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Alternative methods for *in situ* determination of iron oxide in steelmaking slags

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Data are presented on the effect of iron oxide on the electrical conductivity of CaO-SiO_2-FeO-Fe_2O_3 melts, and on limiting current and impedance in direct current or alternating current charge transfer at iron electrodes. The strong influence of iron oxide content can be utilized for *in situ* determination of total iron oxide content and Fe^{3+}/Fe^{2+} ratio. The possible probe designs are presented and the principles and procedures of the measurements are explained.

Keywords: *in situ* probe for iron oxide determination in steelmaking slags, electrical conductivity of CaO-SiO_2-FeO-Fe_2O_3 slags, direct current overvoltage and alternating current impedance at iron/slag electrodes.

Introduction

The most important component of steelmaking slags is the iron oxide since it serves as the oxidizing agent in refining reactions. The measurement of the iron oxide content is performed in the steelworks by taking a sample out of the liquid slag, cooling it and subsequently analysing it. The procedure takes some time. It would be highly desirable, therefore, to develop methods for rapid *in situ* determination. Iron oxide is present in liquid slags in the form of FeO (ferrous oxide) and Fe_2O_3 (ferric oxide). The ratio Fe_2O_3/FeO (or Fe^{3+}/Fe^{2+}) depends on the total iron content, the contents of the other slag components, the temperature, and the oxygen potential. Under reducing conditions mainly FeO is stable, and under oxidizing conditions mainly Fe_2O_3.

If slag and metal are close to equilibrium, the iron oxide content of the slag can be computed from the content of certain elements in the metal and the thermodynamic data for the slag/metal equilibrium. For slag with high iron oxide content, the relevant reaction is [O] + [Fe] = (FeO) which yields $a_{FeO}=K(T)\ a_O$. Hence, the ferrous oxide activity a_{FeO} can easily be obtained by *in situ* measurement of the oxygen activity a_O of the liquid metal with EMF probes involving stabilized zirconia as solid electrolyte. However, in many stages of conventional steelmaking the slag metal reactions are not so close to equilibrium. Consequently, the indirect determination of iron oxide content via metal analysis is not sufficiently accurate, or may even be rather wrong.

The direct *in situ* measurement of iron-oxide content and of Fe^{3+}/Fe^{2+} ratio with EMF probes is possible[1–6]. The oxygen potential has to be fixed, if the oxide content is to be determined, by the presence of metallic iron, which can be performed in various ways. Possible cell designs have been suggested in previous studies[5,6]. However, there are difficulties. The zirconia tubes are attacked by the slag melts. In the practical application, the signal is found to oscillate and there is a large error in the determined iron oxide content. Thus, due to such problems, the direct determination of iron oxide content with EMF cells is not yet widely carried out in industry.

In principle, the iron oxide content can be determined by measurement of such slag properties that are markedly dependent on this component. Besides the thermodynamic activity, certain transport properties can be utilized. They may be easily measurable as such, or it might be possible to measure kinetic phenomena controlled by them. New methods for *in situ* iron oxide determination can be conceived from application of such alternative principles.

In the present paper methods are suggested that are based on transport of electrical charge in the slag melt. The first part deals with the application of electrical conductivity, and in the second part it is proposed to use the measurement of direct current overvoltage and alternating current impedance for *in situ* analysis of iron oxide.

Conductometric measurement of iron oxide content

The electrical conductivity of steelmaking slags depends markedly on composition. There is an increase with basicity and with temperature, and a very strong effect of ferrous oxide content. Figure 1 shows selected data for CaO-SiO_2-FeO-Fe_2O_3 melts with a basicity of $CaO/SiO_2=0.74$ at low oxygen pressure when most of the iron is divalent (FeO)[7,8]. The increase with iron content is larger than by a factor of thirty in the range of 0 to 40 mass % Fe. This strong variation would be very suitable for measurement of iron content of the slag. For 1600°C the function

$$\log\kappa\left(\Omega^{-1}cm^{-1}\right) = -0.62 + 0.0385(\%Fe) \qquad [1]$$

can be used to represent the data. Also, the Fe^{3+}/Fe^{2+} ratio has a strong influence, Figure 2[8]. The variable x at the abscissa is the ratio $Fe^{3+}/(Fe^{2+} + Fe^{3+})$. At x=0 all the iron is divalent and at x=1 all the iron is trivalent. At low iron contents the slags are completely ionic conductors and the electrical conductivity decreases with increasing Fe^{3+} fraction. This decrease is because the mobility of Fe^{2+} is very high[9] (much higher than than that of Ca^{2+}) and that of Fe^{3+} is comparatively small. The dependence on oxidation state is linear in this range, viz.

