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Evaluation and control of iron and steelmaking slags through electrochemical FeO sensors

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One of the greatest obstacles to the application of physical chemistry principles to the elucidation of slag-metal reactions is a lack of knowledge of activities of the reacting species. To a large extent, oxygen potential of the slag phase governs iron and steelmaking practice. Without oxygen control by means of appropriate sensors, the behaviour of the other elements cannot be managed. In this paper, measurements of the FeO activity with various types of electrochemical FeO sensors will be described together with examples of their applications for improved strategies toward better practice for ladle metallurgy and sulphur and manganese distributions between slag and metal phases during steelmaking. Measurements of FeO activity have also been made in order to improve dephosphorization reactions. This type of work has led to significant reduction in volume of slag generated within the steelmaking vessel, which in turn has important implications for refractory wear, metal yield, alloy recovery and improved productivity. Finally, an on-line sensor is described that permits the oxygen potential to be determined for both the metal phase and the slag phase during steelmaking in the BOF.

Introduction

In our efforts to characterize and improve the performance of an existing process or in our quest to generate useful knowledge as a basis for the development of new manufacturing routes, measurements and models should be considered as two interdependent requirements. Without measurements, our models are incomplete and unsatisfactory. Without models, we fail to realize, or perhaps even comprehend, the potential significance of our measurements. Sometimes in our enthusiasm, we construct sophisticated elegant models and forget the reality of the actual manufacturing process. In this computer age, we need to remember again the importance of observations and accurate measurements. In addition, as engineers and applied scientists, we have an obligation and a responsibility to facilitate the transfer of new knowledge into the realm of operating practice. In this context, attention is focused on the thermodynamic activities of components in metallurgical slags.

The studies of chemical reaction between liquid steel and molten slags involve complicated slag systems of at least eight important components, i.e., CaO, MgO, MnO, FeO, SiO_2, Al_2O_3, P_2O_5, CaF_2 and often a number of others such as Na_2O, TiO_2, and Cr_2O_3. One of the greatest obstacles to the applications of physico-chemical principles to the elucidation of slag-metal and slag-gas reactions is a lack of knowledge of the activities of reacting species. Since iron oxide in slag participates in numerous reactions among metal, slag and gas, the evaluation of the activities of ferrous oxide is of primary consideration.

Since the 1950s, a number of experimental determinations of the activities of ferrous oxide have been conducted. Because of such concerted efforts of many laboratories during the last five decades, approximately two thousand data were obtained for the FeO activities, while there are many duplicate measurements. Our knowledge of the activity of FeO is, nevertheless, still far from satisfactory. For example, consider a slag of 40-CaO, 10-MgO, 5-MnO, 20-SiO_2, 10-Al_2O_3, 3-P_2O_5, 2-CaF_2 and 10-FeO in pct by weight. The literature data obtained during the last half century do not allow us to evaluate the a_{FeO} values of this slag. From this example, it is evident that experimental determination of the FeO activities is still required. However, if we intend to determine the activities of FeO in eight-component slags at reasonable intervals of mole fraction of the constituent components, activity measurement must be conducted until a multitude of data are obtained. Even if the activity determinations were focused on slags of high basicity, e.g. $X_{CaO}/X_{SiO_2} > 2$, over a hundred thousand data for a_{FeO} would be required. When then can we have enough data to know the FeO activities of multi-component slag at any given composition?

As is well known, high temperature experiments are time consuming and involve various difficulties. The conventional experimental technique for determination of ferrous oxide activity consists of equilibrating molten slags

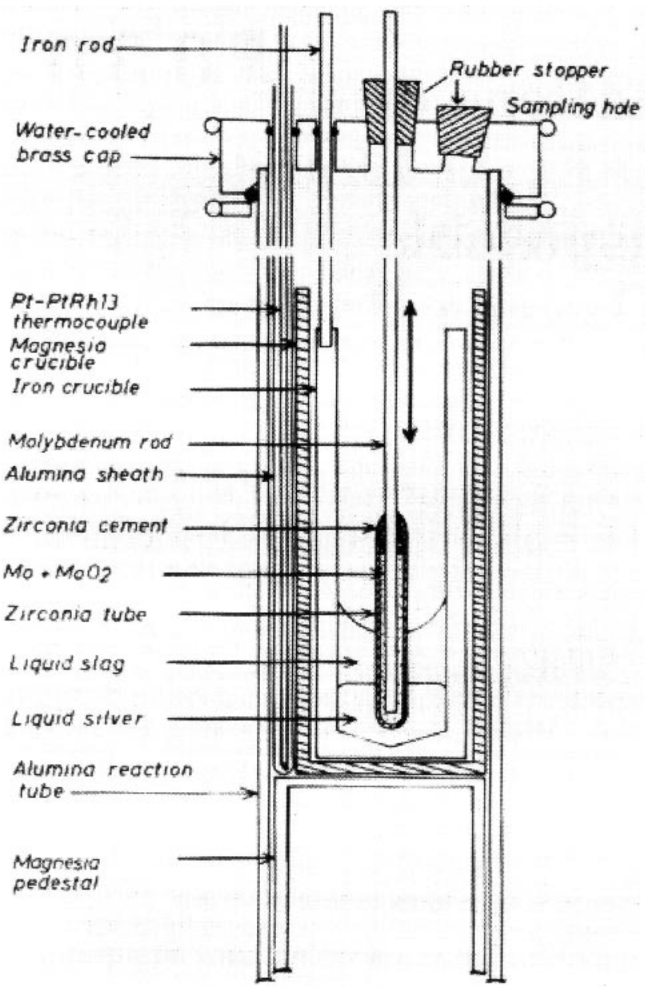

Figure 1. Experimental set-up for measurements of ferrous oxide activity

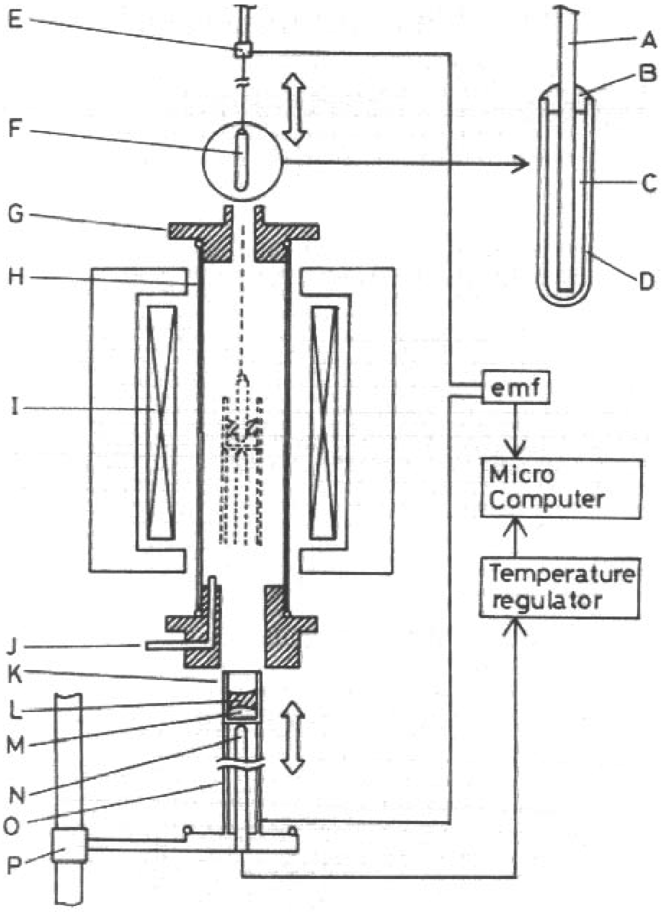

Figure 2. Schematic illustration of automatic activity determinator. A, Mo rod; B, Zirconia cement; C, Mo + MoO_2 reference electrode; D, Zirconia tube; E, Elevator mechanism; F, Zirconia cell; G, Water-cooled brass flange; H, Transparent silica tube; I, Tungsten filament; J, Ar inlet; K, Iron crucible; L, Slag sample; M, Silver; N, Pt-PtRh13 Thermocouple; O, Stainless steel pedestal; P, Elevator mechanism

