

THE EFFECT OF IRON OXIDE ON THE CHEMICAL DIFFUSIVITY OF OXYGEN IN SLAGS

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ABSTRACT

Chemical diffusion of oxygen in iron oxide containing slags was studied by oxidation of the melts contained in a 10 cm long capillary at temperatures in the range of 1350 to 1650 °C. The experiments were carried out under conditions where interferences from rate controlling steps other than diffusion in the melts were minimised. Depending on the iron oxide content and temperature of the melts, the values of diffusivity determined ranged from 5×10^{-5} to 8×10^{-3} cm²/s. For a given temperature, the diffusivity increased by two orders of magnitude as the iron oxide content was increased from 7 to 80 wt%. The activation energy determined was also strongly dependent on the iron oxide content and decreased from about 91 to 16 kcal/mol, with increasing total iron oxide content (7 to 80 wt%). The effect of basicity on the diffusivity of melts studied appears to be insignificant.

1. INTRODUCTION

In many pyrometallurgical processes the rate of mass transfer in molten slags is of some significance. Oxygen diffusion is a key step in a number of reaction sequences and knowledge on how fast it can diffuse in metallurgical slags is often sought. The presence of iron oxide, or in general transition metal oxides, can enhance the rate of transport of oxygen through a slag medium. Recent studies by Sasabe and Jikibi¹ highlighted the effect of iron oxide content on oxygen transport in slags. These researchers found that the permeability of oxygen through CaO-SiO₂-Al₂O₃ melts increased by several orders of magnitude as a small amount of iron oxide was added to the melts. Another study by Sasabe and Asamura² showed that the addition of a small amount of transition metal oxide, such as iron oxide, MnO or NiO to CaO-SiO₂ slags increased the rate of oxygen transport by up to 10 orders of magnitude. The strong effect of the iron oxide has been

attributed to the multi-valency of iron and to the ability of its oxides to alter the structure of metallurgical slags.

As a transition metal, iron exhibits multiple valency and its two highest oxidation states are commonly found together in most metallurgical slags. Thus development of an understanding of how iron oxide affects the diffusion of oxygen in slags is important and has been the subject of a number of investigations. The diffusion of oxygen in pure liquid iron oxide, as a limiting case has received some attention and interest in the past. Turkdogan and Grievson³ and later Mori and Suzuki⁴ attempted to determine the chemical diffusion of oxygen by oxidation/reduction of melts. However, according to an analysis by Belton⁵ these reaction rates were measured under the influence of other rate determining steps and the results do not reflect the actual magnitude of the diffusivity. Recently the present authors have studied the diffusion of oxygen in pure iron oxide and in high and low iron content slags by oxidation of slag contained in a capillary⁶⁻⁹. These measurements were carried out under conditions that minimised the limitations of previous work on liquid iron oxide. Results from these studies are presented here and comparison is made with recent data by Xie and Belton on diffusivity of iron in low iron containing slags^{10,11}.

2. EXPERIMENTAL

The experimental technique used in this work has been described in some detail elsewhere^{6,9}. Master slags were prepared by mixing appropriate amounts of high purity Fe₂O₃, CaCO₃ and SiO₂. The mixtures were then pre-melted in a Pt-Rh crucible, quenched, pulverized and remelted to ensure good homogeneity. The water quenched product from the pre-melted slag was then pre-reduced in an atmosphere of CO-CO₂ to ensure that the starting composition of the samples for the diffusion runs were close to the required equilibrium composition.

The apparatus used for the diffusion runs consisted of a vertical tube furnace with MoSi₂ resistance heating and a gas purification and mixing unit. The furnace tube was fitted with appropriately placed thermal shields to obtain a hot zone of about 10 cm long for the experiments. The temperature was monitored with a Pt-6%Rh/Pt-30%Rh thermocouple, which was in contact with the bottom of the crucible. Slag samples were held in a platinum lined magnesium capillary crucible (7 mm ID and 100 mm high) which was suspended from the bottom of an alumina gas delivery tube. The gas delivery tube had an alumina nozzle of 3 mm ID and the tip of the nozzle was kept about 20 mm above the surface of the melt.

