Improving Sulfide Shape Control in High-Quality Heavy Plate Steel Grades at ArcelorMittal Coatesville

This study was undertaken to establish steelmaking parameters to ensure sulfide shape control without undue MnS stringers and oxide inclusions. New tools were used to characterize sulfide and oxide inclusions in steel grades and plate products, and results of trials conducted in steel refining and casting to improve cleanliness and shape control are presented. The trial data were examined with inclusion analysis achieved using an automated scanning electron microscope applied to tundish and plate steel samples. It was shown that to control sulfide shape, it is necessary to desulfurize the steel to very low levels, <10 ppm S in this case, and prevent steel reoxidation during casting. Specific ratios among sulfur, oxygen and calcium were found to be necessary to ensure adequate shape control. Successful implementation of modified practices has not only resulted in improved shape control in certain plate products, but application of these practices to other steel grades has significantly improved overall cleanliness, thus improving overall customer satisfaction.

One of the prime objectives in steel refining processes is to control the solid inclusions of aluminum: their amount, composition, size and other properties. The presence of these inclusions has been shown to affect the ability to reach long cast sequences. Calcium treatment in steel is a common practice to modify alumina inclusions, and Al-rich Ca-aluminate and Mg-aluminate (spinel) inclusions, into low-melting-point calcium aluminates. However, excess addition of calcium in steel with high sulfur or lower oxygen content results in the formation of solid calcium sulfide (CaS) inclusions that are deleterious to continuous casting operations. Ideally, calcium additions should provide enough calcium to form liquid oxide inclusions containing about 50% CaO and 50% Al$_2$O$_3$, yet allow the sulfur in the melt to precipitate as either CaS or CaS-MnS at lower temperatures than casting. This is known as “shape control” in the classical literature of Ca treatment, where MnS and complex Ca-Mg-Si-aluminates are modified to achieve inclusion shapes conducive to finishing operations and for subsequent in-use product properties.

Thermodynamically, Ca will react with oxygen or sulfur until the contents of reactant reach very low levels, transforming most of the available oxygen in the form of inclusions. In practice, Ca control in steel is an art and consequences of either under- or overinjection of Ca result in high-melting-point solid Ca-aluminates and CaS inclusions. In certain studies, only 50% of total inclusions present as liquid Ca-aluminates were found sufficient for stable casting. Additionally, it was shown that CaS forms as a transient phase during Ca-modification of alumina and spinel inclusions, even for very low-S-containing melts. Whereas some of the transiently formed CaS can still be present in the steel after completion of Ca treatment, it will not contribute toward clogging but rather act as a buffer against reoxidation that typically occurs during start-up or ladle exchange in otherwise well-protected tundish pouring operations. Since the formation of monocalcium-dialuminate (CaO.$2$Al$_2$O$_3$) inclusions by transformation of CaO...
to CaS is possible,\textsuperscript{10} a controlled amount of CaS in liquid steel is desired by steelmakers. Therefore, control of both total oxygen and sulfur concentrations before Ca-injection in Al-killed steels is necessary. Similarly, measures for optimal Ca-injection into the ladle are necessary and have been a subject of past research.\textsuperscript{11,12}

For heavy plate-grade steels and sour gas-resistant steels used in offshore applications, a low crack length ratio (CLR) in the NACE TM0284 test\textsuperscript{25} is a common requirement. In most cases, higher CLR values are an indication of hydrogen-induced cracking (HIC). Higher CLR values have been reported due to the presence of elongated inclusions in steels, and in many cases, they were elongated MnS inclusions.\textsuperscript{13–17} Previous studies reported controlled applications of Ca treatment to reduce or eliminate elongated MnS inclusions from such products. Nagasuki\textsuperscript{13} developed a factor that is correlated to the length of stringers and suggested that this factor needs to be higher than 1.5 to achieve good shape control. Using this factor for ultralow-S and O steels (S <10 ppm, O <10 ppm), the calculated Ca required for successful inclusion modification is 22 ppm. Jehan\textsuperscript{14} and Herbert\textsuperscript{15} proposed a Ca/S ratio of steel higher than 2 in high-strength, low-alloy steels for MnS shape control, although cautiously advised that a very high Ca/S ratio will be detrimental due to possibility of forming oxide stringer inclusions. In other studies,\textsuperscript{16,17} MnS inclusions disappeared from HIC-resistant steels when Ca/S ratio exceeded 2.0. Notably, the average CLR values in Ca-treated plate steels were much higher when the S content exceeded 30 ppm in comparison to heats with S lower than 10 ppm, and were three times higher when Ca treatment wasn’t used. While these studies showed the use of an index, viz. Ca/S ratio to diagnose the steels with poor HIC properties, they could not explain the outliers with high CLR values due to other stringer inclusions, and especially where and when to measure this ratio and how to effectively control it.

Haidar\textsuperscript{18–20} developed an atomic concentration ratio (ACR) that was correlated to the length and area of A-type inclusions in HIC-resistant plate steels, and a minimum ACR value of 1.8 was predicted to obtain less than 1% elongated features. In the calculation of ACR, the effective Ca/S ratio was calculated by deducting the Ca associated with oxygen (present as Ca-aluminate inclusions) by considering the Ca/O ratio of the steel. A higher ACR was achieved using Ca-injection (or rare earth element injection), and an ACR of 0.6 was noted from the thickness distribution of elongated inclusions. While this was sufficient to obtain good centerline in slab-cast heats, ACR of 1.5 was considered better to obtain inclusion lengths smaller than 10 µm. In other studies,\textsuperscript{21} the Ca/O ratio of steel was related to the propensity of HIC in plate steels, and a range of 1.0–2.0 was postulated to obtain globular Ca-aluminate inclusions.

To control the Ca content to achieve good shape control, a Ca-injection practice was developed by Abraham\textsuperscript{22,23} where the CaSi injection amount increased as a function of sulfur content up to 30 ppm S, beyond which the CaSi injected amount was held constant to avoid tundish nozzle clogging. A previous laboratory study by one of the current authors\textsuperscript{24} showed that MnS length in slab samples in the longitudinal direction decreased with decreasing S content of Ca-injected heats. While no effect of Mn content (up to 1.3%) on MnS inclusion length was noticed, steel reoxidation doubled the MnS elongation. Notably, at Ca/S greater than 2 when Ca/O ratio of steel was higher than 0.6, more than 50% of the Ca-aluminate inclusions were liquid. Also, Türkdoğan\textsuperscript{4} pointed out that both Ca and O content must simultaneously be either lower or higher, and preferred S content lower than 15 ppm for combined lower Ca and O contents for acceptable sulfide shape control of Al-killed steels. The study also noted tolerance of higher S levels for higher Mn content of steels.

