Introduction

Since the paper by Towers et al. on the diffusion of Ca$^{2+}$ in molten CaO-SiO$_2$ slags, many studies have been devoted to the diffusion of ionic and molecular species through molten slags and glasses. However, many aspects of this field of study are still unexamined. This project aims to enhance current knowledge by providing a comprehensive understanding of the diffusion of metals cations (including transition metals) and silicon (as silicate anions) in multi-component systems.

Tracer studies are limited in that they apply only to the limiting case where the concentration gradient of all other species is zero. Once a concentration gradient of a second species is introduced, cross-effects from one species impart a flux on other diffusing species, causing a departure from the ideal tracer diffusivity to multi-component diffusivity. As industrial smelting systems are complex, with multiple species and multiple concentration gradients, evaluation of the cross-effects between slag components is necessary.

This project aims to investigate the interactions between ionic species in molten slags, and to develop a model to predict the diffusivity of a species in a multi-component system.

Diffusion method

The semi-infinite capillary method was employed. This method has been presented previously. Capillaries were mounted in resin and polished to reveal a longitudinal cross section. The concentrations of each species were measured along the length of the capillary using electron or X-ray microprobes.

Figure 1 shows a sample 5-component diffusion experiment, in which manganese, iron, calcium and silicon are the diffusing species. Equation [1] gives the concentration profile of each element:

\[ \frac{C - C_s}{C_o - C_s} = \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \]

where $C_s$ is the crucible concentration, $C_o$ is the initial capillary concentration, $x$ is distance from the capillary/crucible interface, $C$ is the concentration at any point $x$ along the dimension of diffusion, $t$ is time and $D$ is the coefficient of diffusion.

The following assumptions are made:

• Diffusion is single-dimensional
• There are no wall effects. This was verified by determining concentrations across the capillary
• The concentration at the crucible/capillary interface is constant
• There are no convection currents in the capillary. This is achieved through maintaining a temperature gradient, and placing the densest slag in the capillary.

The ‘effective diffusion coefficient’ for each diffusing species was determined by applying Equation [1] to the experimental data using a non-linear fitting routine. The flux of each species was calculated using the effective diffusion coefficient and Fick’s First Law.

Calculation of predictive models

The following diffusion experiments were conducted:

• Three component (diffusion of Mn-Fe, Mn-Ca, Mn-Si)
• Four component (diffusion of Mn-Ca-Si)
• Five-component (diffusion of Mn-Fe-Ca-Si).

Experiments were conducted with varying concentration gradients. The effective binary diffusivity, and subsequently the flux, was calculated for each diffusing species.

Multi-component diffusion coefficients, $D_{ij}$, were calculated according to Equation [2]
where $J_i$ is the flux of species $i$, $N$ is the number of diffusing species, $D_{ij}$ is the flux of species $i$ induced by the concentration gradient in species $j$. The ferrous 3-component system has a relatively high electrical conductivity, meaning regions of electric charge will not develop as readily, reducing cross effects. It is expected that iron and manganese will have very similar diffusion properties, as both have very similar chemical and physical properties. If this is the case, increasing the respective concentration gradients by an equal amount should not increase the flux ratio between the two. Effective diffusivities of manganese and iron in 3-component systems are equal to the values of $D_{MnMn}$ and $D_{FeFe}$ respectively for any slag with an equivalent basicity.

3-Component experiments involving diffusion of calcium and manganese in a non-ferrous slag reveal the magnitude of the cross-effect induced by the calcium concentration gradient on the flux of manganese. $D_{CaMn}$ and $D_{MnCa}$ are small compared to experimental error, and are probably not significant when other greater cross-effects are considered.

Cross-effects will be negligible in the Ca-Mn system. It is reasonable to assume that the cross-effect of calcium on manganese will be approximately equal to the cross-effect of manganese on calcium, as both species are discrete cations of similar size with a 2+ charge (although manganese has a small proportion of the 3+ state, the small size of the cross-effect and errors involved render this irrelevant). Therefore $D_{CaMn} = D_{MnCa}$.

As cross-effects between cations are negligible, only the Si-(Mn/Ca/Fe) cross-effects need to be evaluated for a predictive model. This is achieved by evaluating the change in flux of a species with varying silicon concentration gradient.

