Instant Control of Metallurgical Slags in EAFs and Ladles Utilizing an Electrochemical Sensor

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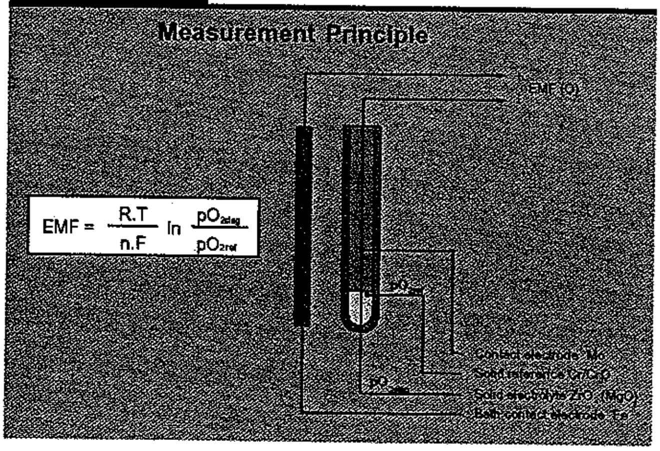
On-line slag control enabling immediate metallurgical corrections to ladle slags became possible only recently. A new method to measure slag oxygen activity in-situ within seconds is presented and compared to standard analytical methods.

Slag/metal reactions are of key importance during metallurgical operations, especially electric arc furnace (EAF) superheating and secondary metallurgy influencing chemical composition and steel cleanliness. Whereas liquid steel temperature and chemical analysis can be kept under control using special sensors and samplers, on-line slag control became possible only recently. A new method to measure slag oxygen activity in-situ within seconds is presented here.

The new method enables immediate metallurgical corrections to ladle slags. In the EAF superheating period, slag metallurgy can thus be corrected by adapted oxygen and carbon injection, burnt lime and/or MgO addition. Benefits for EAF foamy slag practice can be optimized. Additions of ladle slag modifiers after tap or during various treatment stages can be optimized. Based on the slag's measured FeO content, further decisions can be made regarding desulfurization practice, fade of deoxidants and castability. Using this method to control the slag's reoxidation potential, significant improvement of steel cleanliness can be expected. A comparison of the new method and standard analytical methods is presented along with plant results.

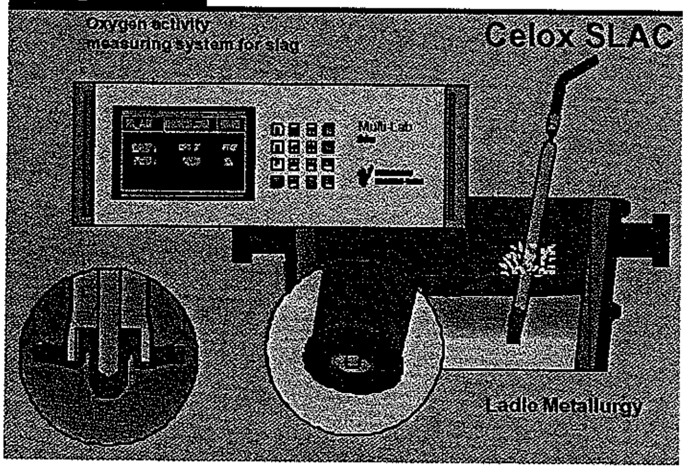
Traditional methods for slag oxygen control have all been off-line until now, as based

Figure 1



The slag sensor is based on a galvanic cell, where the EMF generated is proportional to slag oxygen activity: Mo/Cr-Cr_2O_3//ZrO_2//aO(slag)/Fe liq./Fe.

Figure 2



The measurement procedure follows the standard practice of probe immersion into liquid steel.

