85th Steelmaking Conference Proceedings, ISS-AIME, Warrendale, PA, 2002 pp. 431-452.

EVALUATION AND CONTROL OF STEEL CLEANLINESS — REVIEW

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Key words: Steel Cleanliness, Inclusions, Size Distribution, Morphology, Total Oxygen, Nitrogen Pick-up

INTRODUCTION

The demand for cleaner steels increases every year. In addition to lowering non-metallic oxide inclusions and controlling their morphology, composition and size distribution, clean steel requires lowering other residual impurity elements such as sulfur, phosphorus, hydrogen, nitrogen and even carbon [1, 2], and trace elements such as As, Sn, Sb, Se, Cu, Pb, and Bi[3]. **Table I** lists the influence of common steel impurities on steel mechanical properties [1].

Table I Influence of typical impurities on mechanical properties [1]

Element	Form	Mechanical properties affected
S,O	Sulfide and oxide inclusions	• Ductility, Charpy impact value, anisotropy • Formability (elongation, reduction of area and bendability) • Cold forgeability, drawability • Low temperature toughness • Fatigue strength
C,N	Solid solution	• Solid solubility (enhanced), hardenability
	Settled dislocation	• Strain aging (enhanced), ductility and toughness (lowered)
	Pearlite and cementite	• Dispersion (enhanced), ductility and toughness (lowered)
	Carbide and nitride precipitates	• Precipitation, grain refining (enhanced), toughness (enhanced) • Embrittlement by intergranular precipitation
P	Solid solution	• Solid solubility (enhanced), hardenability (enhanced) • Temper brittleness • Separation, secondary work embrittlement

Inclusions generate many defects in the steel product. For example, **L**ow **C**arbon **A**l-**K**illed steel (LCAK steel) coils at the Midwest Division of National Steel[4] suffer from cracked flanges, which were caused by inclusions identified as alumina from deoxidation and reoxidation product, calcium aluminates from tundish slag, and entrained mold slag inclusions. 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 consist of aluminates originating from deoxidation and complex non-metallic inclusions from entrained mold slag, as documented in many studies such as at Inland Steel No.4BOF Shop [5] and at Great lake works of National steel [6].

Steel cleanliness depends on the amount, morphology and size distribution of non-metallic inclusions in steel. The definition of 'clean steel' varies with steel grade and its end use, as shown in **Table II.**

Table II Steel cleanliness requirements for various steel grades

Steel product	Maximum impurity fraction	Maximum inclusion size
IF steel	[C]≤30ppm, [N]≤40ppm, T.O≤40ppm [7], [C]≤10ppm[8], [N]≤50ppm[9]	
Automotive & deep-drawing Sheet	C]≤30ppm, [N]≤30ppm [10]	100μm [10, 11]
Drawn and Ironed cans	[C]≤30ppm, [N]≤30ppm, T.O≤20ppm [10]	20μm[10]
Alloy steel for Pressure vessels	[P]≤70ppm[12]	
Alloy steel bars	[H]≤2ppm, [N]≤10-20ppm, T.O≤10ppm [13]	
HIC resistant steel (sour gas tubes)	[P]≤50ppm, [S]≤10ppm[12, 14]	
Line pipe	[S]≤30ppm [12], [N]≤35ppm, T.O≤30ppm [13], [N]≤50ppm[9]	100μm[10]
Sheet for continuous annealing	[N]≤20ppm[12]	
Plate for welding	[H]≤1.5ppm[12]	
Bearings	T.O≤10ppm[12, 15]	15μm[13, 15]
Tire cord	[H]≤2ppm, [N]≤40ppm, T.O≤15ppm[13]	10μm[13]
Non-grain-orientated Magnetic Sheet	[N]≤30ppm [9]	
Heavy plate steel	[H]≤2ppm, [N]30-40ppm, T.O≤20ppm[13]	Single inclusion 13μm[10] Cluster 200μm[10]
Wire	[N]≤60ppm, T.O≤30ppm[13]	20μm[13]

The inclusion size distribution is very important because large macroinclusions are the most harmful to mechanical properties. One kg of typical LCAK steel contains $10^7 – 10^9$ inclusions, [3] including only 400 80μm-130μm inclusions, ten 130-200μm inclusions and less than one 200-270μm sized inclusions. [16] 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 [17]. 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 II include restrictions on the maximum inclusion size. The importance of inclusion size distribution is

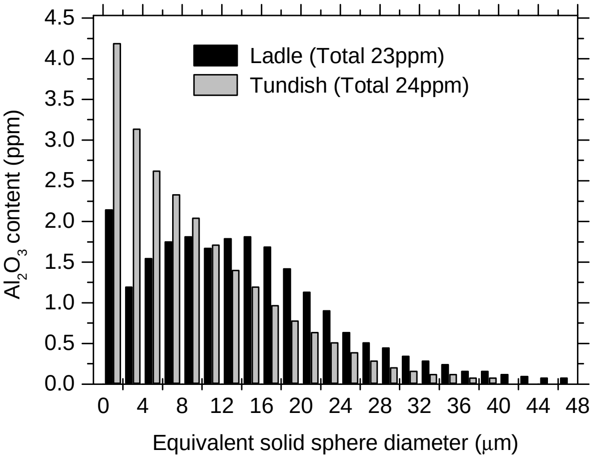


Fig.1 Al_2O_3 inclusion size distribution in ladle and tundish further explained by **figure 1** [18], which shows the measured content of inclusions larger than 30 μm to drop from 1.61 ppm in a ladle to only 0.58ppm in the tundish. Thus, the tundish steel is cleaner, despite having a slightly higher total oxygen content and more total inclusions.

Non-metallic inclusions come from many sources including [4, 6, 19-22]:

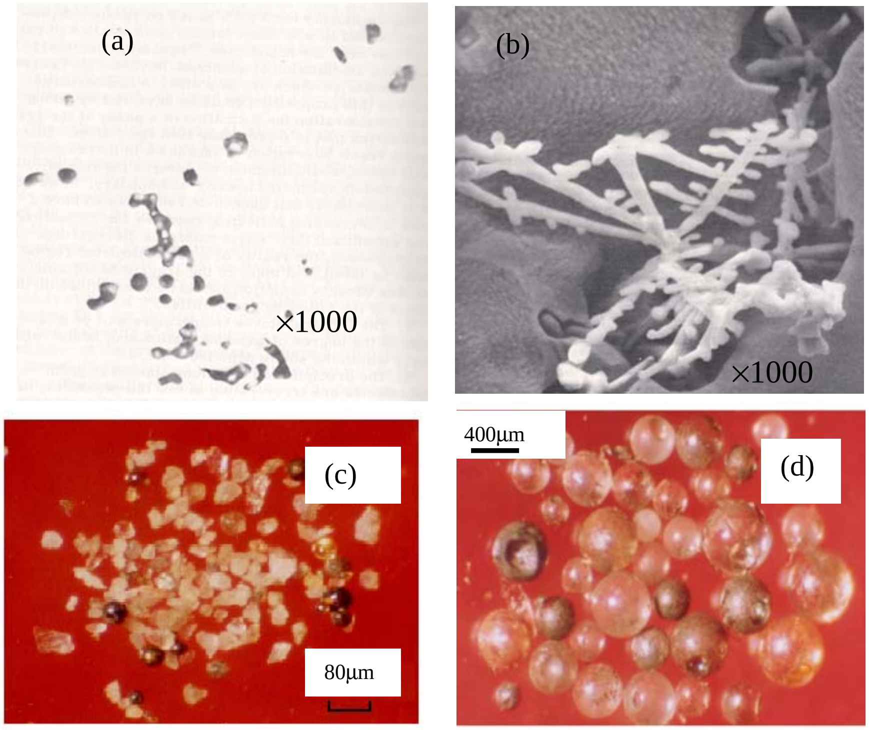
① Deoxidation products, such as alumina inclusions cause the majority of indigenous inclusions in LCAK steel. They are generated by the reaction between the dissolved oxygen and the added deoxidant, such as aluminum. Alumina inclusions are dendritic when formed in a high oxygen environment, as pictured in **Figs. 2a** and **2b** [23], or may result from the collision of smaller particles, including some of those in **Fig. 2c** [24].

