Diffusion of Transition Metals in Slags

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Abstract

The chemical diffusivity of manganese has been determined over a range of slag compositions. Diffusion coefficients have been obtained using the slag reservoir method, where a capillary of silica-lime-alumina slag is brought into contact with a reservoir of a similar slag containing an amount of diffusing species. An Electron Microprobe and X-Ray Microprobe were used to obtain slag compositions at points along the length of the capillary, at 0.10mm intervals. Diffusivities of manganese followed expected trends. Increasing temperature and increasing slag basicity resulted in increasing diffusivity. Diffusivities were in the order of 10^{-6} cm^{2}s^{-1}. The effect of fluorine addition was also investigated. Firstly as a uniform concentration, with CaF_2 present in both the capillary and the reservoir, and secondly, as a concentration gradient, with CaF_2 present in only the reservoir. In both cases, diffusivities were increased markedly over the corresponding experiment without fluorine addition. A comparison between the two showed that diffusivities were greater with the fluorine concentration gradient. This indicates the fluorine is acting to increase diffusivities by i) lowering slag viscosity and ii) providing electrical neutrality to facilitate the transport of the Mn^{2+} ions.

Introduction

The study of diffusion in slags is an important area of metallurgical research. Slags act as a repository for impurities that must be drawn from the metal, and the rate at which this removal occurs is a measure of the overall efficiency of the smelting process. Fruehan and Bhagavatula [1] stated the kinetics of ferromanganese smelting to be dependent on slag phase mass transport. As such, studies of diffusion of metallic species through slags gives a good indication of overall process kinetics.

This project has focused on the diffusion behaviour of manganese and iron in silicate slags. Coefficients of diffusion have been determined with changing slag basicity, temperature and in presence of fluoride.

Microprobe Analysis

Radiotracer methods, first published by Towers *et al.* [2] have the advantage of being relatively cheap and simple, but there are a number of disadvantages, for example, the obvious health risks and large errors inherent in determining distance and precise levels of radioactivity. Generally the method accuracy is only slightly better than one order of magnitude

A recent development in instrumental analysis by Rontgenalytik Messtechnik GmbH, Germany, is the μ-XRF Spectrometer, reported by Haschke *et al.* [3]. This involves the use of x-ray excitation focused with poly-capillary lenses to a diameter of around $50\mu m^2$. Induced fluorescence is measured with an energy dispersive detector. This instrument has been used to determine multi-element slag concentration profiles, to determine coefficients of diffusion of transition metals.

Experimental Methods

CaO-SiO_2-Al_2O_3 slags were prepared from analytical grade reagents. The mixture was roasted at 1000°C for 24 hours and fused under vacuum for degassing and filled into 2 or 3mm internal diameter platinum capillaries. Slag containing the diffusing species was prepared with the same concentration of oxides, with 10% manganese dioxide added. This mixture was roasted at 1000°C for 24 hours then fused under vacuum and ground. Manganese containing slag powders were placed in a platinum crucible. Capillaries were suspended into the powder so the open end was immersed. The crucible was placed into a the cool zone of a tube furnace under an argon atmosphere at 1520°C. To commence diffusion, the crucible was raised , which rapidly heated to 1500±5°C. Diffusion time started when the crucible reached 1450°C. After liquidus temperature was reached, the slag capillary was in contact with a reservoir containing the diffusing species. This method contains several assumptions:

i)   Diffusion inside the capillary is 'single dimensional'
ii)   There are no wall-effects due to the capillary effect. This capillary size is standard in the diffusion experiments mentioned above.
iii)   The concentration of the reservoir at the point adjacent to the capillary opening is constant.
iv)   There are no convection currents in the capillary. This is overcome by maintaining a temperature gradient.