**Plant Processes, Scope of Problem, Sampling and Analytical Techniques**

ArcelorMittal Coatesville is a specialty plate manufacturing facility. The steelmaking shop is equipped with an electric arc furnace (EAF), a ladle metallurgy furnace (LMF), a vacuum tank degasser (VTD) and a curved-mold continuous caster (CC). The heat size is 150 MT. Additionally, the shop has capabilities to teem ingots to make thick and heavy plates. Slab casting is conducted as a single-heat batch operation due to the existing design of the tundish car. The steelmaking process for the ASTM 516 pressure vessel steel grade chosen for this study follows EAF → LMF → VTD → CC. Slag raking is conducted before LMF treatment and then again before VTD operation, as part of a low-ladle slag practice. The steel flow from the tundish to the mold is controlled by a stopper rod, while the tundish size is 6 MT. Due to the batch casting operation, the tundish nozzle and the submerged-entry nozzles are seldom clogged, partly due to the low residence time of inclusions in the small tundish.

The generic chemistry of the steels reported in this study is listed in Table I. Scrap is melted in the EAF using three charges followed by carbon injection through injection burners. The heat is tapped using an open-pour practice into a ladle where slag deoxidizers (and modifiers) and alloys are added after completion of tapping. The ladle is slagged off and the steel is deoxidized using Al at the beginning of LMF treatment, followed by lime and fluorospar addition for steel desulfurization. This is followed by
temperature adjustment and trim alloy additions to complete the LMF treatment process. The ladle slag is raked again before starting the VTD for the hydrogen removal process, which employs Ar stirring through a porous plug. After degassing is complete, the vacuum tank cover is opened and CaSi wire injection is made, followed by a short, gentle Ar stir. The ladle is then transferred either to the slab caster or the ingot teeming location. The cast product is hot-rolled and heat treated at ArcelorMittal Coatesville before being transferred to specialty plate customers and users.

In the past decade, unexpected HIC test failures were found in both ingot-cast and slab-cast product. This coincided with a time when customers were requesting lower CLR values (5% CLR) than in the past (15% CLR). Occasional CLR values as high as 40% were reported. CLR, an indication of HIC, was measured using the standard NACE testing method\textsuperscript{25} and was benchmarked against previously supplied ArcelorMittal Coatesville cast products. Scanning electron microscopic (SEM) examination of cracked HIC specimens taken from quarter and center thickness showed elongated inclusions in both the longitudinal and transverse rolling directions; while most features were identified as MnS, Ca-aluminate oxide inclusion stringers were also noted with the use of electron dispersive x-ray (EDX) analysis. The MnS features were sometimes 500 µm long and 20 µm wide, with the average aspect ratio greater than 100. These unexpected large inclusions called for an in-depth review of manufacturing practices, and a team comprising quality control, operations, technology, commercial, and research and development personnel was formed to diagnose the root cause of the problem, perform trials, and implement robust solutions to avoid similar occurrences in these (and other) plate steel grades.

Table 2 lists the samples collected during the standard and trial industrial heats. Also listed are the analytical techniques that were used on these samples. Complete descriptions of these techniques can be found elsewhere.\textsuperscript{26,27} For the most part, the lollipop samples were analyzed using ASCAT\textsuperscript{TM} software.\textsuperscript{28} Using an automated SEM, the size, area and chemistry of each inclusion found on 100 mm\textsuperscript{2} of steel sample surface was recorded. The inclusions were then classified into size ranges, and inclusion families based on normalized EDX composition. Lollipop and thin pin samples were also used to measure the total oxygen (TO) content by sectioning the thicker area closer to the sampler inlet. The TO content was analyzed using a LECO combustion analyzer. In addition, thin pin samples and plate product samples were also used for preparing remelt buttons,\textsuperscript{29} which were analyzed using a cathodoluminescence microscope (CLM) followed by manual microscopy to identify inclusion morphologies. Plate samples sectioned from different widths and thicknesses were also subjected to NACE HIC testing to determine CLR values.

Results and Discussion

Diagnosing Shape Control — At ArcelorMittal Coatesville, it was a normal practice to perform optical microscopy on plate samples to provide a semi-qualitative rating for shape control. Whereas this technique was fairly useful, it was laborious and dependent on operator interpretation. A rapid technique wasn’t available to quantify the success (or failure) of sulfide shape control in the final product, and only CLR values on finished plate were available. While complete heat chemistries and steelmaking and casting process data were available, it wasn’t sufficient to point to the root cause of the problem, and plant operations could not determine the reasons for not meeting shape control in selected plate grades.

Table 2

| Characterization Techniques Employed on Samples Collected During Trials |
|-----------------------------|----------|---------|--------|---------|
| Techniques/samples          | Lollipop | Thin pin | Plate  | Ladle slags |
| Total oxygen                | ✓        |         |        |          |
| Automated scanning electron microscopy (SEM) | ✓ | ✓ |     |
| Cathodoluminescence microscope (CLM)-SEM | ✓ | ✓ |     |
| X-ray fluoroscopy           | ✓        |         |        | ✓        |
| NACE testing                |          |         |        | ✓        |

Table 1

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<th>Steel Chemistry Range in Mass Percent</th>
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CaO-Al₂O₃-MgO. In those studies, the Ca/Al ratio and specific regions of ternary diagrams were correlated to the castability of steel having acceptable inclusion modification. The studies typically reported Ca treatment as the means of inclusion shape modification in Al-killed steels. In the current study, although the oxide ternary diagrams mentioned above were useful to distinguish heats with perfectly good and poor shape control, in many situations, especially for borderline cases, they could not explain the disconnect between inclusion modification noted on tundish samples and quality ratings on corresponding plate samples. In contrast, the Ca-S-Mn ternary diagram showing the distribution of sulfide precipitates in tundish samples had a success rate of more than 90% in matching qualitative shape control ratings on product samples. It should be noted that sulfide features are precipitates in these steels, since CaS does not form in these steels at liquid steelmaking temperature (from thermodynamic calculations) and MnS precipitates out during solidification. In addition to successful application of the Ca-S-Mn ternary diagram, the MnS and CaS area fraction in tundish samples were found to be useful in diagnosing and explaining the shape control issues in these heats. Although the ladle and tundish samples are fast-cooled samples, and aluminum and sulfur segregation occurs in slabs (or ingots) during cooling and solidification, and the fact that MnS stringers are usually noticed and accounted for in product samples, characteristics of MnS precipitates in tundish samples hold information on the state of oxide inclusions and sulfur distribution when present in liquid steel. This fact will become clearer with thermodynamic calculation results shown later for some selected heats.