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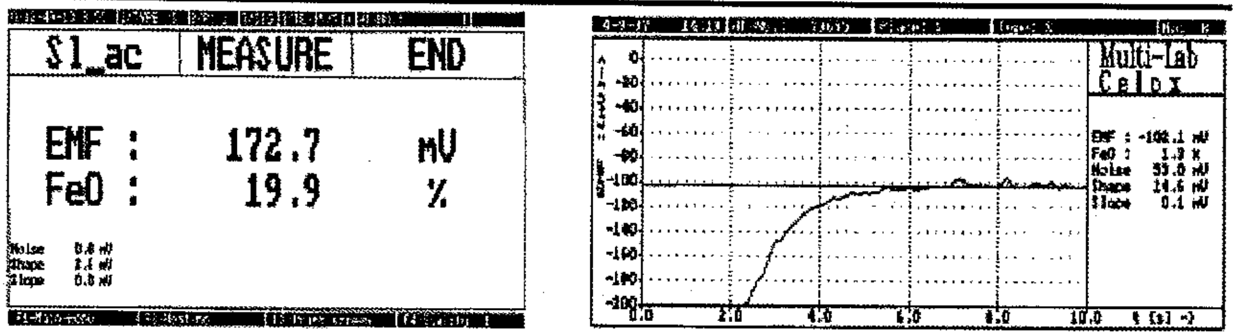
Figure 3

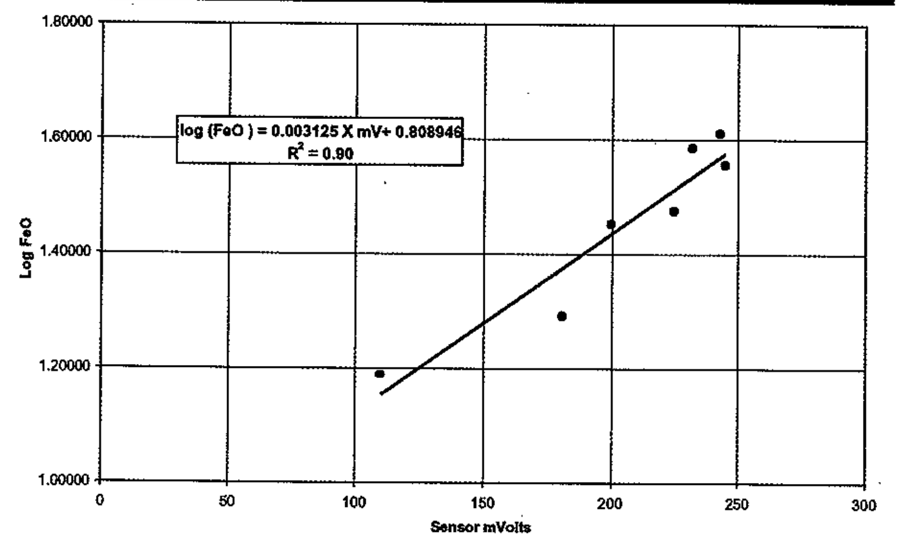


(a) (b)

Typical reading (a) and display (b) when using an electrochemical sensor. Note the trace stabilization.

on sampling methods followed by downstream lab sample analysis. Today, x-ray spectrometry is the industrial standard, whereas wet analysis, potentially offering a higher degree of precision but being time consuming, is the exception. Newly developed laser spectrometry on slag samples provides a solution for steel shops not operating an x-ray spectrometer. One of the concerns when running slag analysis on the same analyzer as steel samples is that dust from slag samples might deteriorate the x-ray spectrometer's vacuum chamber. The innovative method presented here consists of on-line slag oxygen control via an electrochemical sensor.

Figure 4



The correlation of EMF (in mV) to log FeO in the high-Fe_2O_3 range in an EAF application.

