State of the Art in Evaluation and Control of Steel Cleanliness

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(Received on June 11, 2002; accepted in final form on November 7, 2002)

This paper first reviews the current "state-of-the-art" in the evaluation of steel cleanliness, discussing over 20 different methods. The demand for cleaner steels requires lowering non-metallic oxide inclusions and also controlling their morphology, composition and size distribution. Because no single method can measure all of these aspects accurately, it is best to combine several methods together to quantify steel cleanliness in a given operation. Owing to the cost, time requirements, and sampling difficulties, steel cleanliness is widely inferred using total oxygen, nitrogen pick-up, and other indirect methods. Recent cleanliness values using these indicators are summarized for LCAK at many steel plants around the world.

Secondly, this paper reviews operating practices to improve steel cleanliness at the ladle, tundish and continuous caster, emphasizing findings quantified with plant measurements. Inclusions come from many sources, including deoxidation, reoxidation, slag entrapment, refractory wear, and chemical reactions. They generate many defects such as cracks and slivers in the steel product. Steel cleanliness is controlled by attention to a wide range of important operating conditions throughout the steelmaking and casting processes. For ladle operations, FeO and MnO in the slag, ladle treatments, and inclusion modification are discussed. For tundish operations, tundish depth and capacity, casting transitions, refractory lining, tundish flux; gas stirring, and flow controls are discussed. Important transfer operations from ladle to tundish and from tundish to mold, such as argon protection, sealing issues, and SEN clogging are summarized. Caster operations reviewed include the effect of casting speed, fluid flow pattern control, surface level control, and caster curvature.

KEY WORDS: steel cleanliness; inclusions; total oxygen; nitrogen pick-up; ladle; tundish; mold; caster; plant measurement.

1. Introduction

The demand for cleaner steels increases every year. In addition to lowering non-metallic oxide inclusions and controlling their size distribution, morphology, and composition, clean steel requires control of sulfur, phosphorus, hydrogen, nitrogen and even carbon, and minimizing metallic impurity elements such as As, Sn, Sb, Se, Cu, Zn, Pb, Cd, Te and Bi. These requirements vary with steel grade and its end use, as shown in Table 1. Thus, clean steel for one application is often unacceptable for a different application.

Metallic impurity elements, which are traditionally found only in trace amounts, are becoming an increasing problem due to their accumulation in the scrap supply. These elements cause intergranular segregation leading to cracks, detrimental precipitates and other problems, which are often manifested as slivers in the final product. These elements can be difficult to remove in steelmaking and refining, but can be lowered by carefully controlling the scrap charge, or by charging blast furnace iron, direct-reduced iron, or other relatively pure iron source. These trace element aspects of cleanliness are reviewed elsewhere,

so the remainder of this paper reviews oxide inclusion cleanliness, focusing on Low Carbon Al-Killed steel (LCAK steel).

Inclusions can generate many defects in the steel product. For example, LCAK steel cans suffer from cracked flanges due to lack of formability, while axels and bearings suffer fatigue life problems. Both formability and fatigue life are highly affected by sulfide and oxide inclusions in the steel. Sliver defects occur as lines along the steel strip surface parallel to the rolling direction. Slivers plague LCAK steel sheet for automotive applications, causing both cosmetic surface imperfections and formability problems. They usually consist of aluminates originating from deoxidation or from complex non-metallic inclusions from entrained mold slag, as documented in many studies, such as at Inland Steel, National Steel, and Kawasaki Steel.

In addition to the amount of inclusions, steel cleanliness depends greatly on the size distribution, morphology and composition of non-metallic inclusions in the steel. The inclusion size distribution is particularly important, because large macroinclusions are the most harmful to mechanical properties. One kg of typical LCAK steel contains 107–109 inclusions, including only 400 80–130 µm inclusions, ten 130–200 µm inclusions and less than one 200–270 µm sized inclusion. Obviously, detecting the rare large inclusions is very difficult. Though the large inclusions are far outnumbered by the small ones, their total volume fraction
may be larger.20) Sometimes a catastrophic defect is caused by just a single large inclusion in a whole steel heat. Thus, clean steel involves not only controlling the mean inclusion content in the steel but also on avoiding inclusions larger than the critical size harmful to the product. To this end, many products in Table 1 include restrictions on the maximum inclusion size. The importance of inclusion size distribution is further illustrated in Fig. 1, which shows the measured content of inclusions larger than 30 μm to drop from 1.61 ppm in a ladle to only 0.58 ppm in the tundish.21) Thus, the tundish steel is cleaner, despite having a slightly higher total oxygen content and more total inclusions.

Non-metallic inclusions come from many sources:17,22–26) 1) Deoxidation products, such as alumina inclusions cause the majority of indigenous inclusions in LCAK steel. They are generated by the reaction between the dissolved oxygen and the added deoxidant, such as aluminum. Alumina inclusions are dendritic when formed in a high oxygen environment, as pictured in Figs. 2(a) and 2(b),27) or may result from the collision of smaller particles, including some of those in Fig. 2(c).28) 2) Reoxidation products, such as alumina, are generated when i) the Al remaining in the liquid steel is oxidized by FeO, MnO, SiO2 and other oxides in the slag and refractory linings, or ii) by exposure to the atmosphere; 3) Slag entrapment, when metallurgical fluxes are entrained in the steel, occurs especially during transfer between steelmaking vessels. This forms liquid inclusions that are usually spherical, as shown in Fig. 2(d).28) 4) Exogenous inclusions from other sources, include loose dirt, broken refractory brickwork and ceramic lining particles. They are generally large and irregular-shaped. They may act as sites for heterogeneous nucleation of alumina and might include the central particle pictured in Fig. 2(c).28) 5) Chemical reactions, for example produce oxides from inclusion modification when Ca treatment is improperly performed.29,30) Identifying the source is not always easy, as for example, inclusions containing CaO may

| Steel product                  | Maximum impurity fraction                              | Maximum inclusion size |
|-------------------------------|-------------------------------------------------------|------------------------|
| IF steel                      | [C]≤0.03ppm, [N]≤0.04ppm, T.O.≤0.04ppm                | 100μm*                 |
| Automotive & deep-drawing    | [C]≤0.03ppm, [N]≤0.03ppm                              | 100μm*                 |
| Sheet                         |                                                       |                        |
| Drawn and ironed cans         | [C]≤0.03ppm, [N]≤0.05ppm, T.O.≤0.02ppm                | 20μm*                  |
| Alloy steel for Pressure      |                                                       |                        |
| vessels                        |                                                       |                        |
| Alloy steel bars              | [P]≤0.006ppm                                         |                        |
| HIC resistant steel (sour      |                                                       |                        |
| gas tubes)                    |                                                       |                        |
| Line pipe                     | [S]≤0.05ppm, [N]≤0.05ppm T.O.≤0.05ppm                 | 0.5μm*                 |
| Sheet for continuous annealing|                                                       |                        |
| Plate for welding             | [H]≤0.015ppm                                         | 15μm*                  |
| Tire cord                     | T.O.≤0.01ppm                                         | 10μm*                  |
| Non-grain-oriented Magnetic    |                                                       |                        |
| Sheet                         |                                                       |                        |
| Heavy plate steel             | [H]≤0.02ppm, [N]≤0.04ppm T.O.≤0.01ppm                 | 20μm*                  |
| Wire                          | [N]≤0.02ppm                                           | 20μm*                  |

Fig. 1. Al2O3 inclusion size distribution in ladle and tundish.21)

Fig. 2. Typical inclusions morphology and compositions.
Steel cleanliness is controlled by a wide range of operating practices throughout the steelmaking processes. These include the time and location of deoxidant and alloy additions, the extent and sequence of secondary metallurgy treatments, stirring and transfer operations, shrouding systems, tundish geometry and practices, the absorption capacity of the various metallurgical fluxes, and casting practices. Steel cleanliness is an important topic that has received much attention in the literature. An extensive review on clean steel by Kiessling in 1980 summarized inclusion and trace element control and evaluation methods, especially for ingots. More recent reviews of this topic have been made by Mu and Holappa which added extensive thermodynamic considerations. McPherson and McLean reviewed non-metallic inclusions in continuously casting steel, focusing on the inclusion types (oxides, sulfides, oxysulfides, nitrides and carbonitrides), inclusion distributions and methods to detect inclusions in this process.

This paper reviews the current “state-of-the-art” in steel cleanliness. First, the methods for evaluating steel cleanliness are reviewed. Indirect measures, such as total oxygen (T.O.) and nitrogen pick-up, are used to summarize steel cleanliness for LCAK at many steel plants around the world. Next, operating practices to improve steel cleanliness at the ladle, tundish and continuous caster and during transfer operations are reviewed. Industrial measurements on steel cleanliness are used to illustrate every point. This paper aims to provide useful information for the production of clean steel, focusing on the control of alumina inclusions.