Each run involved equilibrating a 5 to 6 cm deep melt in the crucible under a controlled atmosphere, prior to oxidation by pure oxygen for a pre-determined period. The crucible containing the melt was then quickly withdrawn

from the furnace and water quenched. The solidified rod of the slag was sectioned into several discs and the discs were analysed for total and ferrous iron contents by titration technique and for other elements by the ICP technique. After the analysis, concentration profiles of ferrous and ferric iron were determined. These profiles formed the base for further analysis to extract diffusion data.

3. RESULTS AND DISCUSSION

The diffusion experiments were carried out for iron oxide, calcium ferrite, iron silicate and low iron oxide calcium silicate melts. The results of the studies in each system include equilibrium studies and diffusivity measurements.

Using pre-reduced powder, a series of equilibrium measurements were carried out in which a sample of 5 to 8 grams of slag was equilibrated in CO₂-CO mixtures of different compositions, air or Ar-5 vol% O₂. The as-quenched slag sample had a generally uniform shrinkage hole at the centre. The directly-measured length of the sample was in close agreement with that calculated from the sample weight and the nominal cross-section of the crucible and the published density data.¹²⁻¹⁵

Figure 1 shows typical results obtained for the fraction of ferrous iron over the total iron (Fe²⁺/Fe_t) for each section versus the distance from the surface of the melt. It was found that the procedure used gave homogeneous slag samples with compositions very close to the equilibrium compositions with the gas phase within about 2 to 3 hours.

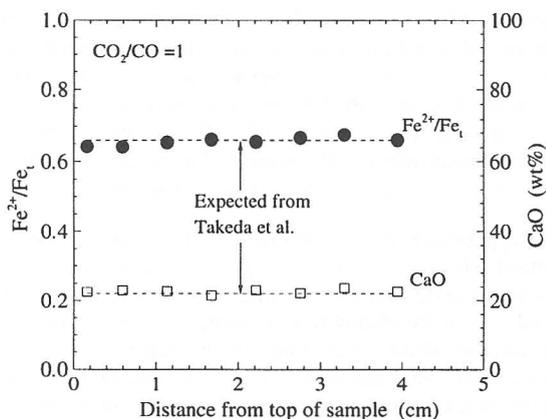


Figure 1: Concentration profiles of the quenched 20 wt% CaO calcium ferrite slag sample pre-equilibrated in CO₂-50 vol% CO at 1350 °C. Dotted line represents equilibrium according to Takeda et al.¹⁶

The equilibrium attained within the depth of the samples showed good agreement with the data reported in

the literature. In the pure iron oxide system equilibrium data were in agreement with the data of Darken and Gurry¹⁶, in the calcium ferrite system the data were in agreement with those of Takeda et al.¹⁷ and in iron silicate with a collection of equilibrium data by various workers^{9, 14, 19, 20}. In the case of low iron oxide containing calcium-silicate slags, due to lack of equilibrium data, some additional equilibrium experiments using shallow melts were carried out by the present authors. The compositions in deep melts were then compared with the determined equilibrium data by the present workers as well as with those by Larson and Chipman¹⁹ and Engell and Vygen¹⁴.

For diffusion experiments after equilibration had been achieved, the flowing gas was changed to oxygen for 3 to 5 minutes for high iron contents slags and for more than 1 hour for low iron content slags. Concentration profiles were obtained by plotting the slag composition, C_x, in terms of Fe²⁺/Fe_t versus the distance, x. Figure 2 shows the concentration profiles in a calcium ferrite system.

As illustrated by the profiles in Figure 2, there are considerable changes in composition across the slag samples, with Fe²⁺/Fe_t varying from the pre-equilibrated value of about 0.7 to the surface value of less than 0.1. In all of the systems, the smoothed curves extended to a point at the surface corresponding to the expected equilibrium ratio of ferrous to total iron with oxygen partial pressure of 1 atm. It is worth noting that the oxidation state of the melts at distances of greater than 3 cm from the surface remained essentially the same as the starting equilibrium composition, according to both the present and the literature equilibrium data.