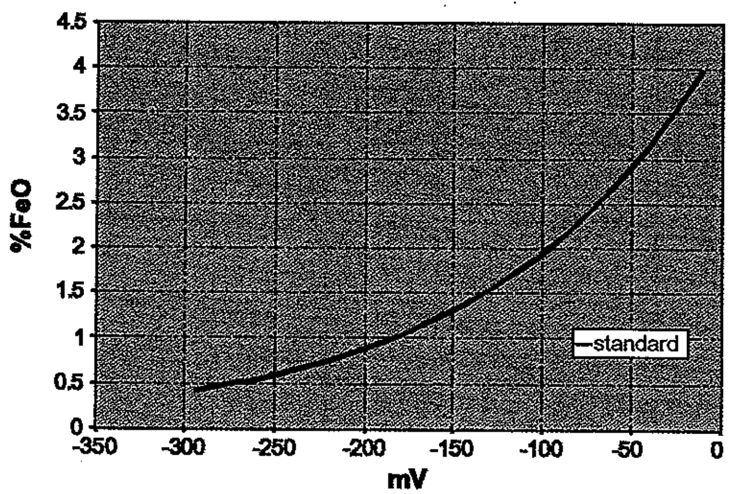
The Electrochemical Sensor Measurement Principle

The principle of using an electrochemical sensor to measure liquid steel temperature and perform chemical analysis is illustrated in Figure 1. Its design is similar to the well-known probe for oxygen activity measurements in liquid steel.

Measuring Equipment and Procedure — For metallurgical and quality control reasons outlined below, the sensor measurement should be considered a control standard just like steel temperature, steel oxygen activity and chemical composition. Mechanical immersion devices and data computing equipment are already present, and the sensor is compatible with existing pole hardware. Using dedicated software, a single immersion lance is sufficient to run thermocouple, steel oxygen and slag oxygen readings. Preconditions for good slag sensor reading are as follows:

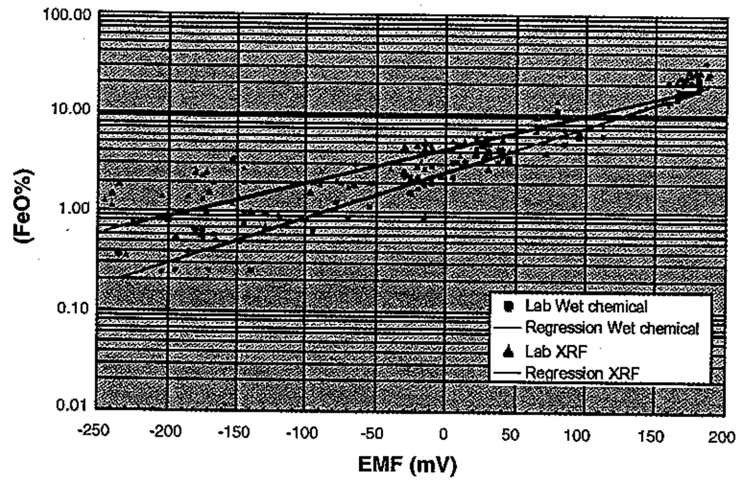
- Temperature range: 1570–1650°C.
- Homogenous, liquid slag.
- Stationary condition around the sensing head (low turbulence).

Figure 5



Correlation of EMF (in mV) to %FeO in the low-FeO range in a ladle application.

Figure 6



Correlation of sensor EMF output versus wet and XRF analytical methods.

Figure 2 illustrates the measurement procedure using the electrochemical sensor. Direct immersion into the slag is not practical due to the low density and corresponding low heat capacity of the slag. Also, finding the correct ladle top slag level and the associated precise positioning of the sensor would require dedicated positioning and holding equipment. The probe can be immersed as a normal oxygen sensor. As the sensor is immersed, the measuring head passes through the ladle top slag, where a small amount of slag adheres to the zirconia cell. The surrounding steel reheats the thin layer of slag, and an EMF is generated. A typical reading is shown in Figure 3.

The Correlation of EMF to Slag FeO

Figure 4 shows the correlation of EMF to slag FeO. The results were obtained from an EAF in the refining stage. The respective database is small but significant.