2. Methods to Evaluate Steel Cleanliness

In order to study and control steel cleanliness, it is critical to have accurate methods for its evaluation. The amount, size distribution, shape and composition of inclusions should be measured at all stages in steel production. Measurement techniques range from direct methods, which are accurate but costly, to indirect methods, which are fast and inexpensive, but are only reliable as relative indicators.

2.1. Direct Methods

There are several direct methods to evaluate steel cleanliness, which are summarized as follows and compared in Table 2.

2.1.1. Inclusion Evaluation of Solid Steel Sections

Several traditional methods directly evaluate inclusions in a two-dimensional section through solidified product samples. The last five of these methods add the ability to measure the composition of the inclusions.

1) Metallographic Microscope Observation (MMO): In this traditional method, two-dimensional slices through steel samples are examined with an optical microscope and quantified by eye. Problems arise when interpreting slices through complex-shaped inclusions. For example, Fig. 2(a) shows a slice through the single inclusion revealed in Fig. 2(b), which might mistakenly be interpreted as a cluster of smaller inclusions. In addition, small inclusions are too time-consuming to count with this method and large inclusions are too rare. Although there are some methods to relate two-dimensional results to three dimensional reality, this is very problematic.

2) Image Analysis (IA): This enhancement to MMO improves on eye evaluation by using high-speed computer evaluation of video-scanned microscope images to distinguish dark and light regions based on a grayscale cutoff. This method can easily evaluate larger areas and greater inclusion numbers than MMO, but is subject to errors such as mistaking scratches, pitting, and stains for non-metallic inclusions.

3) Sulfur Print: This popular and inexpensive macrographic method distinguishes macro-inclusions and cracks by etching sulfur-rich areas. It is subject to the same problems as other 2-D methods.

4) Scanning Electron Microscopy (SEM): This method clearly reveals the three-dimensional morphology and the composition of each inclusion examined as shown in Fig. 2(b). Composition is measured with Electron Probe Micro Analyzer (EPMA). Extensive sample preparation is required, however, to find and expose the inclusion(s).

5) Optical Emission Spectrometry with Pulse Discrimination Analysis (OES-PDA): The OES method analyzes elements dissolved in liquid steel. Ovako Steel improved this technique to measure the total oxygen content, microinclusion size distribution and composition within 10 min of collecting the sample. Inclusions cause high-intensity spark peaks (relative to the background signal from the dissolved elements), which are counted to give the PDA index.

6) Laser Microprobe Mass Spectrometry (LAMMS): Individual particles are irradiated by a pulsed laser beam, and the lowest laser intensity above a threshold value of ionization is selected for its characteristic spectrum patterns due to their chemical states. Peaks in LAMMS spectra are associated with elements, based on comparison with reference sample results.

7) X-ray Photoelectron Spectroscopy (XPS): This method uses X-rays to map the chemical state of individual inclusions larger than 10 μm.

8) Auger Electron Spectroscopy (AES): This method uses electron beams to map the composition of small areas near the surface of flat samples.

2.1.2. Inclusion Evaluation of Solid Steel Volumes

Several methods directly measure inclusions in the three-dimensional steel matrix. The first four of these scan the sample with ultrasound or X-rays. The last four of these volumetric methods first separate the inclusions from the steel.

1) Conventional Ultrasonic Scanning (CUS): This non-destructive method detects and counts inclusions larger than 20 μm in solidified steel samples.

2) Mannesmann Inclusion Detection by Analysis Surfboards (MIDAS): Steel samples are first rolled to remove porosity and then ultrasonically scanned to detect both solid inclusions and compound solid inclusions/gas pores. This method was recently rediscovered as the Liquid Sampling Hot Rolling (LSPH) method.
3) Scanning Acoustic Microscope (SAM)\(^{41}\): In this method, a cone-shaped volume of continuous-cast product is scanned with a spiraling detector, such as a solid ultrasonic system, which automatically detects inclusions at every location in the area of the sample surface, including from surface to centerline of the product.

4) X-ray Detection\(^{42}\): An inclusion distribution can be constructed by dividing a sample into several wafers and subjecting each to conventional X-rays to print penetrameter radiographs for image analysis.

5) Slime (Electrolysis)\(^{28,39}\): In this accurate but time consuming method, a relatively large (200 g–2 kg) steel sample is completely dissolved in acid (HCl) and the nonmetallic inclusions which remain are collected for inspection, counting and further analysis. Alternatively, in order to protect FeO inclusions, most of the dissolution can be accomplished by applying electric current through the steel sample immersed in a FeCl\(_2\) or FeSO\(_4\) solution. This method was used to reveal the individual, intact inclusions in Fig. 2.

6) Electron Beam melting (EB)\(^{43}\): A sample of Al-killed

| Method    | Advantages                                                                 | Shortcomings                                                                 |
|-----------|-----------------------------------------------------------------------------|------------------------------------------------------------------------------|
| MMO       | - Inclusion amount, size distribution (mainly 5-30μm) & morphology possible | - No composition data<br> - Two dimensional<br> - Time consuming<br> - Error from eye |
| IA        | - Inclusion size distribution measured                                      | - No composition or morphology data<br> - Overpredict inclusions amount (Error from machine) |
| Sulfur Print | - Large area coverage<br> - Inexpensive                                    | - No amount, composition or size distribution<br> - Only for macroinclusions |
| SEM and EPMA | - 3-dimensional morphology revealed<br> - Composition measured             | - Measures only individual inclusions<br> - Time consuming                   |
| OES-PDA   | - Measures total oxygen, size distribution and composition<br> - Fast        | - No morphology data<br> - Only for inclusions smaller than 12μm               |
| LAMMS     | - Inclusion composition measured                                           | - No morphology or size distribution data                                    |
| XPS       | - Inclusion composition measured                                           | - No amount, morphology or size distribution data<br> - Only for inclusions larger than 10μm |
| AES       | - Inclusion composition measured                                          | - No amount, morphology or size distribution data                             |
| CUS       | - Size distribution (>20 μm) measured                                      | - No morphology or composition data                                           |
| MIDAS/LSHP | - Detects rare large inclusions                                            | - No morphology or composition data<br> - Only for inclusions larger than 40μm<br> - Both gas and inclusions are counted |
| SAM       | - Large, representative area measured<br> - Automated                      | - No morphology or composition data                                           |
| X-rays    | - Inclusion amount Measured                                                | - Time consuming to dissolve entire large sample                              |
| Slime     | - Accurate inclusion amount measured<br> - Captures rare large inclusions   | - No morphology data<br> - Only for Al-killed steel<br> - Low-melting-point inclusions easily fuse and agglomerate |
| EB melting | - Accurate inclusion amount measured<br> - Captures rare large inclusions   | - Low-melting-point inclusions easily fuse                                    |
| EB-EV     | - Accurate inclusion amount measured<br> - Size distribution estimate      | - No morphology data<br> - Only for Al-killed steel<br> - Low-melting-point inclusions easily fuse |
| CC Melting | - Accurate inclusion amount measured                                      | - No morphology data<br> - Needs other methods to infer 3-D size distribution<br> - Low-melting-point inclusions easily fuse |
| FTD       | - Inclusion composition and total oxygen measured                          | - No size distribution or morphology data                                     |
| Coulter Counter Analysis | - Size distribution (1 - 70μm ) measured                              | - No morphology or composition data<br> - The sample matrix must first be dissolved. |
| Photo Scattering Method | - Size distribution measured                                                | - The sample matrix must be dissolved.                                       |
| LDPSA     | - Size distribution (>0.4 μm) measured                                     | - No morphology or composition data<br> - The sample matrix must be dissolved. |
| Ultrasonic Techniques for Liquid | - On-line detection in liquid amount and size distribution measured     | - Both gas and inclusions are counted as inclusions<br> - Only commercial for aluminum |
| LIMCA     | - On-line detection in liquid (3-dimensional size distribution measured)   | - Both gas and inclusions are counted as inclusions, No morphology or composition data<br> - Only proven for water and aluminum |
| Confocal Microscope | - Reveals transient behavior and morphology development in liquid steel | - Measures only individual inclusions<br> - Surface phenomena only<br> - Time consuming and expensive |
steel is melted by an electron beam under vacuum. Inclusions float to the upper surface and form a raft on top of the molten sample. The usual EB index is the specific area of the inclusion raft. Figure 3 compares EB and MMO measurements of the same samples, and shows only qualitative agreement. An enhanced method (EB-EV—Extreme Value) has been developed to estimate the inclusion size distribution. This is done by measuring the maximum inclusion size in several fields of the raft and extrapolating the results over the entire raft, assuming an exponential inclusion size distribution.