with liquid iron. Chemical analysis for oxygen made on samples taken from liquid iron yields values of ferrous oxide activities. Alternatively, molten slags contained in an iron crucible are brought into equilibrium under a stream of CO-CO_2 or H_2-H_2O. These techniques, however, require a relatively complex experimental set-up and long duration. An alternative approach is to derive theoretical formula that can express the activities as a function of temperature and composition. Recent progress in this area is noted. From an alternative point of view, however, a thermodynamic model is not required, provided experimental data for a_{FeO} are obtainable within a reasonable period of time and at a reasonable cost.

With recent progress in the area of solid state ionics, an electrochemical technique based on magnesia-stabilized zirconia now allows rapid determination of ferrous oxide activity within homogeneous and heterogeneous slag systems[1]. By using this technique, the FeO activity has been measured for many different slag systems by Iwase and co-workers[2,3].

Figure 1 shows the experimental set-up used by the present authors for laboratory experiments. An iron crucible is heated in a resistance furnace together with liquid silver and slags. The equilibrium oxygen partial pressures for $Fe(s) + (FeO)_{slag}$ are determined by using an electrochemical sensor incorporating magnesia-stabilized zirconia as electrolyte and Mo + MoO_2 mixture as reference electrode. This research has led to the manufacture of an analytical instrument for the determination of FeO activities[4]. A schematic diagram and photograph of the automatic activity determinator are shown in Figures 2 and 3, respectively. With this facility, in-plant determinations of FeO activities in industrial slags are obtainable within five minutes.

Application of automatic facility for fundamental studies

Activity measurement by means of the automatic facility was conducted for the system CaO-SiO_2-FeO at 1673 K in order to demonstrate the applicability of the equipment. For this particular system, attention should be focused on the pioneering work of Shumann and Ensio[5] based on the gas equilibration technique. The iso-thermal section of the phase diagram of this system is given in Figure 4. For the slags on lines G-Fe_xO and H-Fe_xO, i.e., X_{CaO}/X_{SiO_2} = 66.6/33.3 and 61/39, respectively, the FeO activities as determined by the automatic equipment are given in Figure 5. For slags on lines G-Fe_xO, two-phase coexistence would occur at compositions between points 5 and G($2CaO \bullet SiO_2$) of Figure 4. Within this two-phase region, all the

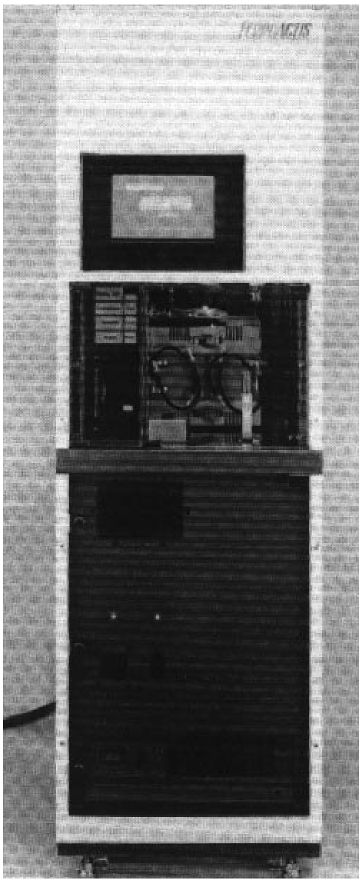

Figure 3. Photograph of the automatic activity determinator

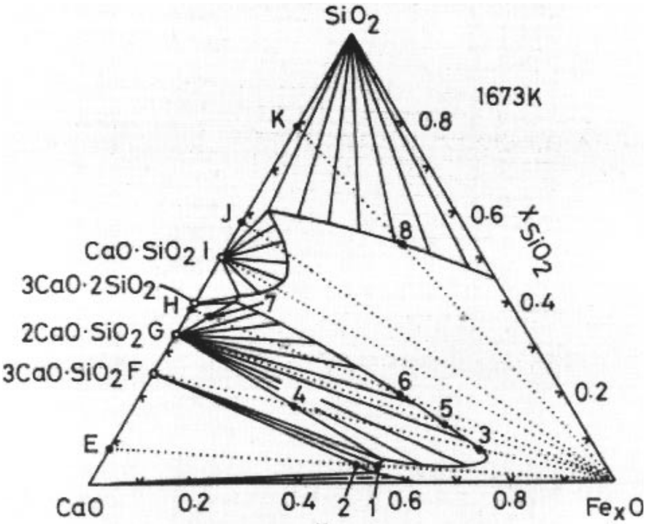

Figure 4. Iso-thermal section of the phase diagram of the system CaO-SiO_2-FeO at 1673 K

conjugation lines pass through point G(2CaO•SiO_2). Hence, the FeO activities should be independent of the slag compositions, and this is observed between point 5' and G' of Figure 5. For the slag of H-Fe_xO, on the contrary, line H-Fe_xO of Figure 4 intersects the conjugation lines within the two-phase region. Hence, the FeO activities decrease with a decrease in FeO mole fractions, as given by curve 6'–7' of

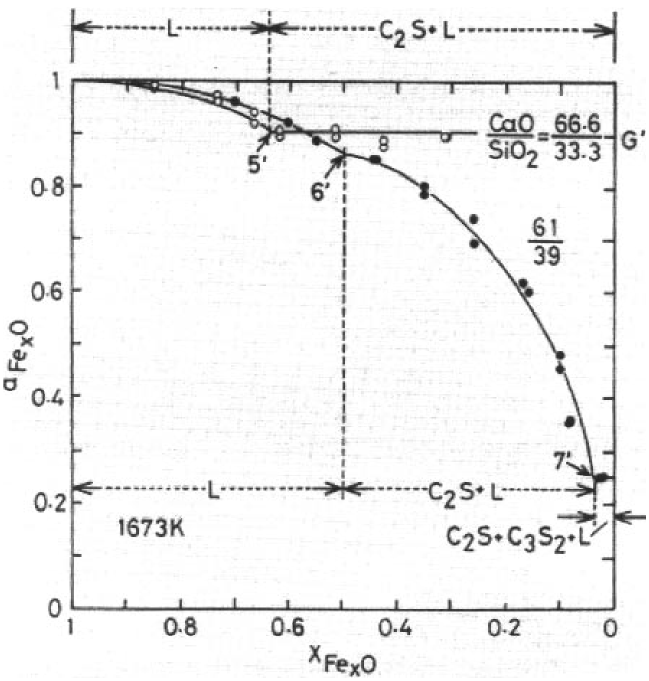

Figure 5. Activities of FeO as the function of FeO mole fraction at 1673 K for slags of $XCaO/XSiO_2$ = 66.6/33.3 and 61/39

Figure 5 Thus, the FeO activities determined through the automatic facility are consistent with the phase diagram..