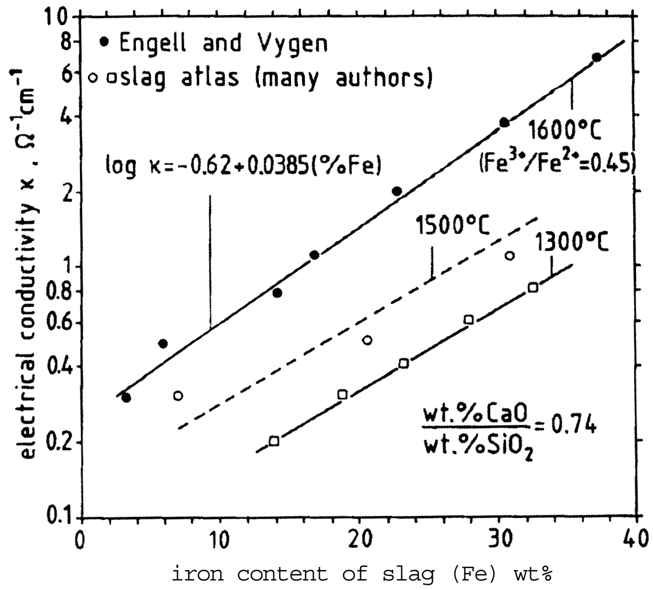

Figure 1. Selected electrical conductivity data of CaO-SiO$_2$-FeO melts[7,8]

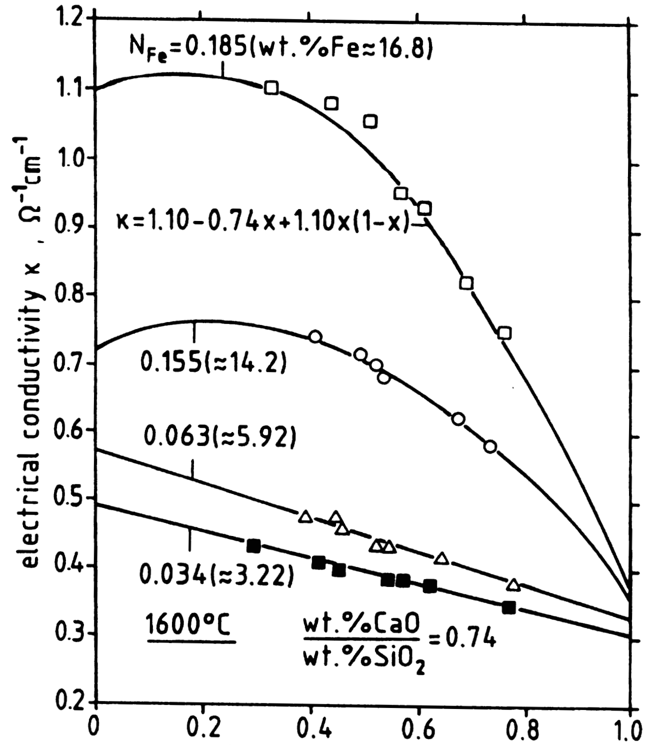

Figure 2. Electrical conductivity of CaO-SiO$_2$-FeO-Fe$_2$O$_3$ melts at various total iron contents as a function of trivalent iron fraction at 1600°C. Engell and Vygen[8]

$$\kappa = A - Bx \qquad [2]$$

where A is the conductivity of the slag with all the iron being divalent and **A-B** that of the slag with all the iron being trivalent. At high iron contents there is a maximum of the electrical conductivity at intermediate x, which can be explained by assuming partial electronic conduction. That is, the electrical conductivity is composed of a part due to ionic transport, which can be taken to be linear, Equation [2], and a part due to electron transport, which is parabolic, κ_e = Cx(1-x). Hence, the function for the electrical conductivity is[8].

$$\kappa = A - Bx + Cx(1-x) \qquad [3]$$

The electron conductivity is caused by direct electron transfer between Fe^{2+} and Fe^{3+} ions, which may occur by a simple bi-ionic collision mechanism[8]. That is, an electron jumps, during a collision between a trivalent and a divalent iron ion, from the divalent to the trivalent ion. The number of collisions is proportional to the product of both concentrations, hence the parabolic concentration dependence of the electron conductivity.

The electrical conductivity of slags has been measured using various cell designs. One electrode may be the metallic crucible and the other a rod immersed in the slag, or the electrodes may be parallel platelets, or one electrode may be a hollow cylinder and the other a wire (rod) in the central axis of the cylinder. The geometry (immersion depth, spacing) of the electrodes has to be controlled precisely to avoid errors in the measurement. The best design is that of two parallel wires (rods) because the resistance between the wires is comparatively insensitive to a variation of wire spacing (most of the voltage drop is in the vicinity of the wires where the current density is highest)[10]. The four poles have to be applied, one pair of poles serving for the current passage, the other for the potential measurement. It is very important to use alternating current of high frequency to avoid overpotentials due to the electrode reaction. Conductivity measurements in ionic melts with direct current (which unfortunately are reported quite frequently) are always wrong.