After the required time had expired, the crucible was lowered to the furnace cool zone, lowering the temperature to around 1000°C, well below slag liquidus temperature, in around 3

minutes. In a 300 minute diffusion experiment, this time can be seen as negligible. Once cooled, the capillaries were mounted in a 1in. diameter resin block, and polished to reveal a continuous longitudinal cross section of slag. The EMP or μ-XRF instruments were used to give a concentration profile of all elements at 0.1mm intervals along the length of the capillary. Probe operating conditions are shown in Table 1.

Coefficients of diffusion were determined by a non-linear fitting routing using the relevant solution of Fick's Second Law:

$$C = C_0 \, erfc \, \frac{x}{2\sqrt{Dt}}$$ (1)

where C is the concentration at any distance x (cm) along the capillary, C_0 is the concentration at the interface where $x = 0$, t is time (s) and D is the coefficient of diffusion (cm^2s^{-1}). The routine finds D and estimates where $x = 0$.

Effect of Slag Basicity on Coefficient of Diffusion
The coefficient of diffusion of manganese was determined in three slag compositions, with 10% MnO_2 in the reservoir at 1500±5°C. Results are outlined in Table 2. Slag basicities are calculated using the optical basicity method outlined in Sommerville and Yang [4]. *Figure 1* shows the concentration profiles of manganese. Fit of the experimental data to the theoretical model is excellent, with standard errors in the order of 2%. Some deviation occurs in the region of the interface. This is more pronounced as the distance diffused is decreased. This could be explained by a departure from the assumption regarding concentration at the interface. Diffusion of manganese into the capillary must be accompanied by diffusion in the opposite direction of other slag components. This will in turn dilute the reservoir slag in the region of the slag-slag interface.

Effect of Calcium Fluoride Addition
Calcium fluoride, as fluorspar, is often used as a fluxing agent in smelting processes to drastically lower liquidus temperature and slag viscosity [5]. Figure 2 shows a comparison of concentration gradients of manganese in the same slag under identical conditions. A uniform concentration of fluoride created by addition of 1% calcium fluoride to both the capillary and reservoir approximately doubles the coefficient of diffusion (Table 2). This can be most likely attributed to the network modifying nature of fluoride, which decreases slag viscosity and decreases restriction to mass transfer. This effect was seen with three slag compositions. Anion concentration gradients can increase diffusivity of cations along a concentration gradient through charge balancing. A fluoride gradient was created by addition of fluoride to the reservoir only. This had the effect of increasing the coefficient of diffusion further. Diffusion of a charged species requires either simultaneous diffusion of an oppositely charged species or counter-diffusion of an like-charged species. Fluoride provides a mobile negative charge with little network interaction.

Effect of Manganese Concentration
Three concentrations of manganese (5%, 10% and 20%) were diffused through an identical slag at 1500°C. Concentration profiles are shown in Figure 3. It can be seen that the larger manganese oxide concentration led to an increase in coefficient of diffusion (see Table 2). Fick's second law states that under ideal conditions diffusion behaviour is independent of

concentration. In a real slag system, this will not be the case as the diffusing species alters the nature of the medium. Manganese oxide is a basic oxide. The optical basicity coefficient derived from average electron density is 0.95 [6], compared with 1.00 for calcium oxide. As a result, an increased concentration of manganese oxide at any point within the silica rich slag will result in increased depolymerisation. It has been shown that coefficients of diffusion of manganese increase as the extent of depolymerisation is increased.

Diffusion of Calcium, Silicon and Aluminium

Determining concentration of all elements present at all points along the capillary axis enables determination of coefficients of diffusion of silicon, calcium and aluminium in a direction counter to that of manganese. Diffusion out of the capillary follows a variation on Fick's second law, eqn. 2:

$$C = C_{max} - (C_{max} - C_0) erfc \frac{x}{2\sqrt{Dt}} \tag{2}$$

Such values are indicative of the nature of bonding within the liquid slag. Diffusion of manganese into the capillary must be accompanied by diffusion of the opposite direction of other slag components. The extent of this diffusion is indicative of the network forming/modifying properties of the particular component. Figure 4 shows the concentration profile of silicon, aluminium and calcium after diffusion of manganese into the capillary. Scatter due to surface imperfections becomes more pronounced in as atomic number decreases. Coefficients of diffusion for each are shown in Table 2. Values of Λ_{th}, the optical basicity coefficient, are taken from Mills and Sridhar [6].   Such a correlation between D and Λ_{th} has been seen with a variety of experimental parameters.