7) Cold Crucible (CC) melting: Inclusions are first concentrated at the surface of the melted sample as in EB melting. After cooling, the sample surface is then dissolved, and the inclusions are filtered out of the solute. This method improves on EB melting by melting a larger sample and being able to detect SiO2.

8) Fractional Thermal Decomposition (FTD): When temperature of a steel sample exceeds its melting point, inclusions can be revealed on the surface of the melt and decomposed. Inclusions of different oxides are selectively reduced at different temperatures, such as alumina-based oxides at 1 400 or 1 600°C, or refractory inclusions at 1 900°C. The total oxygen content is the sum of the oxygen contents measured at each heating step.

2.1.3. Inclusion Size Distribution After Inclusion Extraction

Several methods can find 3-dimensional inclusion size distributions after the inclusions are extracted from the steel using a method from 2.1.2 5)–7).

1) Coulter Counter Analysis: This method, by which particles flowing into this sensor through its tiny hole are detected because they change the electric conductivity across a gap, measures the size distribution of inclusions extracted by Slime and suspended in water.

2) Photo Scattering Method: Photo-scattering signals of inclusions (that have been extracted from a steel sample using another method such as slime) are analyzed to evaluate the size distribution.

3) Laser-Diffraction Particle Size Analyzer (LDPSA): This laser technique can evaluate the size distribution of inclusions that have been extracted from a steel sample using another method such as Slime.

2.1.4. Inclusion Evaluation of Liquid

There are several approaches can be used to detect the inclusion amount and size distribution in the molten melts.

1) Ultrasonic Techniques for Liquid System: This method captures the reflections from ultrasound pulses to detect on-line inclusions in the liquid metal.

2) Liquid Metal Cleanliness Analyzer (LIMCA): This on-line sensor uses the principle of the Coulter Counter to detect inclusions directly in the liquid metal. Commonly this method is used for aluminum and other metals, and it is still under development for steel.

3) Confocal Scanning Laser Microscope: This new in-situ method can observe the behavior of individual inclusions moving on the surface of the molten steel, including their nucleation, collision, agglomeration, and pushing by interfaces.

2.2. Indirect Methods

Owing to the cost, time requirements, and sampling difficulties of direct inclusion measurements, steel cleanliness is generally measured in the steel industry using total oxygen, nitrogen pick-up, and other indirect methods.

2.2.1. Total Oxygen Measurement

The total oxygen (T.O.) in the steel is the sum of the free oxygen (dissolved oxygen) and the oxygen combined as non-metallic inclusions. Free oxygen, or “active” oxygen can be measured relatively easily using oxygen sensors. It is controlled mainly by equilibrium thermodynamics with deoxidation elements, such as aluminum. The equilibrium between aluminum and oxygen during deoxidation is shown in Fig. 4 and for low Al content, is represented by Eq. (1), which includes the effect of temperature.

![Fig. 3. Comparison between EB method (x coordinate) and MMO method (y coordinate) for Al-killed steel samples.](image)

![Fig. 4. Equilibrium between aluminum and oxygen in steel (1 873 K).](image)
1) T.O. in LCAK steel has steadily decreased with passing years, as new technology is implemented. For example, T.O. at Nippon Steel dropped from 40–50 ppm in 1970’s, to 20 ppm in 1990’s;
2) Plants with RH degassing achieve lower T.O. (10–30 ppm) than plants with ladle gas-stirring (35–45 ppm).
3) T.O. generally drops after every processing step: 40 ppm (ladle), 25 ppm (tundish), 20 ppm (mold), and 15 ppm (slab).

2.2.2. Nitrogen Pickup

The difference in nitrogen content between steelmaking vessels (especially ladle and tundish) is an indicator of the air entrained during transfer operations. For example, Weirton restricts nitrogen pickup from ladle to tundish to less than 10 ppm for critical clean steel applications. After deoxidation, the low dissolved oxygen content of the steel enables rapid absorption of air. Nitrogen pickup thus serves as a crude indirect measure of total oxygen, steel cleanliness, and quality problems from reoxidation inclusions, as indicated in Fig. 5. Note that oxygen pickup is always many times greater than the measured nitrogen pickup, due to its faster absorption kinetics at the air steel interface. In addition, nitrogen pickup is faster when the oxygen and sulfur contents are lower. Thus, to reduce nitrogen pickup, deoxidation is best carried out after tapping. Plant measurements confirm this, as nitrogen pickup reduced from 10–20 ppm for deoxidation during tapping to 5 ppm after tapping.

Tables 4 and 5 summarize minimum nitrogen pick-up and nitrogen contents measured in LCAK steel at every processing step for several steel plants. Measurements in the tundish and mold were excluded because they tend to be high due to sampling. These two tables reveal the following conclusions:

1. Nitrogen in LCAK steel slabs is about 30–40 ppm at most steel plants. It is controlled mainly by the steelmaking converter or electric furnace operation, but is affected by refining and shrouding operations.
2. Nitrogen pick-up is deceasing with passing years, owing to new technology and improved operations. For example, at Sollac Dunkirk Works, nitrogen pick-up from tundish to mold decreased from 9 ppm in 1988, to 1 ppm in 1992.
3. Generally, nitrogen pick-up can be controlled at 1–3 ppm from ladle to mold. With optimal transfer operations to lessen air entrainment, this pickup can be lowered during steady state casting to less than 1 ppm. Nitrogen pick-up is discussed further in the Transfer Operations section of this paper.

2.2.3. Dissolved Aluminum Loss Measurement

For LCAK steels, aluminum loss also indicates that reoxidation has occurred. However, this indicator is a less accurate measure than nitrogen pickup because Al can also be reoxidized by slag.