Multi-component diffusion coefficients, in the form of the diffusion coefficient matrix, for a slag of basicity 0.65 and temperature of 1500°C, are shown in Table I. This matrix was also evaluated for other slag basicities. A model was devised to predict diffusivity of various species in slags of a given optical basicity. This model is shown in Equation [3], where $D_{ij}$ is the multi-component diffusion coefficient, $\Lambda_i$ is the optical basicity coefficient for the component oxide and $\Lambda$ is the optical basicity of the slag. Oxide basicity values were taken from Sommerville and Yang. These values were also used in the NPL viscosity model. Selected values are listed in Table II.

$$D_{ij} = (9.3 \times 10^{-10}) \Lambda_i e^{12.55 \Lambda_j} \left(\text{cm}^2\text{s}^{-1}\right)$$  \hspace{1cm} [3]$$

Equation [3] can be used to evaluate $D_{ij}$ or $D_{Si}$, i.e., $D_{MnMn}$, $D_{MnSi}$, $D_{FeMn}$, $D_{FeSi}$, $D_{CaCa}$, $D_{CaSi}$. These values can be applied to Equation [2], along with calculated capillary and crucible slag compositions, to determine effective diffusivities for varying silicon concentration gradients.

Figure 2 shows experimental and predicted diffusion coefficients for manganese. Data points are effective diffusion coefficients calculated from Equation [1]. Fitted lines are effective diffusion coefficients, taking into account slag basicity and concentration gradients of all species. The oxidation state of manganese does not change significantly over the basicity range studied and as such there is no need to account for the different basicity of the Mn3+ species.

Figure 3 shows experimental and predicted diffusion coefficients for iron, for three and five component experiments. The proportion of the Fe3+ ion increases exponentially with slag basicity, to a Fe3+/Fe2+ of 0.6 at an optical basicity of 0.8. The heavier lines represent predicted diffusivity of the Fe2+ species, and the lighter line represent the Fe3+ species. The transformation of Fe2+ to Fe3+ is clearly predicted in the upper result set.

![Figure 1. Concentration profiles of manganese, iron, calcium and silicon from a 5-component experiment, fitted by Equation [1]](image1)

![Figure 2. Experimental and predicted diffusion coefficients of manganese, for 3 (O), 4 (□) and 5 (∆) component experiments at 1500°C](image2)
Figure 4 shows calculated and predicted diffusivities for calcium, determined for 4-component experiments. Experimental data closely follows predicted values across the basicity range studied.

Figure 5 shows calculated and predicted diffusivities for silicon, determined for 4 and 5 component experiments. Obviously, silicon deserved different treatment to the metal cations, due to the incorporation of silicon in molecular networks. No cross-effects are assumed to act on silicon, due to the differences in ionic size. The statistical quality of the model when applied to silicon is poorer than for other species. Presentation of these data is for comparison only, but the fit of the data is still reasonable.

Discussion and conclusions

The slag reservoir method proved to be a reliable method and was bound by Fick’s Second Law of diffusion. The close fit of diffusion profiles to the predicted mathematical profile indicates the assumption of constant reservoir-capillary concentration was justified, and that the mass transfer within the system was diffusion-controlled. Microprobe analysis allowed the study of multi-component diffusion systems, where more than one species is diffusing. This allows a more accurate simulation of industrial systems, and evaluation of the cross-effects between multiple diffusing species. Microprobe analysis is more accurate than tracer measurement, and can be fully quantified with calibration. The distance component of the concentration profile in each experiment contained negligible measurement error, compared to the significant error involved when sectioning is required, as in tracer studies.

The diffusivity of metal cations was found to increase exponentially at 1500°C with increasing optical basicity in the composition range studied. The diffusivity varied from about 1.0 to 5.0 × 10⁻⁶ cm²/s⁻¹ over the composition range studied. The relative diffusivity of species was found to be dependent on the optical basicity coefficient (Λ). Transition metals did not exhibit greater rates of diffusion than non-transition metals, as has been reported in a previous study. The diffusivity of iron was found to be dependent on the relative proportions of the II and III oxidation states. At higher basicity or high oxygen partial pressure, the increased concentration of the III state has the effect of decreasing the overall diffusivity relative to other species. As manganese is almost always in the II state regardless of composition, the rate of diffusion is constant relative to non-transition metals.

An analysis of slag structure by Raman spectroscopy revealed that all experimental slags consist of a wide range of silicate anions, from monomeric species to tetrahedrally coordinated silicon present simultaneously. The relative proportion of larger silicate anions was found to increase with decreasing slag basicity, corresponding to the decrease in diffusivity. Figure 6 shows the Raman spectrum for the 0.8 basicity slag. Absorption bands for each silicate species are located according to Mysen et al. The Raman spectra supported the theory that alumina exists as AlO₂⁻ tetrahedra and, as such, alumina has no chemical interaction with cationic species.

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References


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Figure 6. High-frequency Raman spectrum of a quenched experimental slag with an optical basicity of 0.8 (54CaO-6Al2O3-40SiO2), showing resolved bands for component silicate structures.