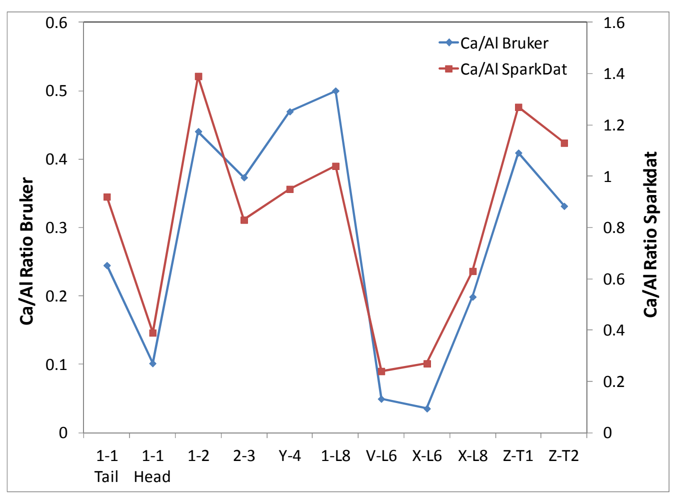


Figure 24b. Comparison of the Ca/Al ratio for different OES-PDA technologies

The solubility of Mg in steel is very low (a few ppm) so that ICP technology is sometimes used for Mg analysis.[64] The direct measurement of Mg in the steel was attempted with a Mg-channel on the spectrometer but all the samples reported Mg levels < 1ppm. However, the raw Mg channel count information from Sparkdat showed a very good correlation with the inclusion Mg levels from the SEM results (Figure 25). Overall Mg counts (PDA) remain the same but the MgO in the inclusions as determined by the SEM decreases after Ca treatment (≈ 25 to ≈3% Mg). The Mg counts for the "After Ca" samples in this figure support previous theories that during Ca treatment the MgO from the spinel inclusions are reduced by the Ca and go into solution in the steel as Mg.[15,64] Further examination of the detailed SparkDat solubility data confirms that the average soluble fraction of Mg increases from 0.10 to 0.88 as a result of Ca treatment. Combining OES-PDA with a Mg-channel also allows for the differentiation between dissolved and undissolved Mg – representing Mg - in the steel and in the inclusions respectively.

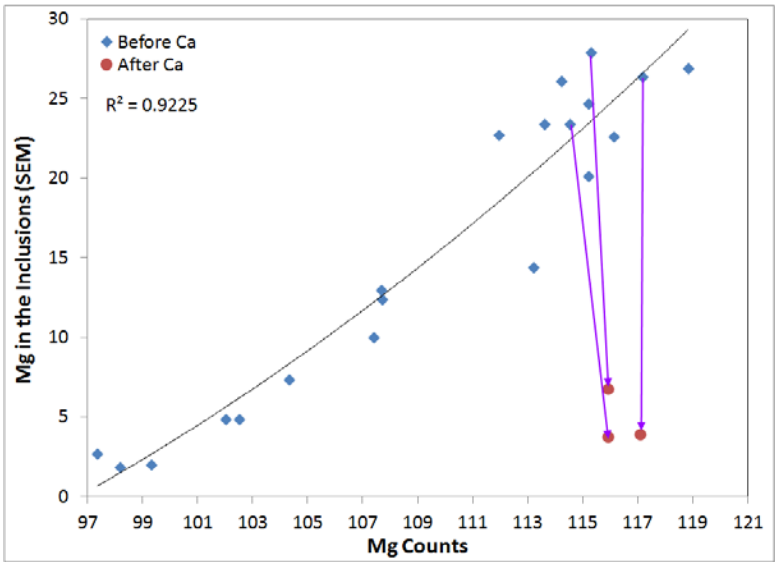


Figure 25. Relation between the Mg content of the inclusions as determined by SEM versus the SparkDat Mg counts. The purple connecting lines show the Mg level of the inclusions for the specific heats before and after Ca treatment.

The direct measurement of the amount of CaS inclusions using OES-PDA

The presence of CaS inclusions is typically an indication of excess Ca addition or Ca addition at high S levels. Excessive amounts of CaS inclusions can cause clogging and affect steel quality.[65] Figure 26 shows the defect and EDS spectrum of a CaS stringer in product sample that failed a quality inspection.

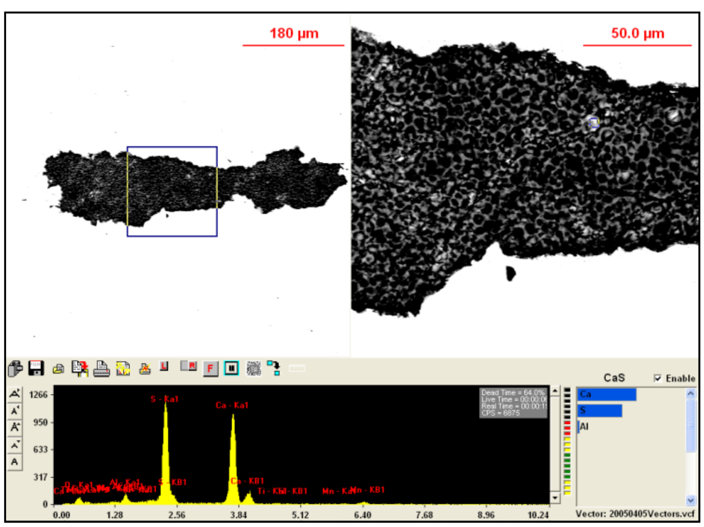


Figure 26. Screen shot of an EDS spectrum of a CaS stringer

This study confirms that OES-PDA is a very effective tool to detect CaS inclusions in the steel.[21] Figures 27a and 27b show the SEM results for well modified and over modified inclusions, respectively. Figure 28a shows the corresponding Sparkdat inclusion results of these two samples. A significant shift from the CA-group to the three CaS-rich inclusions groups can be observed. Figure 28b shows a good correlation of the two OES-PDA technologies used to determine the CaS fraction in steel. The values in this figure are different because different formulas are used to calculate the CaS fraction.

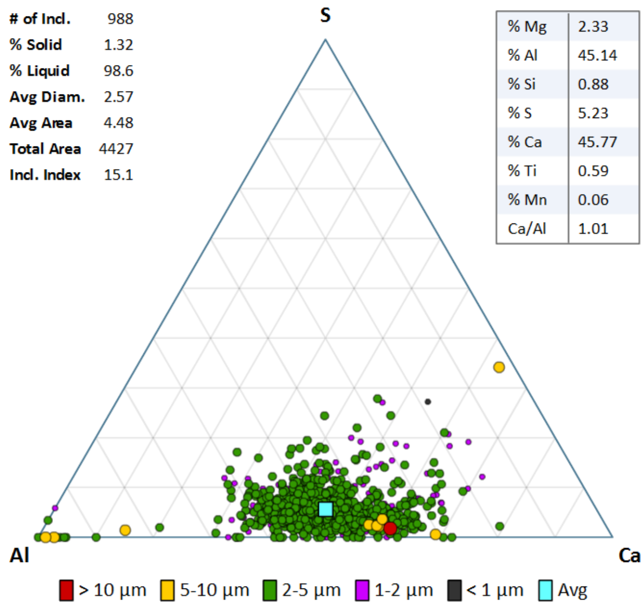


Figure 27a. SEM inclusion results showing well-modified inclusions.