Sensors based on conductivity measurement have been proposed for determination of the Cr$_2$O$_3$ content of stainless steel slags[11]. But it is not known how widely such sensors are applied in the steelmaking industry The suitable sensor would be simple, Figure 3. It has two wire electrodes. The leads a-a are connected to the current source (high frequency generator) and the leads b-b to a high impedance voltmeter. The voltage E is measured at a frequency in the frequency range where it is independent of frequency (10 to 100 kHz). Then the ohmic resistance is obtained as R_s=E/I where I is the current, and the conductivity as κ=k_{cell}i/E where i is the current density at the surface of the wires. The cell constant k_{cell} is determined by calibration with aqueous solutions or salt melts of known conductivity.

To convert the conductivity signal to iron oxide content the basicity and temperature must be known. For measurement in steelmaking slags with high iron content, inert metal electrodes, (Pt, Rh, Ir) might be used if the Fe^{3+}/Fe^{2+} ratio is in the region of the conductivity maximum (viz. Fe^{3+}/Fe^{2+} 0.5, x 0.3) and, consequently, does not exert much influence. Otherwise, the defined oxidation state must be established at the electrodes which is that in equilibrium with metallic iron. This can be obtained by a cylinder of metallic iron around the electrodes, which reduces trivalent iron to the equilibrium content before melting, Figure 4.

An elegant way would be to use 'active' electrodes (metallic iron if the measurement is below about 1450°C, or an iron-iridium alloy). In composition ranges where the electrical conductivity depends on total iron content and on Fe^{3+}/Fe^{2+} ratio, both data could be obtained by a combination of conductivity measurement involving Fe electrodes (total iron) and inert electrodes (Fe^{3+}/Fe^{2+}). The two data could be measured with the same probe consisting of four electrodes (one noble metal pair, one Fe (or Fe-Ir) pair).

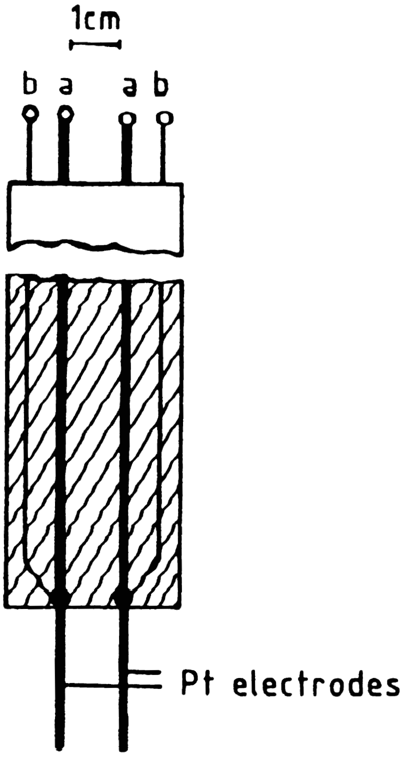

Figure 3. Conductivity probe

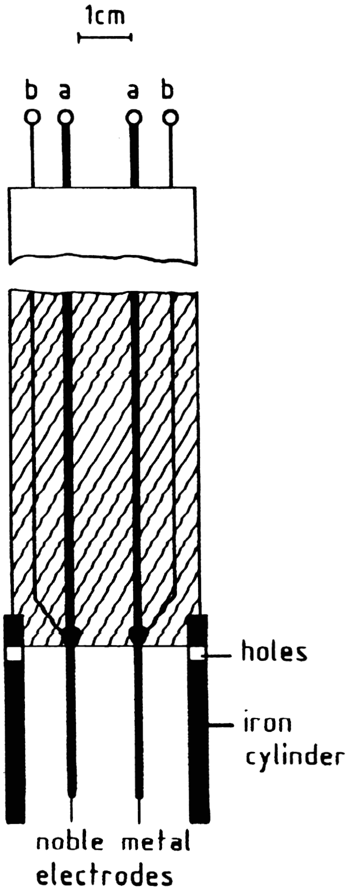

Figure 4. Conductivity probe with iron cylinder for reduction of trivalent iron

It should be mentioned that the total iron content of the slag increases when the slag is at a higher oxidation state and is reduced by metallic iron. The reaction is

$$Fe + 2Fe^{3+} = 3Fe^{2+} \qquad [4]$$

Thus, three divalent iron irons are made from two trivalent ions. The following equation has been derived for the total iron content after equilibration with metallic iron $(\%Fe)_{Fe}$ as a function of the iron content of the bulk slag $(\%Fe)_s$[5]

$$(\%Fe)_{Fe} = \frac{100(2+x_s)(\%Fe)_s}{100(2+x_{Fe})+(x_s-x_{Fe})(\%Fe)_s} \qquad [5]$$

The index *s* refers to the bulk slag (at some distance from the probe) and Fe to the equilibrium with metallic iron. The maximum difference between $(\%Fe)_{Fe}$ and $(\%Fe)_s$ will result if x_s=1 (all the Fe is Fe^{3+} in the bulk slag) and x_{Fe} =0 (all the Fe is Fe^{2+} at the iron electrode). For instance, if $(Fe)_s$=5%, $(Fe)_{Fe}$ would be 7.3%. However, in reality the difference is smaller. But it follows that Reaction [4] can have a noticeable effect on the measurement of total iron content.