2.2.4. Slag Composition Measurement

Firstly, analysis of the slag composition evolution before and after operations can be interpreted to estimate inclusion absorption to the slag. Secondly, the origin of a complex oxide inclusion can be traced to slag entrainment by matching the mineral and element fractions in the slag with the
| Steel Works                  | Refining Method | Ladle | Tundish | Mold | Slab  | Year | Ref. |
|-----------------------------|-----------------|-------|---------|------|-------|------|------|
| **America**                 |                 |       |         |      |       |      |      |
| Inland No.4 BOF shop        | LMF             | 30    | 24      | 21   | 15    | 1990 | 52   |
| Aramco Steel, Middletown   | Works           | 60-105| 15-40   | mean 25 | 16.9-23.8 | 1991 | 50   |
| Aramco Steel, Ashland Works|                 |       |         |      |       |      |      |
| US Steel, Lorain Works      |                 | 16.3  |         |      |       | 1993 | 50   |
| National Steel, Great Lake  |                 |       | 13-17   |      |       | 1991 | 52   |
|                            |                 |       | <31-36  |      |       | 1991 | 52   |
|                            |                 |       | <31-36  |      |       | 1994 | 52   |
|                            |                 |       |         |      |       | 1995 | 52   |
| Some plant in North America |                 | 20-35 | 20-30   | 10-15 |       | 1991 | 50   |
| Timken Steel, Harrison Plant|                 | 20-30 |         |      |       | 1991 | 50   |
| Usiminas, Brazil            |                 | 19    |         |      |       | 1994 | 50   |
| Dofasco, Canada             |                 | 13    |         |      |       | 1994 | 50   |
| LTV Steel, Cleveland Works  |                 | 21-27 |         |      |       | 1995 | 50   |
| Sammi Atlas Inc., Atlas     |                 |       |         |      |       | 1995 | 50   |
| Stainless Steels            |                 |       |         |      |       | 1995 | 50   |
| Lukens Steel                |                 | 16-20 |         |      |       | 1995 | 50   |
| Weirton Steelmaking shop    |                 | 23±10 |         |      |       | 1995 | 50   |
| **Europe**                  |                 |       |         |      |       |      |      |
| Cokerill Sambro/CRM          |                 | <30   | (20°)   |      |       | 1991 | 50   |
| Mannesmannrohren-Werke,     |                 | <20   |         |      |       | 1991 | 50   |
| Hüttenerwerk Hackingen      |                 |       |         |      |       |      |      |
| One steel Plant in Finland  |                 | 48±12 | 32      | 38   | 17    | 1993 | 50   |
| Hüttenerwerke Krupp         |                 |       | 10-20   |      |       | 1998 | 50   |
| Mannesmann                  |                 |       |         |      |       |      |      |
| Dillingen, Germany          |                 | 10-15 | 11      |      | ≤15   | 1993 | 50   |
|                            |                 |       |         |      |       | 1994 | 50   |
|                            |                 |       |         |      |       | 2000 | 50   |
| Hoogovens Ijmuiden,         |                 | 15-32 |         |      |       | 1994 | 50   |
| Netherlands                 |                 |       |         |      |       |      |      |
| British Steel, Ravenscraig  |                 |       |         |      |       | 1985 | 50   |
| Works,                      | DH              |       |         |      |       | 1985 | 50   |
|                            | Lime-spar deep  |       |         |      |       | 1985 | 50   |
|                            | injection       |       |         |      |       |      |      |
| British Steel               | <10             |       | 15.4    |      |       | 1985 | 50   |
| Linz, Austria               |                 | 16    |         |      |       | 1998 | 50   |
| Voest-Alpine Stahl Linz     |                 | 27±4  |         | 21±2 |       | 1998 | 50   |
| GmbH                        |                 |       |         |      |       |      |      |
| Sollac Dunkirk, France      |                 | 20-50 |         |      |       | 1997 | 50   |
| Sidmar, Belgium             |                 | 37    |         |      |       | 2000 | 50   |
| **Asia**                    |                 |       |         |      |       |      |      |
| Kawasaki Steel, Chiba works |                 | 40    |         | 20   |       | 1989 | 50   |
| Kawasaki Steel, Mizushima   |                 |       |         |      |       |      |      |
| Works,                      | LF+RH           | 30    | 34.7    | <30  | <55   | 1986 | 50   |
|                            | KTB             |       | <25-40  |      |       | 1991 | 50   |
|                            |                 |       |         |      |       | 1996 | 50   |
| NKK, Traditional RH         |                 | 17    |         |      |       | 1993 | 50   |
| NKK, PERM for RH            | PERM for RH     | 7     |         |      |       | 1993 | 50   |
| NKK, Traditional VOD        | VOD             | 33.8  |         |      |       | 1993 | 50   |
| NKK, PERM for VOD           | PERM for VOD    | 25.1  |         |      |       | 1993 | 50   |
| NKK, Kehin, #1              |                 | <20   |         |      |       | 1991 | 50   |
| NKK, Kehin, #5              |                 | <28   |         |      |       | 1991 | 50   |
| Kobe Steel, Kakugawa Works  |                 | 15-45 |         |      |       | 1992 | 50   |
| Kobe Steel                  |                 | 25    | 22      |      |       | 1992 | 50   |
| Nippon Steel, Nagoya Works  |                 | 10-30 |         |      |       | 1989 | 50   |
| Nippon Steel, Yawata Works  |                 |       |         |      |       | 1974 | 50   |
|                            | Ar stirring      | 82    | 45      |      | 44    | 1974 | 50   |
| Nippon steel, Yawata works  |                 | 26    |         |      |       | 1989 | 50   |
| The Japan Steel Works,      |                 | Ladle | Refining | 20  |       | 1987 | 50   |
| Miiroan Plant               |                 |       | Furnace (LRF) |       |       |      |      |
| POSCO                       |                 | 25-31 |         |      |       | 1993 | 50   |
|                            |                 |       | <27     |      | <10*  | 1993 | 50   |
|                            |                 |       |         |      |       | 1991 | 50   |
| **China**                   |                 |       |         |      |       |      |      |
| China Steel, Taiwan         |                 | <30   |         |      |       | 1994 | 50   |
| Baosteel, China             |                 |       |         |      |       |      |      |
| CAS-OB                      |                 | 172.5 | 93      |      |       | 1999 | 50   |
| CAS                         |                 | 77    | 57      |      |       | 1992 | 50   |
| CAS                         |                 | 73-100| 38-53   |      |       | 1992 | 50   |
| CAS                         |                 |       | 23      |      |       | 1992 | 50   |
| WISCO, No.1 Works, China   |                 | LF-VD | ≤515    |      |       | 1999 | 50   |
| WISCO, No.2 Works, China   |                 |       |         |      |       |      |      |
| RH                          |                 | 71-73 |         |      |       | 1995 | 50   |
| RH-KTB                      |                 | 43-75 |         |      |       | 1995 | 50   |
| RH (Pressure Vessel Steel)  |                 | 28-34 |         |      |       | 1995 | 50   |
| WISCO, No.3 Works, China   |                 |       |         |      |       |      |      |
| Punzhuihua Iron and Steel   |                 | 35-41 |         |      |       | 1999 | 50   |
| (Group) Co., China          |                   |       |         |      |       |      |      |
| RH-MFB                      |                 | 20-24 |         |      |       | 2000 | 50   |
| Maanshan Iron & Steel Co.   |                 |       |         |      |       |      |      |
| Ltd., China                 | ASEA-SKF        | 18-24 |         |      |       | 2000 | 50   |

(* ultra clean steel).
inclusion composition. These methods are not easy, however, due to sampling difficulties and because changes in the thermodynamic equilibrium must be taken into account.

2.2.5. Submerged Entry Nozzle (SEN) Clogging

Short SEN life due to clogging is sometimes an indicator of poor steel cleanliness. The composition of a typical clog during LCAK steel continuous casting is: 51.7% Al₂O₃, 44% Fe, 2.3% MnO, 1.4% SiO₂, 0.6% CaO, which shows that nozzle clogs are often caused by a simultaneous buildup of small alumina inclusions and frozen steel. Thus, SEN clogging frequency is another crude method to evaluate steel cleanliness. The cause and prevention of SEN clogging was reviewed by Kemeny and Thomas.

2.3. Final Product Tests

The ultimate measure of cleanliness is to use destructive mechanical tests to measure formability, deepdrawing,
and/or bending properties of the final sheet product, or fatigue life of test specimens or product samples. Other sheet tests include the Hydrogen Induced Crack test and magnetoscopy. These tests are needed to reveal facts such as the potential benefit of very small inclusions (<1 μm), which should not count against cleanliness.

The previous discussion shows that there is no single ideal method to evaluate steel cleanliness. Some methods are better for quality monitoring while others are better for problem investigation. Thus, it is necessary to combine several methods together to give a more accurate evaluation of steel cleanliness in a given operation. For example, Nippon Steel used total oxygen measurement and EB melting for small inclusions, and Slime method and EB-EV for large inclusions. Usinor used total oxygen measurement with FTD, OES-PDA, IA and SEM for small inclusions, and Electrolysis and MIDAS for large inclusions. For example, Fig. 8 compares inclusion distributions through the thickness of two slab samples measured with T.O., PDA and Image analysis. All three approaches show that steel A has fewer inclusions than steel B on average, and there is a peak between the loose-side surface and the center. Baosteel employed total oxygen measurement, MMO, XPS, and SEM for small inclusions, Slime and SEM for large inclusions, nitrogen pickup for reoxidation, slag composition analysis to investigate inclusion absorption and slag entrainment.

3. Ladle Operations for Clean Steel

Steel refining and continuous casting operations control steel cleanliness. For example, a systematic study of inclusion removal found that ladle treatment lowered inclusions by 65–75%; the tundish removed 20–25%, although reoxidation sometimes occurred; and the mold removed 5–10% of the inclusions. Thus, ladle operations are particularly important and include control of tap oxygen, FeO and MnO in the slag, ladle stirring, and inclusion modification treatment.

3.1. Tap Oxygen

Tap oxygen content is measured during tapping the ladle or before deoxidant addition. The tap oxygen content is typically high, ranging from 450–800 ppm at Weirton, 800–1200 ppm at Great Lake Division of National Steel, 250–650 ppm at Nippon Steel, 600 ppm at Voest-Alpine Linz, and 700–900 ppm at WISCO No. 3 Works for IF production. Aluminum additions to deoxidize the melt create large amounts of Al₂O₃ inclusions. This suggests that a limitation on tap oxygen content should be imposed for clean steel grades. However, as shown in Fig. 9, there is no correlation between tap oxygen and steel cleanliness. This is consistent with claims that 85% of the alumina clusters formed after large aluminum additions readily float out to the ladle slag, and that the remaining clusters are smaller than 30 μm. Naturally, the decision to ignore tap oxygen depends on the time available to float inclusions and on the availability of ladle refining, which can remove most of the generated inclusions. Figure 10 shows how RH treatments reach the same final T.O. level, regardless of initial tap oxygen, so long as the degassing time is long enough, for example, 15 min. A final consideration is that the tap oxygen content affects the decarburization rate, important for producing ultra low carbon steel.