Activities of ferrous oxide in BOF slags

In 1953, by using slag-metal equilibrium data, Turkdogan and Pearson[6] gave iso-activity curves for FeO drawn on a pseudo-ternary composition triangle of (CaO + MgO + MnO)-(SiO_2 + P_2O_5)-FeO, Figure 6. Keeping their iso-activity curves in mind, by using the automatic activity determinator, activity measurements were extended to industrial slags taken from two different basic oxygen furnaces[7]. If plotted on the pseudo-ternary composition triangle, the slag compositions could be expressed by open and solid circles of Figure 7. The FeO activities as evaluated by the determinator are compared with those by Turkdogan and Pearson in Figure 8.

In contrast to those by Turkdogan and Pearson, the measured values for a_{FeO} are relatively insensitive to the variation of slag basicity $B = (X_{CaO} + X_{MgO} + X_{MnO}) / (X_{SiO_2} + X_{P_2O_5})$, for the region between B = 78/22 and 88/12. As stated by Turkdogan[8], their iso-activity curves are useful for the study of the slag-metal reaction in steelmaking; however, such data are not suitable for more exacting thermodynamic computations. Thus direct determination of the FeO activities based upon the automatic facility is highly desirable.

Evaluation and control of secondary steelmaking slags

Traditionally many of the objectionable oxide inclusions in steel have been attributed to deoxidation practices. Significant effort has been concentrated on deoxidation practice specifically designed to control the type and distribution of nonmetallic inclusions. At the present time, with argon rinsing, the oxide inclusions remaining dispersed in the metal at the time of casting are less than

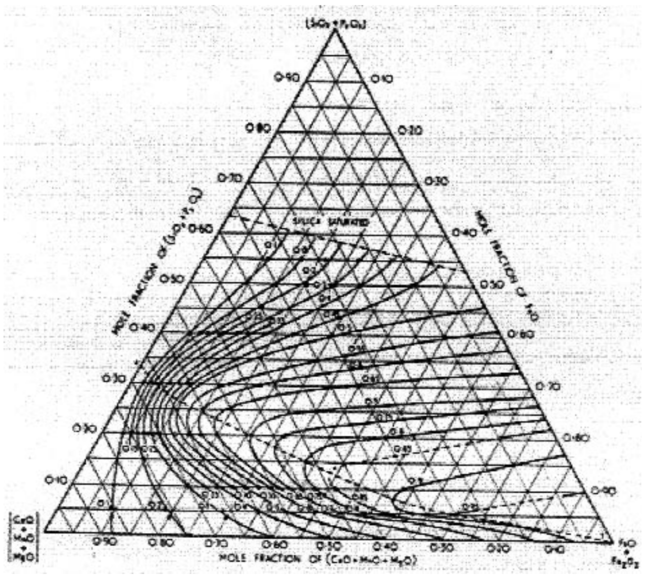

Figure 6. Iso-activity curves for ferrous oxide in pseudo-ternary system of (CaO + MgO + MnO)-(SiO_2 + P_2O_5)-FeO after Turkdogan and Pearson

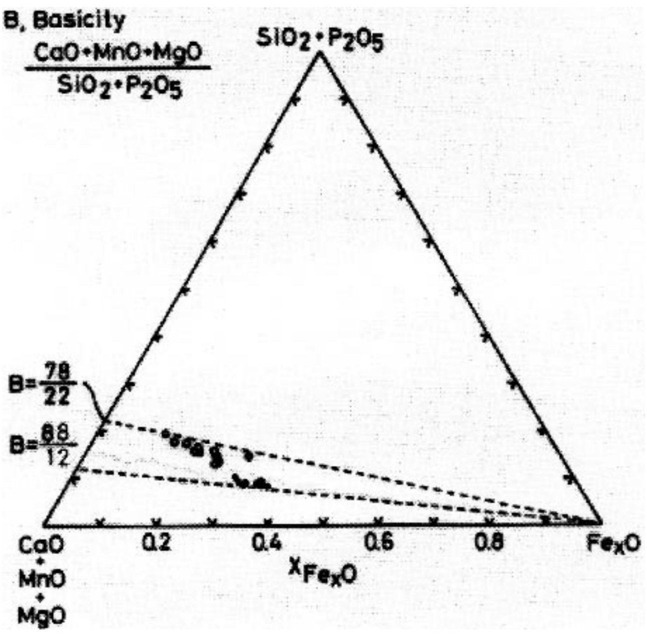

Figure 7. Compositions of BOF slags taken from two different BOF vessels

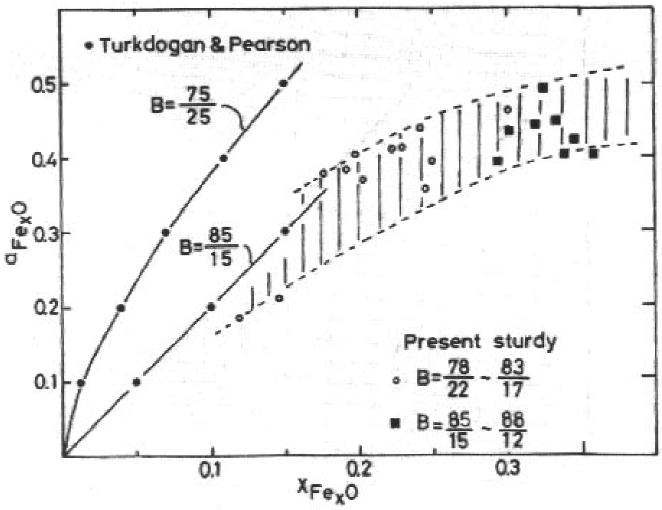

Figure 8. Activities of ferrous oxide as the function of concentration in comparison with those by Turkdogan and Pearson

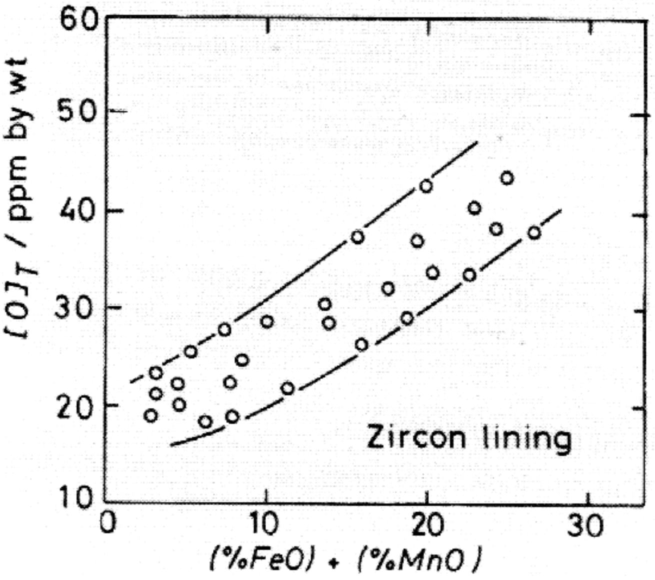

Figure 9. Relation between total oxygen content, $[O]_T$, at tundish and empirical parameter, *(%FeO)* + *(%MnO)* for ladle slags

about 5 microns in diameter[9]. Following the argon rinse, the total concentration of oxygen in aluminum-killed steel should be about 20 ppm or less, corresponding to about 0.01 volume per cent alumina inclusions. In continuous casting with open stream pouring, however, inclusions of 5 to 100 microns and 0.1 to 0.3 volume per cent are not unusual. Farrell, Bilek and Hilty[10] showed that these large inclusions are caused by reoxidation of molten streams. Large inclusion count and size frequently observed in practice are primarily due to reoxidation of the metal during teeming and/or poor practice during mold additions.