In a previous publication, one of the current authors reported the use of remelt buttons prepared from tundish samples of the heats that showed good and poor shape control. In addition, automated SEM inclusion analyses showed that the area fraction ratio of MnS/CaS inclusions in the tundish samples matched satisfactorily with the corresponding qualitative rating on the plate samples of these heats. Figs. 1 and 2, reproduced from a previous publication, highlight that in good heats, the MnS/CaS ratio was lower than 1, inclusions were mostly liquid Ca-aluminate-CaS inclusions, and most of the sulfur was precipitated as CaS features (with Mn<20%). The heat rated as poor (Fig. 2) had a good fraction of CA and CA₂ inclusions with all sulfide features present as MnS. The average Ca/Al ratio of oxide inclusions was 2.2 in Heat 2 versus 0.6 in Heat 5, likely due to differences in steelmaking processing conditions. The usefulness of relatively faster automated SEM analysis was the first successful step in eliminating the need of manual microscopy on plate samples for customer qualification (or postmortem analyses on high-CLR-ranked products).

Effects of Ladle Refractory: A common perception in plant operations was that heats produced in dolomite (CaMg(CO₃)₂) refractory-lined ladles showed higher success of sulfide shape control than for the heats made using an alumina-magnesia-carbon (AMC) lining. The supporting theory behind such observations was higher consumption rate (or wear) of the dolomite

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**Figure 1**

![Graph showing MnS/CaS ratio in tundish samples of five heats](image1)

**Figure 2**

![Diagrams showing composition of oxide and sulfide inclusions in tundish samples of two strand-cast heats rated as “good” and “poor.”](image2)
refractory lining. Fig. 3 shows four times higher area fraction of CaO+MgO features in heats made in dolomite refractory ladles. In a study by Story, the effect of refractory ladle lining on steel cleanliness was discussed; a slight increase in magnesia-spinel inclusions population in MgO-C ladles was noted in comparison to AMC ladles, but the overall steel quality wasn’t affected. In heavily stirred ladles at the LMF, the effect of reduction of MgO in the ladle slag on inclusion density and composition superseded the effect of MgO from refractories of MgO-C ladles. In a recent study, Ca transfer to inclusions forming Ca-aluminates in higher-Al-content (~2%) steel was reported. Thermodynamically and kinetically, reduction of CaO in dolomite ladles is possible under vacuum treatment and strong reducing conditions such as low-ladle slag FeO content and higher Al content. The latter two conditions were present in the current study during the dehydrogenation cycle in the VTD treatment, causing Ca transfer to the steel and inclusions. Therefore, it is possible that excess Ca supplied by dolomite refractory ladles helped in achieving good shape control in past commercial heats. However, the results shown in Fig. 3 do not fully support this hypothesis. As shown, the MnS/CaS number density or area fraction ratio measured in tundish samples corresponded well to the relative quality rating given to the plate samples, while the shape control failures occurred both in AMC and dolomite ladles. Also, certain heats produced in both ladle types had good to moderate shape control, and there were situations in which heats produced in dolomite ladles showed poorer shape control (e.g., Heats R0426 and R0477 in Fig. 4) than heats refined in AMC ladles. Fig. 5 shows ternary diagrams of example heats produced in dolomitic ladles that showed good and poor shape control. Interestingly, both heats had very low S (<10 ppm) and reasonably close TO content (~18 ppm). The data in Figs. 4 and 5 showed that heats made in AMC ladles can attain as good sulfide shape control as with dolomite ladle heats, and therefore other steelmaking factors had to be considered.

Thermodynamic calculations were performed using CEQCSI for selected heats that showed poor MnS/CaS number density and area fraction ratio measured in tundish samples in heats produced in two ladle types. G, M and P represent “good,” “moderate” and “poor” ratings given to corresponding plate samples from manual microscopy.

**Figure 3**

Average area fraction of CaO-MgO inclusions in heats produced in two ladle types used at ArcelorMittal Coatesville. All heats had S <30 ppm, Al <0.05%, Ca-treated and dehydrogenized.

**Figure 4**

MnS/CaS number density and area fraction ratio measured in tundish samples in heats produced in two ladle types. G, M and P represent “good,” “moderate” and “poor” ratings given to corresponding plate samples from manual microscopy.

**Figure 5**

CaO-S-Al₂O₃ and Ca-S-Mn ternary diagrams showing composition of oxide and sulfide inclusions in the tundish samples of two heats rated as “good” and “poor” (Heats R0489 and R0477 in Fig. 4), both produced in dolomitic ladles. Both heats had <10 ppm S and were strand cast. The average composition is shown with the red point.
shape control. For this purpose, tundish steel chemistry, including TO, was used as input. The results for Heat R0477 made in a dolomitic ladle and Heat R0448 made in AMC ladle are shown in Figs. 6 and 7, respectively. Both heats had close S, N and TO contents, although Heat R0488 had twice the oxide inclusions area fraction than in Heat R0477. As shown in Fig. 6, the predicted inclusions at 1,525°C are solid CA2 inclusions, also represented as partly liquid oxide inclusions in the CaO-S-Al2O3 diagram in Fig. 5. This implies that despite the use of a dolomitic ladle, oxide inclusions did not reach C12A7 phase such that S partitioning during solidification was split between CaS and MnS, with MnS becoming the major sulfide phase during later stages of solidification. Similarly, in Heat R0448, the predominant oxide inclusion composition was predicted as CA and CA2, and sulfur partition toward MnS accelerates when CA2 changes to CA6 phase (Fig. 7). Predicted final MnS inclusion content from CEQCSI calculations was higher for Heat R0477 in comparison to Heat R0448, which complemented the measured MnS area fraction in tundish samples of these heats, and was also shown by relative MnS/CaS ratios in Fig. 4. From similar thermodynamic calculations made for other heats, observed and calculated inclusion compositions matched satisfactorily, suggesting that Ca treatment was inadequate in the heats that showed poor shape control produced in both dolomite and AMC ladles. While these results did not show if Ca treatment failed due to either lapses in ladle refining practices or due to reoxidation at the caster or both, they were very useful in explaining that dolomitic ladles are not required to produce heats just for good sulfide shape control — this was especially of interest to plant operations, owing to the higher cost of dolomite refractories. Therefore, in all subsequent commercial heats, AMC ladles were used.

Effects of Higher Manganese Content: Another belief among plant metallurgists was that shape control became poorer with increasing Mn content of the steel grades and steels with higher Mn content needed specific minimum S levels. Fig. 8 shows that shape control qualitative ratings based on manual microscopy performed on plate samples had no relationship with Mn content, even though frequency of good shape control was relatively higher at Mn concentrations of 1.1 and 1.5%. In previous studies, the S content of steel for proper shape control was defined based on Mn ranges of 0.4–0.8% and 1.3–1.5%. Applying those Mn levels to the heats identified in Fig. 8, it was found that good shape-controlled heats had similar S levels (~10 ppm) for both Mn ranges, i.e., 0.4–0.6%, and 1.3–1.5%, while poor shape-controlled heats had three times higher S content for lower Mn range in comparison to the heats with higher Mn range. This latter observation was opposite to the recommendation from the previous work, thus explaining the importance of S content compared to Mn content for the steel grades of interest.

