An electrochemical cell technique based on magnesia-stabilized zirconia has been employed to measure FeO activities within homogeneous and heterogeneous slag systems between 1100 and 1450°C. For the heterogeneous slags, emphasis was given to 3- and 4-phase assemblages in the CaO + P₂O₅ + FeO and CaO + P₂O₅ + SiO₂ + FeO systems. The information generated has permitted new control strategies to be developed for the behavior of phosphorus in liquid iron and for the reduction in steelmaking slag volume. In addition, this work has led to the manufacture of an analytical instrument for the determination of FeO activities. This activity determinator is currently used by a number of major steel companies in different parts of the world.
INTRODUCTION

The studies of chemical reactions in steelmaking processes involve complex slag systems of at least eight important components, i.e., CaO, MgO, MnO, FeO, SiO₂, Al₂O₃, P₂O₅, CaF₂, and often a number of others such as Na₂O, TiO₂ and Cr₂O₃. One of the greatest obstacles to the application of physical chemistry 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 between metal, slag and gas, the evaluation of the activities of ferrous oxide should be first considered. The conventional experimental technique for determination of the FeO activity would consist of equilibrating molten slags with liquid iron. Chemical analysis for oxygen made on samples taken from liquid iron would give the values of FeO activities, \( a_{FeO} \), through the equation:

\[
a_{FeO} = \frac{\%O}{\%O^o}
\]

where \( \%O \) and \( \%O^o \), respectively, are the oxygen contents (pct by weight) in liquid iron in equilibrium with molten slag under consideration and with "pure" liquid FeO, respectively.

Pioneering work of Taylor and Chipman [1] should be noted at this point. Alternatively, molten slags contained in an iron crucible would be brought into equilibrium under a stream of CO-CO₂ or H₂-H₂O. Values of \( a_{FeO} \) can be derived from the expression:

\[
a_{FeO} = \left( \frac{PO_2}{PO_2^o} \right)^{1/2},
\]

where \( PO_2 \) and \( PO_2^o \), respectively, are the equilibrium oxygen partial pressures of mixtures of solid Fe + FeO in liquid slag, and solid Fe + "pure" liquid FeO, respectively. Works by Schuman [2] and Ban-ya and his co-workers [3] are noteworthy. These techniques require, however, a relatively complex experimental setup and long duration.

Because of recent progress in the area of solid state ionics, an electrochemical technique now allows rapid determination of ferrous oxide activity [4]. In the present paper, a description is given of the technique with a particular emphasis on 3- and 4-phase assemblages in the CaO + P₂O₅ + FeO and CaO + P₂O₅ + SiO₂ + FeO systems. The information generated through such measurements has permitted new control strategies to be developed for the behavior of phosphorus in liquid iron and for the reduction in steelmaking slag volume. In addition, this work has led to the manufacture of an analytical instrument for the determination of FeO activities. This activity determinator allows in-plant determinations of the FeO activities in industrial slags, and is currently used by a number of major steel companies in different parts of the world.

RAPID DETERMINATION OF FeO ACTIVITY BY AN ELECTROCHEMICAL TECHNIQUE

A schematic illustration of the experimental apparatus is shown in Figure 1. An iron crucible was charged with about 4 g of slag together with 40 g of pure silver. The crucible and contents were heated to the experimental temperatures in a stream of purified argon within a SiC resistance furnace equipped with a mullite reaction tube 70-mm o.d., 60-mm i.d. and 1000-mm in length.

The electrochemical half-cell, Mo/Mo + MoO₂/ZrO₂(MgO), consisted of a zirconia tube and a two-phase mixture of Mo + MoO₂. A molybdenum rod was used as an electrical lead to the reference electrode, while the liquid silver and a steel rod soldered to the iron crucible made electrical contact with the outer electrode of the zirconia probe. The zirconia probe was first inserted into the furnace about 200 mm above the oxide phase, and then gradually moved downward until the probe contacted both the oxide phase and the liquid
silver. Cell potentials generated were measured by a strip chart recorder of 2 M ohm internal impedance with an accuracy of ±1 mV and more accurately by a digital voltmeter of 100 M ohm input resistance with an accuracy of ±0.1 mV. After stable cell potentials (± 0.2 to 2 mV) were obtained, the zirconia probe was removed from the iron crucible. For a fixed temperature, emf readings were repeated several times at intervals of 30 to 60 minutes until emf reproducibility was established. Reproducibility can also be confirmed by temperature cycling. During emf measurements, samples were taken from the oxide phase to be submitted for chemical analysis and X-ray diffraction. The magnesia-stabilized zirconia tubes used in this study had satisfactory resistance to the FeO-containing slag, which, to a large extent, attacked calcia-stabilized zirconia.