It is to be noted that during steelmaking, molten steel is inevitably brought into direct and/or indirect contact with air. Bare bath, molten streams or turbulence within the mold cavity, all proved ample opportunity for liquid steel to react with the air, which is an unlimited supplier of oxygen.

An obvious solution to this problem of reoxidation is to eliminate open stream pouring between ladle to tundish and tundish to mould by using submerged entry nozzles. Even with such shrouding technologies, however, reoxidation can still occur when the molten steel is in contact with liquid slag containing FeO. The reoxidation of aluminum in liquid steel by ferrous oxide in molten slag can be expressed as:

$$2[Al]_{metal} + 3(FeO)_{slag} = Al_2O_3(s) + 3Fe \qquad [1]$$

Reaction [1] will proceed to the right-hand side with an increase in the activity (or concentrations) of FeO. Normally slags formed during secondary steelmaking processes contain 1 to 10% FeO. Based on practical experience, ladle shop operators pay attention to the concentration of 'total' Fe plus MnO, *(%T.Fe) + (%MnO)* or *(%FeO) + (%MnO)*; manganese oxide can also oxidize aluminium although *(%MnO) << (%T.Fe)*. For example Hara *et al.*[11] have reported such an anticipated effect of FeO in the slag phase as shown in Figure 9. The total oxygen concentration in steel after RH degassing increased with an increase in *(%FeO) +(%MnO)*.

Hence much attention has been given to developing an appropriate practice that can lower the FeO activity in molten slag, especially in secondary refining vessels. In general, metallic aluminium or calcium carbide[12] is spread over molten slag to reduce FeO within slag phase. Currently control strategies for lowering the FeO activity in such practice are based on samples taken from molten slag during ladle treatment. Chemical analysis for Fe and Mn in slags, however, requires at least 10 to 15 minutes, while ladle treatment must be completed within 15 to 20 minutes. Thus knowledge of *(%T.Fe) + (%MnO)* based on chemical analysis does not assist the ladle shop operator to control the molten slag during actual operations.

The automatic activity determinator can be used for slag control in secondary steelmaking. Figure 10 shows the relation between a_{FeO} determined by the automatic facility and *(%T.Fe) + (%MnO)* obtained by chemical analysis for industrial slags taken from different ladle shops[13]. As shown in this figure, the empirical parameter *(%T.Fe) + (%MnO)* is reasonably proportional to the FeO activities. However, FeO activities of slag at one ladle shop are different from those at another even although the empirical parameter *(%T.Fe) + (%MnO)* was the same.

From a thermochemical point of view, this behaviour is quite understandable, if difference in slag basicity is taken into account. In other words, it is evident that the empirical parameter would not be appropriate for close control of the activity of FeO. For practical application of this automatic activity determinator, slag samples would be taken before slag-reduction practice to know the a_{FeO} values. Through such activity measurements, appropriate amounts of aluminium or calcium carbide for slag-reduction can be estimated. Ohnuki *et al.*[14] have reported improved slag-reduction practice with the aid of the FeO activity determinator and the resulting better steel cleanliness.

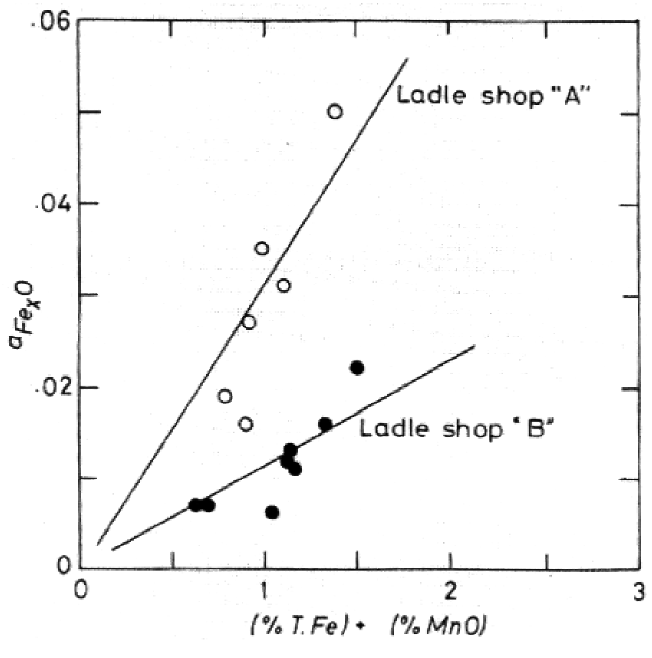

Figure 10. Relation between ferrous oxide activity and the empirical parameter, *(%T. Fe) + (%MnO)* for ladle slags

Application for sulphur and manganese control

The industrial application of the automatic analyser by Ham *et al.*[15] relates to control of desulphurization, which can be expressed as:

$$(CaO)_{slag} + [S]_{metal} + Fe = (CaS)_{slag} + (FeO)_{slag} \qquad [2]$$

The partition ratio for sulphur is given by:

$$\log\{(\%S)/[\%S]\} = -\log a_{FeO} + \log a_{CaO} + constant \qquad [3]$$

Equation [3] implies that a plot of log *(%S)/[%S]* against log a_{FeO} should be a straight line with a slope of -1, if the activity of CaO is kept constant. Although such anticipated relations were obtained with synthetic slags and molten iron equilibrated within small crucibles, for industrial slags this relation was not observed, simply because the a_{FeO} values for industrial slags are normally not known. The relationship between log{*(%S)/[%S]*} and log a_{FeO} obtained by Hamm *et al.* using the determinator is shown in Figure 11. Although the slope is different from the theoretical value of -1, there is a good correlation between the two parameters indicating that the sulphur partition ratio can be monitored and therefore controlled through FeO activity measurements. Similarly, the FeO activities are related to manganese partition as shown in Figure 12[15].