Continuous-Cast Versus Ingot-Cast Product: Another observation in the plant was that more ingot-cast heats failed the NACE test due to poor shape control than the slab-cast heats. Fig. 9 shows area fraction of MnS inclusions measured in plate samples from both ingot and slab-cast heats (second campaign) along with CLR values. While ingot heats showed higher CLR values than slab-cast heats in this campaign, the poor shape control noted in strand-cast heats from Figs. 1–5 suggested that inclusion shape control
failure can occur also in slab-cast heats, although for different reasons. The data in Fig. 9 indicate that elongated MnS stringers (longer than 5 µm) significantly affect CLR ratings. This trend is more noticeable in plate samples from ingot-cast heats. Possible reasons for the higher MnS inclusion area fraction shown in Fig. 9 include central segregation, reoxidation owing to poorly shrouded teeming during ingot casting, and inadequate inclusion modification during steel refining.

Fig. 10 illustrates the average area fraction of MnS inclusions in ingot-cast plate samples in the longitudinal direction and, as shown, the uniformity of MnS inclusion distribution across the plate width indicated that ingot-cast products are not necessarily more sensitive to center segregation for sulfides in comparison to the slabs. Omitting segregation as the primary reason for poor shape control in ingot products, further evaluations were made for other factors. Fig. 11 shows the inclusion composition in last sample at VTD for Heats I3 and I4 (from Fig. 9). As shown, while Heat I3 is perfectly treated for oxide inclusion modification, Heat I4 exhibits signs of insufficient shape control, yet both heats had higher MnS area fraction and CLR measurements in plate samples (Fig. 9). It seems that in some ingot-cast heats steel reoxidation during poorly shrouded teeming was responsible for poor shape control as the relationship between the area fraction of MnS inclusions and TO exhibited an increasing trend, such that TO was higher in the plate samples than the corresponding last VTD samples (Fig. 12). More about steel reoxidation control is discussed in section titled “Area Fraction in Plate Samples and Inclusion Morphology, and the Effect of Steel Reoxidation.”

Development of a Shape Control Index: With the above investigations, it appeared that for some strand-cast heats, shape control wasn’t adequately achieved and detailed examination into steelmaking and casting practices was needed. For ingot-cast heats, it was a mixed case between obtaining the shape control and then maintaining it during the teeming process by avoiding reoxidation. While the steelmaking process was under review, an effort was undertaken to establish a compositional-based index that could be used to

### Figure 8
Frequency of sulfide shape control as function of Mn content of plate steels. The rating “good” or “poor” given to plate samples from manual microscopy.

### Figure 9
Area fraction of MnS inclusions in plate samples from ingot- and slab-cast heats. Crack length ratio (CLR) ratings from NACE testing are also shown.

### Figure 10
Average area fraction of MnS inclusions in rolling direction of plate samples sectioned from quarter width and center location; ingot-cast heats.

### Figure 11
CaO–S–Al₂O₃ diagram showing inclusion composition for last ladle sample in ingot heats I3 (left) and I4 (right) from Fig. 9. The average composition is shown with the red point.

### Figure 12
Area-fraction of MnS vs. TO in end-ladle (blue) and corresponding plate (red) samples for ingot-cast heats.
estimate the success of shape control during on-line production. Tools such as postmortem plate longitudinal manual optical microscopic analyses were considered outdated and even rapid analytical techniques such as automated SEM analysis of steelmaking samples had too delayed a response for making timely decisions for cast product disposition, or rolling and heat treatment adjustments. Some studies\(^{37}\) reported the use of pulse discrimination analysis as an on-line tool to identify the composition of oxide inclusions and their effect on castability. In the current study, the glob index\(^{26}\) obtained on tundish samples did not correlate either with area fraction of liquid and partly liquid inclusions (i.e., C\(_{12}A\) and CA phases) or with Ca/Al ratio of oxide inclusions measured using automated SEM on the same samples. Moreover, the glob index value differences were statistically insignificant for the heats with or without shape control. Therefore, efforts were directed toward the development of a robust technique that could routinely be applied on tundish or stream samples.

Internal comparison among ArcelorMittal plants provided guidelines on computing Ca/S ratio (and Ca/O ratio) of steel and correlating these ratios to MnS inclusion stringer length and density in product samples. While calculating these ratios from liquid steel samples was a fairly quick process, obtaining MnS inclusion stringer information on product samples was overwhelming and laborious. Therefore, an attempt was made to correlate the MnS precipitate information from tundish samples with Ca/O ratios measured in the same samples. Note that in this ratio, total Ca and TO are used (and stated as Ca\(_{\text{total}}\)/TO hereafter), and Ca associated with S has not been deducted. As mentioned earlier, TO content was measured in the tundish samples by sectioning a solid piece close to the sample entry and then machining a 5-mm cylindrical pin for LECO combustion analysis. Ar-purged sampling was used to obtain solid tundish samples.

Results shown in Fig. 13 for several initial heats indicated that a MnS/CaS inclusion ratio greater than 1.0 negatively influenced the shape control of heats. The corresponding Ca\(_{\text{total}}\)/TO ratios were 0.5 or lower. The data in Figs. 1 and 4 when combined with Fig. 13 indicated that adequate shape control was achieved when the Ca\(_{\text{total}}\)/TO ratio is higher than 0.7. To test the validity of this concept, data from additional heats from the second campaign was overlapped in Fig. 13 as cross-dots. All the ingot heats in Fig. 9 ended up in the red circled area in Fig. 13, denoting poor shape control. In contrast, two of the slab-cast heats appeared in the green circled area of Fig. 13, showing adequate shape control. Whereas this verification was helpful, there were outliers in this chart (e.g., Ca\(_{\text{total}}\)/TO ~0.55 and 1.9) that could not fully explain the cases of moderate shape control.