The open-circuit emf, \( E \), of the cell is given by [5]:

\[
E = (RT / F) \ln \left[ \frac{[PO_2(ref)]^{1/4} + [Pe]^{1/4}}{[PO_2(slag)]^{1/4} + [Pe]^{1/4}} \right] + E_I \quad (3)
\]

where \( T \) is temperature, \( E_I \) is thermo-emf between Mo (positive) and Fe (negative), \( R \) is the gas constant, \( F \) is the Faraday constant, \( PO_2(slag) \) is the equilibrium oxygen partial pressure at the slag electrode, and \( Pe \) is the oxygen partial pressure at which the ionic and the n-type electronic conductivities are equal. Values for this parameter were obtained from the relationship reported by Iwase et al. [6]:

\[
\log (Pe / atm) = 20.40 - 6.45 \times 10^4 (T/K) \quad (4)
\]

The oxygen partial pressures at the reference electrode, \( PO_2(ref) \), were calculated using the following equation [7]:

\[
RT \ln PO_2(ref)/kJ \ mol^{-1} = -576.1 + 0.1692 (T/K) \quad (5)
\]

The activities of FeO were determined from the relationship:

\[
a_{FeO} = \frac{PO_2 (slag)}{PO_2 (slag)} \frac{PO_2 (slag)}{PO_2 (slag)} \frac{1}{2} \quad (6)
\]

where \( PO_2 (slag) \) is the equilibrium oxygen partial pressure of the mixture, Fe(s) + pure FeO(l). The standard state for FeO is taken as pure liquid FeO in equilibrium with pure solid iron. Values for \( PO_2 (slag) \) as a function of temperature have been reported by Hoshino and Iwase [8]:

\[
\log \left\{ \frac{PO_2 (slag) / atm}{atm} \right\} = 4.39 - 23,500 / (T/K) \quad (7)
\]

By using this technique, the FeO activity has been investigated for a number of slag systems [9-24].

### NEW CONTROL STRATEGIES TO REDUCE STEELMAKING SLAG VOLUME

Normally the basic oxygen process for steelmaking generates slags at a rate of 120 to 150 kg / ton of steel [25]. The actual composition of BOF slags will vary significantly, depending upon a number of factors, e.g., the sulfur 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 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 amount of recycled slag, in Japan, has to be maintained at a relatively low level. As a consequence, 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. Phosphorus transfer from metal to slag can be represented as follows:

\[
2 [P] + 5 (FeO) = (P_2O_5) + 5 [Fe] \quad (8)
\]
Reaction (8) is essentially an oxidation reaction and is favored by lower temperatures. For this reason, attention has been focussed on dephosphorization of hot metal rather than molten steel. Developments in hot metal processing have been reviewed elsewhere by the present authors [26].

Table 1 gives the compositions of slags formed at the final stages of hot metal dephosphorization. The major components of these slags are CaO, CaF₂ and SiO₂. These slag samples were provided by Japanese steel companies. The initial compositions of fluxes used for hot metal processing are 40-50 FeO, 30-50 CaO and 5-10 CaF₂ in pct by weight. While phosphorus removal by Reaction (8) proceeds toward equilibrium, the activity of FeO inevitably decreases while that for P₂O₅ increases as shown schematically in Figure 2. In practice, despite the relatively high initial concentrations of FeO of 40 to 50 pct by weight, at the final stage, the concentrations have decreased substantially to levels of 1.1 to 2.5 mole pct (1 to 3 pct by weight), while the P₂O₅ contents have increased to 1.1 to 3.4 mole pct (%P) = 1 to 3 pct by weight). The relatively high CaF₂ 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. If lower phosphorus levels are required, then FeO has to be added in order to increase the FeO activity and/or CaO additions would be necessary to lower the P₂O₅ activity. Clearly, such additions result in an increase in slag volume.

Figure 3 shows the isothermal section of the CaO-P₂O₅-FeO system at 1673 K [27]. For convenience, the following notations are used: \( C₄P = Ca₄P₂O₉ \), \( C₃P = Ca₃P₂O₈ \) and \( L = \{CaO + P₂O₅ + FeO\} \) liquid ternary slags. Particular attention should be focussed on the following three-phase regions:

- \( \text{CaO} + \text{Ca}_4\text{P}_2\text{O}_9 + \text{liquid}, \text{i.e. triangle CaO-B-C}_4\text{P} \);
- \( \text{Ca}_4\text{P}_2\text{O}_9 + \text{Ca}_3\text{P}_2\text{O}_8 + \text{liquid}, \text{i.e. triangle } \text{C}_4\text{P} -\text{C} - \text{C}_3\text{P} \).