Slag volume reduction

Normally the basic oxygen process for steelmaking generates slags at a rate of 120 to 150 kg/ton of steel[16]. The actual composition of BOF slags will vary significantly, depending upon a number of factors, e.g., the sulphur and phosphorus levels required in the final product. Some steelmaking slags can be recycled to the blast furnace for recovery of the iron units they contain and because of their beneficial fluxing properties. Chemical composition, and specifically the phosphorus content, is a critical

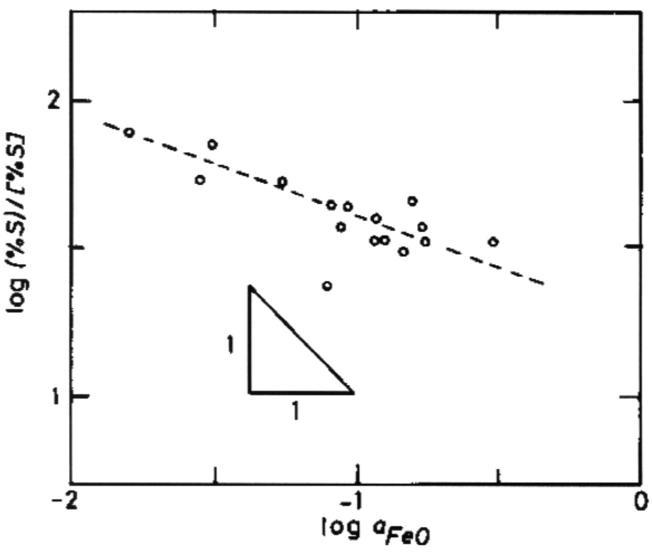

Figure 11. Relation between sulphur partition ratio, *(%S)/[%S]* and FeO activity

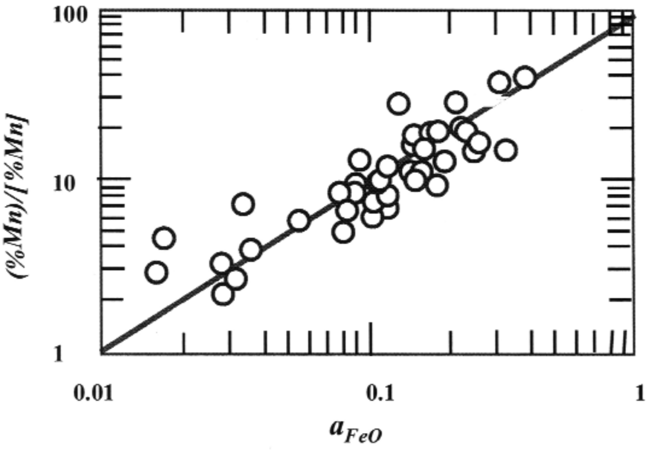

Figure 12. Relation between manganese partition ratio, *(%Mn)/[%Mn]* and FeO activity

consideration in establishing the amount of BOF slags which can be recycled. It is noted that Japanese blast furnace operators rely on the supply of relatively high phosphorus Australian ores. Hence, the amounts of recycled slag, in Japan, have to be maintained at a relatively low level. Therefore, there is a continuous increase in the amount of BOF slag that has to be stored or dumped by the steel plant. From the foregoing comments, it is evident that there is a strong incentive to reduce steelmaking slag volume. The key toward this end is a more effective dephosphorization reaction, which can be represented as follows:

$$2[P]_{metal} + 5(FeO)_{slag} = (P_2O_5)_{slag} + 5[Fe] \qquad [4]$$

Turkdogan and Pearson[17] derived the following expression for the effect of temperature on the equilibrium constant for Reaction [4]:

$$\log K(4) = \log\left\{a_{P_2O_5} / hp^2 a_{FeO}5\right\} = -17.7 + 8.490/(T/K) \qquad [5]$$

Reaction [4] is essentially an oxidation reaction and is favoured by lower temperatures. For this reason, attention has been focused on dephosphorization of hot metal rather than molten steel.

Table I gives the compositions of slags formed at the final stages of hot metal dephosphorization[18]. The major components of these slags are CaO, CaF_2 and SiO_2. The initial compositions of fluxes used for hot metal processing are 40–50 FeO, 30–50 CaO and 5–15 CaF_2 in pct by weight. While phosphorus removal by Reaction [4] proceeds toward equilibrium, the activity of FeO inevitably decreases while that for P_2O_5 increases as shown schematically in Figure 13(a).

In practice, despite the relatively high initial concentrations of FeO of 40 to 50 pct by weight, at the final stages, the concentrations have decreased substantially to levels of 1.1 to 2.5 mole pct (1 to 3 pct by weight), while the P_2O_5 contents have increased to 1.1 to 3.4 mole pct *(%P)* = 1 to 3 pct by weight). The relatively high CaF_2 concentrations should also be noted. It has been considered that calcium fluoride will enhance formation of homogeneous liquid slag because of its relatively low melting temperature (1643 K). Indeed, at temperatures above 1623 K, these industrial slags exist in the liquid state. The phosphorus levels achieved with these slags were in the range 0.016 to 0.112 pct by weight as shown in Figure 14. If lower phosphorus levels are required, then FeO has to be added in order to increase the FeO activities and/or CaO additions would be necessary to lower the P_2O_5 activities, Figure 13(a). Clearly, such additions result in an increase in slag volume.

The present authors have measured the activities of FeO within homogeneous liquid slags[19], the compositions of which are given in Table I. The results are shown in Figure 15; relatively low FeO activities were observed. As information to readers, it is mentioned at this point that the compositions of the homogeneous industrial slags for hot metal dephosphorization as given in Figure 15 are very different from those used in BOF vessels, as in Figure 8.

Dephosphorization with heterogeneous slags

Figure 16 shows the iso-thermal section of the CaO-P_2O_5-FeO system at 1673 K[20]. For convenience, the following notations are used: *C* = CaO, *C_4P* = $Ca_4P_2O_9$, *C_3P* = $Ca_3P_2O_8$ and *L* = {CaO + P_2O_5 + FeO} liquid ternary slags. Particular attention should be focused on the following three-phase regions:

CaO + $Ca_4P_2O_9$ + liquid, i.e. triangle *C*-B-*C_4P*;

$Ca_4P_2O_9$ + $Ca_3P_2O_8$ + liquid, i.e. triangle *C_4P* -C- *C_3P*;

Consider removal of phosphorus from liquid iron by using the three-phase assemblage, *C* + *C_4P* + *L*. According to the Condensed Phase Rule, when three phases coexist in a three component system, there is only one degree of freedom. This implies that for a particular temperature, there is zero degree of freedom. The activities of FeO and P_2O_5 are fixed and therefore independent of the bulk slag composition. If phosphorus removal were conducted with this heterogeneous slag, the FeO and P_2O_5 activities remain constant even although the bulk concentrations of FeO and P_2O_5 are decreasing and increasing, respectively. The

Table I
Composition of industrial slags during final stages of hot metal processing and the corresponding hot metal temperature and phosphorus levels. At temperatures above 1623 K, these industrial slags exist in the liquid state.