Fig. 14 plots the area fraction of MnS against Ca\(_{\text{total}}\)/TO and Ca\(_{\text{total}}\)/S content in tundish samples, and a clearer picture of shape control is observed. Area fraction data on many samples, including on those shown in Figs. 9 and 12, indicated that when the area fraction of MnS increased beyond 1.5 x 10\(^{-6}\), moderate to poor sulfide shape control was observed in the corresponding plate samples. From Fig. 14, this MnS area fraction value corresponds to a minimum Ca\(_{\text{total}}\)/TO ratio of 0.85 and a minimum Ca\(_{\text{total}}\)/S ratio of 1.3. Interestingly, these values of 0.85 and 1.3 also correspond to approximate mass ratios of 12(CaO)/7(Al\(_2\)O\(_3\)) and Ca/S, respectively, whereas 0.55 is the mass ratio of CaO/Al\(_2\)O\(_3\). Based
on this data and from thermodynamic calculations (examples shown in Figs. 6 and 7), it seems that liquid Ca-aluminate inclusions are needed for oxide shape control and, in order to fix S entirely as CaS, a minimum Ca/S in steel needs to be maintained, even just before casting the steel. This information is similar to what has been proposed for shape modification in the literature, where effective inclusion modification requires formation of liquid-Ca aluminate inclusions in molten steel, which then captures S as CaS rings around them during solidification, thus preventing S precipitating with Mn as MnS during solidification, leading to poor shape control. One of the main reasons for formation of such Ca-aluminate inclusions was manganese additions to steelmaking and needed reassessment for future commercial trials. Figs. 15–18 show the relationship between selected steelmaking process variables, inclusion analysis and corresponding shape control.

The Effect of Late VTD Additions: Fig. 15 shows the area fraction of solid Ca-aluminate inclusions and the MnS/CaS ratio of sulfides in tundish samples. As shown in Figs. 6 and 7, these inclusions tend to capture S mostly as MnS during solidification, leading to poor shape control. One of the main reasons for formation of such Ca-aluminate inclusions was late alloy additions in the selected heats during the VTD process. These additions were made during different stages of VTD treatment and consisted of FeSi, FeV, FeMn, Al shot and Mo-oxide additions. Contaminations from such alloys can result in higher TO contents, leading to ineffective Ca modification of inclusions. This was especially concerning since the area fraction of resulting Ca-aluminate inclusions was an order of magnitude higher and MnS/CaS ratio two orders of magnitude higher in the heats with late alloy additions, even when alloys were added in trim amounts (Fig. 15). As previously noted, similar alloys (FeMn, FeSi, etc.) caused formation of solid Ca-aluminate inclusions, resulting in poor cleanliness and clogging of TiSULC grades. In the current study, as a countermeasure, a practice change required all alloy additions to be made at the LMF, thereby eliminating the need of trim additions at the VTD. In addition, certain additions such as FeMn were switched to cleaner ferroalloys for trim additions at the VTD, and if required, were added as early as possible in the process.

Steelmaking and Casting Trials to Obtain Adequate Inclusion Shape Control — As described in the previous section, the sulfide shape control failures were likely related to steelmaking process anomalies and steel reoxidation. Ca_total/TO and Ca_total/S ratios were developed as tools for diagnosing the success of shape control yet they alone could not indicate the source of the problem. The steelmaking and casting process data were thoroughly reviewed for several heats produced in initial campaigns (examples reported in Figs. 1–14). Inclusion analysis data from automated SEM combined with process data indicated that certain steel refining practices contributed to insufficient shape control in steelmaking and needed reassessment for future commercial trials. Figs. 15–18 show the relationship between selected steelmaking process variables, inclusion analysis and corresponding shape control.
The Effects of Lower Sulfur Content: The S distribution in initial industrial heats is shown in Fig. 16. As it can be seen, most heats with good shape control ratings had S content lower than 20 ppm, whereas the distribution of poor shape control heats did not show a clear relationship with the S content. Since the steelmaking has the capability of producing ultralow-sulfur steels owing to LMF and VTD equipment, the variability in the final S content in these heats was an outcome of variable ladle slag-off and incoming S content from the EAF. Nonetheless, in order to obtain the recommended Ca_{total}/S ratio of 2, it was felt that the final sulfur content has to be lower than 20 ppm for the final Ca_{total} content of 40 ppm. If the steel is only desulfurized to 30 ppm, then the final Ca must be close to 60 ppm to respect a Ca_{total}/TO of 1, for 60 ppm final Ca, the acceptable TO can be as high as 60 ppm. Knowing that reaching Ca levels of 60 ppm in the tundish is both difficult and costly, and will significantly deteriorate the steel cleanliness, owing to high volume fractions of inclusions even when the minimum Ca_{total}/TO and Ca_{total}/S ratios are satisfied, operations decided to desulfurize the steel to lower than 20 ppm, and when possible to less than 10 ppm for subsequent heats. For a 100% scrap-based EAF operation, the tap S content in initial heats varied from 250 to 350 ppm. Therefore, to effectively reduce the S content to less than 20 ppm, the following measures were taken. The scrap quality was changed to bundles and busheling, and low-S carbon sources were used at the EAF. The ladle slag volume arriving at the LMF was decreased to avoid sulfur contamination and control phosphorus reversion. Additional lime was added to increase ladle slag lime to alumina ratio more than 2.2. Single-stage Al addition to fully deoxidize steel at the LMF was introduced and low-S containing alloys were used for bulk addition. Because of these modifications, the final S averaged 17 ppm in subsequent trial heats, as shown in Fig. 19.

Improved Calcium Treatment and Argon Stirring: Figs. 17 and 18 show additional VTD practices that needed reconsideration. The amount of CaSi injected varied in the initial heats and was based on the S content in the first VTD steel sample. As shown in Fig. 17, the relative distribution of heats rated good for shape control had a higher amount of CaSi injected. It seemed the variability in CaSi injection amount was either because of a lapse in previous practice on use of CaSi amount as a function of S, poor operator control or likely the inability to control the injection process. In addition, as shown in Fig. 18, the volume of Ar injected through bottom porous plugs was highly variable during the final rinse after completion of Ca injection at the VTD. The MnS/CaS number density ratio in tundish samples increased with increasing stir intensity, particularly when the total injected Ar was higher than 1 ft$^3$/ton. Visual examination of the rinse at the VTD in standard stirring practice showed a large open steel surface under heavy circulation, pointing to one potential source of steel reoxidation.

A previous study$^{22}$ reported variable CaSi addition amount based on S content up to 30 ppm, and about 0.15 kg of pure Ca/MT of steel when S content increased more than 30 ppm. This translated to about 200 lbs. of CaSi for the steel grades of interest in this study. Also, in other ArcelorMittal plants, the Ar flow-rate and final rinse time was half of what was being practiced at ArcelorMittal Coatesville. As mentioned earlier, since the final S content was lowered to less than 20 ppm, subsequent trials were performed using a constant amount of CaSi irrespective to the actual S in the VTD arrival sample. The stir intensity of the final rinse was visually monitored to arrive at Ar flow-rate just sufficient to open a surface plume. The relative stir intensities in trial heats were defined as mild,
The results of these trials are discussed next.