② Reoxidation products, such as alumina generated when 1) the Al remaining in the liquid steel is oxidized by FeO in the slag or 2) by exposure to the atmosphere;

③ Slag entrapment, when metallurgical fluxes are entrained during transfer between steelmaking vessels. They form liquid inclusions that are usually spherical, as shown in **Fig. 2d** [24].

④ Exogenous inclusions from other sources, such as 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 include some of the particles pictured in Fig. 2c [24].

⑤ Chemical reactions, such as the products of inclusion modification when Ca treatment is improperly performed.



(a) Metallographical Microscope Observation (2-Dimensional) of dendritic alumina inclusion [23]

(b) SEM microgragh (3-D) of the same inclusion in (a) after partial slime extraction [23]

(c) Alumina inclusions (Slime test of tundish sample) with various compositions including (Al_2O_3 96.23%, SiO_2 2.32%, MnO 1.3%, FeO 0.14%, CaO 0%, MgO 0%, Na_2O 0%, K_2O 0.06%) and (Al_2O_3 75.43%, SiO_2 19.42%, MnO 1.04%, FeO 2.02%, MgO 2.33%) [24]

(d) Slag inclusions (Slime test of tundish sample) in tundish with typical composition of (Al_2O_3 24.01%, SiO_2 29.03%, MnO 19.68%, FeO 16.39%, CaO 4.08%, MgO 1.41%, Na_2O 1.3%, K_2O 0.71%) [24].

Fig.2 Typical inclusions morphology and compositions

Steel cleanliness is controlled by wide range 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. The first extensive review about clean steel is by Kiessling in 1980 [3] which 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 [25] and by Cramb [11] which add extensive thermodynamic considerations.

This paper reviews the current "state-of-the-art" in steel cleanliness. First, the methods for evaluating steel cleanliness are reviewed. Next, the indirect measures of cleanliness, total oxygen (T.O) and nitrogen pick-up, are summarized for LCAK at many steel plants around the world. Finally, operating practices to improve steel cleanliness at the ladle, tundish and continuous caster are reviewed. Many industrial data about steel cleanliness are gathered. This paper aims to provide useful information for the production of clean steel, focusing on the control of alumina inclusions.

METHODS FOR EVALUATING 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 only reliable as relative indicators.

Direct Methods

There are several direct methods to evaluate steel cleanliness, which are summarized as follows.

Metallographical **M**icroscope **O**bservation (MMO)[3] – 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. 2a shows a slice through the single inclusion revealed in Fig. 2b, 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, [26] this is very problematic.

Image **A**nalysis (IA) [3, 27] – 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 gray-scale 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.

Sulfur **P**rint [17, 24] – 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.

Slime (**E**lectrolysis) [24, 28] – In this accurate but time consuming method, a relatively large (200g – 2kg) steel sample is completely dissolved in acid (HCl) and the nonmetallic inclusions which remain are collected for counting and further analysis. Alternatively, in order to protect FeO inclusions, most of the dissolution is 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.

Electron **B**eam melting **(EB)** [29] **-** A steel sample 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. An enhanced method (**EB-EV** - **E**xtreme **V**alue) has been developed to estimate the inclusion size distribution. [30] 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.

Cold **C**rucible **(CC)** melting [17] **–** 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 slime extraction by reducing the volume of metal to dissolve.

Scanning **E**lectron **M**icroscopy **(SEM)** [31] – This method clearly reveals the three-dimensional morphology and the composition of each inclusion examined as shown in Fig.2b. Composition is measured with **E**lectron **P**robe **M**icro **A**nalyzer **(EPMA)** [32].

Optical **E**mission **S**pectrometry with **P**ulse **D**iscrimination **A**nalysis **(OES-PDA)** [15, 17, 33] **-** The OES method is conventionally used for analysis of dissolved elements in steel. Ovako Steel improved this technique to analyze the total oxygen content, microinclusion size distribution and composition within 10 minutes of collecting the sample. [15] To discriminate solid inclusions (OES-PDA), light logging is made at the frequency of the emission spark. Electrical characteristics are defined to optimize the light ratio between the background signal of the dissolved elements and the disturbance signal due to heterogeneities such as inclusions [28]. The number of high intensity aluminum peaks spark is the PDA index [28].

Mannesmann **I**nclusion **D**etection by **A**nalysis **S**urfboards **(MIDAS)** [14] – 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 **L**iquid **S**ampling **H**ot **R**olling **(LSHP)** method [17].

Laser-**D**iffraction **P**article **S**ize **A**nalyzer **(LDPSA)** [17] **-** This laser technique can evaluate the size distribution of inclusions that have been extracted from a steel sample using another method such as slime.

Conventional **U**ltrasonic **S**canning (**CUS**) [17] – This method can obtain size distributions of inclusions larger than 20μm in solidified steel samples.

Cone **S**ample **S**canning [34] – 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 surface inclusions at every location in the area of the sample, including from surface to centerline.

Fractional **T**hermal **D**ecomposition **(FTD)** [28] – Inclusions of different oxides are selectively reduced at different temperatures, such as alumina-based oxides at 1400 or 1600°C, or refractory inclusions at 1900°C. The total oxygen content is the sum of the oxygen contents measured at each heating step.

Laser **M**icroprobe **M**ass **S**pectrometry **(LAMMS)** [35] – 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.

X-ray **P**hotoelectron **S**pectroscopy **(XPS)** [32] – This method use x-rays to map the chemical state of inclusions larger than 10μm.

Auger **E**lectron **S**pectroscopy **(AES)** [32] – This method use electron beams to map the chemical state of

Photo **S**cattering **M**ethod [26, 36] – 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.

Coulter **C**ounter **A**nalysis [37] This method, which is similar to LIMCA, can be used to measure the size distribution of inclusions extracted by Slime and suspended in water [37].
inclusions larger than sub-μm.

Liquid **M**etal **C**leanliness **A**nalyzer **(LIMCA)** [38] **-** This on-line sensor detects inclusions directly in the liquid. Particles which flow into this sensor through its tiny hole are detected because they change the electric conductivity across a gap.

Ultrasonic **T**echniques for **L**iquid **S**ystem [38] – This method captures the reflections from ultrasound pulses to detect on-line inclusions in the liquid steel.

Indirect Methods

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

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 by equilibrium thermodynamics with deoxidation elements, such as aluminum. The equilibrium constant of the reaction between aluminum and oxygen can be represented by [39]

$$\log K = \log\left([\mathrm{Al}]^2[\mathrm{O}]^3\right) = -62780/T(K) + 20.54 \qquad (1)$$

For example, at 1873K (1600°C), $K=1.05\times10^{-13}$, so if [%Al] = 0.03-0.06, the free oxygen is 3-5ppm. Because the free oxygen does not vary much, the total oxygen is a reasonable indirect measure of the total amount of oxide inclusions in the steel. Due to the small population of large inclusions in the steel and the small sample size for T.O measurement (normally 20g), there are likely no large inclusions in samples. Even if a sample has a large inclusion, it is likely discounted due to anomalously high reading. Thus, T.O content really represents the level of small oxide inclusions but not larger ones. A low T.O content, however, decreases the probability of large oxide inclusions [3] as shown in **figure 3** [24]. Thus total oxygen is still a very important and common index of steel cleanliness.

The T.O. measured in liquid samples clearly correlates with the rate of slivers in the product, as first shown in **figure 4** [40]. In particular, tundish samples are commonly taken to indicate cleanliness for slab dispositioning. For example, Kawasaki [41] requires the T.O in tundish samples <30ppm to warrant shipment of cold-rolled sheet without special inspection. T.O levels between 30 and 55ppm require critical inspection. Heats above 55 are downgraded. The control levels of T.O in steel during every step for LCAK Steel at some steel plants are shown in **Table III**. The blank parts in this table mean no data available from the reference papers.