The results shown in Figure 5 were obtained from ladle top slags of LCAK steel grades. The comparative slag samples had been spoon-sampled and analyzed by wet chemistry and an x-ray spectrometer. It is symptomatic that the generally fine correlation suffers in the very low FeO range of ~ 1 percent FeO (Figure 6). It is suspected that this behavior is due to imperfect slag sample preparation, as the magnetic Fe separation of steel residuals in the slag might not be good enough, and thus nonseparated Fe is calculated as FeO.

Due to the aforementioned sample preparation issue, it is probable that the oxygen slag sensor in the low FeO range is both faster and more precise compared to slag sample analyzing methods. In the high FeO range, sensor and lab results coincide well, leaving the speed advantage to the sensor.

Sensor Applications

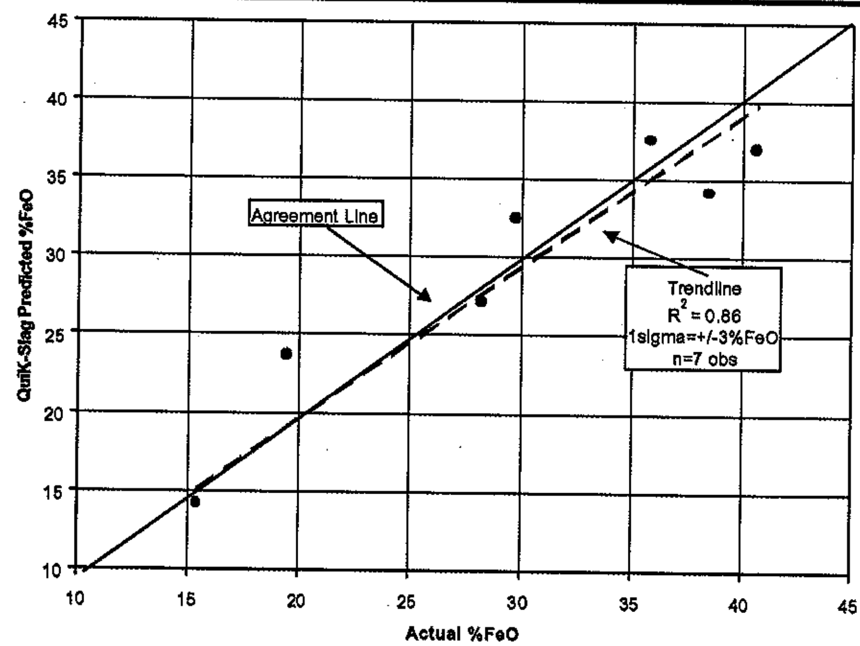
Electric Arc Furnace — Figure 7 compares %FeO measured to lab results. Again, the data used is not yet based on perfect statistics; however, a clear trend line was obtained.

Detailed results are seen in Table 1. Using the suggested formula for FeO measurements in the EAF, a standard deviation of 3 percent FeO can be expected.

Ladle — As opposed to primary steelmaking in the BOF and EAF, where carbon and related steel and slag oxygen activity run through a desired dynamic change, the slag/metal system in ladle metallurgy needs to be balanced. This is shown schematically in Figure 8.

Oxidizing and reoxidizing slag/metal reactions have to be slow or at least be predicted with a high degree of confidence. With excessive oxygen imbalance in steel and slag (e.g., Al-killed steel, high FeO-containing slag), any metallurgical action lacks precise prediction — in particular, the issues of alloy and deoxidizer additions, desulfurization treatment, Ca treatment and rinsing for liquid steel cleanliness.

Figure 7



Comparison of %FeO measured to lab results.