Direct current overpotential and alternating current impedance

Current density-potential curves measured at slag/metal electrodes may show considerable polarization effects. At slag/iron electrodes the anodic and cathodic reactions are

$$Fe(metal) = Fe^{2+}(slag) + 2e^- \qquad [6a]$$

$$Fe^{2+}(slag) + 2e^- = Fe(metal) \qquad [6b]$$

respectively. There is a strong effect of the iron oxide content on the current density-potential relationship in the low concentration range, which can be exploited for the *in situ* analysis of the iron oxide content.

The following data are taken from an investigation, carried out by the author and his associates several years ago, on the fundamentals of current transfer in the electroslag remelting process (ESR)[12]. Current transfer in the ESR process is according to Reactions [6a] and [6b] (at low current density), and the electrochemistry is the same as that in a sensor with two iron electrodes. The experiments were carried out with $CaF_2(FeO)$ and CaF_2-$CaO(FeO)$ slags contained in iron crucibles. The set-up is shown in Figure 5. Two electrodes made of iron wire were immersed, about 1 cm deep, in the slag and served as anode A and cathode C in the measurements with direct current. The voltage between the wire electrodes is determined, in the same manner as in conductivity measurements, via two additional leads (four pole method) to eliminate the ohmic resistance of the current carrying leads. The obtained voltage E is composed of the overpotential η_{AC} and the ohmic voltage drop iaRs, viz.

$$E_{AC} = \eta_{AC} + iaR_s \qquad [7]$$

where *a* is the surface area of the electrode and R_s the ohmic resistance of the slag. The latter can be measured with high frequency alternating current.

Direct current overvoltage

Figure 6 shows current density-overpotential curves for slags with various iron oxide contents. It is evident that the overpotential increases strongly with decreasing iron oxide

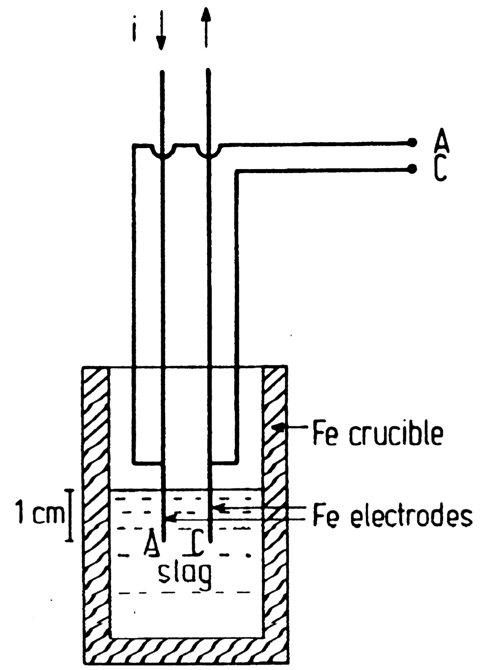

Figure 5. Cell used in experiments on overvoltage and impedance at iron/slag electrodes. Nowack, Schwerdtfeger, and Krause[12]

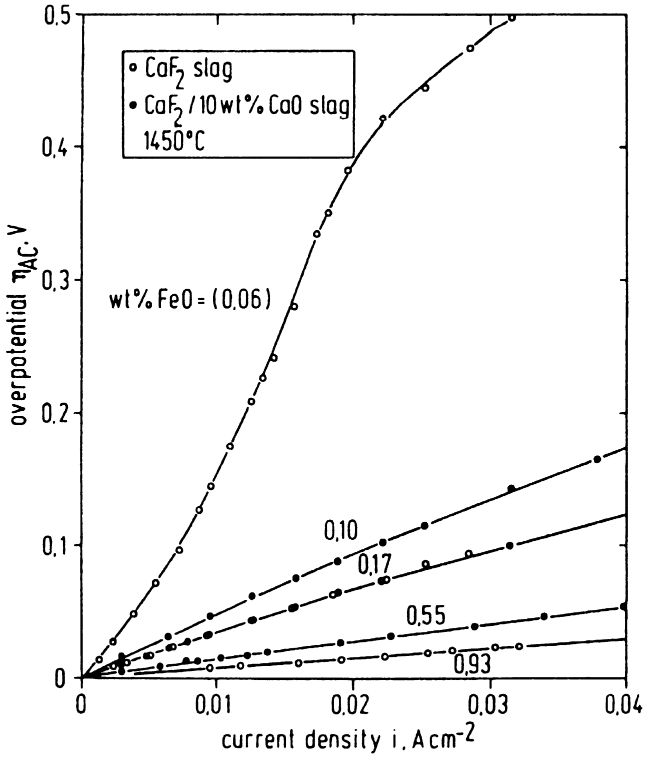

Figure 6. Influence of FeO content on relationship between current density and overpotential. Nowack, Schwerdtfeger, and Krause[12]