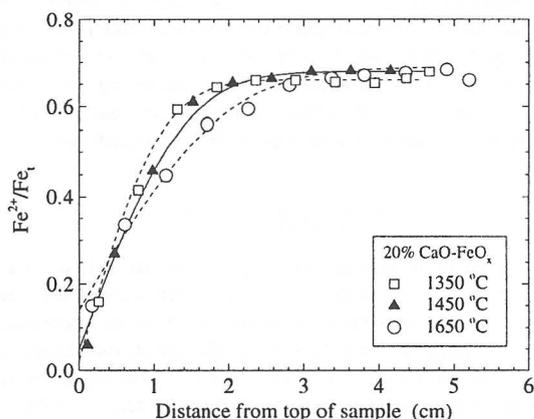


Figure 2: Concentration profiles of Fe²⁺/Fe_t in the samples pre-equilibrated in CO₂ - 50 vol% CO and nominal content of 20 wt% CaO oxidised for 3 minutes in oxygen at 1350, 1450 and 1650 °C.

In the study^{7,9} of inter-diffusivity in calcium silicate slags containing about 7 wt% total iron oxide, the equilibrated melts were also oxidised by pure oxygen. The concentration profiles for different species, obtained in one

of the diffusion experiments are shown in Figure 3. This plot shows that after 90 minutes of oxidation of an equilibrated sample the SiO₂ and CaO concentration remained uniform throughout the sample, while the oxidation state of the melt changed considerably from top to the bottom of the sample.

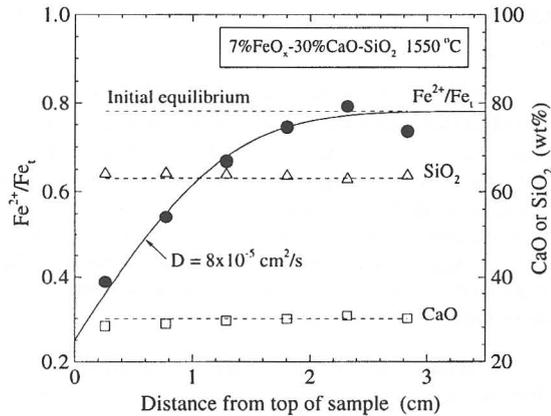


Figure 3: Concentration profile of the quenched low iron slag sample, which was pre-equilibrated in CO₂-20 vol% CO and oxidised by oxygen for about 90 minutes.

When oxygen was for oxidation, the surface composition of the samples was found to be close to the expected equilibrium composition of the slag with pure oxygen. In these experiments the surface composition did not change with oxidation period. Hence, it was assumed that the surface composition during the reaction was constant and in equilibrium with the oxygen gas.

For the determination of diffusivity, the solution of Fick's second law for semi-infinite media;

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \quad \dots [1]$$

with the boundary conditions;

$$C(x, 0) = C_0 \quad 0 < x < \infty$$

$$C(0, t) = C_s \quad t > 0$$

$$C(\infty, t) = C_0 \quad t > 0$$

was applied. In the above equation C_x is the concentration of diffusing species inside the melt at a distance x from the gas-melt interface. C_s is the constant concentration of diffusing species at the surface and C₀ is the uniform concentration of diffusing species throughout the sample at the start of diffusion. To fit the experimentally obtained concentration profiles, calculated values of x/\sqrt{Dt} were plotted against distance, x. The slope of the plot was used to calculate the value of diffusivity. As an example, the

data plotted in Figure 3 were treated according to the above equation and the result are shown in Figure 4.

The curves fitting the concentration profiles, in Figures 2 and 3, have been drawn by applying Equation 1 and the deduced values of D according to the above treatment.

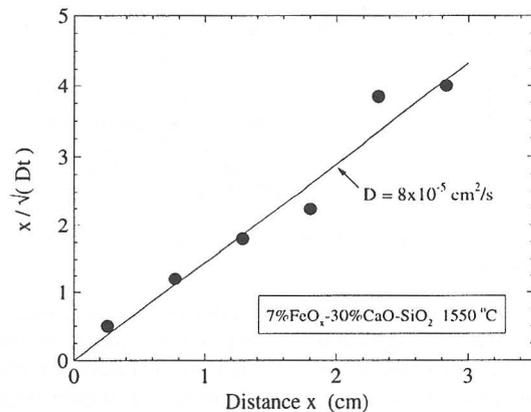


Figure 4: Plot of x/\sqrt{Dt} calculated from the concentration ratio, $(C_x - C_0)/(C_s - C_0)$, versus distance, x, for the experimental results shown in Figure 3. The slope of the line gives D as $8 \times 10^{-5} \text{ cm}^2/\text{s}$.