The following conclusions can be derived from Table III:

① T.O in LCAK steel has steadily decreased with passing years, as new technology is implemented. For example, in Nippon steel, T.O dropped from 40-50 ppm in 1970's [42], to 20 ppm in 1990's [43];

② Plants with RH degassing achieve lower T.O. (10-30ppm) than plants with ladle gas-stirring (35-45).

③ T.O generally drops after every processing step: ladle 40ppm, tundish25ppm, mold 20ppm, and slab 15ppm.

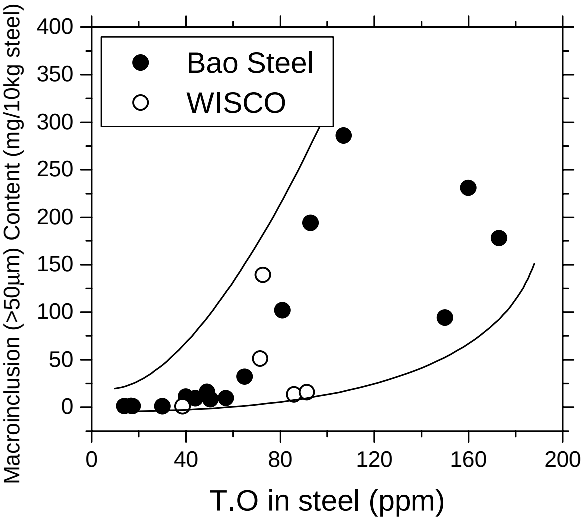


Fig.3 Relationship between T.O and macroinclusions in steel

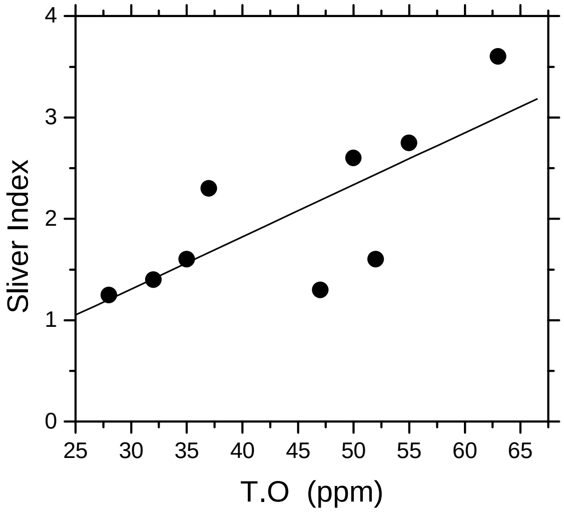


Fig.4 Relationship between T.O in tundish and sliver defect index for product

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 uses a restriction of 10 ppm maximum nitrogen pickup from ladle to tundish for critical clean steel applications.[44, 45] 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 Figs. 4 [40] and **figure 5**[45]. Note that sulphur is a surface active element which reduces the rate of nitrogen pick-up and the oxidation. [46]

Table III The total oxygen during every steps for the production of LCAK steel (* for ultra clean steel).

Steel works	T.O (ppm)					Year	Ref.
	Steel Refining Method	Ladle	Tundish	Mold	Slab		
America							
Inland No.4 BOF shop	LMF	30	24	21	15	1990	[5]
Middletown Works, Armco Steel		60-105	15-40 mean 25		16.9-23.8	1991	[41]
Ashland Works, Armco Steel			16.3			1993	[47]
Lorain Works, BOP shop, U.S. Steel					13-17	1991	[48]
Great Lake Division, No.1CC, National Steel					<31	1991	[41]
Great Lake Division, No.2CC, National Steel					<36	1991	[41]
Some plant in North America		20-35		20-30	10-15	1991	[49]
Cokerill Sambre/CRM					<30	1991	[41]
					<20*	1991	[41]
Timken Company's Harrison Steel Plant				20-30		1991	[50]
Dofasco (Canada)					13	1992	[51]
			19		13.2	1994	[52]
Great Lake Division, No.2CC, National Steel				20-40		1994	[6]
Great Lake Division, No.2CC, National Steel			25-50 mean 40			1995	[4]
Cleveland Works, LTV Steel			21-27			1995	[53]
Atlas Stainless Steels division, Sammi Atlas Inc	Gas stirring treatment	36-45	30-38			1995	[40]
Lukens Steel Company, USA			16-20			1995	[54]
Weirton Steelmaking shop			23±10	22±12		1995	[45]
Europe							
Mannesmannröhren-Werke, Hüttenwerk Huckingen					<20	1991	[41]
Usiminas (Brazil)					20	1993	[55]
Usimina (Brazil)					13*	1993	[55]
One steel Plant in Finland		48±12	32	38	17	1993	[56]
Dillinger (Germany)			10-15	10		1993	[46]
					≤15	1994	[57]
Hoogovens Ijmuiden BOS No.2, Netherlands			LCAK: 15-32			1994	[58]
			IF 20-30			1994	[58]
British Steel					<10	1994	[59]
Linz (Austria)					16	1994	[60]
Dunkirk, Sollac (France)	RH		20-50			1997	[61]
Sidmar (Belgium)		37				2000	[62]
Koerhar Works, Fundia (Finland) (high carbon steel)	Gas stirring	32		23		2000	[63]

Asia							
Chiba works, Kawasaki	RH	40			20	1989	[64]
Mizushima Works, Kawasaki			34.7			1989	[65]
				<30		1991	[41]
	KTB (R=CaO/Al_2O_3)	<25 (R=1.8) <35 (R=1.2) <40 (R=0.8)			<55	1996	[7]
NKK, Traditional RH	RH	17				1993	[66]
NKK-PERM for RH	PERM for RH	7				1993	[66]
NKK, Traditional VOD	VOD	33.8				1993	[66]
NKK-PERM for VOD	PERM for VOD	25.1				1993	[66]
Keihin, #1, NKK					<20	1991	[41]
Keihin, #5, NKK					<28	1991	[41]
Nagoya, Nippon Steel	RH	10-30				1989	[67]
Yamata Works, Nippon Steel	Ar Ladle	82 (152 before Ar)	45		44	1974	[42]
Hachiman works, Nippon steel					26	1989	[43]
POSCO	RH	25-31				1993	[68]
					<27	1991	[41]
					<10*	1991	[41]
China Steel, Taiwan	RH	<30			12	1994	[69]
Baosteel, China	CAS-OB	172.5	93	/	48.8	1992	[24]
	RH	72	/	/	30	1994	[24]
	RH	70	57	21-51	13.8-17.5	1995	[24]
WISCO, China	RH	71-73	/	/	37-39	1995	[70]

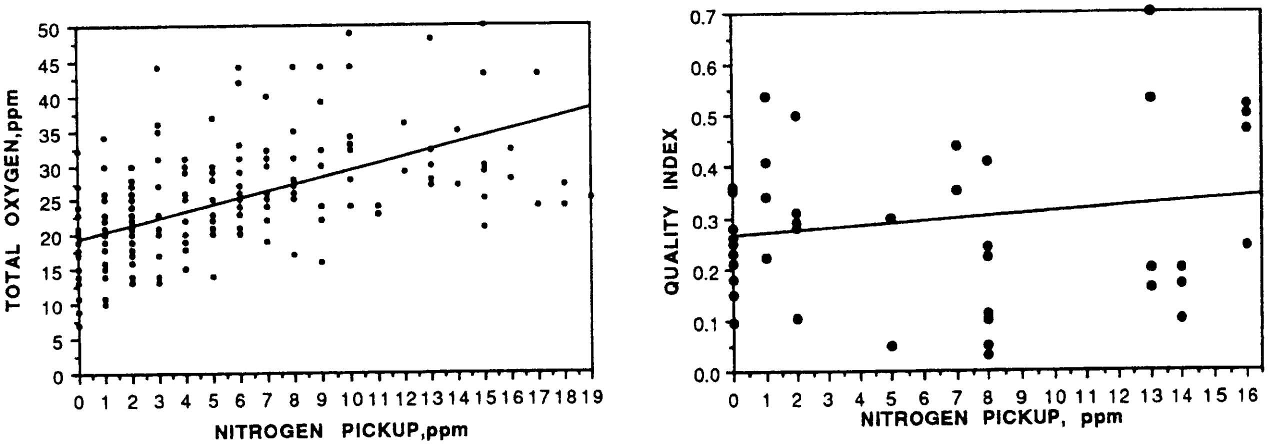


Fig.5 Relationship between nitrogen pickup and total oxygen and steel quality index