content. The theory known from polarography can be used to analyse the current density-overpotential relationship[12,13]. At the anode, Fe^{2+} is transferred into the slag via Reaction [6a], and at the cathode Fe^{2+} is removed from the slag via the reverse Reaction [6b]. Hence, at the anode the Fe^{2+} concentration increases and at the cathode it decreases compared to the bulk concentration $\bar{c}_{Fe^{2+}}$, Figure 7. The resulting gradients are the driving force for the diffusion the Fe^{2+} ions.

At sufficiently low current density, the overpotential is given by

$$\eta_{AC} = \frac{RT}{2F}\ln\frac{c_{Fe^{2+},A}}{c_{Fe^{2+},C}} \qquad [8]$$

The concentration differences are related to the diffusive flux $j_{Fe^{2+}}$ of the Fe^{2+} ions by equations

$$j_{Fe^{2+}} = \frac{i}{2F} = k_{Fe^{2+}}\left(c_{Fe^{2+},A} - \bar{c}_{Fe^{2+}}\right) \qquad [9a]$$

for the anode, and

$$j_{Fe^{2+}} = \frac{i}{2F} = k_{Fe^{2+}}\left(\bar{c}_{Fe^{2+}} - c_{Fe^{2+},C}\right) \qquad [9b]$$

for the cathode in which $k_{Fe^{2+}}$ is the mass transfer coefficient and F the Faraday constant. The limiting current density i_l is defined as the current density in the hypothetical situation in which the cathodic iron concentration $c_{Fe^{2+},c}$ is zero (case (3) in Figure 7) and still the cathodic charge transfer is exclusively by Reaction [6b]. Hence,

$$\frac{i_l}{2F} = k_{Fe^{2+}}\bar{c}_{Fe^{2+}} \qquad [10]$$

By application of [9a],[9b], and [10], Equation [8] can be transformed into

$$\frac{\alpha-1}{\alpha+1} = \frac{i}{2Fk_{Fe^{2+}}\bar{c}_{Fe^{2+}}} = \frac{i}{i_l} \qquad [11]$$

where

$$\alpha = \exp\left(\frac{2F\eta_{AC}}{RT}\right) \qquad [11a]$$

Figure 8 gives the proof of Equation [11]. Figure 9 demonstrates the linear relationship between i_l and (%FeO).

The probe consists of two iron or iron-iridium wires (set-up in Figure 5 without crucible) and is rather similar to the conductivity probe shown in Figure 3. A sketch is given in Figure 10. The mass transfer coefficient $k_{Fe^{2+}}$ which determines the relationship between Fe^{2+} content and limiting current density, Figure 9, depends on the majority components of the slag and can be determined by 'calibration' experiments. Inserting i_l=k'(%FeO) into [10] and solving for (%FeO) yields

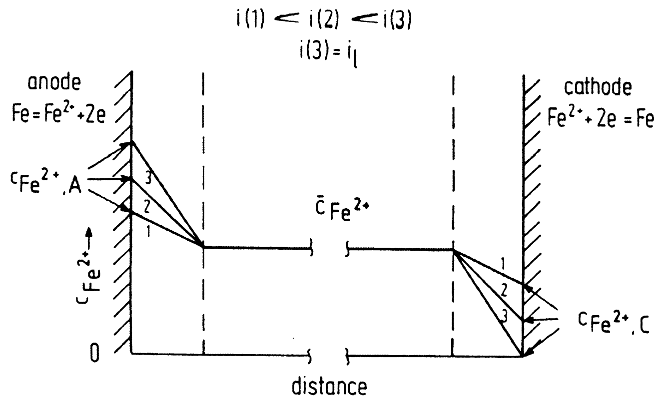

Figure 7. Concentration of Fe^{2+} at anode and cathode during transfer of direct current at iron/slag electrodes