Fig. 19 refers to a temperature measurement station just before the caster where additional steel samples can be collected. Fig. 19 also shows the variability in Ca\textsubscript{total} and TO content, and these measurements were necessary to understand the evolution of Ca\textsubscript{total}/TO and Ca\textsubscript{total}/S in the steelmaking and casting process. As shown, a decrease in the average Ca content from 33 ppm at VTD after Ca treatment to 20 ppm in the standard tundish sample indicates inclusion flotation, since Ca is present mostly in the form of inclusions. An increase in the average TO by 2 ppm in tundish samples possibly shows mild steel reoxidation in the tundish. This is supported by TO trend for an extensively sampled trial heat in Fig. 20, where an increase in TO is noticed between the fourth and sixth samples (more about reoxidation control is discussed in the section titled “Area Fraction in Plate Samples and Inclusion Morphology, and the Effect of Steel Reoxidation”). A separate round robin with other chemical analysis labs was carried out for standard tundish samples, and a variability of 1 ppm each for Ca and S content was recorded. Therefore, even though variability existed in Ca\textsubscript{total} and TO measurements, standard tundish samples were considered reliable and were used for calculating and comparing Ca\textsubscript{total}/TO and Ca\textsubscript{total}/S ratios in the trial heats.

Fig. 21 shows the area fraction of Mn\textsubscript{S} in heats with increased CaSi injection. All heats had standard final rinse practice at VTD. Ca/TO, Ca/S and Ca/Al ratios are shown.

Fig. 22 shows the Ca total, TO and S content of trial heats produced in third campaign. “Buggy” in Fig. 19 refers to a temperature measurement station just before the caster where additional steel samples can be collected. Fig. 19 also shows the variability in Ca\textsubscript{total} and TO content, and these measurements were necessary to understand the evolution of Ca\textsubscript{total}/TO and Ca\textsubscript{total}/S in the steelmaking and casting process. As shown, a decrease in the average Ca content from 33 ppm at VTD after Ca treatment to 20 ppm in the standard tundish sample indicates inclusion flotation, since Ca is present mostly in the form of inclusions. An increase in the average TO by 2 ppm in tundish samples possibly shows mild steel reoxidation in the tundish. This is supported by TO trend for an extensively sampled trial heat in Fig. 20, where an increase in TO is noticed between the fourth and sixth samples (more about reoxidation control is discussed in the section titled “Area Fraction in Plate Samples and Inclusion Morphology, and the Effect of Steel Reoxidation”). A separate round robin with other chemical analysis labs was carried out for standard tundish samples, and a variability of 1 ppm each for Ca and S content was recorded. Therefore, even though variability existed in Ca\textsubscript{total} and TO measurements, standard tundish samples were considered reliable and were used for calculating and comparing Ca\textsubscript{total}/TO and Ca\textsubscript{total}/S ratios in the trial heats.

Fig. 21 shows the area fraction of Mn\textsubscript{S} in heats with increased CaSi injection. All heats had standard final rinse practice at VTD. Ca/TO, Ca/S and Ca/Al ratios are shown.

The area fraction of Mn\textsubscript{S} in heats with varying stirring rinse at VTD. Ca/TO, Ca/S and Ca/Al ratios are shown.

The area fraction of Mn\textsubscript{S} in heats with varying CaSi amount and stirring rinse at VTD. The last two heats R6383 and R6460 showed reoxidation in tundish.
although a direct relationship was not clear from the heats made in earlier campaigns.

**Area Fraction in Plate Samples and Inclusion Morphology, and the Effect of Steel Reoxidation:** Longitudinal sections of plate samples from selected heats were obtained and analyzed by automated SEM to determine characteristics of MnS inclusions. Heats R6383 and R6392 were included since they showed highest and lowest MnS area fraction based on tundish sample inclusion analyses results (Fig. 23). The area fraction results shown in Fig. 24 for plate samples confirmed that Heat R6392 was free of MnS sulfide inclusions, while Heat R6383 had several MnS stringers. Heats R6406 and R6378, on the other hand, showed MnS area fraction results in plate samples contrary to the tundish sample results. Despite a similar S content of 17 ppm in both heats, Heat R6406 had higher TO and lower CaSi injection amounts resulting in slightly higher MnS area fraction in the tundish sample than in Heat R6378 (refer to Figs. 21 and 22). Fig. 24 shows a higher total area fraction of larger MnS inclusions in the plate sample of Heat R6378 in comparison to Heat R6406. An explanation for this observation is not available, although the authors suggest possible reoxidation in Heat R6378 from tundish to mold, which somehow wasn’t captured in the tundish sample chemistry and inclusion analyses, and possibly incorrect sampling in plate sections. Nevertheless, the findings from these heats were helpful in making decisions for practice implementation for sulfide shape control in subsequent trials. It was decided to desulfurize steel to 10 ppm and lower, use 200 lbs. of fixed CaSi injection amount for Ca treatment, use ladle stirring during final rinse at VTD based on small-surface roll area on top of the ladle, and use basic tundish flux to control steel reoxidation during casting in future campaigns. In addition, temperature stirring following VTD treatment was restricted. The heats made using these controlled practices in campaign 4 showed significantly lower MnS area fractions, and Ca\text{total}/TO and Ca\text{total}/S ratios in the required ranges, as shown in Fig. 25. Fig. 25 also shows the results of campaign 3 trial heats, which became a baseline for comparing results of industrial heats produced in campaign 4. All heats of campaign 4 had acceptable shape control as confirmed by 5% maximum CLR from NACE testing.

Heats R6383 and R6392 were further investigated by performing inclusion analysis on remelt buttons prepared from the tundish samples. Fig. 26 with CLM images of Heat R6383 shows that the end-VTD sample had complete modification of oxide inclusions to liquid Ca-aluminates, shown by globular green features, whereas in the tundish sample, reoxidation-type aluminate inclusions were present (red and brown colored dendritic features). The TO content in the end-VTD sample (taken after Ca treatment and final rinse), standard tundish sample, and plate sample for Heat R6383 was 14, 23 and 27 ppm, respectively. In comparison, TO values for Heat R6392 were 15 ppm for the end-VTD sample, 17 ppm in the tundish sample and 18 ppm in the plate samples. The comparison of TO content indicated that severe steel reoxidation occurred during casting of Heat R6383, which typically causes inclusion composition reversion to Al-rich Ca-aluminate inclusions and sulfide partitioning to MnS in cast products.  

**Figure 24**

Area fraction of MnS stringers determined in plate samples of selected heats. Example scanning electron microscope (SEM) images of inclusion stringers are shown.

**Figure 25**

Area fraction of MnS precipitates vs. Ca\text{total}/TO and Ca\text{total}/S ratio in tundish samples of heats made in trial campaigns. The colored lines are manually drawn to indicate the trend.