Tables IV summarizes nitrogen pick-up in LCAK steel at every processing step for several steel plants. From these two tables, the following conclusions can be obtained:

① With new technology and improved operation, nitrogen pick-up has deceased with years. For example, at Dunkirk Sollac works, from tundish to mold, nitrogen pick-up decreased from 9ppm in 1988, to 1ppm in 1992.

② 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 1ppm. The effect of shrouding operations on nitrogen pick-up will be discussed later in this paper.

③ Nitrogen level in LCAK steel slab is controlled to 30-40ppm at most steel plants. It is controlled mainly by the steelmaking converter or electric furnace operation, but is affected by refining and shrouding operations.

Table IV The level of nitrogen pickup Δ[N] for some steel plants

Steel works	Process	Δ[N] (ppm)	year	Ref,
Dofasco	Ladle→tundish Tundish→mold Tundish→mold	<1 1.8 0.3	1992	[51]
	Tundish→mold	0.52	1995	[71]
Weirton Steel Corporation	Ladle→mold	4~10	Before 1993	[44]
	Ladle→mold	<5	After 1993	[44]
Ashland works, Ameco	Tundish→mold	2	1993	[47]
No.4 BOF shop, Inland steel	Ladle→tundish	3	1990	[5]
Fairfield Works, US Steel	Ladle→tundish	4	1995	[72]
		7.5	Before 1995	[72]
Dunkirk, Sollac	Ladle→tundish	0.5-1.3	1995	[73]
	Tundish→mould	1	1992	[73]
	Ladle→tundish	3	Before 1995	[73]
	Tundish→mould	9	1988	[73]
IMEXSA Steel, Mexico	Ladle→mold	5	1996	[74]
Dillinger Steel Plant, Germany	Ladle→tundish	5	1993	[46]
	Ladle→mold	5	1993	[46]
Baosteel, China	Ladle→mold	1-5	1995	[24]
WISCO, China	Ladle→mold	3.8-9.3	1995	[70]

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

Slag composition measurement- Analysis of the slag composition evolution before and after operations can be interpreted to estimate inclusion absorption to the slag. Secondly, slag entrainment from a particular vessel can be determined by matching trace elements in the slag and inclusion compositions. [24]

Submerged entry nozzle (SEN) clogging- Short SEN life due to clogging is often an indicator of poor steel cleanliness. Small alumina inclusions in LCAK steel are known to cause nozzle clogging [28]. The composition of a typical clog during LCAK steel continuous casting is [62]: Al_2O_3 51.7%, Fe 44%, MnO 2.3%, SiO_2 1.4, CaO 0.6%, which reveals a large alumina fraction. Thus SEN clogging frequency is another crude method to evaluate steel cleanliness. The origin, process, and prevention measures for SEN clogging were recently reviewed by Kemeny [19] and Thomas [20].

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, NSC used total oxygen measurement and EB melting for small inclusions, and Slime method and EB-EV for large inclusions. [28] Usinor used total oxygen measurement with FTD, OES-PDA, IA and SEM for small inclusions, and Electrolysis and MIDAS for large inclusions.[28] Baosteel employed total oxygen measurement, Metallographical Microscope Observation, XPS, and SEM for small inclusions, Slime and SEM for large inclusions, nitrogen pickup for reoxidation, slag composition analysis for the inclusion absorption and slag entrainment tracing. [24]

OPERATION PRACTICES FOR CLEAN STEEL

Steel refining and continuous casting operations have important effects on improving steel cleanliness. For example, SOLLAC Dunkirk carried out a systematic study of inclusion removal [61], which indicated that the ladle treatment dropped inclusions by 65~75%; the tundish removed 20~25%, although reoxidation sometimes occurred; and the mold had just a small effect, removing only 5~10% of the inclusions.

Ladle Operations

Tap oxygen-Tap oxygen content is measured during tapping the ladle or before deoxidant addition. The tap oxygen content is typically high, ranging from 450-800ppm at Weirton [45], 800-1200ppm at Great Lake Division of National Steel [75], and 250-650ppm at Nippon Steel Corporation [76]. Aluminum additions then deoxidize the melt, creating larger amounts of Al_2O_3. This suggests that a limitation on tap oxygen content should be imposed for clean steel grades. However, as shown in **figure 6** [45], there is no correlation between furnace practice and steel cleanliness. This agrees with studies [45] of total oxygen content in melt samples, which found 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 7** [24] shows how the T.O decreases with degassing time during RH treatment and reaches the same final T.O level, regardless of different tap oxygen. To achieve this, the degassing time must be long enough, for example, 15minutes. A final consideration is that the tap oxygen content strong affects the decarburization rate for producing ultra low carbon steel.

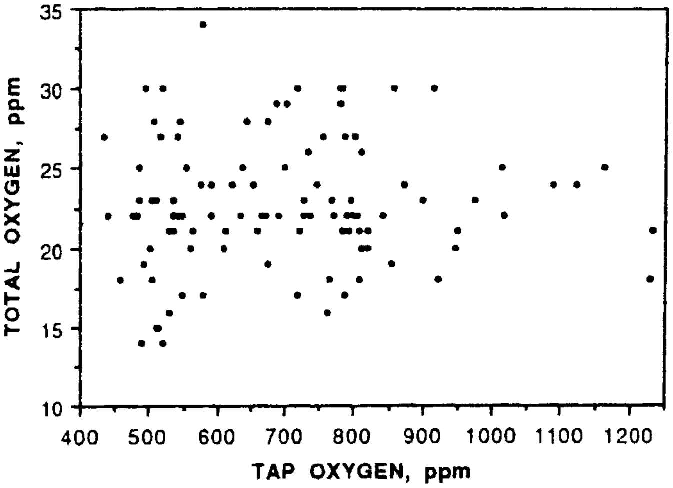


Fig.6 Tap dissolved oxygen and final T.O in tundish

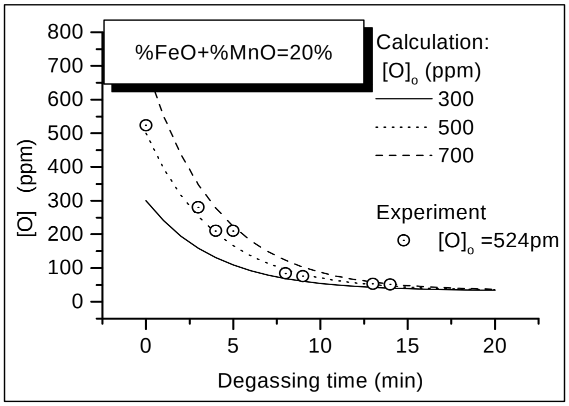


Fig.7 Effect of tap oxygen ($[O]_o$) on the T.O removal in ladle during RH degassing

