

Advanced SEM Methodology for Tracking Reoxidation in the Tundish

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### ABSTRACT

The tundish bath encounters strong reoxidation at caster startup and at ladle exchanges. We use automated inclusion analysis to show the severity of these events on aluminum killed, calcium treated steel. CaS inclusions made during ladle refining dissociate upon reoxidation in the tundish and form higher alumina compounds. The start of a cast sequence may show the lingering effect of oxidation for more than thirty minutes, and a ladle exchange may show it for more than ten minutes. The higher alumina phases formed during these events may contribute to clog events in the flow control casting channel.

## **INTRODUCTION**

In recent years, the extent of our understanding of non-metallic inclusions in steelmaking has moved from the fortunate few to widespread use in steel plant production. Today's universities and plant technical departments conduct research with high value added tools such as the cathodoluminescent microscope and pulse-discrimination optical emission spectroscopy as used by Kaushik et. al. <sup>[1-2]</sup>. We have this common language of inclusions because the scanning electron microscope (SEM) has become readily accessible. Additionally, ever since aluminum has been used in steel, the phenomenon of nozzle clogging has been a significant problem to producers and lasting job security for engineers. The work of Snow and Shea <sup>[3]</sup> in 1949 correlated aluminum deoxidation to the accumulation of solid alumina in the metering nozzle. A modern example of a billet caster submerged nozzle buildup is shown in Figure 1. Samples of nozzle buildup may be impregnated with a liquid epoxy and then polished for a 2-dimensional evaluation, or the same sample may be observed by SEM in the as-received state for a 3-dimensional view. The thin,  $5 - 10 \mu m \log platelets$  here are composed of predominantly CaO'6Al<sub>2</sub>O<sub>3</sub>.



Figure 1. SEM image of a billet caster nozzle buildup in 2- and 3-dimensions, respectively.

## Reoxidation

With high resolution tools at our disposal, and teams of individuals applying creative solutions at the plant, what obstacles remain in the pursuit of clean steel? This target may be broadly summarized with one word: reoxidation. The nature of molten steel is to consume into itself any source of oxygen. The forms that reoxidation may take are many, whether the steel is being refined in the ladle, or transferred to the tundish or mold. More specifically, the initial tundish fill and ladle exchange events are process instabilities that yield higher inclusion content, often sufficient to require a downgrade in quality. Story, et. al., showed a significant pickup of small inclusions (2 - 3 times area fraction) at the time of a new ladle being opened, and an even greater increase of inclusions (5 – 6 times area fraction) at the initial filling of the tundish <sup>[4]</sup>. On a similar note, Chattopadhyay, et. al., described with computational fluid dynamics that pouring with a misaligned ladle shroud could yield a higher inclusion content<sup>[5]</sup>. Thomas described in detail the inclusion morphology changes and total oxygen pickup measured in slab samples taken during a ladle exchange [6]. Potential for emulsification of tundish slag and strong temperature driven flow is evident in Figure 2 as shown here in physical models of the tundish by Morris, et. al., <sup>[7,8]</sup>. The rise of hot water suggests that reoxidation products could be driven toward the surface, but cold water would have the reverse effect <sup>[8]</sup>. SEM evidence of tundish slag entrainment is shown in Figure 3. These examples include  $ZrO_2SiO_2$  ladle sand that was dissolved by tundish slag and then entrained downstream. The small particles of zirconia (bright phase) were precipitated out of an oxide solution on the surface of billet caster submerged entry nozzles. The task of the metallurgist is not only to define the sources of reoxidation, but also to use our tools to determine the effect of countermeasures on clogging and quality in the plant. When considering possible sources of reoxidation in the tundish, we must account for the following:

# Air – Tundish Lining – Ladle Sand – Ladle Slag – Tundish Slag – Shroud Cleaning Residue



Figure 2. Physical modeling images of oil emulsification<sup>[7]</sup> (left) and incoming hot water (red dye) into a colder tundish<sup>[8]</sup>.



Figure 3. SEM images of buildup that contains zirconia rich areas, where the Zr originates from ladle sand.