**Figure 26**

Cathodoluminescence microscope (CLM) images of remelt buttons in Heat R6383. Reoxidation alumina inclusions are shown in red.
of ternary diagrams for tundish and plate samples for these heats, as shown in Figs. 27 and 28, suggested the Ca/Al ratio of oxide inclusions for Heat R6392 was close to twice that of Heat R6383. The shifting of the inclusion population cloud toward alumina in the plate sample of Heat R6383 (CaO-S-Al₂O₃ ternary plot in Fig. 27) suggested significant Al and S enrichment during solidification which wasn’t the case for Heat R6392 (Fig. 28). Noting that the sulfur content of Heat R6383 was more than twice that of Heat R6392, it was anticipated that Heat R6383 would show relatively poor shape control, although examination of Fig. 27 made it clear that steel reoxidation made the situation worse for sulfide shape control. This observation led to examination of conditions that caused steel reoxidation during pouring of ladles into the tundish and during steel flow from tundish to mold.

Visual observations during casting showed formation of a moderate to large open eye several times at the surface of steel bath in the tundish. The location of this open eye was mainly around the ladle shroud. Since the tundish size is 6 tons, the residence time of inclusions in the tundish is short and therefore complete inclusion flotation is not possible. Thus even minor steel reoxidation in the tundish will not only change the inclusion composition, but will also affect the minimal required Ca/TO for adequate shape control. This implied that the VTD is the last stage to refine and float inclusions and supply fully modified inclusion composition to the caster for acceptable shape control. Thus, after development of improved practices at VTD, the focus was shifted on identification of tundish practices that affected shape control, e.g., steel reoxidation, and development of corrective actions for their control.

As mentioned earlier, in campaign 3 heats, tundish flux practice was already modified to use basic flux and increased addition amount to cover the open surface in the tundish. While this practice helped, it was insufficient to control the reoxidation reliably without assistance from an operator. Numerical investigation revealed that incorrect size and location of the impact pad in the tundish and ladle shroud misalignment were two main reasons for frequent open eye formation in the tundish bath. A separate study reported elsewhere was launched to further determine appropriate tundish furniture. In the current study, for subsequent trials in later campaigns, casting operations were monitored and the tundish bath was examined using a mounted optical camera that guided the operators for timely flux additions to control any open eyes. Moreover, as excess Ca acts as a buffer against reoxidation, the CaSi addition amount at VTD was increased to 210 lbs.

For the ingot casting process, reoxidation during open-stream teeming was present (as discussed in the previous section), affecting cleanliness and shape control in the final product. The changes made in steelmaking practices, including an increase in CaSi injection amount, lowering of S content, and the use of a mild stir at the VTD were helpful but inadequate as shape control was unreliable in ingot-cast products. Therefore, an Ar-purged conical shroud made of silica wool was manufactured in-house and trialed. This practice not only protected the steel stream directly in contact with air, but also helped to keep the stream narrow without too much splashing. The shroud was perfected in a few alterations in subsequent trials. Additional key points that helped in the ingot casting process include lowering the mold powder bags in the
ingot molds to a precise height, using hot top boards to improve insulation and minimize contamination and flux entrapment, and keeping runner traps free from debris.

**Final Practice Refinements —** During this study, a few practice refinement strategies were pointed out by plant operations. One school of thought was to eliminate Ca treatment completely if the steel is desulfurized to 8 ppm or lower. The concept behind this approach was to have as low a volume of inclusions as possible free of Ca, and let S precipitate as small MnS inclusions, which would be acceptable to properties in these products. Such a practice was not acceptable to certain customers and the idea was not pursued further. A second approach was to Ca-treat the steel at the end of the LMF process or at the beginning of VTD cycle. The thought was that early Ca treatment will sufficiently modify oxide inclusions and then float large inclusions out during a strong vacuum-assisted rinse employed for H removal in the VTD. Since carbon in steel can thermodynamically reduce Ca under vacuum, it is expected that the Ca loss from the steel will result in a lower total Ca, in addition to lower TO and S contents, and limited Ca-containing oxide inclusions. The expected net result for MnS inclusions in this practice is similar to the practice with elimination of Ca treatment. Plant operations agreed to a trial (termed hereafter as “pre-Ca injection trial”) to test this hypothesis on selected grades, and three heats were produced.

Figs. 29 and 30 show the results of the pre-Ca injection trial heats. The area fraction of MnS precipitates vs. Ca\textsubscript{total}/TO and Ca\textsubscript{total}/S ratio in tundish samples of all heats studied during the project. Pre-Ca injection trial results are also marked. The colored lines are manually drawn to indicate the trend.

**Figure 29**

![Figure 29](image)

Area fraction of MnS precipitates vs. Ca\textsubscript{total}/TO and Ca\textsubscript{total}/S ratio in tundish samples of all heats studied during the project. Pre-Ca injection trial results are also marked. The colored lines are manually drawn to indicate the trend.

**Figure 30**

![Figure 30](image)

CaO-S-Al\textsubscript{2}O\textsubscript{3} and Ca-S-Mn ternary diagrams in the tundish sample for a pre-Ca trial heat. CaSi injection of 220 lbs. and S = 13 ppm.

Ca\textsubscript{total}/S ratio played a role in shape control more than the Ca\textsubscript{total}/TO in these heats. Even though the results of the three pre-Ca injection trial heats showed the possibility of achieving good shape control with limited Ca remaining in the steel (or even by eliminating Ca treatment completely), requalification of a new process route with certain customers would be cost-intensive, time-consuming and affecting productivity, and therefore plant operations...
decided to use the standard production route maintaining best-in-class clean steelmaking practices for the foreseeable future.

Before conclusion of the project, the results obtained in this study were compared with the literature. Heats in campaign 5 and later were used to compare Ca\textsubscript{total}/S ratios measured in the tundish and plate product samples, and the use of Ca\textsubscript{total}/S and Ca\textsubscript{total}/TO in the melt (i.e., from the tundish sample) to the largest sulfide inclusion length analyzed in plate samples. As shown in Fig. 31, a good match was seen between Ca\textsubscript{total}/S ratio in tundish and plate samples. The correlation coefficient between Ca\textsubscript{total}/S and sulfide inclusion length was 0.7, and the relationship trend was similar to what was discussed in the literature. Although a specific relationship between Ca\textsubscript{total}/TO ratio and shape control in product samples was not discussed in previous studies,\textsuperscript{13–20} in this research a strong decreasing trend was noted between MnS length and Ca\textsubscript{total}/TO in tundish samples, as shown in Fig. 31. The results on plate samples substantiated the use of these ratios from melt samples on a routine basis for achieving acceptable sulfide shape control for commercial heats. Table 3 shows some statistics for heats produced in later campaigns, indicating reliable capability at ArcelorMittal Coatesville to produce such steels.