3.2. FeO and MnO in Slag

An important source of reoxidation is the carryover of slag from the steelmaking furnace to the ladle, which contain a high content of FeO and MnO. These liquid oxides react with the dissolved aluminum to generate solid alumi-
na in the liquid steel, owing to the strong favorable thermodynamics of the following reactions:\(^\text{103}\)

\[
\begin{align*}
3\text{FeO} + 2\text{Al} & = \text{Al}_2\text{O}_3 + 3\text{Fe} \\
\Delta G^\circ_2 & = -853 \, 700 + 239.9 \, T \quad (\text{J mol}^{-1}) ....... (2) \\
3\text{MnO} + 2\text{Al} & = \text{Al}_2\text{O}_3 + 3\text{Mn} \\
\Delta G^\circ_3 & = -337 \, 700 + 1.4 \, T \quad (\text{J mol}^{-1}) ....... (3)
\end{align*}
\]

The higher is the FeO and MnO content in the ladle slag, the greater is the potential for reoxidation and the corresponding generation of alumina inclusions. Many slivers in the final product have been traced to reoxidation that originated from FeO in the ladle slag.\(^\text{16,17,111}\) Figure 11 shows how T.O. in the ladle, tundish and mold correlates roughly with the %FeO/%MnO in the ladle slag.\(^\text{16,84,111–113}\) These slag impurities are particularly damaging when the ladle lining material is high in silica. Figure 12 shows a similar influence on the loss of dissolved Al and the increase of tundish inclusions.\(^\text{17,111,114}\)

Countermeasures to lower FeO and MnO contamination are summarized as follows:

1) Minimize slag carryover from steelmaking furnace to ladle during tapping:
   - Increasing aim turndown carbon, avoiding rebloows, thus minimizing the dissolved oxygen content in the steel, can lower the amount of FeO in the furnace slag.\(^\text{16}\)
   - Use of a susblance in the BOF substantially lowers the frequency of rebloows.\(^\text{16}\)

2) Control slag composition:
   - An efficient slag stopper, such as a slag ball (that floats in steel and sinks in slag), can lower the amount of furnace slag carried over to the ladle during tapping to 3 kg/t steel.\(^\text{115}\) To improve yield, other sensors are available, which detect the slag after a little has carried over. These include infra-red\(^\text{116}\) and electromagnetic systems.\(^\text{117}\)
   - The furnace geometry and tap hole location can be designed to minimize vortexing and slag carryover.\(^\text{118}\)
   - A thick ladle slag layer after tapping suggests high slag carryover problems, as shown in the rough relationship in Figure 13.\(^\text{114}\)

3) Adjust tapping practice:
   - Ladle slag depth after skimming should be

\(\%\text{FeO} > \%\text{MnO} > 20\%\)

\[\text{Calculation:}
\begin{align*}
\%\text{FeO} & = \text{tap oxygen (ppm)} \\
\%\text{MnO} & = \text{tap oxygen (ppm)}
\end{align*}
\]

Fig. 10. Effect of tap oxygen on T.O. removal in ladle during RH degassing.\(^\text{150}\)

Fig. 11. Relationship between FeO+MnO in ladle slag and T.O. in steel for Ladle (RH-OB),\(^\text{9,111}\) Ladle (Argon Stirring),\(^\text{112}\) Ladle (different lining),\(^\text{113}\) Continuous casting mold.\(^\text{17}\)

Fig. 12. Effect of FeO+MnO content in ladle slag on lowering dissolved Al (from ladle to mold\(^\text{17}\)) and from ladle to tundish\(^\text{114}\)) and on increasing alumina content (measured in tundish\(^\text{114}\)).

Fig. 13. Correlation of FeO content in ladle slag with ladle slag depth.\(^\text{14}\)
controlled to 25–40 mm.\textsuperscript{16,119)}

2) Use a ladle slag reduction treatment.\textsuperscript{4,16,17,72,111,114,120,121)}

Another way to lower the FeO/H\textsubscript{\textsuperscript{11001}}MnO content of the ladle slag is to add a slag conditioner (i.e. slag reduction or deoxidation treatment), which is a mixture of aluminum and burnt lime or limestone. Table 6\textsuperscript{4,16,17,55,72,88,111,114,119–121)} summarizes the drop in FeO/H\textsubscript{\textsuperscript{11001}}MnO content after ladle slag reduction treatment at several steel plants. On average, this treatment lowers FeO/H\textsubscript{\textsuperscript{11001}}MnO to below 5\%, as shown in Fig. 14.\textsuperscript{72)} SOLLAC Dunkirk reports an accompanying sharp improvement of coil cleanliness.\textsuperscript{72)} Minimizing slag carry-over, together with adding a basic ladle slag and basic lining was found to lower the ladle slag to less than 1–2\% FeO/H\textsubscript{\textsuperscript{11001}}MnO, which lowered T.O. to 10 ppm for LCAK steel.\textsuperscript{115)}

3.3. Ladle Stirring Practice

Ladle stirring and refining processes, such as RH (Rheinstahl Heraeus) ladle degassing, greatly promote inclusion growth and removal. Some metallurgical reactions require strong mixing of metal and slag (e.g. desulphurisation and dephosphorisation), whereas others require gentle mixing at the metal/slag interface and maintenance of an unbroken slag layer (e.g. deoxidation and inclusion removal). Different processes produce different stirring powers, as compared in Table 7. The effect of various ladle treatments on slab inclusion levels is shown in Fig. 15.\textsuperscript{1)} This figure shows the improvement of RH vacuum treatment over Ar-stirring in the ladle in better steel cleanliness, which is consistent with Table 7. The pronounced benefit of calcium-based powder injection may be due in part to its greater stirring power\textsuperscript{1} in addition to its primary effect of deoxidization and liquefying inclusions. Together, RH degassing and Ca treatment dropped T.O. to 15 ppm at some plants.\textsuperscript{106)} The NK-PERM process (modified RH by NKK) can lower the T.O. of LCAK steel to 5 ppm after 20 min de-gassing.\textsuperscript{77)}

The effect of stirring power on the rate of oxygen removal is shown in Figs. 16\textsuperscript{6,77)} and 17,\textsuperscript{113)} which show that increasing stirring rate helps to remove inclusions, unless it becomes excessive. Sufficient stirring time (>10 min)\textsuperscript{22)} after alloy addition is also important, (Fig. 17), to allow the alumina inclusions to circulate up to the slag and be removed. Extremely vigorous stirring or excessive treatment

**Table 6.** Effect of ladle slag reduction treatment reported for LCAK steel.

| Steel Works                  | FeO/MnO composition in ladle slag | Year | Ref. |
|-----------------------------|----------------------------------|------|------|
| LTV Steel, Cleveland Works, | FeO 3.9\%, MnO 1.6\%            | 1993 | 16\textsuperscript{184)} |
|                             | FeO 25.9%, MnO 2.9\%            |      |      |
| Inland Steel, No.4 BOF Shop,| FeO 8.1\%, MnO 5.2\%            | 1990 | 16\textsuperscript{188)} |
|                             | FeO 2.4\%, MnO 1.4\%            |      |      |
| National Steel, Great Lake  | FeO 25\%                        | 1994 | 16\textsuperscript{204)} |
| Div.                        | FeO 8.3\%, Best 2.0\%           |      |      |
| US/SKSteel Company          | FeO 30\%                        | 1991 | 16\textsuperscript{204)} |
|                             | FeO 12.3\%, best 0.64%          |      |      |
| Algoma Steel, Canada        | FeO 1.5\%, MnO 0.8\%            | 1999 | 16\textsuperscript{206)} |
| Sollac Dunkirk, France      | FeO 12-25\%                     | 1997 | 16\textsuperscript{208)} |
| Krupp Stahl AG, Bochum Steelwork, | FeO+MnO<1%                      | 1996 | 16\textsuperscript{188)} |
| POSCO, Kwangyang Works, Korea | FeO+MnO 9-18\%                 | 1998 | 16\textsuperscript{188)} |
| Kawasaki Steel, Mizushima Works, | FeO<2%                        | 1996 | 16\textsuperscript{188)} |
| Chian Steel, Taiwan         | FeO 26.8\%, MnO 4.7\%           | 1996 | 16\textsuperscript{188)} |
| WISCO No.3 Works, China     | FeO<1%                          | 2000 | 16\textsuperscript{188)} |

**Table 7.** Stirring powers reported for different processes.

| Stirring Method                      | Power (Watt/ton) |
|--------------------------------------|------------------|
| Argon gas bubbling                   | 2-130, 43-214    |
| Tapping steel                        | 17-286           |
| DH (Dortmund Hoerder)                | 72-100           |
| ASEA-SKF                             | 7-29, 10-250     |
| PS (Pulsation Mixing)                | 10-600           |
| RH (Raestahl – Heraeus)              | 86-116, 200-400  |
| VOD (Vacuum Oxygen Decarburization) | 10-400 (conventional), 100-800 (NK-PERM) |
| Outlet of SEN in continuous casting mold | 470-800 (NK-PERM) |
| Tundish inlet zone                   | 10-50 (NK-PERM)  |

**Fig. 14.** Reduction of FeO content in ladle slag by ladle slag reduction treatment.\textsuperscript{72)}

**Fig. 15.** Effect of different ladle treatments on inclusion level in slab.\textsuperscript{1)}

**Fig. 16.** Effect of stirring power on deoxidation rate in various refining processes (Ar gas bubbling\textsuperscript{6}; ASEA-SKF\textsuperscript{6}; VOD and RH\textsuperscript{77)}.
time are bad for several reasons. Firstly, faster upward circulation of steel onto the slag layer may expose an “eye” or slag-free region of the steel surface to air reoxidation and perhaps even slag entrainment. Secondly, ladle lining erosion may become a problem. Thirdly, vigorous stirring encourages particle collisions into large macroinclusions. Thomas et al suggest to first stir vigorously to encourage mixing and the collision of small inclusions into large ones, followed by a “final stir” that slowly recirculates the steel to facilitate their removal into the slag while minimizing the generation of more large inclusions via collisions.