### **AUTOMATED FEATURE ANALYSIS (AFA)**

Many metallurgists choose the SEM as a tool for evaluation, and this work was done with an ASPEX PSEM eXplorer. This microscope routinely collects size, shape and chemical information on ~1500 inclusions in an hour. As described by Ahlborg, et. al., this equipment rapidly scans stepwise across polished steel in search of a video level that is dissimilar to the base metal<sup>[9]</sup>. A backscattered electron detector yields an image (BEI) that distinguishes color, or video level, based on average atomic weight. Since the iron base metal is a heavy element, it has a very high video level; oxide inclusions have a lower atomic weight and therefore are much darker than the background. Contrast and brightness are adjusted to set a video level difference between the steel sample and an aluminum tape standard at the start of each run. Once a feature is detected by its BEI video level, the system slows down to measure its shape and chemistry. A feature will be excluded if it is outside the acceptable size range, or if it does not meet chemical criteria. Energy dispersive spectroscopy (EDS) detects characteristic X-rays, where individual element intensities are counted. Iron, or any base metal, is set equal to zero; thus empty voids are not considered in this work. Low atomic weight elements such as carbon, nitrogen and oxygen are excluded as their EDS resolution is not accurate at high beam energy. Pure MnS inclusions (video level ~140) are purposely passed over since they are features of solidification. The list of accepted elements for the target counts / feature include Na, Al, Si, Mg, S, Ca, Ti and Mn. Extra caution is used when considering other elements as the EDS noise level may detract 0.5% or more from the functional composition for each additional element. Table I lists several AFA settings that are used for our inclusion studies, and an example of output with two representative ternary diagrams is shown in Figure 4.

AFA Settings				
Electron beam energy	20 keV			
EDS – silicon drift detector size	30 mm <sup>2</sup> area			
EDS base count rate	30,000 counts/second			
Min / Max EDS time	0.5 sec / 1.0 sec			
Aim EDS counts	2500 counts			
Video level – Steel / Aluminum	200 / 60			
Video level – Detect / Measure range	125 / 175			
Scan magnification / scan step size	450X / 0.88 μm			
Min / Max feature size (maximum diameter)	2.0 μm / 225 μm			
Scan area	100 mm <sup>2</sup>			

Table I. AFA settings for PSEM eXplorer



Figure 4. An example of AFA ternary diagram output for one sample.

## **AFA - Rule Classification**

The volumes of collected data may now be sorted based on unique rule classifications. These may include factors for size, shape, location, video level, EDS counts and chemistry. Pretorius, et. al., developed a robust set of guidelines for distinguishing the various calcium aluminate compounds based on their EDS peak intensities <sup>[10]</sup>. They determined the ideal Al/Ca ratio for each of the five known oxides and allowed a contiguous range of compositions to represent each type. For our projects, additional rules are generated according to the type of steel being analyzed, where our general guidelines for aluminum killed, calcium treated steel are shown in Table II. This set of rules uses three expressions that artificially combine multiple oxide phases: CaAl Liquid for high calcium content, CaAl Solid for low calcium content and CaAl Mushy for an intermediate level of calcium that yields an oxide melting point just above typical casting temperatures. Figure 5 shows a  $CaO - Al_2O_3$  binary phase diagram<sup>[11]</sup> for reference of the several unique oxide phases. Special attention is required to define the other main types of inclusions. Magnesia-alumina Spinel Type is categorized by its Mg/Al ratio and it may contain up to 20% calcium. Ca sulfides are described by having more than 20% of both calcium and sulfur. There is of course overlap of compositions between the types of inclusions, particularly for duplex oxide / sulfide inclusions. Here simplification of the designations allows us to more easily evaluate the change in the steelmaking conditions. Additional effort is needed to exclude or unclassify features that are mostly manganese sulfide and therefore not present during steelmaking. Also to be excluded are various sources of contamination either from sample preparation itself or from the laboratory environment. A feature is checked rule by rule, starting at the top of the file, until it fits a classification.