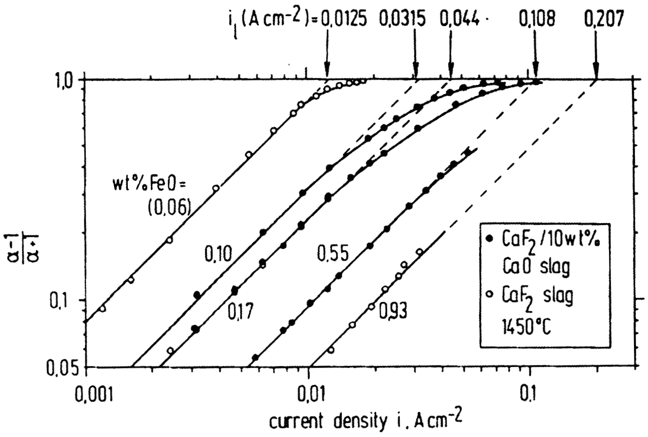

Figure 8. Plot of experimental data according to Equation [11]. Low current density range. Nowack, Schwerdtfeger, and Krause[12]

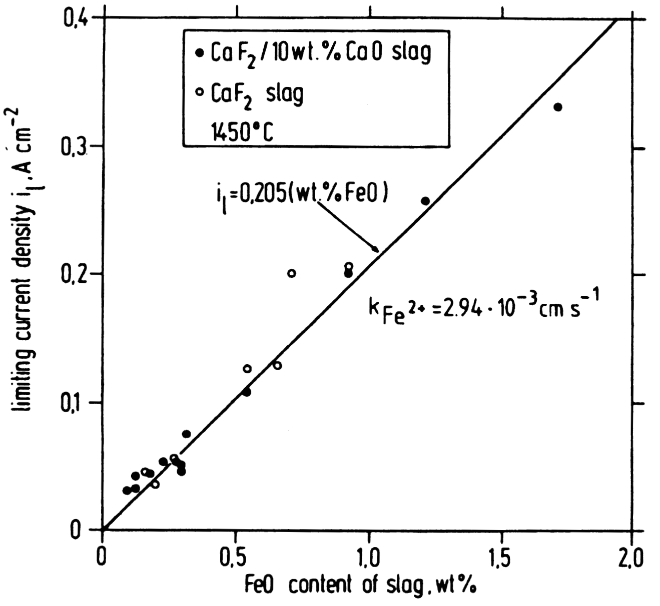

Figure 9. Limiting current density at iron/slag cathode as a function of FeO. The given value of the mass transfer coefficient is derived using Equation [11]

$$(\%FeO) = \frac{i(\alpha+1)}{k'(\alpha-1)} \qquad [12]$$

where

$$k' = \frac{2F\rho k_{Fe^{2+}}}{100M_{FeO}} \qquad [12a]$$

Hence, the FeO content of the slag is obtained from one measured pair of i, η_{AC} values.

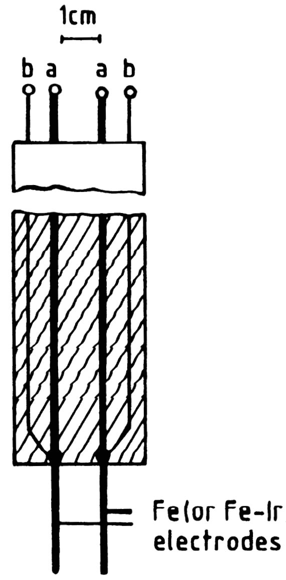

Figure 10. Probe with iron or iron-iridium electrodes

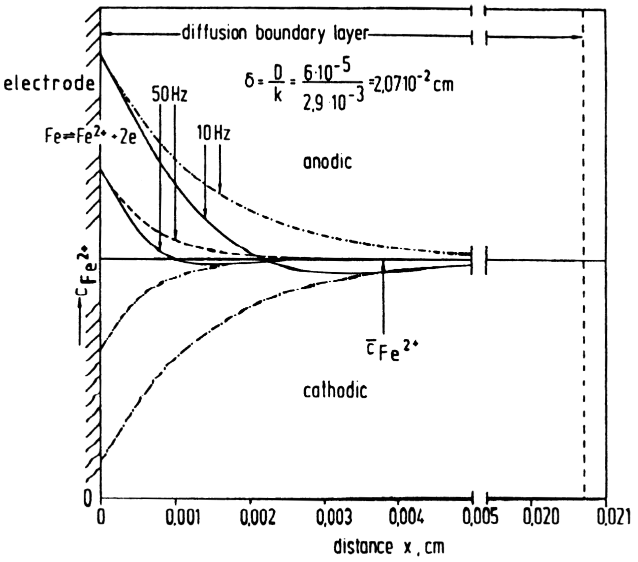

Figure 11. Penetration of Fe^{2+} concentration into the interior of the slag. The solid lines represent the concentration profile for the moment given by $\omega t=3\pi/4$. The dash-dot lines represent the maximum and minimum concentrations attained during the cycle. Nowack, Schwerdtfeger, and Krause[12]