Discussion

Previous studies [7,8] using radiotracers have shown iron to have a coefficient of diffusion around an order of magnitude greater than non-transition metals such as calcium and silicon. This has been explained in terms of electrical conductivity: the partially filled d orbital enables conduction of electrical charge to facilitate the necessary electrical neutrality that accompanies diffusion of a charged species. Such behaviour has not been seen in this project. Coefficients of diffusion have been found to be approximately the same as those of non-transition metals reported earlier. As no diffusion data on manganese has been available previously, it would be premature to give a definitive explanation for this.   A study of diffusion of iron with this method would provide an interesting comparison.

Experimental results involving fluoride addition suggest the diffusion rate is enhanced through two means. Firstly, through the decrease in slag viscosity upon fluoride addition. This effect has been shown in previous studies. Secondly, as the fluoride gradient further increased the coefficient of diffusion, through electrical neutrality. The fluoride provides a mobile negative charge to maintain charge balance as manganese ions diffuse through the slag, thus acting as a driving force for the diffusion.

Microprobe analysis enables analysis of the diffusion behaviour of all slag components present, which can provide more detailed information of the slag structure than previously. The coefficients of diffusion of calcium, aluminium and silicon support existing knowledge on the network forming/modifying properties of each. Correlation was seen between the

coefficient of diffusion and optical basicity coefficient and slag viscosity data shown in Turkdogan [9].

Conclusions

The x-ray microprobe employed in this study is a very valuable tool for slag analysis, enabling detailed determination of concentration profiles. This allows determination of coefficients of diffusion to a greater degree of accuracy than before. Manganese diffusion behaviour followed the trends found with other metals. Although results for iron found previously suggest transition metals have coefficients of diffusion an order of magnitude greater than other metals, results obtained for manganese do not support that. Further study of diffusion of iron with this method may help clarify this discrepancy.

Acknowledgments

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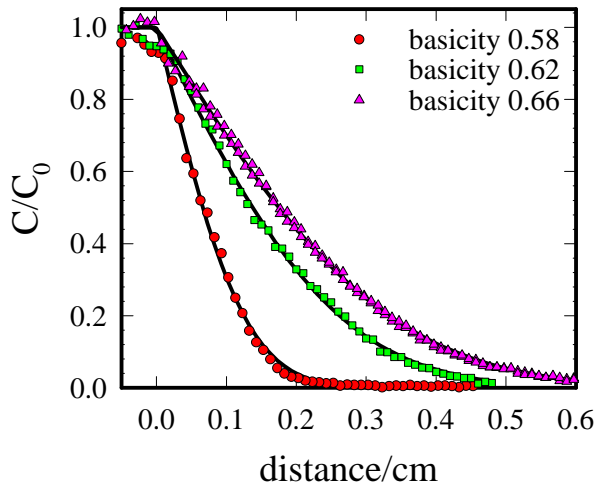
Figure 1
Relative concentration profiles of
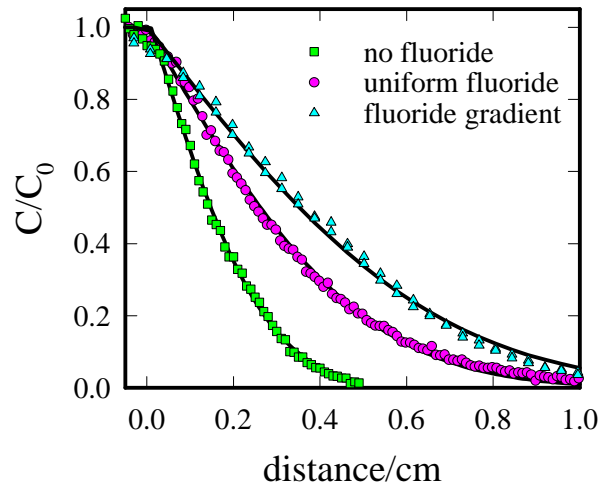manganese in CaO-SiO$_2$-Al$_2$O$_3$ slags