Table 1

Sensor Measurements in an EAF (January 2002)

Heat No.	Temp.	CX ppm	Cx mV	QuiK-Slag EMF	logFeo			Predicted FeO*	Diff. (actual vs. predicted)
					CaO	Fe_2O_3	Mn_2O_3		
K7561-1	2839	623	238	245	29.29	35.80	7.35	38	–2
K7574-1	2923	347	168	181	32.78	19.46	8.85	24	–4
K7575-1	2930	121	89	110	34.04	15.40	8.30	14	1
K7577-1	2911	443	189	225	26.31	29.80	7.86	33	–3
K7577-2	2847	353	193	200	31.09	28.26	7.14	27	1
K7731-1	—	—	—	243	25.31	40.64	7.65	37	4
K7732-2	2920	646	214	232	22.20	38.48	8.26	34	4
Avg.	2895	422	182	205	29	30	8	29	0
Min.	2839	121	89	110	22	15	7	14	–4
Max.	2930	646	238	245	34	41	9	38	4
Std. dev.	40.8	196	51	48	4	10	1	8	3

*Predicted %(FeO) = log10 (0.003125 x QslagmV + 0.808946)

Slag Carryover During Furnace Tapping — Even with today's methods using slag stoppers, EBT or slag-detecting devices, slag carryover continues to be a concern, as unknown quantity and oxygen potential of primary steelmaking slag added to ladle slag formers influence said metallurgical ladle operations. Figure 9 illustrates how primary steelmaking slag added to ladle slag formers influences metallurgical ladle operations.

A sensor measurement after tapping should be the basis for decisions on the following:

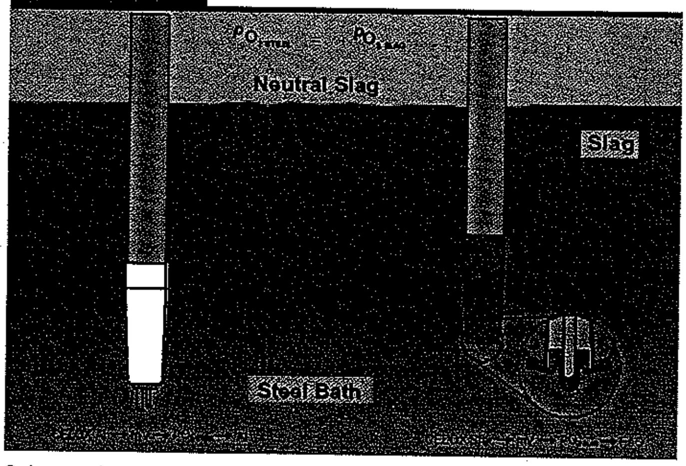
- Ladle slag skimming
- Ladle top slag treatment by adding slag modifiers, such as aluminum, calcium carbide or additional slag formers to dilute FeO down to an acceptable level.

Steel Desulfurization — A diagram from the related work of Andersson et al.[1] on molten slags is presented in Figure 10.

The absolute figures may be prone to discussion, but the tendency to cut desulfurization time from seven to two minutes with different ladle top slags (6 and 2 percent FeO, respectively) for the same sulfur drop stresses the importance of controlling slag oxygen activity. Depending on the slag's oxygen activity, it can be determined if top slag desulfurization will result in sufficiently low sulfur content, or if additional means such as calcium additives have to be used.

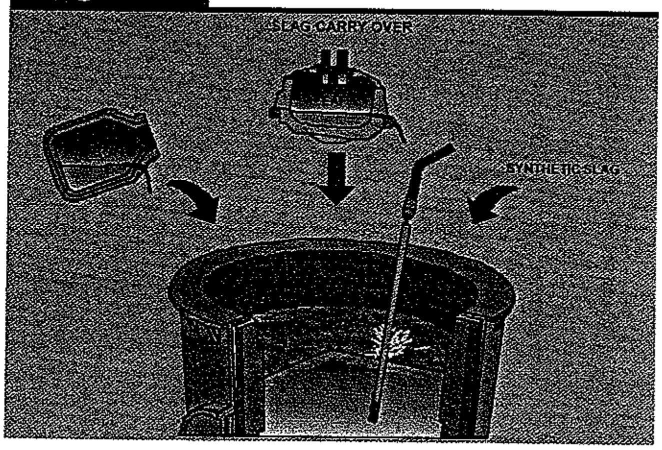
Aluminum Trim and Fade — High-FeO ladle slags not in equilibrium with Al-killed steel cause steel reoxidation and aluminum fade,