The implementation of the aforementioned practices in steelmaking and casting operations at ArcelorMittal Coatesville has resulted in achieving significant improvements in HIC-sensitive and other specialty plate-grade steels. Not only has the cleanliness of studied grades significantly improved, but acceptable shape control has also resulted in better in-use properties such as lower CLR and higher impact energy. The implementation of clean steel practices to other grades have also shown increased productivity, higher quality and reduced costs due to the elimination of reprocessed heats, resulting in higher customer confidence in the products.

### Summary and Conclusions

The work reported here was conducted at ArcelorMittal Coatesville over a period of several years with the aim of improving steel cleanliness, sulfide shape control and rejection performance on specialty plate grades. Steelmaking process data, inclusion analyses made on steel samples collected from standard and trial heats in several campaigns, and product test data were used to determine the success of the trials. A summary of the major results is presented below.

1. Unexpected failures of HIC properties of pressure vessel plate steel due to elongated MnS inclusions were reported. Improved reliability of Ca treatment needed for adequate shape control of inclusions was indicated.

2. ArcelorMittal Coatesville performed optical microscopy on plate product samples to provide qualitative ratings indicative of shape control. The research conducted here demonstrated that tundish samples can be used to assess the success of sulfide shape control by measuring the MnS/CaS area fraction (or number density) ratio.

3. Poor shape control was attributed to insufficient Ca treatment, and was found to be independent of the ladle refractory lining and the Mn content of steel. Thermodynamic calculations and inclusion analyses made on remelt buttons of heats with poor shape control indicated that completely modified Ca-aluminate inclusions (7CaO.12Al\textsubscript{2}O\textsubscript{3}) are required for S partitioning as CaS during solidification, even for ultralow-S-containing steels. Al-rich solid Ca-aluminate inclusions tend to cause S to precipitate as MnS, leading to poor sulfide shape control.

4. Ingot-cast heats had generally inferior HIC properties than slab-cast product. Total oxygen in end-ladle and plate product samples implicated steel reoxidation during ladle teeming. Among several steps taken to reduce steel reoxidation, hot top boards were used, an improved Ar-purged shroud was manufactured and mold powder bags were hung lower in the molds.

5. Inclusion analysis data of continuous cast heats showed a relationship between area fraction of MnS in tundish samples with melt Ca\textsubscript{total}/TO and Ca\textsubscript{total}/S ratios. Total Ca in steel samples is used to calculate these ratios without subtracting the Ca associated with S. From these relationships, minimum ratios for achieving acceptable shape control were

| Table 3 | Elemental Capability to Produce Plate-Grade Steels for Shape Control |
|---------|------------------|-----------------|----------------|----------------|-----------------|----------------|
|         | Ca\textsubscript{total} | S   | TO  | N   | H   | P   | Ca\textsubscript{total}/TO | Ca\textsubscript{total}/S |
| Average | 22               | 10  | 16  | 62  | 2.3 | 44  | 1.3                        | 2.2                        |
| Std. dev.| 3.6             | 4.2  | 3.8  | 11  | 0.6  | 6.2  | 0.2                        | 0.5                        |
developed and are now used to predict sulfide shape control success.

6. Steelmaking factors that affected shape control were S content of steel, late alloy additions at VTD, CaSi injection amount and final rinse conditions. It was determined that to obtain good shape control in all plate products, S content lower than 10 ppm, CaSi amount of 1.2 lbs./ton of steel and a mild stirring were necessary to achieve the recommended \( \text{Ca}_{\text{total}}/\text{TO} \) ratio of 1.0 and \( \text{Ca}_{\text{total}}/\text{S} \) ratio of 2.0. Changing scrap charge was the key step in reaching <10 ppm timely without modifying slag chemistry or increased Ar flow.

7. Steel reoxidation in the tundish during slab casting made it difficult to achieve the recommended \( \text{Ca}_{\text{total}}/\text{TO} \) ratio. Reoxidation also caused poor sulfide shape control in the plate product even when satisfactory clean steelmaking practices had been achieved. This development was expected since thermodynamically Al-rich Ca-aluminates formed during reoxidation affect shape control. Severe reoxidation was confirmed from visual examination of the casting process, leading to the use of a basic tundish flux and constant monitoring of the steel bath using an optical camera to avoid open eye formation.

8. Injection of Ca during the start of VTD treatment cycle (pre-Ca injection practice) was as good in achieving shape control as with the standard practice of Ca-injection at the end of the VTD process. Pre-Ca injection trial heats showed minimal MnS features in the product samples, even though \( \text{Ca}_{\text{total}}/\text{TO} \) and \( \text{Ca}_{\text{total}}/\text{S} \) in melt samples did not meet recommended values. This route wasn’t pursued further due to expensive customer process requalification requirements.

9. Verification of recommended \( \text{Ca}_{\text{total}}/\text{TO} \) and \( \text{Ca}_{\text{total}}/\text{S} \) ratios in the tundish samples was made by identifying a relationship between these ratios and the largest sulfide length in corresponding plate samples. This verification enabled elimination of tedious qualitative optical microscopy on plate samples as a quality control method.

10. The Ca/Al ratio of oxide inclusions measured in tundish samples was neither helpful in identifying steelmaking factors that caused poor shape control nor useful in distinguishing the levels of trial variables that affected inclusion modification. In most trial heats, the Ca/Al ratio from melt samples suggested good inclusion modification, while mixed shape control results were seen in the corresponding plate samples. Whereas this ratio still required timely automated SEM inclusion analysis, \( \text{Ca}_{\text{total}}/\text{TO} \) and \( \text{Ca}_{\text{total}}/\text{S} \) ratios were available within a few hours and therefore were adopted by plant operations for heat qualification. This is the first published study where the use of these ratios for real-time determination of shape control has been reported.

11. The collective teamwork of research and development, operations, technology, and quality control staff helped in developing and implementing required clean steel practices to achieve satisfactory sulfide shape control in steel grades of interest. The capabilities of steel producing were reinvented and improved to achieve more tightly controlled chemistry specifications of S, TO, P and H content of steels. Application of these practices has led to zero rejections, reduced costs, enhanced capability to supply maximum 5% CLR specified products and improved customer satisfaction.

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References


18. O. Haida, “Mechanism of Sulfide Shape Control in Continuously Cast HSLA Steel Slabs With Ca and/or Rare Earth Elements,” English Reprint of Tetsu To Hagane, Vol. 60, No. 3, 1980, pp. 48–56.


28. Automated Steel Cleanliness Assessment Tool (ASCAT), RJ Lee group, Pittsburgh, Pa., USA.


35. Chemical Equilibrium Calculation for the Steel Industry, ArcelorMittal Global R&D.