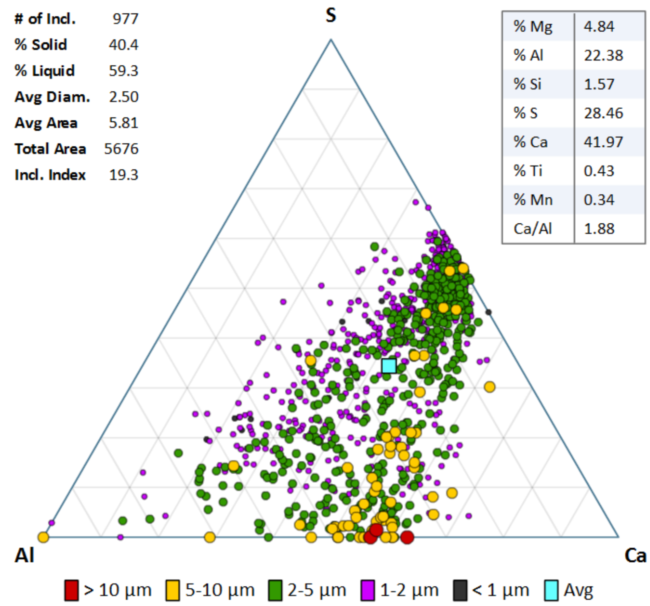


Figure 27b. SEM inclusion results showing CaS and over-modified inclusions

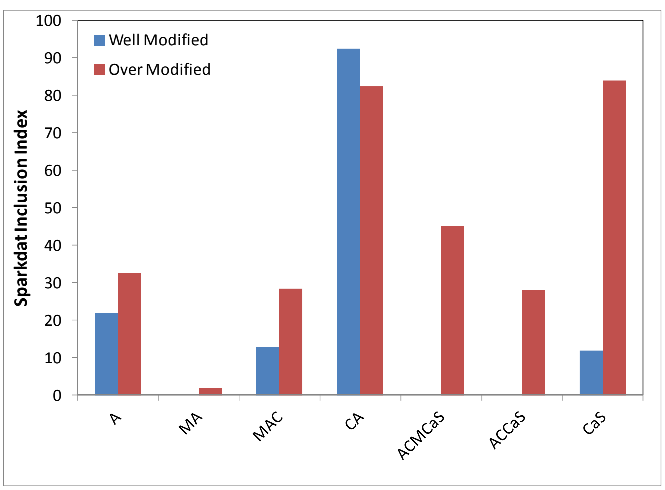


Figure 28a. SparkDat results showing the effect of Ca over-modification on the inclusion distribution

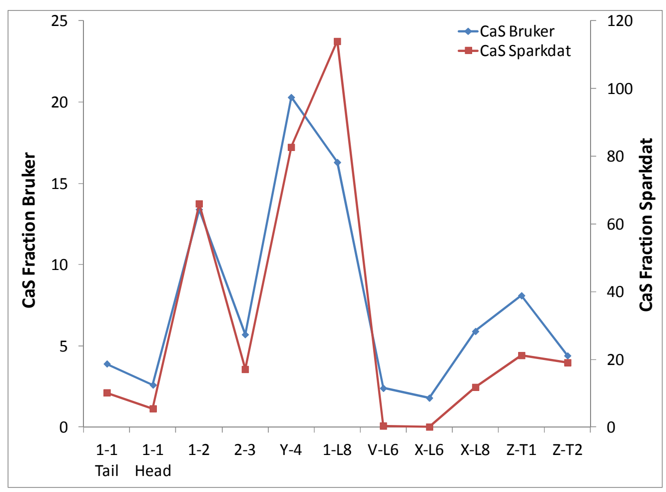


Figure 28b. Comparison of the different OES-PDA technologies to detect CaS inclusions in the steel

The measurement of MnS inclusions and the impact of MnS inclusions on steel quality

In recent papers MnS inclusions have received increased attention since they have a significant impact on the mechanical properties of the steel. One reference states the coarse crystallized MnS from the liquid steel can be problematic.[66] Increasing number of studies are reporting the presence of MnS inclusions in lollipop samples taken from the ladle or the tundish.[52,65,67,68] As thermodynamics predict that MnS will not be stable for the specific chemistry and temperature in the ladle and tundish, it is possible that the MnS form during rapid cooling of the sampled steel in the lollipop. Regardless of how/when they form, the presence of these inclusions has been associated with a higher propensity for casting defects in slab and bloom casters. These MnS inclusions are typically observed in a specific grade family; high Mn (> 0.8), Si-bearing (>

0.15%), Al-killed steel (>0.02).[52,65,67,68] On the CSP casters at Nucor, medium C, high Mn, Si-bearing heats that contained MnS inclusions in the tundish samples showed a significant increase in the frequency of transverse corner cracks and edge problems on the cast slabs. The same observation was made by Ozgu[71] relating the sulfur content in the steel to the ratio of slabs with corner cracks (Figure 29).

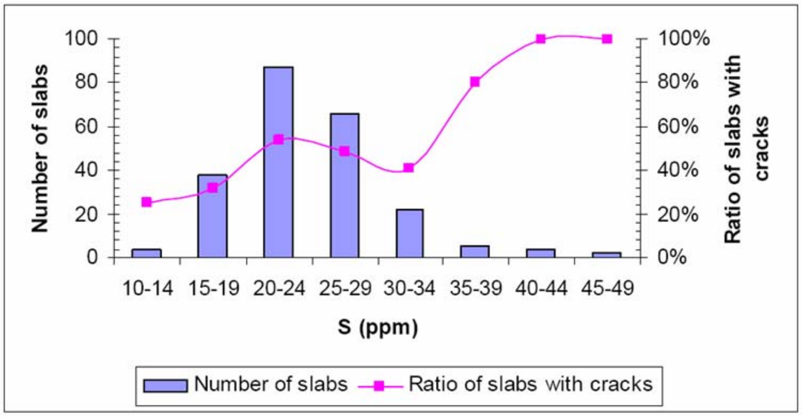


Figure 29. The effect of sulfur content in the steel on the ratio of slabs with corner cracks[71]

Yang et al[57,58] did a detailed study of inclusion evolution as a function of time and their results in Figure 30a show the change in the number MnS inclusions as a function of time and S content. The sulfur content of these samples was added to the graphs from their original publication.

In numerous studies the presence of these MnS inclusions in the tundish sample could be related to some quality defect.[18,68,69,70] Kaushik et al[18,68] showed that tundish samples of medium-C heats with a high MnS inclusion population relative to CaS inclusions, had poor sulfide shape control (Figure 30b). The quantitative rating of each heat (Good vs. Poor) was based on SEM analysis of the plate samples of that heat. Higher CaS/MnS inclusion ratios were also correlated with higher impact energy in the corresponding plate product samples.

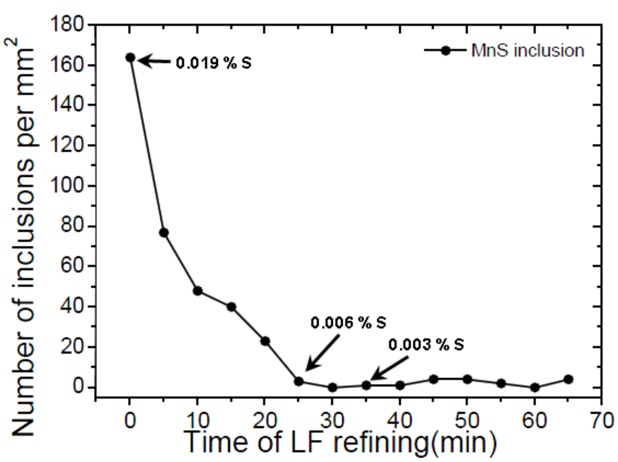


Figure 30a. Decrease in MnS inclusions as a function of time and S content in the steel[57]