FeO and MnO in Slag-An important source of reoxidation is the carryover slag from the converter to the ladle, which contain a high content of FeO and MnO. These oxides react with the dissolved aluminum to generate alumina in liquid steel, owing to the strong favorable thermodynamics of the following reactions [74]:

$$3FeO\ (l) + 2\underline{Al} = Al_2O_3 + 3\underline{Fe(l)} \qquad \Delta G_1^o = -853700 + 239.9T\ \ (J\ mol^{-1}) \qquad (2)$$

$$3MnO + 2\underline{Al} = Al_2O_3 + 3\underline{Mn}\ (l) \qquad \Delta G_1^o = -337700 + 1.4T\ \ (J\ mol^{-1}) \qquad (3)$$

The higher 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 [5, 6, 77]. **Figure 8** shows how T.O in the ladl correlates with the %FeO+%MnO in the ladle slag. [77] **Figure 9** shows a similar influence on the loss of dissolved Al. [6, 78] **Figure 10** quantifies how the metallurgical benefits of tundish inclusion removal may be negated by the FeO and MnO pollution from the ladle slag. [79]

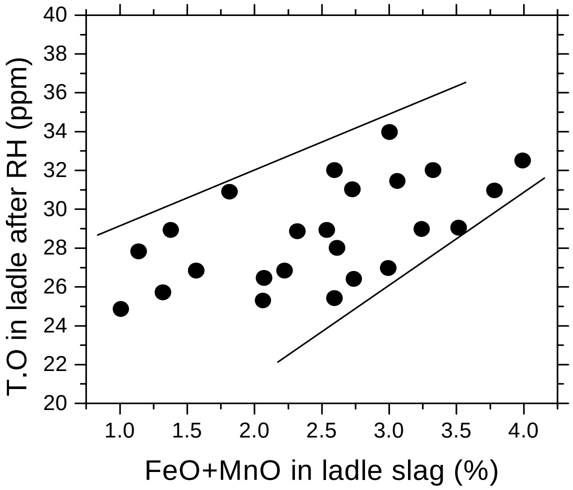


Fig.8 Relationship between the FeO+MnO in ladle slag and the T.O in of steel in ladle

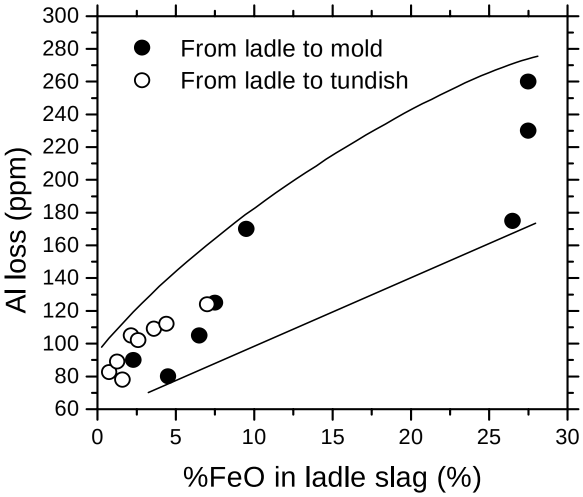


Fig.9 Effect of FeO+MnO content in ladle slag on lowering dissoloved Al (from ladle to mold and from ladle to tundish)

Many countermeasures can be adopted to lower FeO and MnO contamination as follows:

1) Minimize slag carryover from converter to ladle during tapping

- Increasing aim turndown carbon, avoiding reblows, thus minimizing the dissolved oxygen content in the steel, can reduce the amount of FeO in the furnace slag [5].
- Use of a sublance in the BOF has substantially reduced the frequency of reblows [5].
- An efficient mechanical slag stopper, such as a slag ball (that floats in steel and sinks in slag), can help reduce the amount of furnace slag carried over to the ladle during tapping to 3 kg/t steel.[80] Alternatively, other sensors are available. A thick ladle slag layer after tapping suggests high slag carryover problems. For example, at Inland No.4 BOF shop, the ladle slag for critical grades is mechanically skimmed at the Ladle Metallurgy Furnace (LMF) to less than 40mm [5]. At LTV Steel Cleveland Works 1993 [78], the average final ladle slag depth is around 75 mm; at LTV Indiana Harbor Works [81], the depth is 97mm for LCAK, 135mm for high strength low alloy grades, and 140mm for grades requiring coke conditions; at China steel, the depth is 30-100mm[82]; at WISCO #2 (China), the depth is 100-130mm [83]; and at Algoma steel (Canada), the depth is 75mm before skimming and 25mm after skimming [84].

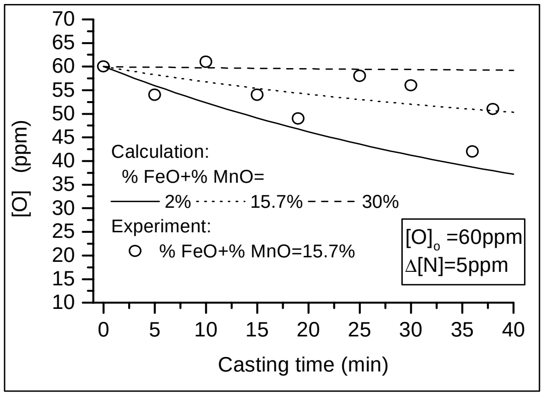


Fig.10 Effect of FeO+MnO content in ladle slag on T.O of steel in tundish

2). Ladle slag reduction treatment [5-7, 61, 77, 78, 82, 85]

Emi found that minimizing slag carryover, together with adding a basic ladle slag and basic lining to lower the ladle slag to less than 1-2% FeO+MnO, can reduce total oxygen to 10 ppm for LCAK steel.[81] Another way to lower the FeO+MnO content of the ladle slag is to add a slag conditioner (ie. slag reduction or deoxidation treatment), which is a mixture of aluminum and burnt lime or limestone. **Table V** summarizes the drop in FeO+MnO content after ladle slag reduction treatment at several steel plants. On average, this treatment lowers FeO+MnO to below 5%, as shown in **figure 11**. SOLLAC Dunkirk reports an accompanying sharp improvement of coil cleanliness. [61]

Table V Effect of Ladle Slag Reduction Treatment for LCAK Steel

Steel Works	FeO+MnO composition in ladle slag		Year	Ref.
	Before reduction treatment	After reduction treatment		
Cleveland Works, LTV Steel	FeO 3.9%, MnO 1.6%	FeO 1.6%, MnO 0.9%	1993	[78]
Cleveland Works, LTV Steel	FeO 25.9%, MnO 2.9%	FeO 4.2%, MnO 2.0%	1993	[78]
No.4 BOF Shop, Inland Steel	FeO 8.1%, MnO 5.2%	FeO 2.4%, MnO 1.4%	1990	[5]
Great Lake Div., National Steel	FeO 25%	FeO 8%, Best 2.0%	1994	[6]
USS/Kobe Steel Company	FeO 30%	FeO 1.23%, best 0.64%	1991	[77]
Algoma Steel (Canada)		FeO 1.5%, MnO 0.8%	1999	[84]
Dunkirk, Sollac (France)	FeO 12-25%	FeO 2-5%	1997	[61]
Bochum Steelwork, Krupp Stahl AG		FeO+MnO%<1%	1991	[49]
Kwangyang Works, POSCO	FeO+MnO 9-18%	FeO+MnO 3-5%	1998	[85]
Mizushima Works, Kawasaki	/	FeO<2%	1996	[7]
Chian Steel, Taiwan	FeO 26.8%, MnO 4.7%	FeO 6.8%, MnO 5.5%	1996	[82]

Effect of RH treatment and ladle stirring-Ladle stirring and refining processes, such as RH (Rheinstahl Heraeus) ladle degassing greatly promote inclusion growth and removal. The effect of various ladle treatments on slab inclusion levels is shown in **figure 12** [1]. This figure shows the improvement of RH vacuum treatment over Ar-stirring in the ladle in improving steel cleanliness, which is consistent with Table IV. The pronounced benefit of calcium-based powder injection is due in part to its greater stirring power [1] in addition to its primary effect of deoxidization and liquefying inclusions. Haastert reported RH degassing and Ca treatment together dropped T.O to 15ppm at some plants [86]. The NK-PERM process (improvement of RH by NKK) can lower the T.O of LCAK steel to 5ppm after 20 min degassing [66]. Excessive stirring is detrimental, however, as the upward circulation of steel onto the slag layer may expose an "eye" region of the steel surface to reoxidation.