Figure 8



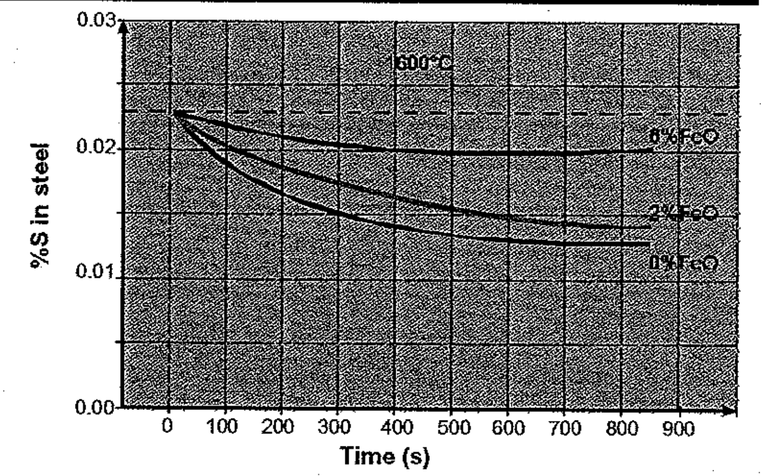
Schematic showing the relationship of steel oxygen activity measurement versus slag.

Figure 9



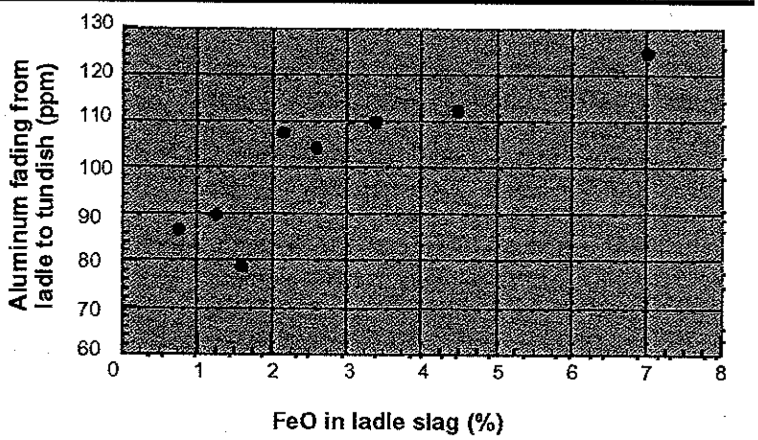
Primary steelmaking slag added to ladle slag formers influences metallurgical ladle operations.

Figure 10



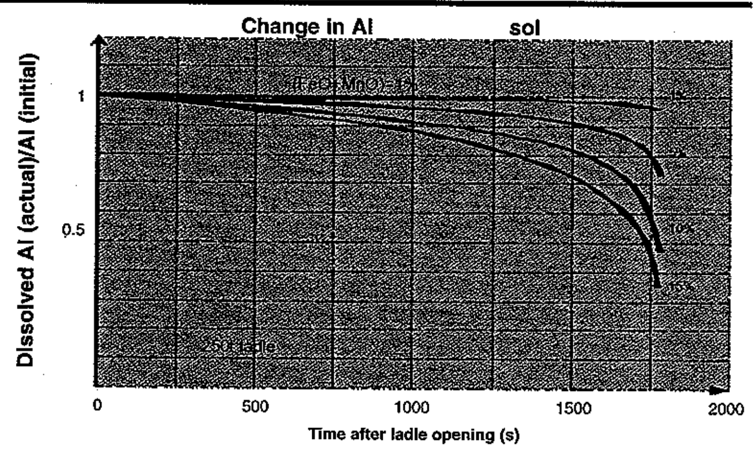
Desulfurization rates for variations in ladle slag %FeO.