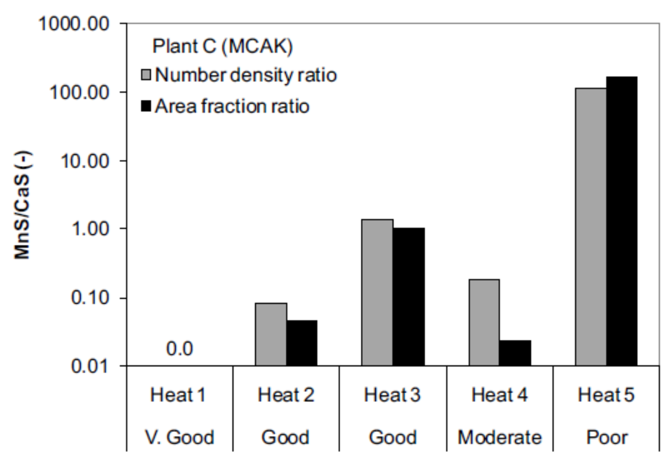
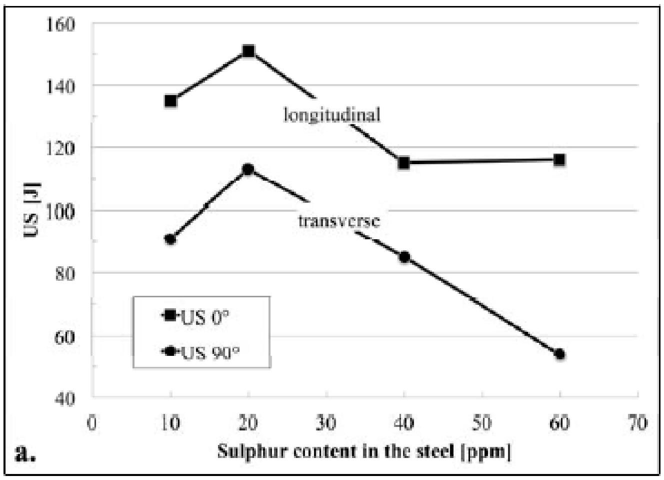


Figure 30b. Ratio of MnS/CaS inclusions in tundish samples of 5 MCAK heats[18]

Kaijalainen et al[70] studied the effect of inclusions on the mechanical properties of an Al-killed, Ca-treated ultra-high-strength-low-alloy (UHSLA) C-Mn-Cr-Mo steel with four sulfur levels (10 ppm to 60 ppm). A significant amount of elongated MnS inclusions were found in the steel with the highest sulfur level (60 ppm) which impaired the impact toughness properties and bendability (especially in the longitudinal direction). Figure 31 shows the toughness and bendability (BI) as a function of sulfur content from their work.



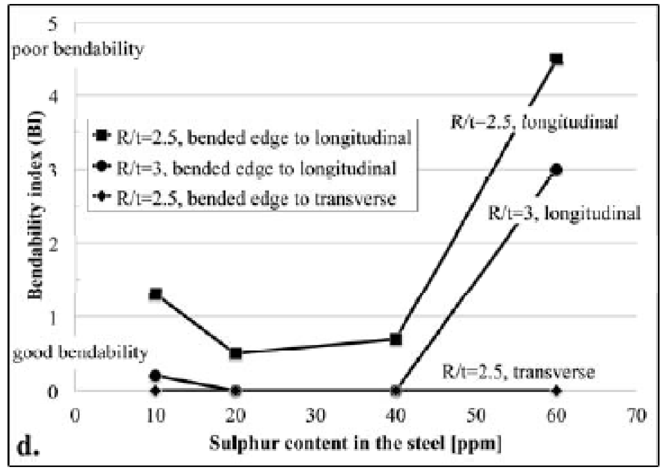


Figure 31a. Effect of sulfur content on impact toughness[70]

Figure 31b. The effect of sulfur on the bendability index [70]

MnS inclusions can be easily detected on the SEM as shown earlier in Figure 4a but SEM analysis are typically post process and are not used as an in-line control tool. It has been demonstrated that OES-PDA is a credible tool to analyze oxide and CaS inclusions in steel but has not been shown to correctly identify MnS inclusions. It is not possible to directly measure Mn and S coinciding peaks with PDA because Mn is typically a bulk element in the steel and it is difficult to separate inclusion outliers from the high steel matrix background. If all the S peaks associated with the other elements (Al, Ca, and Mg) can be accounted for, the remaining S inclusion peaks could probably be associated with Mn as MnS. This was investigated by tracking the inclusions at the LMF on a medium C, High-Mn, Si-bearing steel using the SEM and then running the Sparkdat analyses on the same samples. The results of this study are summarized in Figure 32.

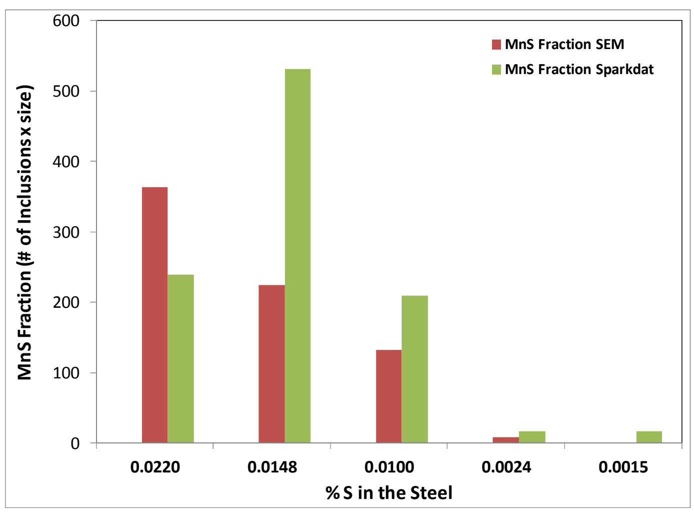


Figure 32. MnS fraction as determined by SEM and Sparkdat as a function of sulfur content in a number of ladle samples

Ca Treatment – The Modification of Solid Al_2O_3 and Spinel Inclusions into Liquid Inclusions

Operations that utilize conventional thick slab casters typically don't attempt to modify the alumina inclusions in the steel. Their clean steel efforts are focused on decreasing the amount of alumina inclusions and minimizing spinels in order to limit slivers and the number of SEN changes. Since the inclusions are solid, clogging will occur, but the extent of clogging is minimized by clean steel practices. In contrast, CSP casters, or other casters with smaller nozzles, cannot tolerate much clogging because the steel flow is controlled with stopper rods with a limited vertical range and the SEN's cannot typically be exchanged during a sequence. The number of heats on a nozzle for these operations is commonly > 12 compared to the 3 - 5 for large slab casters. Liquid inclusions that will result in limited or no clogging are therefore a prerequisite for these operations.

The theoretical aspects of Ca treatment have been discussed in many papers. For most operations the goal of Ca treatment is clear: Modify the solid alumina and spinel inclusions into liquid Ca-Aluminate inclusions without forming too much CaS. Some operations now rely on SEM inclusion results to develop the Ca treatment practices for specific grades that meet this goal. The development of the practices uses sound metallurgical principles and real inclusion results. However, the execution of the practices relies on "Statistical Metallurgy", i.e., the Ca treatment is based on past results and the expected number of inclusions that are typically produced. Unfortunately, every heat produced at the ladle refining station is unique for a number of reasons:

1. The ladles are different (newer or older, colder or warmer, with or without skulls or ladle glaze).
2. The metal tap amount and slag carryover amount and chemistry is different.
3. The tap temperature and oxygen levels are different.
4. The tap metal composition is different (Mn, S, residuals).
5. The plugs stir differently.
6. Some operator variability.
7. The ladle stations could be different so that the alloy entry point in relation to the stir plugs could be different.
8. Different processing and arc times.
9. Past grade history on the ladle and variability in alloy additions.