The deoxidation treatment time should be several times the mixing time, \( t_m \), which has been estimated as a function of stirring power, \( e \), by several researchers. For example, the Nakanishi equation is popular

\[
t_m [s] = 800e [watt/ton]^{-0.4}
\]

The specific stirring powers of different process steps, given in Table 7, can be used to estimate mixing times. For example, an RH treatment with 200–400 W/t stirring power has a mixing time of about 1.2–1.6 min. In industrial refining practice, the pure degassing time is usually 5–10 min, which is 3–6 times this mixing time.

3.4. Inclusion Modification

Calcium treatment of LCAK steel is attractive because it can liquify the oxides and sulphides in molten steel and modify their shape and deformability in the solidified steel. The liquid calcium aluminates coalesce and rise more easily than the clusters of solid alumina inclusions. This facilitates their removal to the slag and lowers T.O., in addition to avoiding nozzle clogging. To achieve liquid inclusions, the calcium must be present in the correct proportion. The acceptable range is narrow and depends on the alumina content, as documented by the equilibrium phase diagram. In addition, the sulfur content must be low in order to maintain liquid inclusions over the range of Al contents found in Al-killed steel, as shown in Fig. 18. Because Ca is so reactive, it is only effective after the steel has been deoxidized and if slag entrapment, especially with FeO and MnO, can be avoided.

4. Tundish Operations for Clean Steel

Important phenomena taking place in the tundish are shown schematically in Fig. 19. Tundish operations greatly affect steel cleanliness, as covered in reviews by McLean and Schade. Depending on its operation, the tundish may act as a further refining vessel to remove inclusions to the slag layer or it may contaminate the steel through slag entrainment, reoxidation, and refractory dissolution. The following important factors are discussed here: tundish depth and capacity, casting transitions, tundish lining refractory, tundish flux, gas stirring, and tundish flow control.

4.1. Tundish Depth and Capacity

Deep tundishes with a large capacity increase the residence time of liquid steel and particles, so encourage inclusion removal as shown in Fig. 20. Deep tundishes also discourage vortex formation, enabling more time for ladle transitions before slag entrainment becomes a problem. Tundish size for LCAK steel has gradually increased worldwide over the past 20 years, typically reaching 60–80 tons with over 70 inches depth.
can be added. Eventually, during steady casting, the T.O. decays to lower levels, consisting mainly of alumina.

One improvement during ladle transitions is to stop the flow of liquid into the mold until the tundish is filled and to bubble gas through the stopper to promote inclusion flotation.22) Another improvement is to open new ladles with submerged shrouding. With this measure, T.O. was decreased at Dofasco from 41±14 ppm to 31±6 ppm with more consistent quality throughout the sequence (Fig. 21 Case II).58)

Near the end of a ladle, ladle slag may enter the tundish, due in part to the vortex formed in the liquid steel near the ladle exit. This phenomenon requires some steel to be kept in the ladle upon closing (e.g. A four tonne “hee”16)). In addition, the tundish depth drops after ladle close, which disrupts normal tundish flow and may produce slag vortexing, slag entrainment, and increased total oxygen in the mold, as reported by Dofasco.59) An electro-magnetic level indicator for ladles is under development.

4.3. Lining Refractory

Dissolved aluminum in the liquid steel may react with oxygen sources in the lining refractory. This oxygen may come from carbon monoxide, when carbon in the refractory reacts with binders and impurities, or from silica refractory decomposition (Eq. (5)).24) Silica-based tundish linings are worse than magnesia-based sprayed linings (Baosteel28) and Inland Steel16).

\[ \text{SiO}_2 + \frac{4}{3} Al = \frac{2}{3} Al_2 O_3 + Si \]
\[ \Delta G^0 = -219400 + 35.7T \text{ (J mol}^{-1}) \] ..........................(5)

The extent of this reaction can be quantified by monitoring the silicon content of the liquid steel.

Another factor is the wear rate of the lining refractories. At Kawasaki Steel Mizushima Works, three types of materials (high Al2O3, Al2O3–SiC–C, and MgO–C with a wear rate of 1.0, 0.34, 0.16 mm/heat respectively) have been adopted at the slag line, where the refractory tends to be damaged by erosive tundish flux and slag, and the MgO–C brick shows the highest durability among the three.18)

4.4. Tundish Flux

The tundish flux provides several functions. Firstly, it must insulate the molten steel both thermally (to prevent excessive heat loss) and chemically (to prevent air entrainment and reoxidation103)). For example, at IMEXSA Steel (Mexico), by changing tundish flux, nitrogen pickup from ladle to mold decreased from 16 to 5 ppm.105)

Secondly, in ideal circumstances, the flux should also absorb inclusions to provide additional steel refining. A common tundish flux is burnt rice hulls, which is inexpensive, a good insulator, and provides good coverage without crushing. However, rice hulls are high in silica (around 80% SiO228), which can be reduced to form a source of inclusions (Eq. (5)). They also are very dusty and with their high carbon content, (around 10% C28), may contaminate ultra low carbon steel.

Basic fluxes (CaO–Al2O3–SiO2 based) are theoretically much better than rice hulls at refining LCAK steels, and much better than magnesia-based sprayed linings (Baosteel28) and Inland Steel16)).
with flux basacity increasing from 0.83 to 11, measured at Kawasaki Steel Mizushima Works.\textsuperscript{76) At Dofasco’s #2 Melt Shop, using basic tundish flux (40% CaO, 24% Al\textsubscript{2}O\textsubscript{3}, 18% MgO, 5% SiO\textsubscript{2}, 0.5% Fe\textsubscript{2}O\textsubscript{3}, 8% C), together with baffles, significantly lowered in total oxygen fluctuation, as compared to the initial flux (3% CaO, 10–15% Al\textsubscript{2}O\textsubscript{3}, 3% MgO, 65–75% SiO\textsubscript{2}, 2–3% Fe\textsubscript{2}O\textsubscript{3}). The T.O. decreased from 41 to 21 ppm during ladle transitions and decreased from 39 to 19 ppm during steady state casting.\textsuperscript{58) However, other results, such as shown in Fig. 22 found no improvement in T.O. between rice hulls and higher basicity flux (25.0% SiO\textsubscript{2}, 10.0% Al\textsubscript{2}O\textsubscript{3}, 59.5% CaO, 3.5% MgO).\textsuperscript{61) This might be because the basic flux still contained too much silica. More likely, the basic flux was ineffective because it easily forms a crust at the surface, owing to its faster melting rate and high crystallization temperature. This crust results in the evolution of an open slag-free eye around the ladle shroud during teeming, which not only provides an excessive area for reoxidation, but also allows a significant radiative heat loss and discomfort for operators on the ladle platform. Also, basic fluxes generally have lower viscosity, so are more easily entrained. To avoid these problems, AK Steel Ashland suggested a two-layer flux, with a low-melting point basic flux on the bottom to absorb the inclusions, and a top layer of rice hulls to provide insulation, which lowered T.O. from 22.4 ppm to 16.4 ppm.\textsuperscript{53) 4.5. Tundish Stirring

Injecting inert gas into the tundish from its bottom improves mixing of the liquid steel, and promotes the collision and removal of inclusions.\textsuperscript{60,79) At Lukens Steel Company, this technology was employed and successfully lowered T.O. to 16 ppm in tundish.\textsuperscript{60) The danger of this technology is that any inclusions-laden bubbles which escape the tundish and become entrapped in the strand would cause severe defects. 4.6. Tundish Flow Control