Figure 11



Example of aluminum fade as a function of FeO in the ladle slag.

Figure 12



Effect of ladle slag oxygen activity (FeO + MnO) on aluminum fades in continuous casting.

making Al-trim additions unpredictable. The resultant problems for the operators include time-consuming chemistry corrections and waiting for lab confirmation. Consequences are often a lost sequence at the caster or a heat degrade due to an unmet fine grain steel matrix structure (minimum 0.015 percent Al for low- and medium-carbon grades). A.W. Cramb[2] has given an example in his "Clean Steel Fundamentals Course" for slag oxygen-related Al-fade from ladle to tundish.

The graph in Figure 12 shows the percentage of Al fade in LCAK steels as a function of time and %FeO + %MnO after ladle opening in continuous casting.

Steel Cleanliness and Clogging — It is generally accepted that there is a correlation of steel reoxidation from ladle slags to total oxygen content in steel and related castability issues. The problem that follows is how to control these issues. There are various technical solutions for different steel grades, practices and different casters.

Figure 13 contains a graph illustrating steel cleanliness in terms of slag oxygen content versus total oxygen.

The slab caster producing LCAK steel grades for drawn and ironed (D&I) can applications requires the lowest total oxygen to avoid any can leakage from exhibiting surface nonmetallic inclusions in extremely thin rolled and deep-drawn D&I cans. (Canning producers specify a maximum leakage of 1 pc within 80Mio cans). Similarly, the thin slab caster struggles with elevated total oxygen and related inclusion levels, as its narrow internal refractory subentry nozzles are not forgiving to clogging. Even with a low FeO range in ladle slags, there is already a significant link to nonmetallic inclusion formation in steel, as shown in Figure 14.

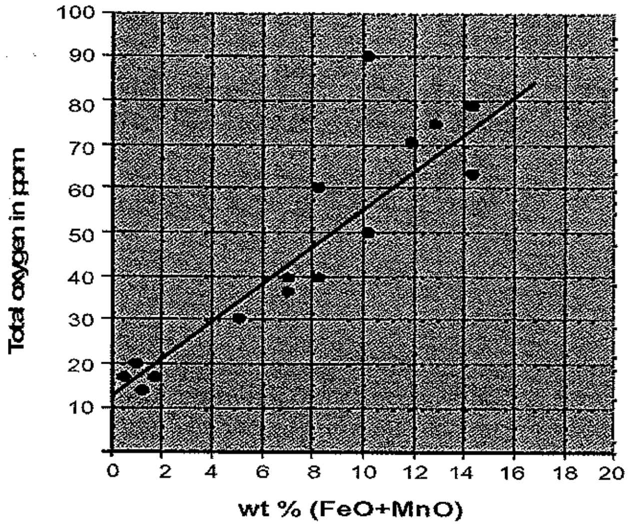
The slag sensor is the means of controlling and thus preventing these specific problems, thereby enabling the use of both statistical means of improving cleanliness/castability and an on-line means of cleaning the heat (e.g., by additional gas rinsing treatment).

Billet casters producing Al fine-grain steels require a certain FeO window in ladle slag to simultaneously guarantee proper castability (low spinels quantity) and a clean as-cast billet (Figure 15).