As a result, the number and type of inclusion before Ca treatment can vary. Using the same amount of Ca for every heat of the same grade typically results in a different level of Ca modification. Hopefully, the resultant inclusions fall "statistically" in the range that is acceptable for good quality and casting. Figures 24a and Figure 33 show the variation in Ca/Al ratio of the inclusions in the tundish samples taken over the early stage of two sequences. The red vertical lines indicate heat transitions. Both these sequences show extensive Ca/Al variations from heat to heat for the same grade of steel and the same Ca practice for that grade. The results in Figure 33 also show the drop in the Ca/Al ratio of the inclusions just after ladle exchange indicating that some reoxidation occurred during the exchange.

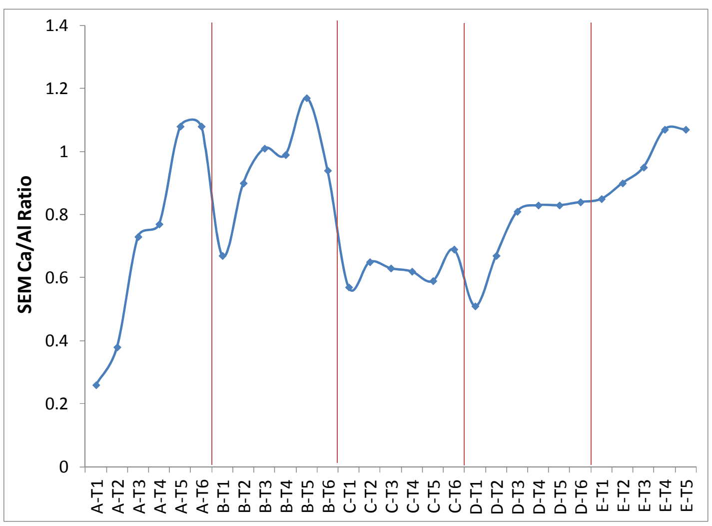


Figure 33. Variation in inclusion SEM Ca/Al ratio for sequence of heats at the caster

The "Holy Grail" of Ca treatment is the addition of Ca based on a specific measured amount of inclusions for that particular heat. This will ensure that the inclusions are completely modified with the ideal target composition every time. OES-PDA could possibly be the technology that will make that possible.

While the amount of Ca required can be determined from inclusion analysis (SEM and possibly PDA), the conditions in the ladle during and after the Ca addition also have a big impact on the extent of modification. The oxidation state of the ladle slag during and after Ca treatment of spinel inclusions is especially important. The added Ca reduces the MgO from the spinel into the steel so that it is now in solution. However, if this steel with a high dissolved Mg content encounter any source of oxygen, then the dissolved Mg will oxidize and secondary reoxidation spinels will form. The effect of reoxidation on secondary spinel formation during a startup heat has been demonstrated in an earlier paper.[15] Any other event after Ca treatment such as alloying, arcing or argon stir high enough to open a big stir eye could cause reoxidation that could compromise the Ca treatment effort. This typically results in a mixture of liquid and solid inclusions that could cause clogging at the caster and ultimately dirty steel.

Some operations (linepipe steel plate) attempt to eliminate low-melting $CaO-Al_2O_3$ inclusions by adding excess Ca to form mostly solid CaO and CaS inclusions to minimize the presence of B-type oxide stringer inclusions in the steel.[59] In the steel grades with high S and Al concentrations it is not possible form liquid inclusions with Ca-treatment without forming CaS.[72] The CaO content in the inclusions is typically limited to about 40% in order to minimize CaS formation.

The experimental study by Verma et al[62] that took metal samples immediately after Ca treatment showed that the modification of spinel inclusions proceeded through a transient CaS formation. The injected calcium reacts with dissolved sulfur to form CaS and reduces the MgO from the spinels and the CaS reacts with the oxide (mainly Al_2O_3) inclusions, returning sulfur to the melt. From this study, it appears that CaS in the steel could act as a Ca "reservoir" to potentially react with Al_2O_3 or other reoxidation inclusions. This hypothesis will be explored further in the thermodynamic evaluation.

Ca analysis on OES

Some operations with very consistent ladle processing times for stainless steel grades have shown good correlation between the Ca calculated from the inclusions and the total calcium content analyzed with OES.[63] However, the authors of this paper have found that the Ca analysis on an OES is typically unreliable as an indication of inclusion modification.[16,17] SEM inclusions analyses is a better reference tool to determine the effectiveness of Ca-treatment. The OES analysis of a dirty heat can indicate a high Ca value but the inclusions could be poorly modified and the Ca analysis on a very clean heat could be very low, even when the inclusions are over-modified. Consider for example the L8 sample in Figure 16b that was taken before Ca-treatment. The OES %Ca value was measured as 9 ppm Ca but the SEM results indicate well modified inclusions (Ca/Al ratio = 0.73) that were 86% liquid.

THERMODYNAMIC CALCULATIONS

Thermodynamic equilibrium calculation programs such as FactSage, ThermoCalc and CEQCSI, have been very useful to simulate inclusion formation and their modification by Ca and the results of these studies have been reported by a number of researchers.[51,75] In this paper FactSage calculations will be used to demonstrate the effect of calcium treatment and the effects of subsequent reoxidation of the steel on the inclusion composition. These reoxidation products typically consist of a mixture of solid and liquid phases (secondary spinels and Ca-Aluminates) that can buildup and adhere to the refractories.

Buildup on the refractories could occur by several mechanisms:

1. A marginal heat from the ladle station where the Ca modification was ineffective and inclusions consisted of a mixture of primary spinels, alumina and some liquid.
2. A good heat from the ladle station but a reoxidation event at the caster that could result in secondary spinels and a liquid phase.
3. Reaction with the refractories (SiO_2 reduction), tundish slags, and glazes.
4. Ca reaction with the decarburized alumina graphite SEN

Good ladle refining practices can eliminate the first mechanism and the effectiveness of the process can be verified by analyzing depart samples from the ladle station. This was discussed in a previous paper where it highlighted the use of SEM inclusion analysis to identify the problem areas that cause clogging and focusing on the appropriate root cause.[16] Reoxidation at the caster is of great concern and its effect can be demonstrated by the use of thermodynamic calculations. All the calculations for this study were performed with FactSage 6.3 using the FTOxide and FTMisc databases. The FTOxide-SlagA, FTOxide-SPINA and FTMisc-FeLQ solution databases were selected for inclusion and steel calculations, respectively.

A generic LCAK-steel with the following composition was considered in the calculations: 0.04 % C, 0.02% Si, 0.6% Mn, 0.035% Al, 0.002% S, 3 ppm Mg and 4 ppm O.

The calculations were performed at 1550°C (2822°F) and only spinel inclusions (26.2% MgO and 73.8% Al_2O_3) were formed in the initial steel condition (Before Ca treatment). Three cases of increasing Ca additions to this steel were simulated to completely modify the spinel inclusions to liquid and Liquid + CaS inclusions. The amounts of the inclusions and the composition of the liquid phases for the three cases are summarized in Table IV

Table IV. Amounts of the inclusions and the liquid phase composition

	Case I	**Case II**	**Case III**
% Liquid	100	74.8	48.1
% CaS		25.2	51.9
Liquid Composition			
% CaO	43.7	49.4	49.4
% Al_2O_3	48.9	43.2	43.2
% MgO	5.8	5.7	5.7
% S	1.6	3.2	3.2

The results of these calculations were saved as input streams for the reoxidation calculations where incremental amounts of oxygen were added to the steel and the change in inclusion composition tracked to simulate "arbitrary" reoxidation . The change in inclusion distribution for Case I is shown in Figure 34a and the change in bulk composition of the inclusions is tracked in Figure 34b.