Sample Code	Slag composition (mole pct)						Hot metal	
	CaO	SiO_2	FeO	CaF_2	P_2O_5	Others*	*T*(K)	*[%P]*
#1	53.0	32.2	1.7	6.8	1.1	5.3	1548	0.112
#2	57.3	28.3	2.5	5.6	1.8	4.5	1548	0.090
#3	58.3	20.8	2.4	10.4	2.6	5.5	1548	0.057
#4	58.9	16.1	2.1	11.1	3.2	8.6	1548	0.016
#5	58.3	11.1	1.6	21.0	3.4	4.6	1573	0.020
#6	60.0	11.6	1.1	21.5	2.1	3.7	1543	0.030

* ‘Others’ means CaS + MgO + MnO + Al_2O_3

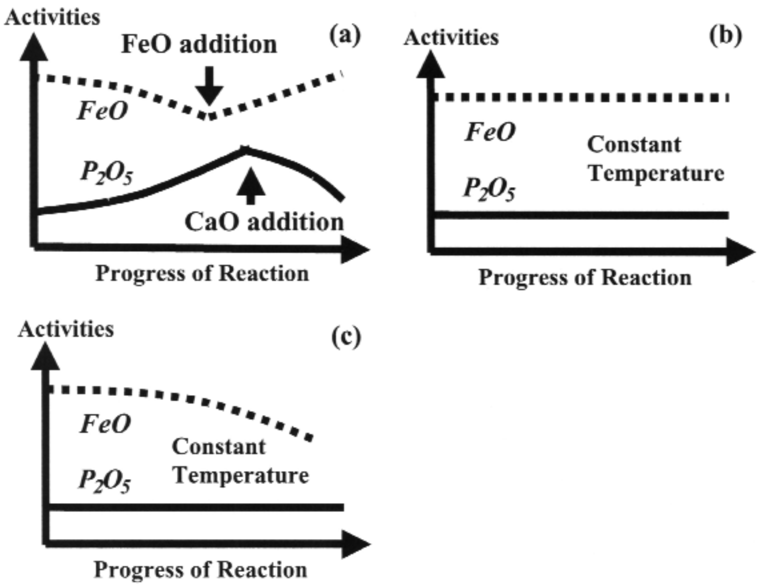

Figure 13. Schematic diagram of dephosphorization reaction; (a) homogeneous liquid slag, (b) heterogeneous slag with zero degree of freedom, (c) heterogeneous slag in which the degree of freedom is greater than unity, saturated with *C+ C$_4$P*

activities of P_2O_5 within the three-phase region $C + C_4P + L$ and $C_4P + C_3P + L$ are fixed through the reaction:

$$4 < CaO > + \left(P_2O_5\right) = \ < Ca_4P_2O_9 > \qquad [6]$$

$$3 < Ca_4P_2O_9 > + \left(P_2O_5\right) = 4 < Ca_3P_2O_8 > \qquad [7]$$

Values for the free energy changes for Reactions [6] and [7] have been reported in the literature[21,22]. A schematic representation of the phosphorus removal process under these conditions is shown in Figure 13(b). Thus, since these heterogeneous slags would not require further additions of CaO and FeO in order to sustain the dephosphorization reaction, the possibility exists for minimizing, or at least lowering, the steelmaking slag volume.

Further consideration should also be given to slags of freedom degree greater than unity, e.g., 5-component slags with 3 phases. At a fixed temperature, the FeO activities within such slags will decrease with a decrease in FeO concentration, as shown in Figure 13(c). If slags are, however, saturated with $C + C_4P$, then the activities of P_2O_5 are still fixed through Reaction [6]. Such fixed P_2O_5 activities would also correspond to reducing slag volume.

The present authors have measured the activities of FeO in the three-phase regions of $C + C_4P + L$ and $C_4P + C_3P + L$ within the CaO + P_2O_5 + FeO system, and in the four-phase region of $C + C_4P + C_5PS$ ($5CaO{\bullet}P_2O_5{\bullet}SiO_2$) + L within the CaO + P_2O_5 + SiO_2 + FeO system. Values for the FeO activities are plotted against the reciprocal temperature as shown in Figure 15. As shown in this figure, the FeO activities within the 3- and 4-phase assemblages are considerably greater than those in the industrial slags (homogeneous liquid slag), thus enhancing conditions for the removal of phosphorus.

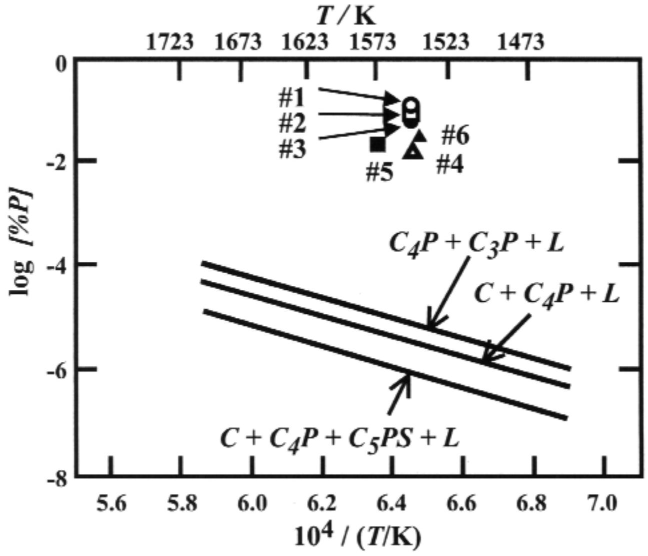

Figure 14. A comparison of the estimated phosphorus contents attainable with the heterogeneous slags, with those actually obtained using the homogeneous industrial slags

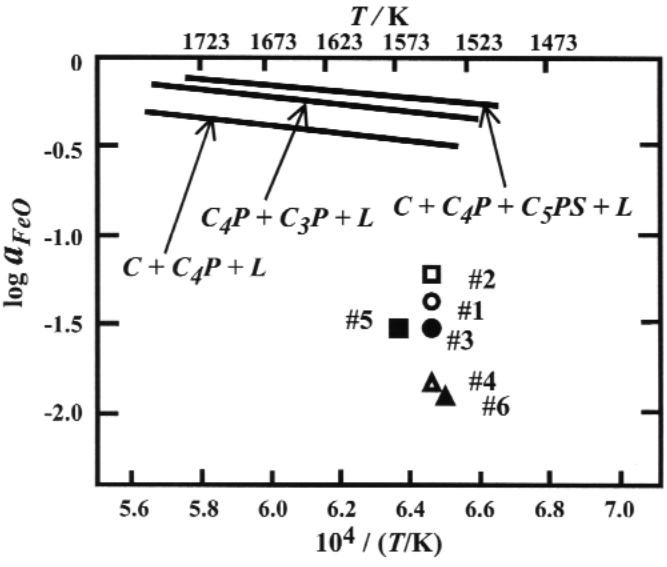

Figure 15. Activities of FeO in the heterogeneous slags compared with those in the homogeneous industrial slags

The activities of P_2O_5 within the three-phase region $C + C_4P + L$ and $C_4P + C_3P + L$, and the four-phase region $C + C_4P + C_5PS + L$ are fixed through either Reaction [6] or [7]. For homogeneous slags, it is well known that the presence of SiO_2 will increase the activity of P_2O_5. In the case of heterogeneous slags, however, the activity of P_2O_5 in $C + C_4P + C_5PS + L$, is identical to that in $C + C_4P + L$. With respect to the stability of C_4P, a few words seem to be pertinent at this point. In industrial slags saturated with solid lime one may detect C_3P rather than C_4P. This is due to the fact that the activities of P_2O_5 as fixed by Equation [6] are very close to those of Equation [7].