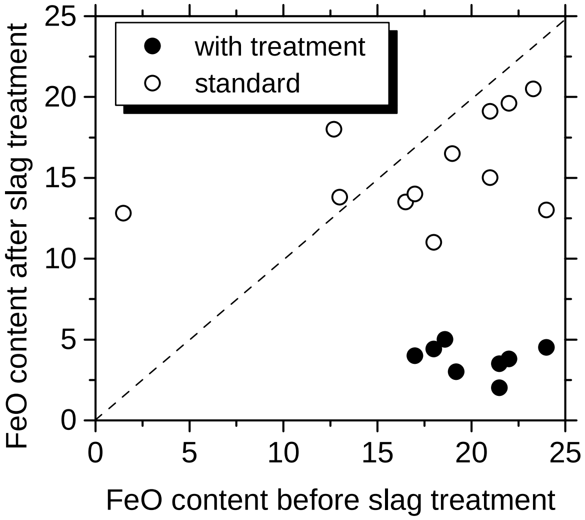
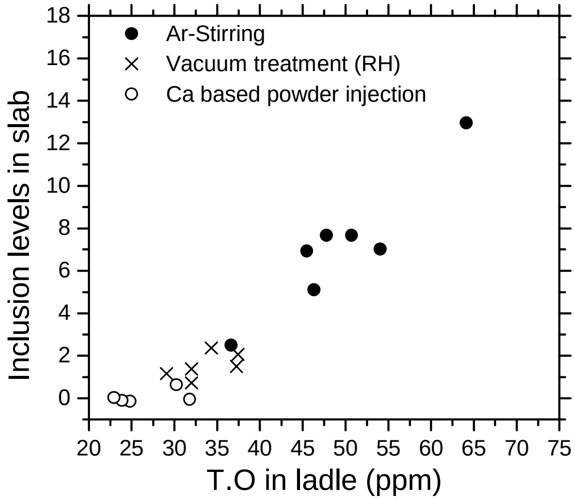


Fig.11 Reduction of FeO content in ladle slag by ladle slag reduction treatment [58]

Sufficient stirring time (> 10 min) [4] after alloy addition is also important, to allow the alumina inclusions to circulate up to the slag and be removed. Too much ladle stirring, however, may be detrimental, as shown in **figure 13** by Atlas Stainless Steel [40], perhaps due to refractory erosion. [40] This phenomena has been theoretically verified by Thomas et al[87], who suggested to first stir vigorously to encourage 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.



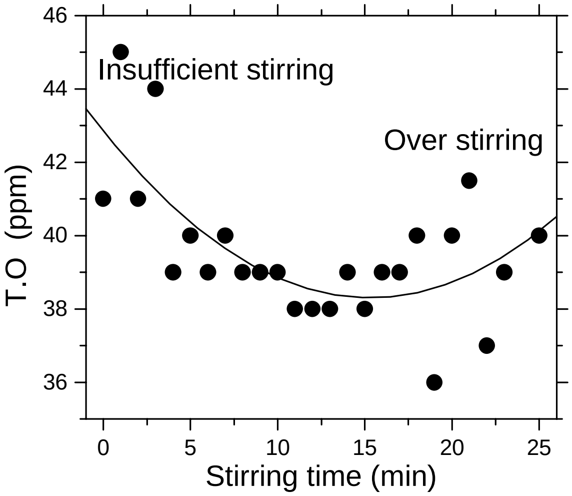


Fig.12 Effect of different ladle treatments on inclusion level in slab[1]   Fig13 T.O in ladle *versus* ladle stirring time [40].

Tundish Operation

Important phenomena taking place in the tundish are shown schematically in **figure 14** [56]. The following factors affecting steel cleanliness are discussed: • Casting transitions; • Tundish lining refractory; • Tundish flux; • Gas stirring; and • Tundish flow control

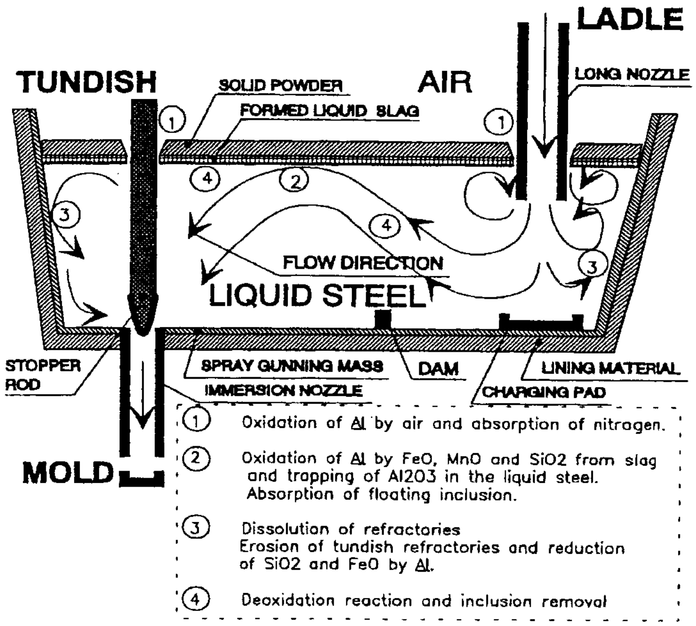


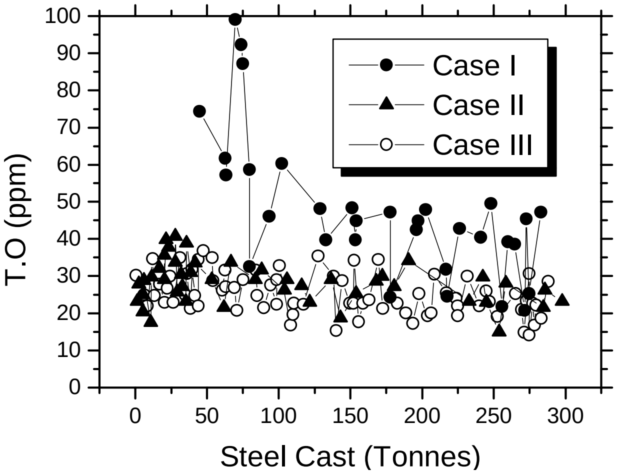
Fig.14 Phenomena in continuous casting tundish

Casting transitions- Casting transitions occur at the start of casting, during ladle exchanges and SEN changes, and at the end of the casting sequence. Inclusions are often generated during transitions and may persist for a long time, thus contaminating a lot of steel [88]. During these unsteady casting periods, slag entrainment and air absorption are more likely, which induce reoxidation problems. At National Steel, for example, T.O. in tundish during transitions is 50-70 ppm, compared with only 25-50ppm at steady state [4]. At other plants, the difference is only 3ppm. Lukens reports transitions to have only 19.2 ppm, relative to 16ppm at steady state [54] and Dofasco reports T.O. of 27±5 ppm during transitions and 24±5 ppm during steady casting [52].

Figure 15 shows the T.O content in the tundish during casting of several individual heats. During the first casting heat, the entrainment of air and slag in the tundish pour box due to the turbulence during ladle open is accompanied by an initial maximum in T.O content in the tundish (including both slag and alumina inclusions). Open pouring at start cast causes T.O in tundish to increase to twice normal levels for more than an entire heat (Fig.15 Case I) [52]. Several minutes of filling are needed before tundish flux 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 bubbling gas through the stopper to promote inclusion flotation [4]. Another improvement effect is to open new ladles with submerged shrouding. With this measure, T.O was decreased at Dofasco from 41±14ppm to 31±6 ppm with more consistent quality throughout the sequence (Fig.15 Case II) [52].