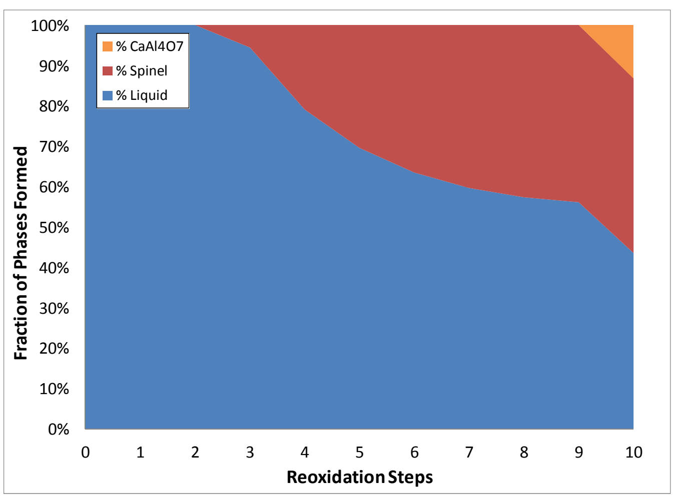


Figure 34a. Distribution of inclusions as a function of reoxidation for Case I

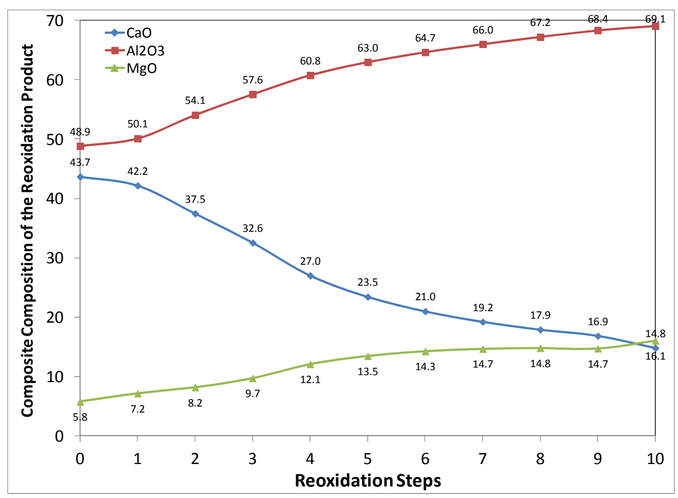


Figure 34b. Change in bulk composition as a function of reoxidation for Case I

The calculation results in these figures clearly show when reoxidation of the steel occurs, secondary spinels form.

The inclusion distributions for the reoxidation sequence for Case II and Case III are summarized in Figures 35a and 35b, respectively.

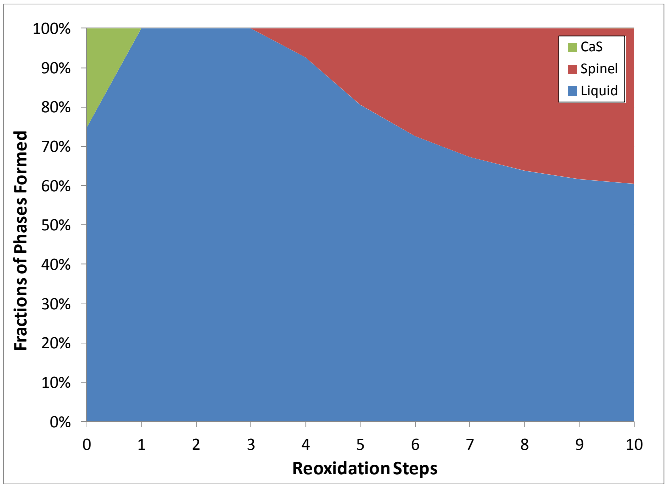


Figure 35a. Distribution of inclusions as a function of reoxidation for Case II

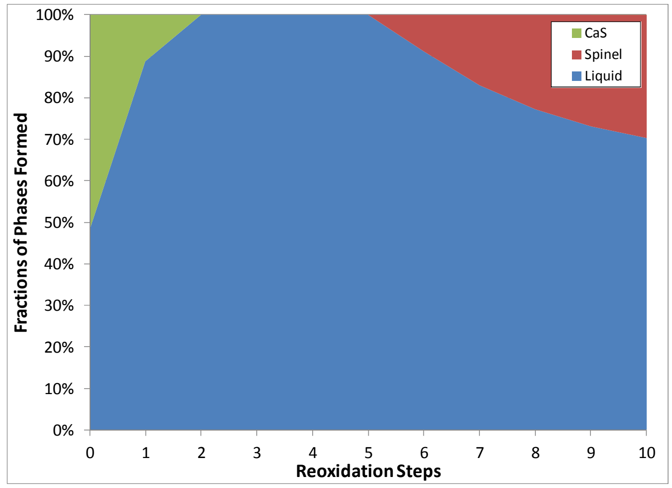


Figure 35a. Distribution of inclusions as a function of reoxidation for Case III

The % Liquid that will be present for the three cases as a function of reoxidation is summarized in Figure 36. These figures clearly show that the CaS inclusions start to disappear as the steel is exposed to oxygen. These CaS inclusions dissociate into Ca and S and effectively act as a Ca reservoir or buffer that supplies Ca to retard formation of spinels during reoxidation. At reoxidation step 6, the % liquid for Case I is only 63%, whereas the % Liquid for Case II and Case III with more initial CaS is 73 and 91%, respectively. These results imply that slight over modification during Ca-treatment to form a small amount of CaS inclusions might be advantageous to protect the steel against reoxidation events at the caster.

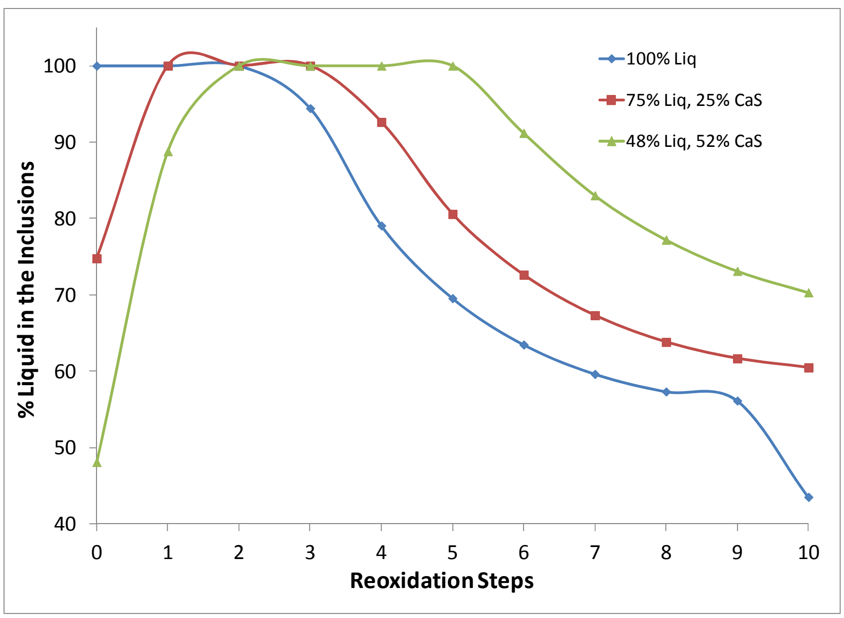


Figure 36. The %Liquid present in the inclusions for the three cases as a function of reoxidation

CLEAN STEEL PRACTICES AT THE CASTER

Sources of Oxygen

Exposure of liquid steel to air is a gross source of oxygen and nitrogen and such events can typically be measured by nitrogen pickup in the steel. Most operations attempt to purge argon around the metal transfer points (ladle to tundish and tundish to mold) in order to minimize air ingress. More subtle, but equally important, are the sources of oxygen in reducible oxides.