Consider removal of phosphorus from liquid iron by using the three-phase assemblage: \( \text{CaO} + C₄P + L \). 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 are zero degrees of freedom, the activities of FeO and P₂O₅ are fixed and therefore independent of the bulk slag composition. If phosphorus removal was conducted with this heterogeneous slag, the FeO and P₂O₅ activities remain constant even although the bulk concentrations of FeO and P₂O₅ are decreasing and increasing, respectively. A schematic representation of the phosphorus removal process under these conditions is shown in Figure 4. 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.

The activities of FeO were determined first for the industrial slags [28], the compositions of which are given in Table 1. The measurements were subsequently extended to the three-phase regions of \( \text{CaO} + C₄P + L \) and \( C₄P + C₃P + L \) within the \( \text{CaO} + P₂O₅ + \text{FeO} \) system. The work was further expanded to incorporate the four-phase assemblage of \( \text{CaO} + C₄P + C₅PS + L \) within the \( \text{CaO} + P₂O₅ + \text{SiO₂} + \text{FeO} \) system, where \( C₅PS \) denotes 5CaO.P₂O₅.SiO₂ i.e. Ca₅P₂SiO₁₂. Phase relationships in the system CaO-P₂O₅-SiO₂-FeO are
illustrated schematically in Figure 5.

From the experimental results, values have been determined for \( \log a_{FeO} \), and plotted against the reciprocal temperature as shown in Figure 6. As shown in this figure the FeO activities within the 3- and 4-phase assemblages are considerably greater than those in the industrial slags, thus enhancing conditions for the removal of phosphorus.

The activities of \( P_2O_5 \) within the three-phase region \( CaO + C4P + L \) and the four-phase region \( CaO + C4P + C5PS + L \) are fixed through the reaction [29]:

\[
4 \text{CaO} + (P_2O_5) = \text{Ca}_4P_2O_9 \\
\Delta G(\theta) / \theta \text{ mol}^{-1} = RT \ln a_{P_2O_5} = -781,500 + 14.7 (T/K)
\]

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 \( CaO + C4P + C5PS + L \), is identical to that in \( CaO + C4P + L \).

The effect of temperature on the activity of \( P_2O_5 \) within the 3-phase assemblage \( C4P + C3P + L \) can be derived with the aid of the following expressions [30]:

\[
3 \text{Ca}_4P_2O_9 + (P_2O_5) = 4 \text{Ca}_3P_2O_8 \\
\Delta G(II) / \theta \text{ mol}^{-1} = RT \ln a_{P_2O_5} = -760,500 + 29.7 (T/K)
\]

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:

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

The results of these calculations are shown in Figure 7 together with the final phosphorus levels achieved with the industrial slags as reported in Table 1. 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. As a consequence of this behaviour, the opportunity is available to considerably reduce the required slag volume.

**FeO ACTIVITY DETERMINATOR**

In view of industrial importance and theoretical interest of the ferrous oxide activities, a number of experimental determinations of the activities of ferrous oxide have been conducted. Because of the concerted efforts of many laboratories during five decades, approximately two thousand data were obtained for FeO activities, and 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-SiO₂, 10- Al₂O₃, 3-P₂O₅, 2-CaF₂ and 10-FeO in pct by weight. No literature data are available for this particular slag.

By using the electrochemical technique incorporating a solid electrolyte, an automatic facility has been developed [31-34]. This equipment has essentially the same design as that shown in Figure 1. A schematic illustration of the automatic activity determinator is given in Figure 8. The electrochemical cell consists of zirconia tube D of 3.6 mm o.d., 2.2 mm i.d. and 32 mm in length, a Mo + MoO₂ mixture C, and a molybdenum rod A of 1 mm diameter and 200 mm length. To operate this system, firstly, the electrochemical cell is attached to the elevator mechanism E. Second, an iron crucible K of 19 mm o.d., 16 mm i.d. and 37.5 mm in length, is placed on a steel pedestal O. The electrical contact to the outer electrode of the zirconia cell is made \( via \) this pedestal. Pure silver M (8 g) is pre-melted...
within the iron crucible. A sample of slag L (1 to 3 g) is charged in the iron crucible. These procedures require manual operations. Subsequent steps, however, will occur automatically upon touching the LCD (Liquid crystal display) of a microcomputer installed within the facility.