The tundish flow pattern should be designed to increase the liquid steel residence time, prevent “short circuiting” and promote inclusion removal. Tundish flow is controlled by its geometry, level, inlet (shroud) design and flow control devices such as impact pads, weirs, dams, baffles, and filters. The tundish impact pad, such as shown in Fig. 23,\textsuperscript{59,135) is an inexpensive flow control device that prevents erosion of the tundish bottom where the molten steel stream from the ladle impinges. More importantly, it suppresses turbulence inside the inlet zone, which lessens slag entrainment.\textsuperscript{135) It also diffuses incoming stream momentum and allows the natural buoyancy of the warm incoming steel to avoid short circuiting, particularly at startup. If properly aligned, and perhaps together with weir(s) and dam(s), a pour pad can improve steel cleanliness, especially during ladle exchanges. For example, adding the pour pad at LTV Steel decreased alumina during ladle transitions from 48 to 15 ppm.\textsuperscript{59) At Lukens Steel, T.O. decreased from 26 ppm (with a domed pad) to 22 ppm (with a hubcap pad).\textsuperscript{60) At POSCO, steel cleanliness was improved by putting 77 holes in their dam, making it act as a partial filter.\textsuperscript{84) At Dofasco’s #2 Melt Shop, using baffles improved product quality, especially at ladle exchanges, thereby making the heat more consistent. (Fig. 21 Case III).\textsuperscript{58) Baffles combined with an initial tundish cover lowered the average T.O. in the tundish during steady state casting from 39 to 24 ppm.\textsuperscript{58) Ceramic filters are very effective at removing inclusions.\textsuperscript{84,130) However, their cost and effective operating time before clogging usually make their use prohibitive. 5. Transfer Operations for Clean Steel

Transfer operations from ladle to tundish and from tundish to mold are very important for steel cleanliness control. McPherson and McLean reviewed various aspects of tundish-to-mold transfer operations, focusing on shroud design variations.\textsuperscript{136) One of the most important sources of oxygen pickup is atmospheric reoxidation of steel during transfer operations. This generates inclusions which cause production problems such as nozzle clogging, in addition to defects in the final product. This phenomenon is minimized by optimizing the use of shrouds, argon injection and submerged entry nozzle (SEN) operations. 5.1. Open Pouring and Shrouding

Using an optimized shrouding system greatly lowers reoxidation during transfer operations. For example, using a ladle shroud lowered nitrogen pickup from 24 to 3 ppm relative to open pouring at Bao Steel.\textsuperscript{29) At US Steel Fairfield Works, replacing the tundish pour box with a ladle shroud and dams lowered nitrogen pickup (ladle to tundish) from 7.5 to 4 ppm, and also lowered slag entrainment during
transitions. At British Steel Ravenscraig Works, improving the shroud system from ladle to tundish, lowered the nitrogen pickup there from 14 to 3 ppm. Shrouding the ladle to tundish stream at another plant lowered the dissolved aluminum loss from 130 to only 70 ppm and to lower the T.O. increase by 12 ppm. When pouring without shrouds, which is common in billet casting, the turbulence of the casting stream is very important. A smooth stream entrains much less oxygen than a turbulent or "ropy" stream. To produce a smooth stream between tundish and mold in these operations, and the metering nozzle edges must be maintained and high speed flow in the tundish across the nozzles must be avoided. A variety of inert gas shrouding systems are also available to help.

5.2. Ladle Opening
A "self-open" ladle opens on its own without having to lance the nozzle. Lancing requires removing the shroud, which allows reoxidation, especially during the first 25 to 50 inches of the cast. Figure 24 shows that lanced-opened heats have total oxygen levels around 10 ppm higher than self-open heats. Carefully packing of the ladle opening sand helps to realize ladle self open. Ladle sand is also a source of reoxidation because of high silica contained.

5.3. Argon Protection and Sealing
Inert gas can protect the steel from air reoxidation in many ways. Tundish flux is added after the steel is already flowing, in order to prevent its entrapment into the steel. Combined with the turbulence of ladle opening, air entrapment is thus a problem for up to 15 min at the beginning of a cast. To combat this problem, the tundish can be purged with inert gas (to displace the air) prior to ladle opening, which lowers both the total oxygen and the nitrogen pickup during startup. A protective tundish cover with carefully sealed edges also helps, lowering T.O. from 41.5 to 38 ppm.

It is very important to carefully seal the joints in the shrouds, both to improve cleanliness and to prevent clogging. Improving the bayonet system between the ladle nozzle and ladle shroud, lowered the nitrogen pickup there from 8 to <1 ppm. Stiffening the SEN holder and increasing its maintenance lowered initial nitrogen pickup from 1.8 to 0.3 ppm.

Argon injection to pressurize the shrouds can help to prevent the liquid steel from air reoxidation through any joints or leaks. Guidelines for minimum argon gas flow to ensure positive pressure inside the nozzle are provided elsewhere. In addition, flooding the joints with argon gas ensures that any leaks aspirate inert gas and not air. Injecting argon into the tundish stopper rod and improved sealing decreased nitrogen pickup from tundish to slab from 5 to 1.8 ppm; lowered T.O in slab from 31 to 22 ppm, decreased the size of alumina clusters in the slab, and the decreased clogging. Elsewhere, argon injection through the stopper rod lowered the number of inclusions detected by MIDAS method by 25–80%. Injecting Ar gas purge through upper plate of the sliding gate lowered the amount of 50–100 μm sized inclusions from 3 to 0.6 per cm², and lowered 100–200 μm macroinclusions from 1.4 to 0.4 per cm².

5.4. Nozzle Clogging
Nozzle clogs are caused by reoxidation, or by the accumulation of solid oxides or sulfides, such as alumina (Al₂O₃) and calcium sulfide (CaS) in the steel. In addition to interfering with production, tundish nozzle/ Submerged Entry Nozzle clogging is detrimental to steel cleanliness for many reasons. Firstly, dislodged clogs either become trapped in the steel, or they change the flux composition, leading to defects in either case. Secondly, clogs change the nozzle flow pattern and jet characteristics exiting the nozzle, which disrupt flow in the mold, leading to slag entrainment and surface defects. Thirdly, clogging interferes with mold level control, as the flow control device (stopper rod or slide gate) tries to compensate for the clog. Changing from a 3-plate slidegate system to a stopper rod system reduced clogging at Dofasco. Many practices can be used to minimize clogging, which are reviewed elsewhere. In addition to taking general measures to minimize inclusions, clogging via refractory erosion can be countered by controlling nozzle refractory composition, (e.g. avoid Na, K, and Si impurities), or coating the nozzle walls with pure alumina, BN, or other resistant material.

5.5. Shroud Material
The refractory at the surface of the shroud walls should be chosen to minimize reactions with the steel that create inclusions and clogging. In addition to silica lining decomposition, discussed previously, other oxygen sources in the refractory can react with Al in the steel to form alumina. These include carbon monoxide when carbon in the refractory reacts with binders and impurities. Incorporating calcia into the nozzle refractory may help by liquefying alumina inclusions at the wall, so long as CaO diffusion to the interface is fast enough and nozzle erosion is not a problem. Nozzle erosion can be countered by controlling nozzle refractory composition, (e.g. avoid Na, K, and Si impurities), or coating the nozzle walls with pure alumina, BN, or other resistant material.

6. Mold and Caster Operations for Clean Steel
The continuous casting mold region is the last refining step where inclusions either are safely removed into the top slag layer or they become entrapped into the solidifying shell to form permanent defects in the product. In 1985, Mepherson used the words "Mold Metallurgy" to emphasize the importance of the mold to improve steel cleanliness. Relevant phenomena in the mold region are shown.
The mold flow pattern is very important to avoid defects because it affects particle transport: removal to the top slag or entrapment by the solidifying shell. The behavior of the top surface of the liquid pool is particularly important because it controls the entrainment of mold slag, surface defects, bubble and particle removal, and many other problems.

6.1. Top Surface Control

Directing too much flow towards the top surface generates surface defects, due to transients, turbulence at the meniscus, and inclusion problems from slag entrainment. However, decreasing surface flows too much can also generate problems. These include surface defects due to the meniscus region becoming too stagnant, and a greater fraction of incoming inclusion particles being sent deep before they can be removed into the slag. Thus, a balance must be found in order to optimize the flow parameters to avoid defects.

6.1.1. Meniscus Stagnation

Most surface defects in the steel product originate in the mold at the meniscus, where the solidifying shell is very thin. The most obvious source of surface defects is the capture of foreign particles into the solidifying shell at the meniscus. If the steel jet is directed too deep or has too little superheat, then the liquid surface will have very little motion and will become too cold. This can lead to freezing of the steel meniscus, which will aggravate the formation of meniscus hooks. This allows inclusions and bubbles to be captured, the latter forming pinholes just beneath the surface of the slab. For example, decreasing surface velocity below 0.4 m/s has been measured to increase surface pinnole defects. To avoid these problems, the flow pattern should be designed to exceed a critical minimum velocity across the top surface, estimated to be about 0.1–0.2 m/s.

6.1.2. Entrainment of Mold Slag

Mold slag can be entrained into the solidifying shell due to vortexing, high velocity flow that shears slag from the surface, and turbulence at the meniscus. Slag entrainment is less likely with deeper nozzle submergence and slower casting speed. To avoid shearing slag in this manner, the surface velocity must be kept below a critical value. This critical velocity has been measured in water–oil models as a function of viscosity and other parameters. Entrainment is more difficult for shallower slag layers, higher slag viscosity, and higher slag surface tension.