Summary

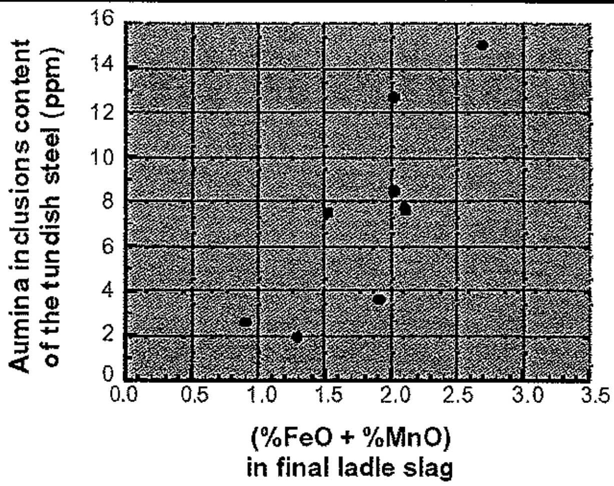
The real-time nature of the slag activity measurement affords the opportunity to open the "sealed book" of direct ladle slag chemistry. For decades, precision sensors in liquid steelmaking were used for on-line control to produce "clean" steel in the required grade and

Figure 13



Steel cleanliness described in terms of relationship of slag oxygen content (FeO + MnO) to total oxygen.

Figure 14



Steel cleanliness described in terms of relationship of slag oxygen content (FeO + MnO) to total oxygen in final ladle slag.

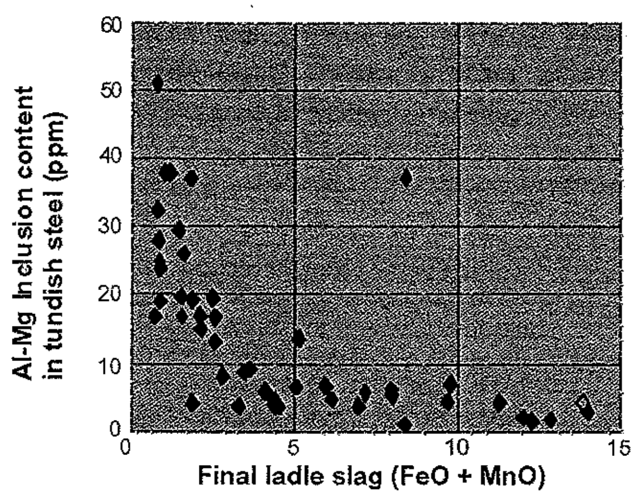
at competitive cost. Precise and reliable sensors make the difference in modern steelmaking as a basis for on-line decision making, either through experienced metallurgists or an expert system. The slag sensor has opened a new chapter in metallurgical control, to the benefit of steel producers.

References

1. Andersson et al., "Slag/metal Reactions During Ladle Treatment With Focus on Desulfurization," *Sixth International Conference on Molten Slags, Fluxes and Salts*, Stockholm, Sweden, and Helsinki, Finland, June 2000.

2. Cramb, A.W., Industrial Seminars: Short Course on Clean Steel With R.J. Fruehan and A. MacLean. ✦

Figure 15



Relationship of slag oxygen activity and spinel-induced clogging.

Did You Know?

2003 Steel Shipments Increase 6.5 Percent From 2002

The American Iron and Steel Institute reported that, for the year 2003, steel shipments were 105,625,000 net tons, representing a 6.5 percent increase from the 99,191,000 net tons shipped in 2002. For the month of December 2003, U.S. steel mills shipped 9,038,000 net tons, a 19.3 percent increase from the 7,577,000 net tons shipped in December 2002 and a 6.5 percent increase from the 8,485,000 net tons shipped in the previous month, November 2003. A year-to-year comparison of shipments shows the following changes within major market classifications: service centers and distributors, up 6.3 percent; automotive, down 5.0 percent; construction and contractors' products, down 8.4 percent; oil and gas, up 8.6 percent; machinery, industrial equipment and tools, down 2.5 percent; appliances, utensils and cutlery, up 9.0 percent; containers, packaging and shipping materials, down 9.3 percent; and electrical equipment, down 10.2 percent.