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 (eg. a four tonne "heel" [5]). 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 [52]. An electro magnetic level indicator for ladles is under development.



Case I: The first heat in the tundish; **Case II**: The itermediate heats with Bell shrouds and initial tundish covers; **Case III**: intermidiate heats with baffles and initial tundish covers

Fig.15 The T.O content in Tundish versus time for different heats

Lining refractory- Dissolved aluminum in the liquid steel reacts with an oxygen source 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.(7)) [20]. Silica-based tundish linings are worse than magnesia-based sprayed linings (Baosteel[24] and Inland Steel [5]).

$$SiO_2\ (s)\ (l) + 4/3\underline{Al} = 2/3Al_2O_3\ (s) + \underline{Si}\ (l) \quad \Delta G_1^o = -219400 + 35.7T\ \ (J\ mol^{-1}) \qquad (4)$$

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

Tundish flux – The tundish flux must provide several functions. Firstly, it must insulate the molten steel both thermally (to prevent excessive heat loss) and chemically (to prevent air entrainment and reoxidation [74]). For example, at IMEXSA Steel (Mexico) [74], by changing tundish flux (with lower SiO_2 content), nitrogen pickup from ladle to mold decreased from 16 ppm to 5ppm.

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 crusting. However, rice hulls are high in silica and ($SiO_2 \cong 80\%$ [24]), which can be reduced to form a source of inclusions (Eq.(7)). They also are very dusty and with their high carbon content, ($C \cong 10\%$ [24]), may contaminate ultra low carbon steel.

Basic fluxes ($CaO-Al_2O_3-SiO_2$ based) are theoretically better than rice hulls at refining LCAK steels, and have been correlated with lower oxygen in the tundish. For example, the T.O decreased from 25-50ppm to 19-35ppm with flux basacity increasing from 0.83 to 11, measured at Kawasaki Mitsushima [65]. At Dofasco's #2 Melt Shop, using basic tundish flux (CaO 40%, Al_2O_3 24%, MgO 18%, SiO_2 5%, Fe_2O_3 0.5%, C8%), together with baffles, significantly lowered in total oxygen fluctuation, as compared to the initial flux (CaO 3%, Al_2O_3 10-15%, MgO 3%, SiO_2 65-75, Fe_2O_3 2-3%). The T.O decreased from 41 to 21ppm during ladle transitions and decreased from 39 to 19 ppm during steady state casting. [52] However, other results, such as shown in **figure 16** [45]

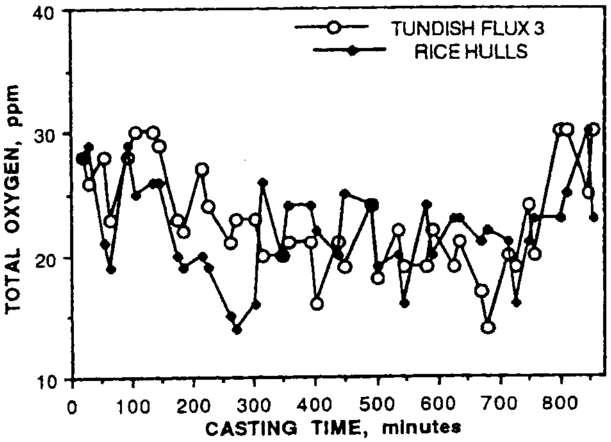


Fig.16 Effect of tundish flux on the T.O in tumdish

found no improvement in T.O between rice hulls and higher basicity flux (SiO_2 25.0%, Al_2O_3 10.0%, CaO 59.5%, MgO 3.5%). 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[24], owing to its faster melting rate and high crystallization temperature. 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 22.4ppm to 16.4ppm [47].

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. At Lukens Steel Company, this technology was employed and successfully lowered T.O to 16 ppm in tundish [54]. The danger of this technology is that any inclusions-laden bubbles which escape the tundish and become entrapped in product, they would be severe defects

Tundish flow control-The tundish flow pattern should be designed to increase the liquid steel residence time, prevent "short circuiting" and promote inclusions 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 is an inexpensive flow control device that suppresses turbulence and prevents erosion of the tundish bottom where the molten steel stream from the ladle impinges the tundish. The incoming stream momentum is diffused and allows the naturally buoyancy of the warm incoming steel to avoid short circuiting, particularly at startup. Together with weir and dam, the TURBOSTOP pour pad improved steel cleanliness, especially during ladle exchanges.[53] At Lukens Steel, T.O decreases from 26ppm (with a domed pad) to 22ppm (with a hubcap pad) [54]. At POSCO, steel cleanliness was improved was improved by putting 77 holes in their dam, making it act as a partial filter [68]. At Dofasco's #2 Melt Shop, using baffles improved product quality, especially at ladle exchanges, thereby making the heat more consistent. (Fig.15 Case III) [52]: baffles combined with an initial tundish cover lowered the average T.O. in tundish during steady state casting from 39±8 to 24±5 ppm [52]

Transfer Operations

One of the most important sources of oxygen pickup is atmospheric reoxidation of steel during transferring from ladle to tundish or from tundish to mold. This generates inclusions which cause production problems such as nozzle clogging, in addition to defects in the final product. Optimization of shrouding system is very important to prevent this phenomenon. Using a shroud lowered nitrogen pickup from 24 to 5 ppm relative to open pouring at Bao Steel [24]. At Fairfield Works (US Steel) [72], replacing the tundish poor box with a ladle shroud and dams lowered nitrogen pickup (ladle to tundish) from 7.5ppm to 4ppm, and also lowered slag entrainment during transitions.

Ladle opening- Ladle self open is a heat in which the ladle nozzle does not have to be lanced open, but opens on its own. When the nozzle has to be lanced open, the shroud must be removed. The cast is unshrouded from ladle to tundish during the first 25 to 50 inches of the cast, and reoxidation by air therefore occurs. **Figure 17** depicts the total oxygen levels for the self-open and lanced-open cases at Lukens Steel

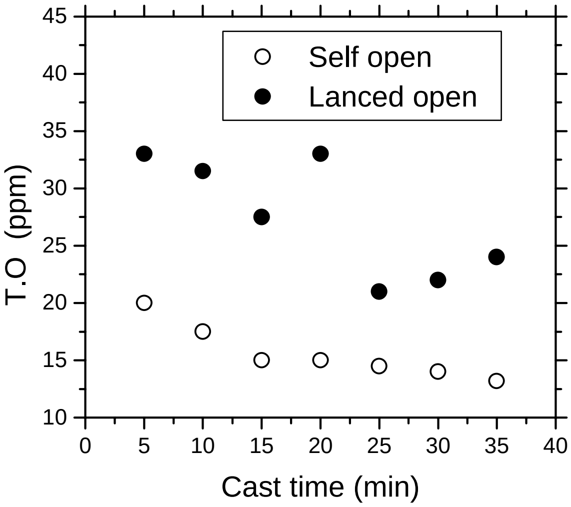


Fig.17 Total oxygen levels created by the self-open and the lanced-open cases

Company, which shows that lanced-opened heats have total oxygen levels around 10 ppm higher than self-open heats [54]. Carefully packing ladle opening sand will be helpful to realize ladle self open.

Argon protection - Argon protection is used to prevent the liquid steel from air reoxidation [20]. When adding the tundish flux too early, the flux can be entrapped into liquid steel and cast into the slab, thus normally no protective cover for the first few minutes of a cast. Also at the period of ladle opening, air is very easy to reach liquid steel. The effects of these two factors can last up to 15 minutes into the cast for 60 ton tundish [54]. To counteract this problem, Lukens Steel explored methods of purging the tundish with inert gases (to displace the air) prior to opening the ladle into the tundish [54]. Another measure to improve shrouding system is to incorporate an appropriate gas injection. At Atlas Stainless Steels division of Sammi Atlas Inc., the level of T.O in tundish decreased from 41.5ppm to 37.9ppm by improving the shrouding system [40].