The ladle well-block sand could contain chromite with Fe_3O_4 and Cr_2O_3 but the most important oxide is SiO_2, which could be in the sand, the tundish cover and the refractories. The typical oxidation reactions with SiO_2 are the following:

$$2\,[Al] + 3\,(SiO_2) = Al_2O_3(incl) + 3\,[Si] \tag{2}$$

$$[Mg] + 2[Al] + 2\,(SiO_2) = MgAl_2O_4(incl) + 4\,[Si] \tag{4}$$

$$[Ti] + (SiO_2) = TiO_2(incl) + [Si] \tag{5}$$

It is especially the use of rice hulls as a primary tundish cover or secondary cover over a basic tundish flux that could be significant source of oxygen since the reaction between SiO_2 from the rice hulls and CaO-containing ladle slag carryover can result in a liquid tundish slag with a high silica activity. The kinetics of slag-metal reactions is typically much faster than refractory-metal reactions. Slagging off the tundish might be a required practice in some operations to make clean steel. A basic tundish slag with a low silica activity is desirable for the last-minute absorption of inclusions and to protect the steel from the atmosphere. Some research is underway to engineer tundish slags by using more exotic raw materials to actively assist in the cleanup of the steel.[36]

Startup Heats and Ladle Exchange

Despite extensive efforts, such as Ar flushing of the new tundish, tundish covers and basic tundish starting cover, extensive reoxidation of the steel occurs during a startup heat. The total oxygen and inclusion composition result in Figures 17 and 24a clearly show the reoxidation on a startup heat. The SEM and PDA results of the inclusions show that some reoxidation is also observed during ladle exchange as shown by Figures 24a and 33. These results are not surprising since the ladle nozzle is typically above the steel bath in the tundish when the ladle is opened, resulting in direct exposure to air and significant mixing of ladle sand, tundish cover, and tundish slag. Different ladle shroud designs have been developed to allow for submerged ladle open with decreased risk of blow back. Impact pads used in the tundishes are now also engineered refractories developed using water models and CFD modeling. These impact pads are designed to minimize turbulence at the nozzle/cover interface, maximize residence time, promote surface directed flow, and distribute the steel homogeneously in the tundish.

An excellent tracer study by Cicutti et al[77] highlighted the effect of tundish operation on steel cleanliness. Tundish slags were doped with BaO to investigate if they contributed to defects during casting. Their study found that the inclusions in the product contained the presence of BaO (4 to 9%) and that ladle exchange had a big impact on tundish slag entrapment. The entrapment became worse as the sequence progressed because of the amount of slag accumulated in the tundish and the probability of slag emulsification increased. Figure 37a shows the inclusion density for transient slabs compared to steady state slabs and Figure 37b shows the frequency of inclusions with BaO in transition and steady state slabs. Plant remedies included a limit on the sequence length for steels with higher cleanliness requirements and the reduction of casting speed during ladle changes to minimize tundish weight variations.

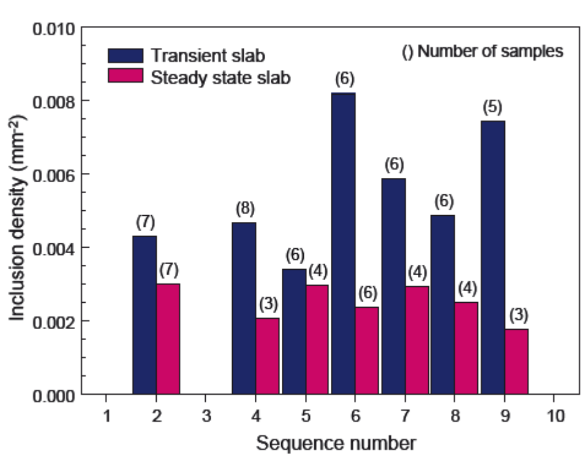


Figure 37a. Evolution of inclusion density along sequence for transition and steady state slabs[77]

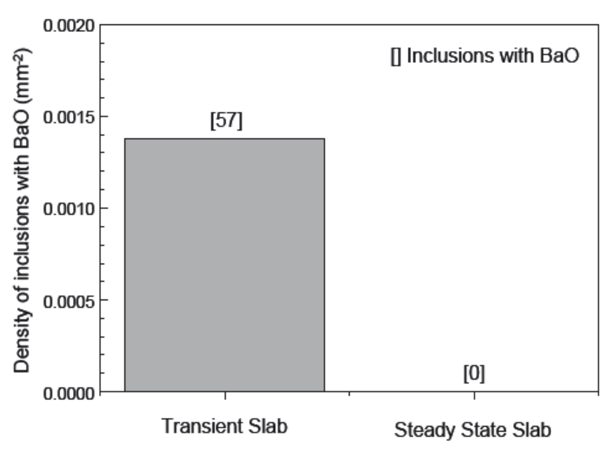


Figure 37b. Frequency of inclusions with BaO in transition and steady state slabs[77]

EMS Stirring

Electro-Magnetic Stirring (EMS) has been widely applied in slab and bloom casters. A number of studies have shown that EMS enhances the inclusion removal from the mold and can significantly affect the quality of cast steel (Figure 38).[47] It reported in earlier papers that EMS improved coil surface quality for high throughput (high casting speeds and wide slabs), but recent studies have shown that coil surface quality is also improved when throughput is low.[47] While EMS stirring has been effective to remove smaller sized inclusions, the it depresses the flotation of larger inclusions (> 100 um), especially at increased stirring intensity[46] Computer simulation studies have indicated that the location of the EMS could also have an impact on liquid steel flow and steel cleanliness.[48] It found that the optimized location was at an intermediate distance from the top of the mold (510 mm) versus 450 mm and 690 mm. These results from this study suggest that different quality conditions might exist for operations that use EMS stirring and move the SEN during a casting sequence to minimize slagline refractory wear.

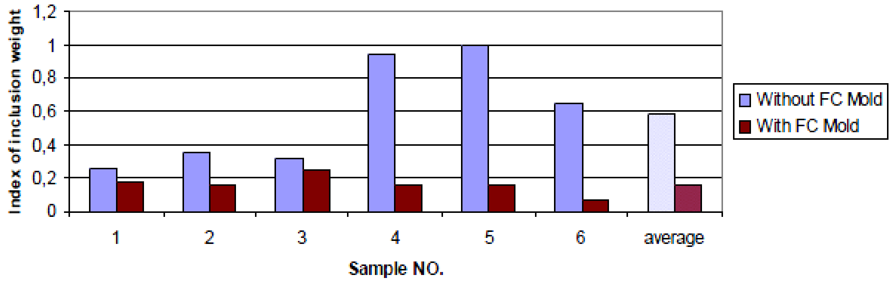


Figure 38. Effect of FC Mold on subsurface inclusions[47]

Argon Purging in the Tundish

An earlier discussion clearly showed the benefits of increased stirring on cleanliness in the ladle. A number of studies indicate that argon purging in the tundish might have similar benefits. Some of the technologies in use today are the MicroClean™ Tundish Gas Diffuser (TGD) and the CALDE™PLUG (Figures 39a and 39b). The principle behind these technologies is that the steel in the tundish will pass through a curtain of argon bubbles that will capture the solid inclusions and float them into the tundish slag.