Measurement with alternating current

The overpotential is again caused by Reactions [6]. But if alternating sinusoidal current is transferred between the iron (or iron-iridium) electrodes the iron concentration at the electrodes changes periodically. In the anodic half cycle of the current Fe^{2+} is added into the slag, and in the cathodic half cycle Fe^{2+} is discharged again, Figure 11. If the concentration changes are confined to regions within the boundary layers the concentration profile is obtained by the solution of Fick's second law. The theory is explained in texts on electrode kinetics[12,13]. The equation describing the relationship between voltage E and current density i is given by

$$E = \hat{\eta}\sin\left(\omega t - \frac{\pi}{4}\right) + \hat{i}aR_s\sin\omega t \qquad [13]$$

with

$$\hat{\eta} = \frac{RT\hat{i}}{2F^2\bar{c}_{Fe^{2+}}\sqrt{\omega D_{Fe^{2+}}}} \qquad [14]$$

where $\hat{\eta}$ and $\hat{i}$ are the amplitudes of overvoltage and current density, ω, is the angular frequency of the current, t time and $D_{Fe^{2+}}$ the diffusivity of the iron ions in the slag. Note that the overvoltage lags behind the ohmic voltage drop (or current) by a phase shift of $\pi/4$. Consequently, the amplitudes (or effective values) have to be added vectorially, viz.

$$\hat{E}^2 = \left(\hat{i}aR_s + \frac{\hat{\eta}}{\sqrt{2}}\right)^2 + \frac{\hat{\eta}^2}{2} \qquad [15]$$

From [15] and [14] one obtains

$$\left(\frac{\hat{E}}{a\hat{i}}\right)^2 - R_s^2 = \frac{4R_sK}{\sqrt{\omega}} + \frac{8K^2}{\omega} \qquad [16]$$

where

$$K = \frac{RT}{4F^2 a\hat{c}_{Fe^{2+}}\sqrt{2D_{Fe^{2+}}}}. \qquad [16a]$$

The experiments were carried out with the cell shown in Figure 5 using $CaF_2(FeO)$ and CaF_2-$CaO(FeO)$ slags. Figure 12 gives examples for the measured density-voltage relationship. Again the curves are seen to depend strongly on the FeO content. The theory can be tested by checking Equation [16]. That is, plotting $[(\hat{E}/a\hat{i})^2 - R_s^2]\omega$ against $\sqrt{\omega}$ should yield straight lines. From the slope and the intersection at the ordinate the numerical value of K can be derived. The test is performed in Figure 13. Thus, in order to determine the iron content in the slag, $\hat{E}$ and $\hat{i}$ have to be measured at a specified frequency ω (or several frequencies). Then K is obtained from Equation [16] and (%FeO) from Equation [16a]. In principle, again one pair of $\hat{E}$, $\hat{i}$ values suffices. The values of $D_{Fe^{2+}}$ and R_s depend on temperature and on the majority components of the slag, and are obtained with calibration experiments. Figure 14 shows the dependence of K on (%FeO) as evaluated from the data of the previous investigation[12].

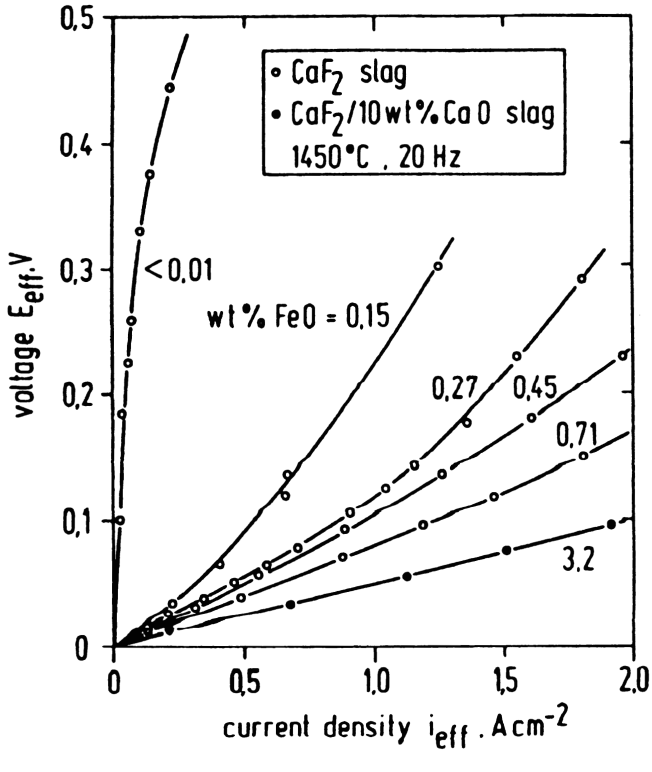

Figure 12. Influence of FeO content on relationship between current density and voltage at iron/slag electrode. Nowack, Schwerdtfeger, and Krause[12]