The determined average chemical diffusivity of oxygen in pure iron oxide was about $3 \times 10^{-3} \text{ cm}^2/\text{s}$ with Fe²⁺/Fe_t of 0.25 to 0.77 at 1615 °C. Choosing iron oxide as a reference system, the effect of additives or slag basicity on diffusivity was studied by adding up to 30 wt% CaO or 15 wt% SiO₂ to iron oxide. Calcium silicate slags with 7 wt% total iron oxide and at two different basicities (CaO/SiO₂ = 0.54 and 1) were also studied. In high iron content systems (liquid calcium ferrite and iron silicate) the magnitude of diffusivity remained essentially the same and the diffusivity values were in the range of $2 \times 10^{-3} \text{ cm}^2/\text{s}$ and $8 \times 10^{-3} \text{ cm}^2/\text{s}$ for the temperature range of 1350 to 1650 °C. These values are considerably greater than previously reported by Turkdogan and Grieveson for liquid iron oxides¹². In calcium silicate melts containing about 7 wt% total iron oxide, the determined values of diffusivity were relatively low, $5 \times 10^{-5} \text{ cm}^2/\text{s}$ to $2 \times 10^{-4} \text{ cm}^2/\text{s}$ in the temperature range of 1500 to 1600 °C. The diffusivity in these slags is one to two orders of magnitude smaller than in high iron content slags, indicating a strong effect of iron content of slags on diffusivity. It was also found that the diffusivity is not strongly dependent on the basicity of slags. The diffusivity data obtained for both high and low iron content slags are compared in Figure 5.

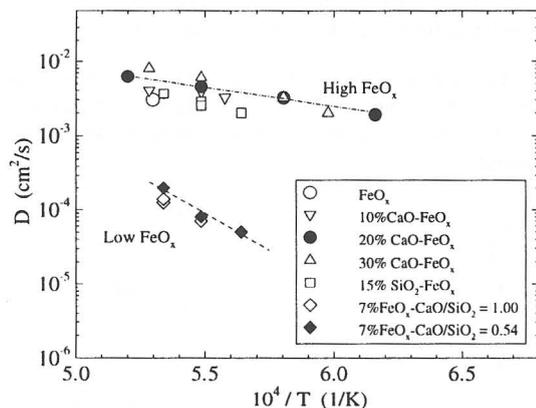


Figure 5: Comparison of the measured diffusivity of oxygen in melts.

In the present work, the diffusion runs covered a wide range of oxidation state. In pure iron oxide melts the Fe^{2+}/Fe_t values ranged from 0.25 to 0.77. In calcium ferrite melts it ranged from 0.05 to 0.7 and in iron-silicate from 0.25 to 0.82. In order to investigate the effect of oxidation state on diffusivity, several experiments were carried out within narrower ranges of oxidation states. In the iron oxide melts, three experiments were carried out at higher oxidation states by pre-equilibrating the melts with CO_2 , Ar-5 vol% O_2 and air and subsequently oxidising in pure oxygen. The calculated diffusivity from samples with the ranges of $Fe^{2+}/Fe_t=0.47$ to 0.25, 0.38 to 0.25 and 0.30 to 0.25 was $3.0 \times 10^{-3} \text{ cm}^2/\text{s}$, $4.5 \times 10^{-3} \text{ cm}^2/\text{s}$ and $3.5 \times 10^{-3} \text{ cm}^2/\text{s}$, respectively. These values are in close agreement with the average diffusivity ($3.0 \times 10^{-3} \text{ cm}^2/\text{s}$) for the overall range ($Fe^{2+}/Fe_t=0.77$ to 0.25). Experiments aimed at a more reducing range of concentration were also performed by oxidation of the melts with gases other than pure oxygen. The diffusivity determined from different models⁸ for variable surface concentrations showed that there is no significant difference in diffusivity for the range of oxidation of $Fe^{2+}/Fe_t=0.77$ to 0.72 ($2.9 \times 10^{-3} \text{ cm}^2/\text{s}$), $Fe^{2+}/Fe_t=0.77$ to 0.62 ($3.0 \times 10^{-3} \text{ cm}^2/\text{s}$) and overall range $Fe^{2+}/Fe_t=0.77$ to 0.25 ($3.0 \times 10^{-3} \text{ cm}^2/\text{s}$).