Figure 2
Relative concentration profiles of
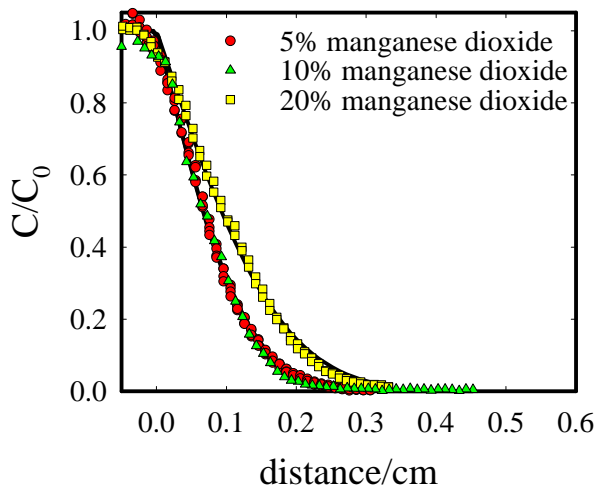manganese with fluoride addition

Figure 3
Relative concentration profiles of
manganese with changing manganese
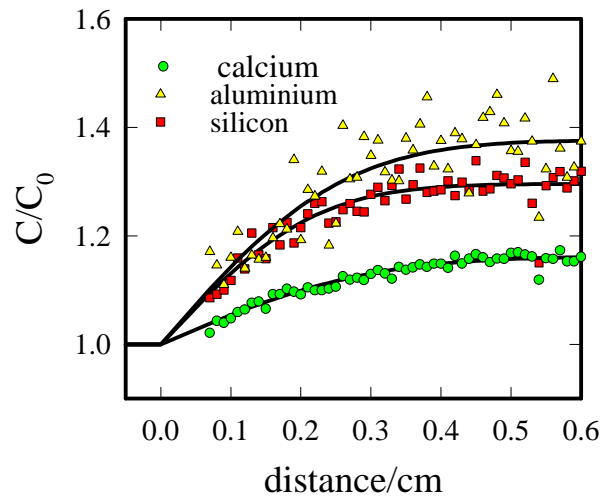reservoir concentration

Figure 4
Concentration profiles of calcium, silicon
and aluminium after diffusion of
manganese

Table 1 *Operating conditions of the μ-xrf spectrometer*

Exciting Voltage	40kV
Tube Current	70μA
Beam Diameter	50μm
Measuring Time	10s
Elements Detected	Fluorine and heavier
Detection Limits	10^{-2} %

Table 2 *Coefficients of diffusion at 1500°C for various experimental conditions*

Element	Slag Basicity	Conditions	D/cm^2s^{-1}
Mn	0.66	10% MnO_2	1.8×10^{-6}
Mn	0.62	10% MnO_2	1.2×10^{-6}
Mn	0.58	10% MnO_2	0.3×10^{-6}
Mn	0.66	No fluoride	1.8×10^{-6}
Mn	0.66	Uniform fluoride	4.2×10^{-6}
Mn	0.66	Fluoride gradient	7.1×10^{-6}
Mn	0.58	5% MnO_2	0.3×10^{-6}
Mn	0.58	10% MnO_2	0.3×10^{-6}
Mn	0.58	20% MnO_2	0.5×10^{-6}
Ca	0.66	$\Lambda = 1.00$	1.5×10^{-6}
Al	0.66	$\Lambda = 0.60$	1.0×10^{-6}
Si	0.66	$\Lambda = 0.48$	0.8×10^{-6}