Sealing issues-To decease the nitrogen pickup during continuous casting, the following factors are usually considered, such as sealing of shroud from ladle to tundish, and submerged entry nozzle (SEN) from tundish to mold. At Dofasco #2 Melt Shop, by improving bayonet system between ladle nozzle and ladle shroud, the nitrogen pickup from ladle to tundish was reduced to <1ppm at steady state (before improvement, this value is 8 ppm nitrogen pickup), and the initial nitrogen pickup from tundish to mold was found 1.8ppm, with the stiffened holder and increased maintenance of the holders, nitrogen pickup was reduces to 0.3 ppm. [51]

Nozzle Clogging – In addition to interfering with production, tundish nozzle / Submerged Entry Nozzle clogging is detrimental to steel cleanliness for three 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 tries to compensate for the clog. At Dofasco #1 Caster, with a 65 tonne tundish, changing from a 3-plate slidegate system to control steel flow from tundish to mold to a stopper rod system was reported to reduce clogging.[71] Many practices can used to minimize clogging, which are reviewed elsewhere. [19, 20] In addition to taking general measures to minimize inclusions, clogging via refractory erosion can be countered by controlling nozzle refractory composition, (eg. avoid Na, K, and Si impurities), or coating the nozzle walls with pure alumina, BN, or other resistant [20].

Mold and Caster Operation

The continuous casting process involves many phenomena, shown in **figure 18** [89], which have far-reaching consequences on strand quality. Inclusions carried into the mold through the nozzle include deoxidation products, nozzle clogs, and entrained of tundish/ladle slag (reoxidation by SiO_2, FeO, MnO in slag), and reoxidation products from air absorption from nozzle leaks. Mold slag may be entrained by excessive top surface velocities or level fluctuations. New inclusions may precipitate as the superheat drops, such as TiO_2 inclusions in Ti-treated steels. On the other hand, inclusions can be removed into the slag / steel interface by buoyancy flotation, fluid flow transport, and attachment to bubble surfaces. The mold 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

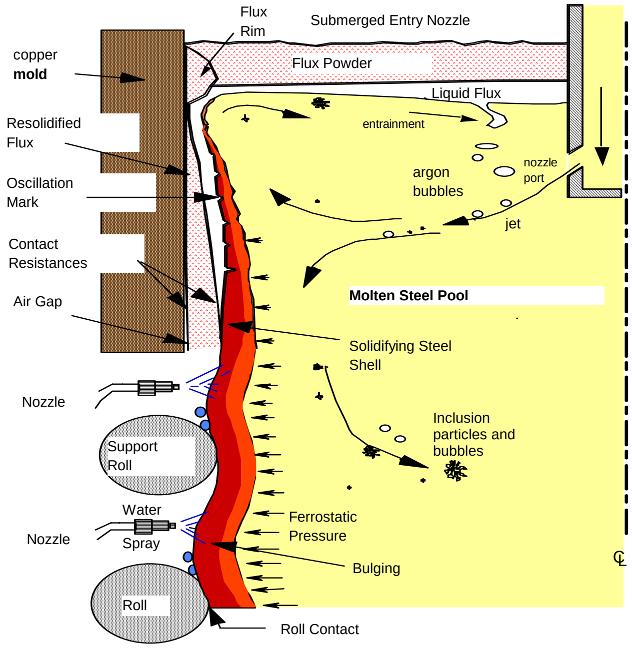


Fig.18 Schematic of phenomena in the mold region of a steel slab caster

permanent defects in the product. Significant insight into inclusion entrapment has been obtained in the past through collecting statistical data and conducting trails on the operating steel caster. Knoepke found that increasing steel flow rate increased the level of pencil blisters (from argon bubble entrapment) significantly, while it reduced the level of slivers (from slag entrainment). [90] Abbel measured the inclusion and bubble distribution in steel slabs and observed that individual 1-mm bubbles were often coated with inclusion clusters, and could be carried from far upstream, even if no gas was injected into the tundish nozzle. [91] 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. Defects are often found associated with transients in the process, such as changes in casting speed, tundish changes, or clogged nozzles. [92] Pencil pipe defects occur intermittently and are rare, relative to the quantity of injected gas [93]. Quan et al obtained the following conclusion by mathematical simulation that 80% the particle were eventually removed to meniscus (20% entrapped in product), and a given particle circulate for up to 300seconds before being removed or entrapped. [94]

In curved-mold machines, inclusions are preferentially trapped 1-3m below the meniscus [93]. Thus, inclusions concentrate at one-eighth to one-quarter of the thickness from the top of the inside radius surface [95, 96], in addition to the surfaces, as verified by AK Steel Middletown Works (**figure 19**) [41]. Harrison Steel Plant at Timken Company reports that electromagnetic stirring of outer strands can improve the steel cleanliness, lowering T.O in slab from 30ppm to 20 ppm [50]. Curved mold machines are known to entrap many more particles than straight (vertical) mold caster [97], because the inclusion spiral upwards the inside radius, where they collect at a specific distance through the thickness [91], corresponding to 2-3m below the meniscus [93].

It was reported that the cast speed has effect on slivers [40]: high speeds and high variation in casting speed result in a higher rate of slivers. Adequate stable casting speeds can be obtained with the use of a stopper. With a stopper, the speed is no longer determined by the level of steel in the tundish, but by the level of steel in the mold [40]. It is better to control mold level control in the range ±3mm [5].

A profitable tool for optimizing the fluid flow and therefore improving slab quality is the electromagnetic brake (EMBR) [98], which bends the jet and shortens its impingement depth, inclusions thus move more upwards, tend to top powder or be captured by the solidified shell at the surface of slab. As shown in **figure 20**, the inclusion distribution across slab width shows a shift to the slab surface after using EMBR.

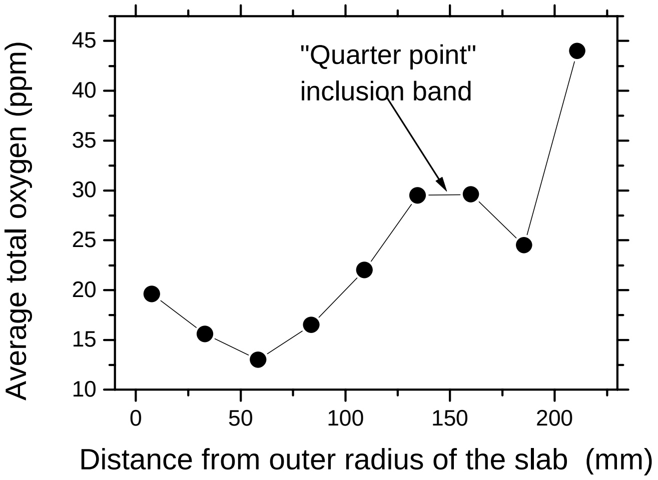


Fig.19 Average total oxygen along the thickness of slab

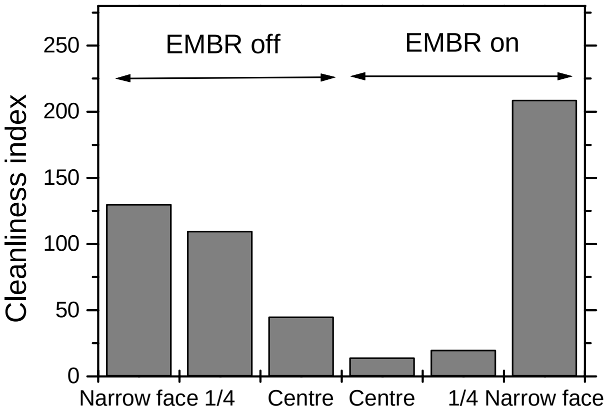


Fig.20 Effect of EMBR on steel cleanliness

SUMMARY

This paper first reviews the different definitions of clean steel, depending on steel grade and application. Next, the different methods to evaluate it are reviewed, including both direct and indirect methods. There is no single ideal method to measure 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.

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