For 20 wt% CaO- FeO_x melts at 1450 °C, a range of initial oxidation state of the melts was established by using CO_2 -50 vol% CO, CO_2 -4.8% CO and pure CO_2 for pre-equilibrating the melts. These gases produced progressively more oxidising conditions and hence lower initial concentration of Fe^{2+}/Fe_t , which covered a range from 0.25 to 0.68. The derived diffusivity at 1450 °C for the composition range of $Fe^{2+}/Fe_t = 0.05$ to 0.2, 0.05 to 0.37 and 0.05 to 0.68 were about $4.5 \times 10^{-3} \text{ cm}^2/\text{s}$, 3.7×10^{-3}

⁸ To account for the differences between the surface and equilibrium Fe^{2+}/Fe_t in runs, where the oxidant was not pure oxygen, application of diffusion coupled models which account for variation in the surface concentration during the diffusion process were developed and used.⁹

cm^2/s and $3.2 \times 10^{-3} \text{ cm}^2/\text{s}$, respectively. These values show only a weak dependence on the oxidation state of the melts. For 15 wt% SiO_2 in iron silicate slag, the diffusivity obtained at 1550 °C for the concentrations of $Fe^{2+}/Fe_t = 0.255$ to 0.815, 0.815 to 0.7 and 0.255 to 0.57 were about $2.8 \times 10^{-3} \text{ cm}^2/\text{s}$, $3.0 \times 10^{-3} \text{ cm}^2/\text{s}$ and $2.5 \times 10^{-3} \text{ cm}^2/\text{s}$, respectively. In this system the apparent small variation with the oxidation state of the melts is also insignificant with respect to the experimental uncertainty in the data.

In each system, the narrow concentration ranges were selected so that both reducing and oxidation sections of the overall range could be examined. The determined diffusivity in narrow ranges of concentration showed good agreement with the average diffusivity determined for overall ranges within experimental uncertainty. These findings suggest that there may only be a rather mild dependence of the chemical diffusivity of oxygen on the state of oxidation of the slag.

To acquire information on the activation energy of diffusion, experiments were carried out at different temperatures for fixed slag compositions. The temperature dependence of diffusivity was deduced from these results.

Figure 2 shows the concentration profiles obtained at 1350, 1450 and 1650 °C for nominal content of 20 wt% CaO in calcium ferrite melts oxidised for 3 minutes in oxygen. There seems to be an effect of temperature on the oxygen concentration profile in this slag. In general, in slags with high iron content, temperature dependence of concentration profiles is observed, but is not pronounced.

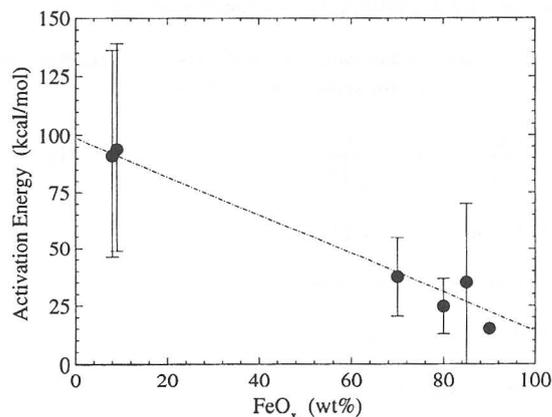


Figure 6: Variation of activation energy for chemical diffusivity of oxygen with iron oxide content of slags.

According to the results shown in Figure 5, the variation of logarithm of diffusivity values with the reciprocal of temperature indicates an Arrhenius type dependence. The deduced activation energy for each system was obtained from the slope of the respective line

in Figure 5. The variation of activation energy with iron content of slag is shown in Figure 6. The uncertainty in the activation energy is based on 30% uncertainty in determined diffusivities. This Figure shows that the activation energy increases as the iron content of slag decreases.

It appears that the variation of activation energy with iron content could be linear. However, to confirm the validity of this finding, some studies need to be performed for intermediate composition ranges of 10 to 70 wt% iron oxide. Through extrapolation of data shown in Figure 6, the activation energy for pure iron oxide should be about 10 kcal/mol (41.8 kJ/mol). The relatively large variation of the activation energy from 16 to 91 kcal/mol (67 to 380 kJ/mol) for high and low iron content of slags, respectively, lead one to expect that different mechanisms are operating for diffusion of oxygen in different slags.