Figure 39a. Photograph of the MicroClean™TGD

Figure 39b. Photograph of the CALDE™PLUG

Extensive trials with the MicroClean™TGD at Nucor's Decatur division demonstrated that the technology worked as advertised. In a caster sequence, the diffuser was turned on and turned off during the cast for a number of heats. Tundish samples were collected during each event and analyzed on a SEM. Figures 40a show the ternary plot of the inclusions when the diffuser was turned off and Figure 40b show the plot when the diffuser was turned on. The results show that the Diffuser did not have an impact on the liquid inclusions but it certainly removed most of the solid inclusions. The number and volume of solid alumina and spinel inclusions are plotted for 4 heats in Figure 41 with the diffuser turned on and off. The impact of the diffuser on inclusion size is shown in Figure 42. The diffuser was effective decreasing all solid inclusions of all sizes but it appeared to be more effective in removing the larger inclusions (> 3 μm). While the diffuser technology might not make a dirty heat full of liquid inclusions clean, it appears to be effective to remove the solid inclusions that could potentially agglomerate with the liquid inclusions and cause a buildup. These solid inclusions could originate from a marginal heat from the LMF or because of reoxidation events at the caster. Feedback from the Decatur plant indicates that clogging on specific heats could also be effectively decreased by increasing the argon flow through the diffuser.

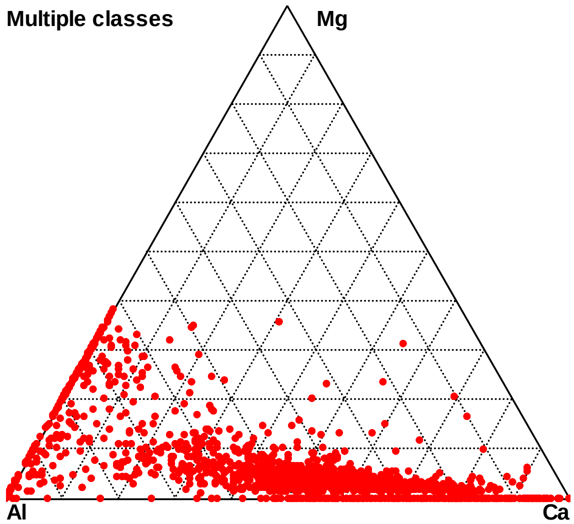


Figure 40a. Ternary Inclusion plot of tundish sample with diffuser turned off

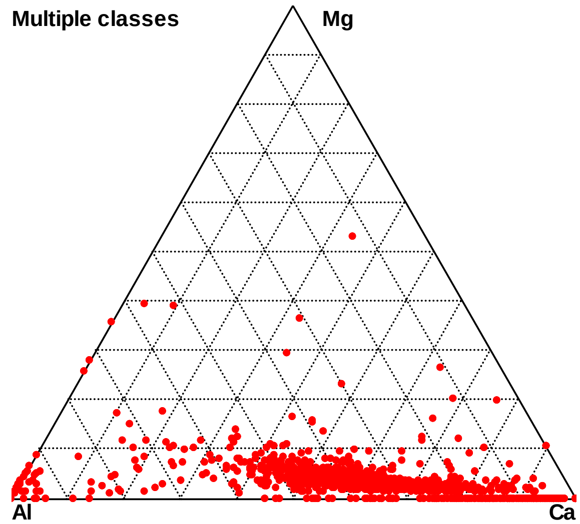


Figure 40b. Ternary Inclusion plot of tundish sample with diffuser turned on

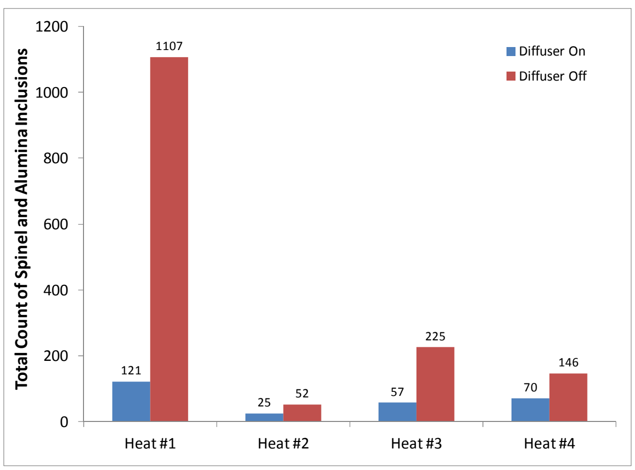


Figure 41a. Total count of spinel and alumina inclusions for a number of heats with the diffuser on and off

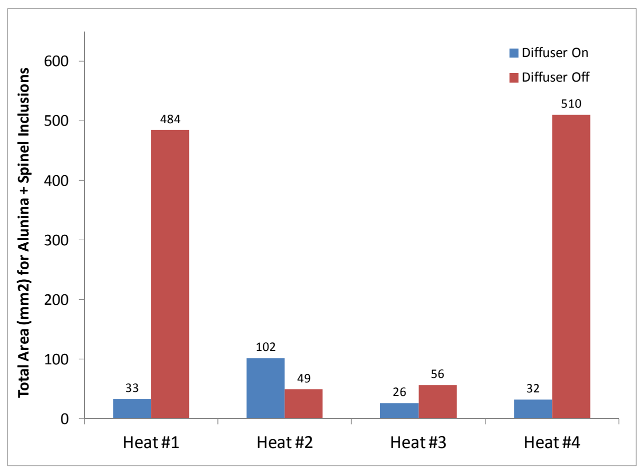


Figure 41b. Total Area of spinel and alumina inclusions for a number of heats with the diffuser on and off

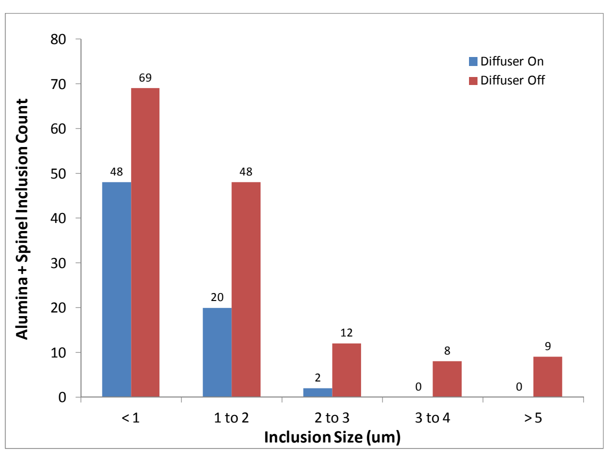


Figure 42. The count of spinel and alumina inclusions for the diffuser on and off as a function of inclusion size

Cicutti also did a study on the effect of argon stirring in the tundish. Trials were conducted by installing this device in one half of a two strand tundish and comparing the inclusion density for the two strands. The density of inclusions larger than 10 μm measured in both strands did not show a clear difference between slabs cast with and without the argon barrier (Figure 43a). However, when only inclusions larger than 30 μm were considered, the density observed in those slabs cast with argon barriers was clearly lower as seen in Figure 43b.