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Inclusion Type	Classification Rules (At%)			
{Unclassified}	Various contaminants			
{Unclassified MnS}	Mn>25 and S>10 and (Al+Ca)<50			
Spinel Type	Mg/(Al+Mg+Ca)>0.1 and Al>30 and Ca<20			
Ca Sulfides	Ca>20 and S>20			
CaAl Liquid	(Ca+Al)>50 and Al/Ca<0.8			
CaAl Mushy	(Ca+Al)>45 and Al/Ca<1.5			
CaAl Solid	(Ca+Al)>45 and Al/Ca<3			
Alumina	Al>50			



Figure 5. Calcium aluminate phase diagram from the American Ceramic Society <sup>[11]</sup>, notation added.

#### METALLURGICAL REACTIONS

Turkdogan's "Physical Chemistry of Ironmaking and Steelmaking" [12] shows that efficient desulfurization is performed after deoxidation with aluminum. As shown in Figure 6, an increase in aluminum lowers the sulfur content when in equilibrium with a high lime slag. Larsen and Fruehan<sup>[13]</sup> advance this relationship by applying it to inclusions in calcium treated steel as a function of oxygen activity. Figure 7 shows their calculation of oxygen versus %CaO in inclusions, where C and A represent CaO and Al<sub>2</sub>O<sub>3</sub>, respectively. The equilibrium oxygen content remains stable for the solid aluminates, whereas it is dramatically lower for liquid aluminates. This is due to the activity of alumina being much lower in the high calcium phases. Equation 1 represents the reaction between calcium aluminate and CaS inclusions, and Al and S content in the steel <sup>[9,13,14]</sup>.



 $3 (CaO) + 2 \underline{Al} + 3 \underline{S} = (Al_2O_3) + 3 CaS$ (Eq. 1)

where:

Thus higher aluminum and sulfur content can increase CaS formation in the ladle. Our mission is to use this platform of sulfide inclusion formation and to show how it is reversed when oxygen may be added downstream. Reoxidation in the tundish would destabilize the sulfides formed in Equation 1. Theoretically, sulfur would be liberated from the sulfides in proportion to the severity of reoxidation. A dissolved oxygen test potentially has the sensitivity to measure the impact, but it is not typically available at the caster. A calculation with a ThermoCalc based software package was made for illustration. Figure 8 shows a 100 ppm addition of oxygen in 1 ppm steps to aluminum killed steel with 32 ppm CaS and 23 ppm C12A7 inclusions. Figure 8 is different from figure 7 only in that it accounts for CaS in addition to calcium aluminate inclusions. The first stage shows oxygen activity remaining low while there is still CaS present; the next stages correspond to higher oxygen activities with the stable phase being C12A7 "Liquid", CA "Mushy" and finally CA2 + CA6 "Solid".



Figure 8. Thermocalc simulation showing dissolved Al and O content with 100 ppm added oxygen in CaS saturated steel.

#### **RESULTS AND DISCUSSION**

Tundish refractory designs and process changes are often evaluated based on final product quality results, which may take many weeks to obtain. Our goal was to gain an understanding of process inclusions for baseline and trial conditions which may serve as a predictor for downstream quality results. After much evaluation of ladle, tundish, mold and product samples, we chose to conduct our studies in a single location, most often the tundish, with an emphasis on sampling the steel many times to observe the relative change. It became apparent that each heat would have a distinctive inclusion footprint. Also, of the many types found within a heat, the types were grouped together depending on closely associated stable phases. For example, heats with much CaS could be found with high calcium ("Liquid") aluminates but not much of the low calcium ("Solid") aluminates. This suggests that thermodynamics is the guiding force that determines the possible reactions, but that they do not reach equilibrium. Analysis of used refractory revealed a discrepancy between tundish inclusions and the corroding species. Figure 9 shows a stopper tip to have spinel, CA and CA2 phases on the tip even though each heat cast was characterized to be rich with CaS inclusions. If sulfide inclusions dissociate at or near the refractory interface, the resultant lime rich oxides would have a very high capacity for corrosion. The findings of Tiekink et. al. <sup>[15]</sup> agree with this disparity.



Figure 9. SEM/EDS of stopper tip shows no CaS even though the tundish inclusions were primarily CaS.