The phosphorus concentration in the liquid iron phase, $[\%P]$, attainable through equilibration with the 3- and 4-phase assemblages, can then be estimated from the relationship:

$$\log[\%P] = \log\left\{a_{P_2O_5} / K(4) a_{FeO^5}\right\}^{1/2} \qquad [8]$$

The results of these calculations are shown in Figure 14 together with the final phosphorus levels achieved with the industrial slags as reported in Table I. It is evident from this graph that the residual phosphorus concentrations attainable by using the heterogeneous slag systems are three to five orders of magnitude lower than those obtained with the industrial slags. Because of this behaviour, the opportunity is available to considerably reduce the required slag volume. Based upon these considerations, the Fukuyama works of NKK (now JFE Steel), a very small slag volume of 50 kg/ton-steel has been achieved.

Phosphate capacities

As an alternative to Reaction [4], the dephosphorization reaction can be expressed in the following terms:

$$2[P] + 3\left(O^{2-}\right) + (5/2)O_2 = 2\left(PO_4^{3-}\right) \qquad [9]$$

$$K(9) = a_{PO_4^{3-}}{}^2 / h_{P^2} a_{O^{2-}}{}^3 p_{O_2}{}^{5/2} \qquad [10]$$

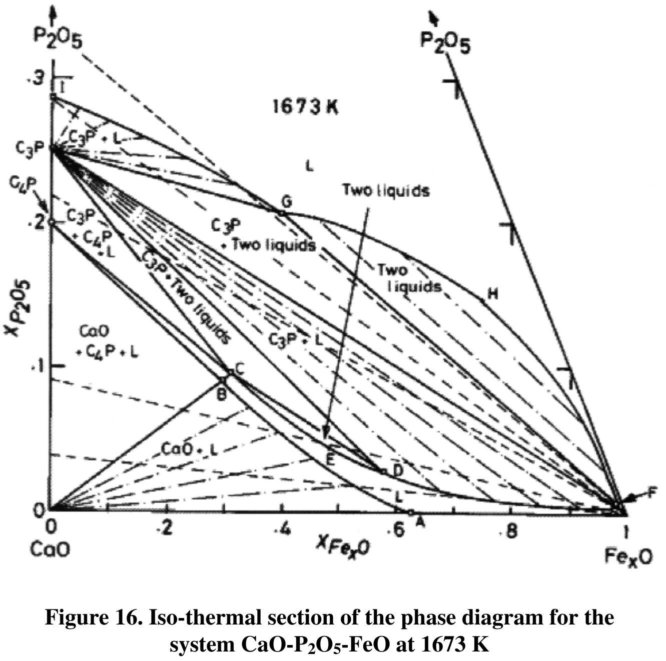

Figure 16. Iso-thermal section of the phase diagram for the system $CaO-P_2O_5-FeO$ at 1673 K

The equilibrium constant for Reaction [9], *K(9)*, cannot be determined by experiment, since activities of ions are, in principle, not measurable. Equation [10] can be rewritten as:

$$\left\{\left(\%PO_4^{3-}\right)/[\%P]P_{O_2}{}^{5/4}\right\} = a_{O^{2-}}\, 3/2\, K(9)^{1/2} f_P \left(f_{PO4}{}^{3-}\right)^{-1} \qquad [11]$$

The left-hand side of Equation [11] is defined as the phosphate capacity, $C_{PO_4^{3-}}$, i.e.

$$C_{PO_4^{3-}} \equiv \left\{\left(\%PO_4^{3-}\right)/[\%P]P_{O_2}{}^{5/4}\right\} \qquad [12]$$

where the concentrations of phosphorus in liquid slag and molten iron, $(\%PO_4^{3-})$ and $[\%P]$, and oxygen partial pressure, P_{O_2}, are all measurable quantities. According to Equation [11], the phosphate capacity increases with an increase in oxygen anion activity, i.e. with slag basicity. Because of higher phosphate capacity, lower phosphorus residuals can be achieved in the liquid iron.

Since the 1970s, considerable efforts have been devoted to exploring slags of higher phosphate capacities. An excellent overview on the phosphate capacity of various slags and fluxes has been published by Sano[23]. With only a few exceptions, despite all of these efforts, steelmaking slag volume has not decreased substantially during the past decade[24]. Experimental determinations of phosphate capacity are normally based upon the equilibration of homogeneous liquid slag with phosphorus-containing molten alloys under a controlled oxygen partial pressure. From chemical analysis of metal and slag samples, values can be calculated for the phosphate capacity. Based on the foregoing discussion, it is evident that, while the concept of 'phosphate capacity' is valid for homogeneous liquid slags, it is not appropriate for heterogeneous slag systems.

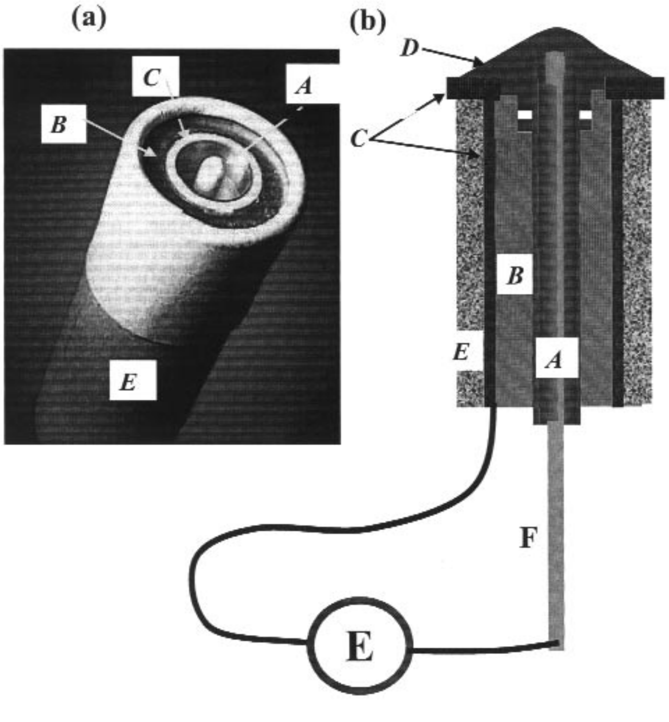

Figure 17. Photograph (a) and schematic illustration (b) of on-site FeO sensor. A, Zirconia electrolyte containing reference electrode; B, Ceramic body; C, Steel ring; D, Slag; E, Ceramic body; F, Molybdenum rod

On-site FeO sensor

The automatic activity determinator is now used by several steel companies in different parts of the world. The application of this technology has recently been expanded to allow rapid on-site determinations of FeO activity or concentrations. Figure 17 shows the schematic diagram of such an on-site FeO sensor and Figure 18 illustrates schematically how measurements are made. A relationship between measured emf and FeO concentrations, *(%FeO)*, as determined through chemical analysis is given in Figure 19.

On-line FeO sensor for BOF

An alternative approach to measure FeO activities or oxygen potentials in the slag phase is to install the conventional oxygen sensor designed for molten steel applications. Figure 20 shows schematically such an on-line FeO sensor installed within the sub-lance system of a BOF. As is well known, the sub-lance installed within a BOF normally allows metal sampling and determinations of carbon through liquidus temperature measurements.