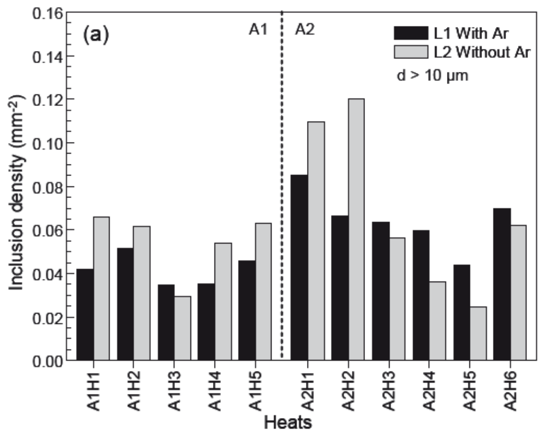


Figure 43a. The effect of argon barriers on inclusion density for inclusions with d > 10 um

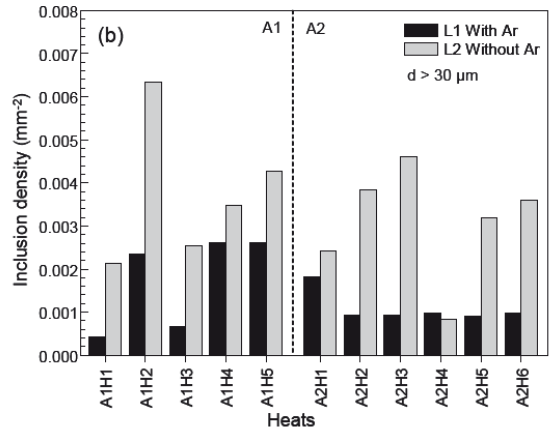


Figure 43b. The effect of argon barriers on inclusion density for inclusions with d > 30 um

Mold level and Stopper Rod Variations

The formation of sliver defects and quality of the final steel product are closely related to the transient liquid steel flow in the mold. Excessive liquid steel surface velocity can shear off and entrain liquid mold slag droplets, leading to the entrapment of inclusions in the solidifying shell and sliver defects in the final products. The release of clogging material from the SEN can send these agglomerations into the mold and also cause meniscus level fluctuations, both events potentially resulting in sliver formation.[39] Figures 44a and 44b show the effect of mold level variation on steel quality.[78]

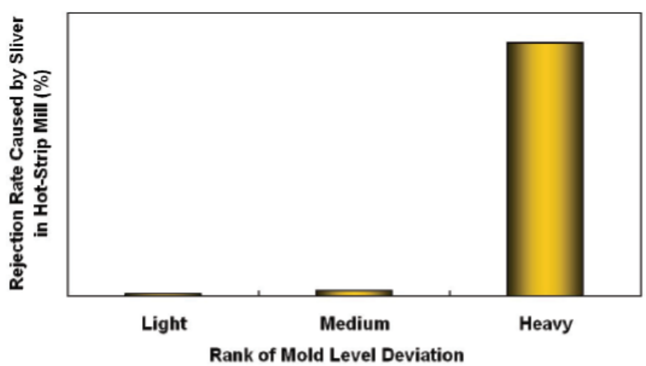


Figure 44a. Relationship between mold level deviation and rejection rate caused by silver in hot-strip mill.[78]

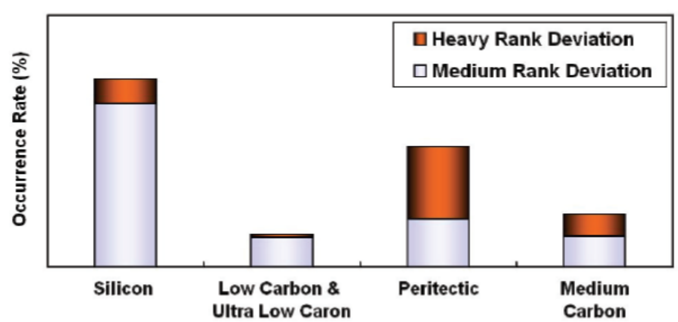


Figure 44b. Occurrence rate of medium and heavy rank mold level deviation on different steel grades.[78]

Possible reasons for an unstable mold level are the following:

1. Inadequate or slow feedback and control from the mold level sensor and stopper rod mechanism.
2. Bulging of the shell during solidification.
3. Poor alignment of the rolls in the lower sections of the caster.
4. Sudden changes in casting speed.
5. The use of argon in the submerged nozzle or too high argon flow rates.
6. Unsteady hydraulic pressure which provides the power to the driven roll to squeeze the slab.
7. Stopper rod clogging and subsequent flushing events.

Figure 45 shows the effect of mold level deviation on the defect rate as measured at the inspection stations in the cold mill.

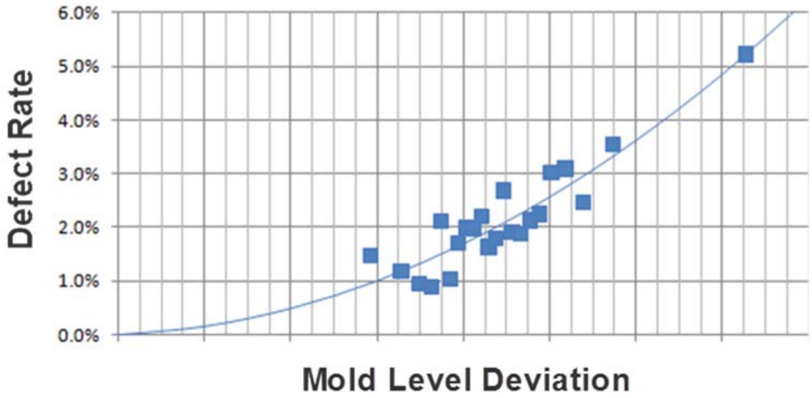


Figure 45. The effect of increasing mold level deviation on the defect rate

Figure 46a shows the stopper rod trace for heat that had extensive clogging at the caster. The subsequent heat at the caster had inclusions that were well-modified, so that a flushing event occurred during that heat (Figure 46b) which resulted in defects in the coil. These events are fairly easy to detect and the corresponding coils are typically flagged for follow-up or automatically downgraded.

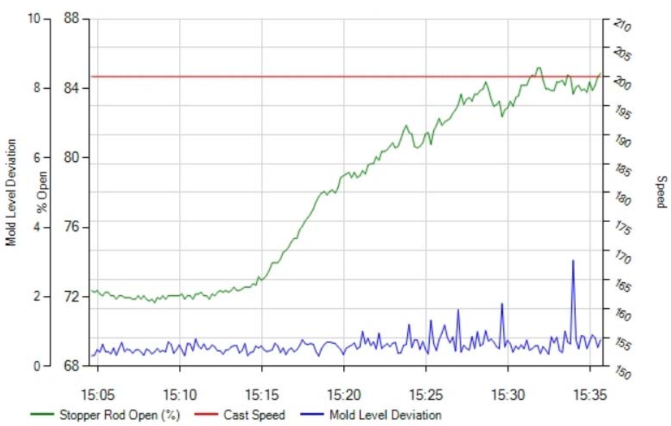


Figure 46a. Stopper rod trace of a heat that clogged

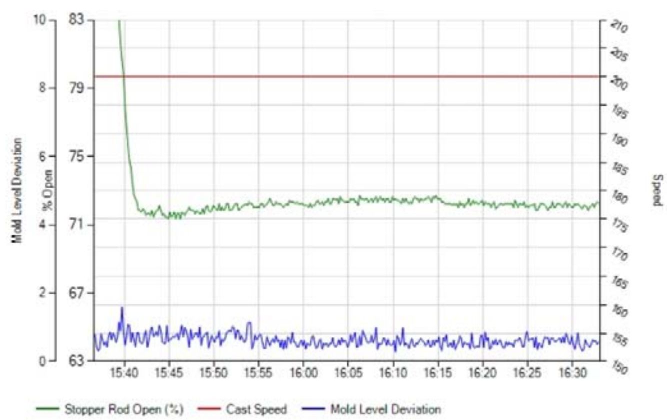


Figure 46b. Stopper rod wash of subsequent heat

CONCLUSIONS

In conclusion, the control of inclusions in the product and process requires an understanding of mechanisms of formation and modification and preferably removal. The key for the industry is to incorporate the large body of work available - often for very specific conditions of product or process - into clean steel practices that can deal with the day to day variability of steelmaking process and produce a consistent product, fit for purpose.

Techniques exist to quantify and classify inclusions after production, but not during real time processing. This makes it difficult to control what cannot be measured. PDA with OES has been a promising technology to enable real time quantification of inclusions and how to respond to variations. This paper reviewed and summarized what the authors believe to be the pertinent industry knowledge regarding steel cleanliness.

ACKNOWLEDGEMENTS

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