When climbing this 'Mt. Everest' of steel inclusion data, caution must be used in its interpretation. For example, a tundish design study could be undertaken by repeated sampling in a single location for the baseline and trial conditions. This, though, assumes that all incoming heats were refined in the same manner and therefore would provide similar starting points for the inclusions. Often, this is not the case. Figure 10 shows an extreme difference of two calcium treated heats of the same grade from steel plant 'X'. One heat consisted of predominantly *CaAl Liquid* and *Ca Sulfides*, whereas the other heat was mostly composed of *CaAl Mushy* and *CaAl Solid*. Those non-startup heats clearly did not have the same steelmaking conditions. Furthermore, it is essential that a single grade of steel be chosen for the evaluation. Figure 11 shows an average



Figure 10. Steel plant 'X' heat to heat comparison of tundish samples on the same grade (2 samples).

Figure 11. Steel plant 'Y' average of fifteen heats with multiple tundish tests on two grades of steel (60 samples).

of thirty tundish samples for two different grades made by steel plant 'Y'. The low carbon steel yielded more *Solid* and *Mushy* inclusions, which corresponds to higher oxygen ( $\underline{O}$  and  $O_{TOT}$ ) than the medium carbon steel which was replete with *Ca Sulfides*. Thus, the steel grade is just as important as calcium treatment in determining the population of non-metallics.

### **Tundish Sampling Program**

Many of our early studies were focused on aluminum killed, calcium free steel due to nozzle clogging or quality issues. It was readily observed that a proper tundish design evaluation would require a large number of samples to account for the various forms of transient reoxidation that occur. The first heat on a sequence was recognized as a strong oxidizer, and, to a lesser degree, so was each ladle transition. We chose to collect samples as often as possible, just after opening a heat, in order to capture the transition effect. This period may need to be adjusted based on tundish size and throughput. Later samples were spread out over the balance of the heat. This practice allows us to recognize the dirty steel, and by contrast the clean steel toward the end of the heat that contains primarily unaffected ladle inclusions. An example evaluation for aluminum killed, Ca-free steel is shown in Figure 12. This chart plots the inclusion count (alumina) during the 2<sup>nd</sup> through 5<sup>th</sup> heats of a sequence from steel plant 'Z'. In this study of a single strand slab tundish, samples were collected over the nozzle well area. At that location, the 22 MT capacity tundish allowed for a peak in inclusion count 2 to 6 minutes after the ladle was opened. The transient event was much more prominent on the 2<sup>nd</sup> and 4<sup>th</sup> heats. This period of oxidation makes high alumina inclusions and agglomerations which dilute the incoming ladle inclusions that generally contain about 4% magnesia.



Figure 12. Steel plant 'Z' tundish design evaluation from a single grade of aluminum killed, Ca-free steel (29 samples).

The inclusion composition hinted toward each transient event, and the inclusion count may not have captured the event in each of these aluminum killed heats. This uncertainty left us wanting for a more sensitive method to define reoxidation in the tundish. We found our answer in repeating this type of study on steel systems with calcium treatment, particularly those that form CaS. Figures 13A and 13B represent the average chemistry and inclusion count, respectively, for steel plant 'Z' calcium treated steel. The first heat on the tundish clearly shows a change in composition and types that progress toward a lower state of oxidation. Each of the sequenced heats shows a similar change, only to a lesser degree. In all cases, there is an inverse relationship between %Al and %S in the inclusion. This is governed by the temporary loss of CaS inclusions and their replacement by various CaAl phases. Each of these heats may have approached equilibrium in the tundish, but further sampling around the 40 minute mark would be needed for confirmation. We estimate that the latter samples in a heat deliver inclusions that were made in the ladle, without much change due to local reoxidation. Though there will be variation from heat to heat, we can still assess the relative level of reoxidation by following the loss of %S or decrease in count of CaS inclusions. For example, the second heat shown in Figure 13A shows a low sulfur value of 15% at 2 minutes that rises to 19% at 40 minutes. This 4% increase in sulfur implies a certain level of reoxidation, which in this case corresponds to a swing of 262 CaS inclusions per cm<sup>2</sup>. Several other heats should be measured in the same way, with an eye toward correlating real events (non-free open, low tundish weight, slag carryover, etc.) to the observed change in inclusion type.