The iron crucible is moved upward, via an elevator mechanism P, into a transparent silica reaction tube H of 48-mm o.d., 44-mm i.d., and 238 mm in length. The tube is sealed and flushed with a stream of argon. By means of an infrared ray generated by four tungsten filaments I, the furnace is subsequently heated to the desired temperature of 1673 to 1723 K within 2.5 minutes in conformance with the computer program.

The furnace temperature is measured with a Pt-PtRh13 thermocouple N placed below the iron crucible and monitored on the LCD. Upon temperature reaching the pre-determined value, the electrochemical cell is lowered until it contacts both the molten silver and the slag. Open-circuit cell voltages generated between the molybdenum rod and the steel pedestal are monitored on the LCD of the microcomputer. Normally stable cell potentials are obtainable within 0.5 to 1 min. After stable EMFs (±0.8 mV) were obtained for at least 1 minute, the electrochemical cell is removed from the iron crucible, which is, in turn, lowered and abandoned in order to prepare for subsequent activity determinations. The cell potential is then converted to the FeO activity and displayed on the LCD.

With this facility, "on-floor" activity determinations are possible and a result is obtainable within 5 minutes. Since important steelmaking reactions, e.g., desulfurization and dephosphorization, are related to the FeO activities, this equipment is now used by a number of major steel works. An example of the industrial application of this analyzer by Hamm et al [35] relates to control of desulfurization, which can be expressed as:

\[(\text{CaO}) + [\text{S}] + \text{Fe} = (\text{CaS}) + (\text{FeO})\]  \hspace{1cm} (14)

The partition ratio for sulfur is given by:

\[\log\left\{(\%S)/(\%S)^0\right\} = - \log a_{\text{FeO}} + \log a_{\text{CaO}}\] \hspace{1cm} (15)

Equation (15) implies that if the activity of CaO (i.e., the basicity of the slag) is kept constant, a logarithmic plot of \((\%S)/(\%S)^0\) against \(a_{\text{FeO}}\) should be a straight line with a slope of -1. The relationship between \(\log\left\{(\%S)/(\%S)^0\right\}\) and \(a_{\text{FeO}}\) as obtained by Hamm et al is shown in Figure 9. Although the slope was different from the theoretical values of -1, there is a good correlation between the two parameters. This indicates that the sulfur partition ratio can be monitored and therefore controlled through FeO activity measurements.

**CONCLUDING REMARKS**

Since ferrous oxide participates in numerous steelmaking reactions, attention should be focussed on the activity of FeO. Nevertheless, our knowledge on thermochemical properties of ferrous oxide is far from satisfactory because of experimental difficulties at high temperatures. By employing an electrochemical technique incorporating zirconia as electrolyte and Mo + MoO$_2$ as reference electrode, the activity of ferrous oxide in steelmaking slags can be determined more readily than by conventional techniques. Based upon information generated through activity measurements in conjunction with Gibbs' phase rule, a new control strategy for the reduction of steelmaking slag volume has been proposed. In addition, an automatic analyzer for the rapid determination of the activity of FeO in metallurgical slags has been developed. With this equipment, "on-floor" activity determinations are possible, since a result is obtainable within 5 minutes.
REFERENCES
vol. 16, 1989, 45-52
Figure 1  Experimental setup for FeO activity determinations.
Figure 2  Schematic diagram of dephosphorization reaction with homogeneous liquid slag.
Figure 3  Isothermal section of the phase diagram for the system CaO + P₂O₅ + FeO.
Figure 4  Schematic diagram of dephosphorization reaction with heterogeneous slags and zero degrees of freedom.

Figure 5  Phase relationships in the system CaO + P2O5 + SiO2 + FeO.
Figure 6  Activities of FeO in the heterogeneous slags compared with those in the homogeneous industrial slags.

Figure 7  A comparison of the estimated phosphorus contents attainable with the heterogeneous slags compared with those actually obtained using the homogeneous industrial slags.
Figure 8  Schematic illustration of automatic activity determinator. A, Mo rod; B, Zirconia cement; C, Mo + MoO₂ 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,
Table 1 Composition of industrial slags during final stages of hot metal processing and the corresponding hot metal temperature and phosphorus levels

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Slag composition (mole pct)</th>
<th>Hot metal</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>SiO₂</td>
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<tr>
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</tr>
<tr>
<td>#6</td>
<td>60.0</td>
<td>11.6</td>
</tr>
</tbody>
</table>

* “Others” means CaS + MgO + MnO + Al₂O₃