6.1.3. Level Fluctuations

Many surface defects form at the meniscus due to fluctuation of the liquid steel level on the top surface of the mold cavity. It is well known that automatic level control is better than manual level control. Figure 26 shows the variation in cleanliness at the start of casting with accidental disruption of automatic level control. Fig. 26. Variation in cleanliness at the start of casting with accidental disruption of automatic level control. Fig. 26. Variation in cleanliness at the start of casting with accidental disruption of automatic level control.

Fig. 25. Schematic of phenomena in the mold region of a steel slab caster.

Fig. 26. Variation in cleanliness at the start of casting with accidental disruption of automatic level control.
To decrease these problems, the top surface velocity should be kept below a critical maximum velocity, which has been estimated to be 0.3 m/s\(^{154}\) or 0.4 m/s.\(^{147}\)

6.2. Flow Pattern Control

In slab casting, the mold flow pattern varies between the two extremes shown in Fig. 27: single roll and double roll.\(^{155}\) For the “single roll” flow pattern, surface velocities and level fluctuations are high, so mold slag entrainment and surface defects are likely. The optimal flow pattern for slab casting is likely a stable, double-roll flow pattern from a bifurcated nozzle that is not too deep. The mold flow pattern is controlled by adjustable parameters such as nozzle geometry, nozzle submergence depth, argon gas injection rate, and the application of electromagnetic forces. It also depends on parameters which generally cannot be adjusted to accommodate the flow pattern, such as the position of the flow control device (slide gate or stopper rod), nozzle clogging, casting speed, strand width, and strand thickness. All of these parameters together form a system that should be designed to produce an optimal flow pattern for a given operation.

6.2.1. Flow Pattern Stability

The first requirement to improve steel cleanliness by the mold flow pattern control is to minimize transients during the operation. It was observed that inclusion entrapment varies from side to side, which suggests a link with variations in the transient flow structure of the lower recirculation zone, and the asymmetrical flow pattern, which could be induced by nozzle clogging as shown in Fig. 28,\(^{63}\) by turbulence as investigated by Thomas et al. (mathematical simulation)\(^{156}\) and Gupta (water model),\(^{157}\) and by excessive argon gas injection.\(^{149}\) It is especially important to keep nearly constant the liquid steel level in the mold, powder feeding rate, casting speed, gas injection rate, slide gate opening, and nozzle position (alignment and submergence). Next, the steady mold flow pattern must be designed and controlled.

6.2.2. Casting Speed

Increasing casting speed tends to increase transient turbulent fluctuations, and worsens the extent of flow pattern asymmetries. This in turn worsens detrimental surface turbulence and level fluctuations.\(^{158}\) Improving internal cleanliness often requires limiting the maximum casting speed, such as employed by Inland to avoid pencil pipe defects.\(^{159}\) Lower casting speed and avoiding variations in casting speed both reduce the rate of slivers.\(^{51}\) More precisely, it is important to lower the liquid mass flow rate in order to control the jet velocity exiting the nozzle.\(^{159}\)
6.2.3. Nozzle Geometry

The nozzle is one of the few control parameters that is relatively inexpensive to change, yet has a profound influence on the flow pattern and thus on quality. Nozzle parameters include bore size, port angle and opening size, nozzle wall thickness, port shape (round vs. square vs. oval), number of ports (bifurcated vs. multiport), and nozzle bottom design (well vs. flat vs. sloped). Using a large bore or large port area can slightly lower the jet speed exiting the nozzle and accommodate some clogging, but this is at the expense of increased swirl and variability in the flow.\textsuperscript{139,160} Flow pattern is controlled mainly by the angle of the lower ports. A shallow port angle was found to increase defects due to powder entrapment while a deep angle increased defects due to alumina.\textsuperscript{112} This tradeoff shows that nozzle geometry must be chosen, together with every other flow-control parameter, to produce an optimal flow pattern that balances between these two problem types.

6.2.4. Argon Gas Injection

In addition to helping to reduce nozzle clogging, argon is injected into the nozzle to help influence and control the flow pattern in the mold. For example, Fig. 27 shows that low gas flow tends to double-roll flow pattern, while a high argon flow rate induces single-roll flow.\textsuperscript{155} Gas injection also makes the flow pattern more variable, as it alternates between single and double roll. To maintain a stable double-roll flow pattern, which is often optimal, the argon should be kept safely below a critical level.\textsuperscript{155,161} Excessive argon injection may generate transient variation of the jets entering the mold, introduce asymmetry in the mold cavity,\textsuperscript{149} and increase surface turbulence. Argon gas bubbles may also be trapped in the solidifying steel shell to form blister defects, such as pencil pipe in the final product.\textsuperscript{149,153,159,162} Gas bubbles also capture inclusions as they flow in the mold.\textsuperscript{163} Figure 29 shows a typical bubble coated with inclusion clusters.\textsuperscript{153} A tremendous number of alumina particles can be captured by a single bubble, as shown in Fig. 30, especially a large bubble owing to its larger surface area.\textsuperscript{164} This phenomenon is good for inclusion removal if the bubbles float out. The fundamentals of inclusion removal by bubble flotation in liquid steel is reviewed by Zhang et al.\textsuperscript{165} However, inclusion-coated bubbles are very bad for steel cleanliness if they are entrapped by the solidifying shell. Entrapped solid oxide particles eventually lead to surface slivers or internal defects.\textsuperscript{153} Even if no gas is injected into the tundish nozzle, defects can form from bubbles originating far upstream.\textsuperscript{163}

6.2.5. Submergence Depth

Increasing submergence depth naturally shifts the flow pattern downward, which lessens fluctuation and instability of the steel/slag interface,\textsuperscript{166} and tends to improve surface quality, as shown in Fig. 31.\textsuperscript{166} However, too deep submergence may send more particles deep into the lower recirculation zones, where a greater fraction may become entrapped. Deeper submergence may lead to inadequate liquid slag layer thickness, meniscus freezing, and problems feeding slag into the interfacial gap, especially near the SEN. This increases problems with longitudinal cracks and transverse depressions, as shown in Fig. 31.\textsuperscript{166} For a given operation, an optimum submergence depth should exist.\textsuperscript{154,166}

6.2.6. Electromagnetic Forces

Electromagnetic forces can be applied to the molten metal in a number of ways to substantially alter the flow pattern in the strand. Timken Harrison Plant reports that electromagnetic stirring of outer strands can improve the steel cleanliness, lowering T.O in the billet from 30 to 20 ppm.\textsuperscript{41} Another example is the electromagnetic brake (EMBR),\textsuperscript{167} which bends the jet and shortens its impingement depth, to lessen the likelihood of capture by the solidified shell deep in the strand.

6.2.7. Caster Curvature

Curved mold machines are known to entrap more parti-
cles than straight (vertical) mold casters, because the particles gradually move upwards towards the inside radius while they spiral with the liquid in the lower recirculation zone. Most particles are captured 1–3 m below the meniscus, independent of casting speed, which corresponds to a specific distance through the strand thickness. Often, inclusions concentrate at one-eighth to one-quarter of the thickness from the top of the inside radius surface, in addition to the surfaces, as verified by AK Steel Middletown Works (Fig. 32). Figure 33 shows the difference of inclusion and pinhole distributions along the slab thickness between curved (S-type) and vertical bending (VB-type) caster. The vertical bending caster has fewer inclusions and pinholes, which are distributed deeper, relative to the curved caster. Particle entrapment defects such as pencil pipe can be lessened if at least the top 2.5 m section of the caster is straight (vertical).

7. Summary

This paper first reviews the different definitions of clean steel, depending on steel grade and application. Next, the different methods to evaluate steel cleanliness, so it is best to couple several methods together to give a more accurate evaluation. Many plants control total oxygen content and nitrogen pickup in Low Carbon Al-killed steel, which are summarized for many plants. Finally, operation practices to improve steel cleanliness at the ladle, tundish, transfer, and caster are reviewed. Ladle operations should minimize FeO and MnO in the slag, optimize ladle stirring practice, and possibly modify inclusions with Ca treatment. Tundish operations should employ a large, deep vessel with a nonreactive lining and a stable basic flux cover. It should be optimized with flow controls such an impact pad to remove inclusions, especially during transitions. Transfer operations should employ open ladles with optimized, nonreactive refractory shrouds, argon gas protection, sealing and care to avoid reoxidation, slag entrainment and nozzle clogging. Finally, mold operations should optimize casting speed, nozzle geometry, gas injection, submergence depth, and electromagnetic forces in order to maintain a stable mold flow pattern that encourages inclusion removal while avoiding the creation of new defects. The top portion of the caster should be vertical to minimize inclusion and bubble entrapment on the inside radius.

Acknowledgments

The authors are grateful for support from the National Science Foundation (Grant No. DMI-0115486) and the Continuous Casting Consortium at University of Illinois at Urbana-Champaign.

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