In addition, an oxygen sensor can also be installed to measure the oxygen partial pressures within the metal phase. An electrical contact to molten steel for a conventional oxygen probe is made by a molybdenum or steel rod encased within the sensor body. For on-line FeO sensors, electrical contact to molten steel is made through the trunnion ring, Figure 20. When the sub-lance is moved downward, the oxygen sensor is brought into contact with liquid slag and subsequently molten steel. The sub-lance is then moved upward. Figure 21 indicates the oxygen potential within molten steel and liquid slag during a period when the sub-lance is moved upward. As shown in this figure, output voltage signals yield oxygen partial pressures of $\log\{P_{O_2}(\text{atm})\} \approx -11.0$ for the metal phase and subsequently $\log\{P_{O_2}(\text{atm})\} \approx -9.0$, indicating that the oxygen potential in the slag phase is about two orders of magnitude higher than that in the metal phase.

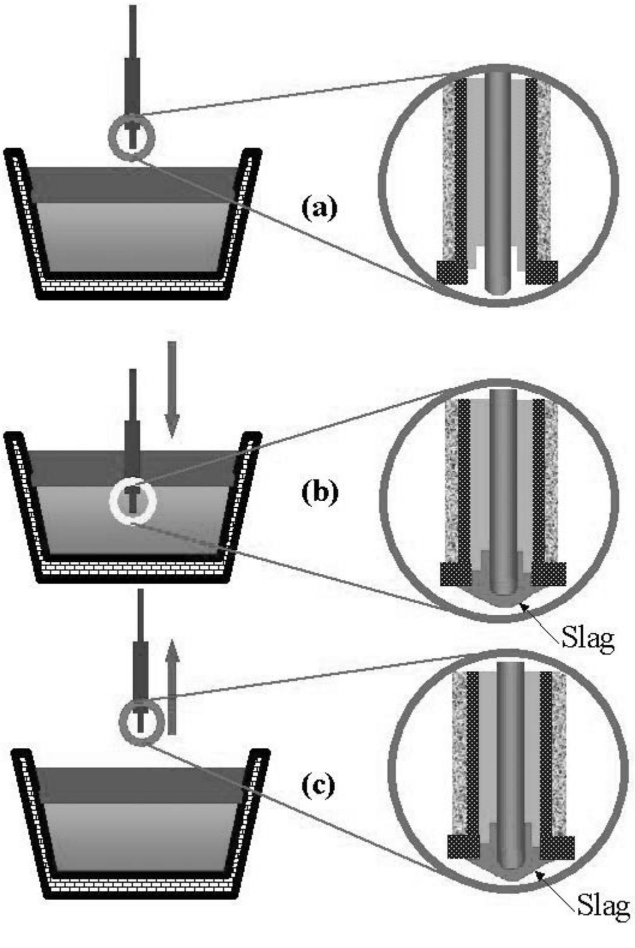

Figure 18. Schematic illustration to show how emf measurements are made with the on-site FeO sensor. (a) Before immersion into liquid slag; (b) After immersion in molten steel through liquid slag. Liquid slag is adhered on to the steel ring; (c) After removed from liquid steel. Slag is still adhered on to the steel ring. Hence emf is still generated between reference electrode and slag

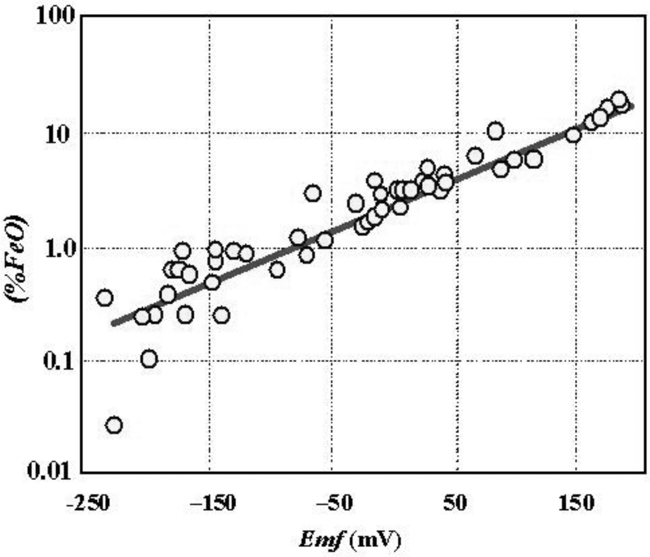

Figure 19. Relation between FeO concentration, (%FeO), determined through chemical analysis and cell potential, emf/mV, measured by the on-site FeO sensor

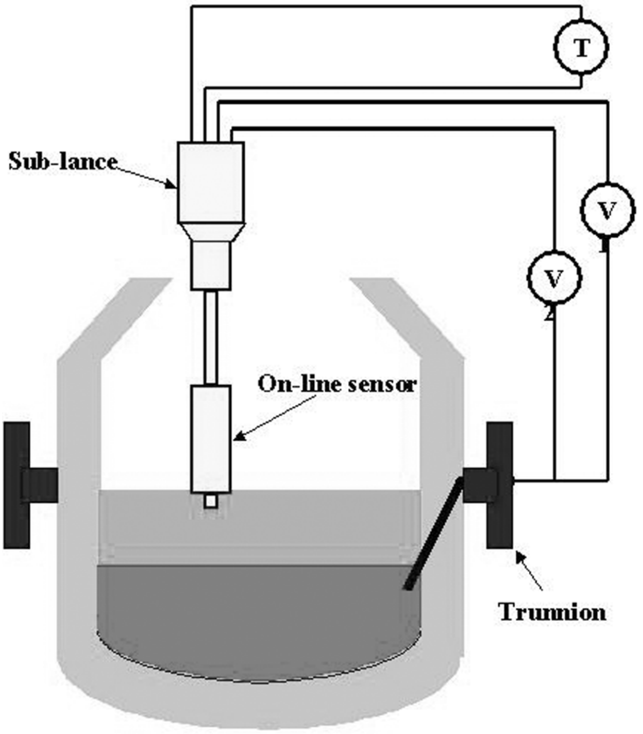

Figure 20. Schematic illustration of on-line FeO sensor

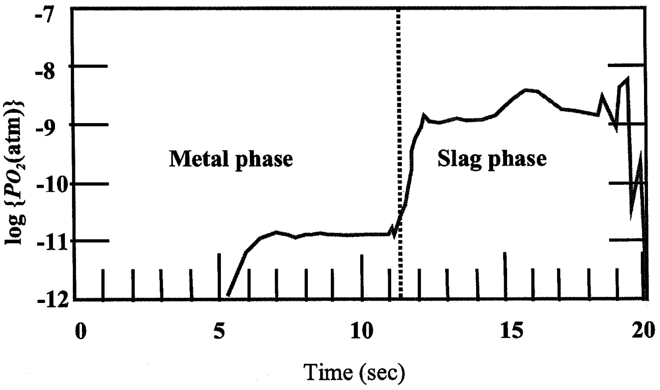

Figure 21. Measured oxygen potentials, log PO_2 in the metal and slag phases

Conclusion

To a large extent, oxygen potential of the slag phase governs iron and steelmaking reactions. Oxygen measurements obtained by means of appropriate sensors designed for slag control, are an essential requirement in order to manage the behaviour of other elements such as sulphur and phosphorus. Without measurements, we fail to understand the reality of the actual manufacturing process.

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