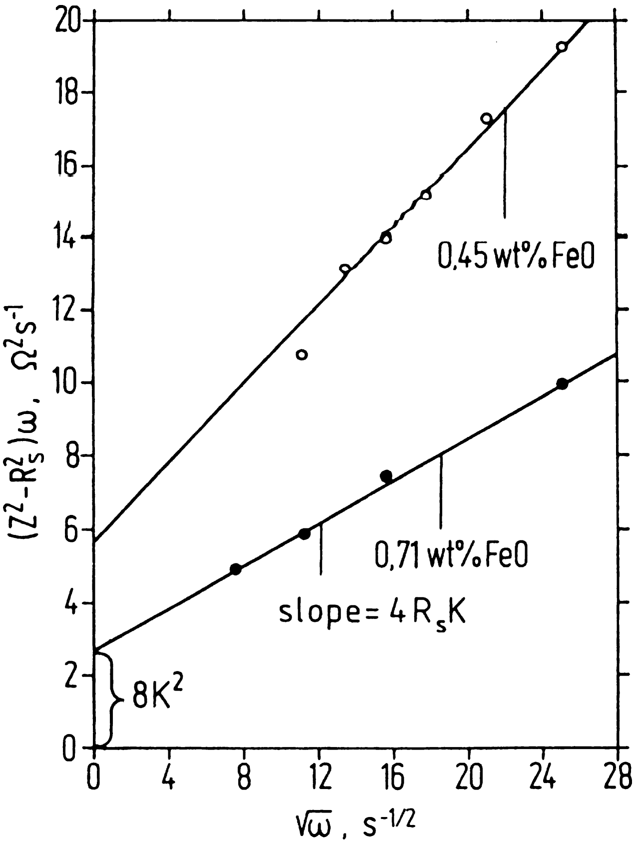

Figure 13. Plot of experimental data according to Equation [16]. Z is given by $\hat{E}/a\hat{i}$. Nowack, Schwerdtfeger, and Krause[12]

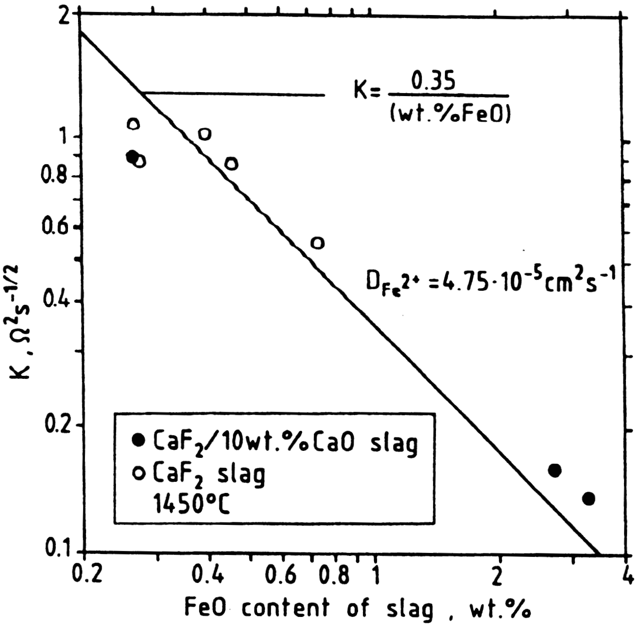

Figure 14. Influence of FeO content on K (Equation [16a]). K is evaluated from the data of the previous investigation[12]

Conclusions

The *in situ* determination of iron oxide content and of oxidation state Fe^{3+}/Fe^{2+} of steelmaking slags based on the measurement of electrokinetic properties and phenomena may be possible and may be more reliable than EMF measurements involving solid electrolytes. In the present paper it is proposed to utilize the strong dependence of electrical conductivity on FeO content on the slag for iron oxide determination. Also, current transfer phenomena at iron or iron-alloy electrodes as direct current overvoltage or alternating current impedance depend strongly on iron oxide content and could serve as indicators of iron oxide content.

The conductometric determination seems to be very suitable for slags with high iron oxide content, viz. BOF and EAF slags. The overvoltage measurements are sensitive at low iron oxide content and could be applied to reduced slags, viz. BOF and ladle slags. The probes would be rather simple. The electronic equipment to be used is standard in aqueous electrochemical testing. So, the measurement in total is also simple.

It is proposed to explore these alternative methods by more experimentation, both in the laboratory and in the steel plant. One aim would be to develop the high-melting iron alloys (Fe-Ir or others) with defined iron activity[14] constituting the suitable electrode metal. Reliable data of slag properties (electrical conductivity, mobility of ions) have to be used for converting the sensor signal to iron oxide content. Such data are scarce at present. So there is an initial handicap for application of the new methods.

However, this situation is not different from that thirty years ago when the EMF technique for soluble oxygen measurement in liquid steel became available. The necessary data (in this case, free energies of reference oxide metal mixtures and interaction coefficients of elements in liquid steel) were measured rather fast subsequently at many places, and this would also occur with the necessary electrokinetic data.

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