Figure 13A. Tundish evaluation over 4 heat duration from steel plant 'Z' on the same grade (31 samples).



Figure 13B. Tundish evaluation over 4 heat duration from steel plant 'Z' on the same grade (31 samples).

#### CONCLUSION

A method to evaluate tundish reoxidation with automated SEM/EDS has been described. The plan included collection of multiple tundish samples on several heats from a single grade, with an emphasis on times that correlate to the transient reoxidation events. Though the events could be characterized by counting alumina inclusions from aluminum killed steel, we found it to be advantageous to perform the study on calcium treated steels, particularly those that form CaS. This allowed us to measure tundish reoxidation with greater sensitivity due to the loss of CaS in the presence of oxygen. This methodology is now being used to thoroughly evaluate a tundish configuration in about one week, which is significantly less time than what is required to obtain downstream quality results.

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#### REFERENCES

- 1. P. Kaushik, H. Pielet, and H. Yin, "Inclusion characterisation tool for measurement of steel cleanliness and process control: Part 1," *Ironmaking & Steelmaking*, Volume 36, Number 8, November 2009, pp. 561-571.
- 2. P. Kaushik, H. Pielet, and H. Yin, "Inclusion characterisation tool for measurement of steel cleanliness and process control: Part 2," *Ironmaking & Steelmaking*, Volume 36, Number 8, November 2009, pp. 572-582.
- 3. R. B. Snow, J. A. Shea, E. E. Marbarker, and V. Benedict, "Mechanism of erosion of nozzles in open-hearth ladles," *Journal of American Ceramic Society*, 32 (1949), pp. 187–194.
- 4. S. R. Story, G. E. Goldsmith, R. J. Fruehan, G. S. Casuccio, M. S. Potter, and D. M. Williams, "Study of Casting Issues using Rapid Inclusion Identification and Analysis," *AISTech 2006 Proceedings*, Vol. I., pp. 879-889.
- 5. K. Chattopadhyay, M. Isac, and R. I. L. Guthrie, "Effect of Ladle Shroud Alignment on Steel Quality in a Four-strand, Deltashaped, Tundish," *AISTech 2010 Proceedings*, Vol. I, pp. 1311-1320.
- 6. P. Thomas, "Variations in Steel Cleanness during Transient Continuous Casting Practices," *Materials Science and Technology*, Vol. 21, 2005, pp. 334-338.
- 7. J. Morris, and E. Wotsch, Vesuvius physical model documentation, 2011.
- 8. J. Morris, and D. Zacharias, Vesuvius physical model documentation, 2010.
- 9. K. Ahlborg, R. J. Fruehan, M. S. Potter, S. R. Badger, and G. S. Casuccio, "Inclusions in Aluminum-Killed Steel with Varying Calcium Additions," *ISSTech 2003 Proceedings* Vol. I, pp. 177-194.
- E. B. Pretorius, H. G. Oltmann, and T. Cash, "The Effective Modification of Spinel Inclusions by Ca Treatment in LCAK Steel," *Iron & Steel Technology*, July 2010, pp. 31-45.
- 11. American Ceramic Society Phase Equilibria Diagram Database 3.0.1.
- 12. E. T. Turkdogan, "Physical Chemistry of Ironmaking and Steelmaking," United States Steel Research Laboratory, May 1982, pp. 234b.
- 13. K. Larsen, and R. J. Fruehan, "Calcium Modification of Oxide Inclusions," *Iron & Steelmaker*, Vol. 17, No. 7, July 1990, pp. 45-52.
- 14. S. R. Story, T. J. Piccone, R. J. Fruehan, and M. S. Potter, "Inclusion Analysis to Predict Casting Behavior," *Iron & Steel Technology*, September 2004, pp. 163-169.
- W. Tiekink, B. Santillana, R. Kooter, F. Mensonides, B. Deo, and R. Boom, "Calcium: Toy, Tool or Trouble?" AISTech 2006 Proceedings, Vol. II, pp. 395-403.