Recently Xie and Belton have studied the kinetics of dissolution of iron from a rotating disc of iron into slags containing 41%CaO-38%SiO₂-21%Al₂O₃ and 3 to 9 wt% Fe₂O₃ at 1360 °C^{10,11}. In this study the derived mass transfer coefficients were found to be a function of the rotation speed and average total iron concentration and independent of oxidation state of slags. The chemical diffusivity of the iron species in this study was estimated to have a linear variation with the total iron content of slag as shown in Figure 7.

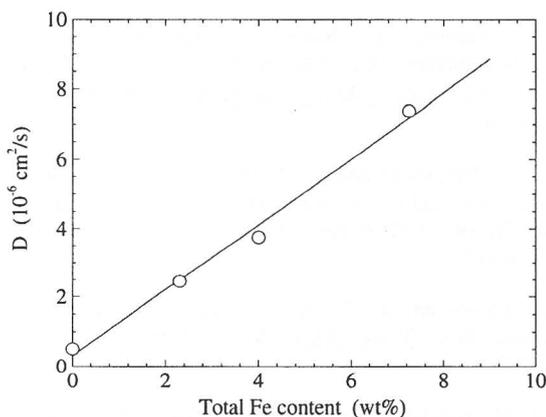


Figure 7: Deduced values of the diffusivity of iron as a function of the average total iron concentrations within the diffusion boundary, after Xie and Belton.^{10,11}

Figure 8 shows the values of diffusivities for different low iron oxide content calcium silicate slags versus temperature in the present work. The estimated value of diffusivity for 5 wt % total iron content slag at 1360 °C from the work of Xie and Belton is also shown in this Figure. Apparently this value is of similar magnitude to the extrapolated value from the present work. This

agreement between inter-diffusivities derived from two different measurement methods is significant. While the imposed gradient differs in the two techniques (oxygen for oxidation method and iron for rotating disc) the inter-diffusivity appears to be the same. This agreement could be an indication that the same diffusion mechanism governs both systems.

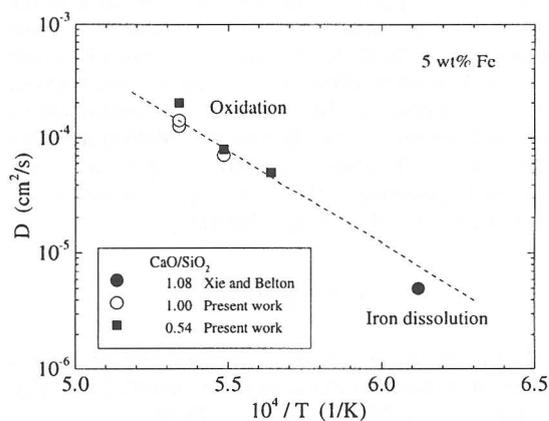


Figure 8: Comparison of inter-diffusivity in low iron content liquid slags.

4. CONCLUSIONS

Chemical diffusion of oxygen in slags containing iron oxide was studied through oxidation of deep capillaries containing melts by oxygen, over a temperature range of 1350 to 1650 °C. The results obtained show that:

- When oxygen was used for the oxidation reaction, interference from rate determining steps, other than diffusion in melts, is minimised and the oxidation state of melt at the gas-slag interface is close to the expected equilibrium between gas and slag.
- Depending on the iron oxide content and temperature of the melts, the determined values of diffusivity ranges from 5×10^{-5} to 8×10^{-3} cm²/s.
- For a given temperature, the diffusion coefficient increased by about two orders of magnitude as the iron oxide content of the melts was increased from 7 to 80 wt%.
- The determined activation energy for oxygen diffusion in slags decreased from about 91 kcal/mol to 16 kcal/mol as the iron oxide content was increased from 7 to 80 wt%, respectively.
- There did not seem to be a strong dependence of the chemical diffusivity of oxygen on the oxidation state of slags, within the range covered.

- In low iron oxide containing calcium silicate based slags, the determined diffusivity of oxygen is in good agreement with the diffusivity of iron deduced from dissolution of iron in slags.

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