

FACTORS AFFECTING THE DIFFUSIVITY OF IONS IN LIQUID SLAGS

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ABSTRACT

Although diffusion is an important process in many heterogeneous pyrometallurgical reactions the factors which influence diffusivity values are not well understood. This is particularly so for the diffusivities of transition metal ions in slag metal reactions. These ions exhibit multiple valencies and the valency or range of valencies present in a particular melt may be expected to depend on the basicity of the slag, however the basicity is defined. As the slag becomes more acidic in nature it may be expected that the valency of the transition metal present will reflect this and increase. In the case of many transition metals this means that the metallic ion will be part of a more complex anion while in a basic slag the valency will decrease and the ion will remain a simple cation. This will, in turn affect the network forming or network modifying ability of the metallic ion species and consequently it may be expected to affect the diffusivity of the ion. This paper discusses some of the factors that influence the diffusivity of ions in liquid silicate slags and attempts to relate the diffusion phenomenon to the interaction of the diffusing ion to the silicate network in the slag. The paper initially considers a typical ternary slag of 40% CaO, 20% Al₂O₃, 40% SiO₂ which is often chosen for its applicability to ironmaking and for the fact that it has a relatively low glass transition temperature (about 1265°C) enabling a wide range of temperatures to be

studied. The effect on the diffusivity of the various species of removing the alumina and the silica respectively are then examined. Transition metal diffusion is explored through some initial measurement of diffusivities in calcium silicate slags of varying lime silica ratios. It is concluded that, although data is at present sparse, the effect of basicity on diffusivities, especially of transition metals is significant. Diffusivities as measured range over several orders of magnitude.

1. INTRODUCTION

Diffusion through the slag at the interface between slag and metal is an important rate controlling step in many slag metal reactions of relevance to extractive metallurgy. Considering its importance it is perhaps surprising that so few measurements of diffusivity have been reported in the literature. This may be a reflection of the difficulties that are encountered in attempting to make such measurements accurately and a great deal of effort must be put into eliminating, or at least minimising, sources of error in these experiments. Much of the current work on diffusivity measurement involves the use of radioisotopes and radioisotope laboratories must be properly licenced to satisfy the relevant Occupational Health and Safety Codes. This, together with the usual hazards of high temperature experimentation probably acts as a considerable disincentive to laboratories wishing to set up suitable equipment and facilities. Nevertheless some measurements have been made and some general pictures emerge of the way in which diffusing species interact in the liquid slag network.

Diffusing species, particularly the electronically charged species that are diffusing in liquid slags may be expected to interact with the slag matrix. Thus the so called network forming species such as silicon and titanium, characterised by a strong tendency to form covalent bonds with

| Slag Composition wt% | | | | Diffusing Species | | Effect on Silicate | Diffusivity; Dcm ² s ⁻¹ | |
|----------------------|--------------------------------|------------------|--------------------------|-------------------|------------------|--------------------|---|------------------------|
| CaO | Al ₂ O ₃ | SiO ₂ | Other | Cation | Anion | | 1450°C | 1600°C |
| 40 | 20 | 40 | | Al ⁽²⁾ | | n.f. | 4.3 x 10 ⁻⁷ | 7.0 x 10 ⁻⁷ |
| | | | | Si ⁽³⁾ | | n.f. | 1.8 x 10 ⁻⁶ | 2.8 x 10 ⁻⁶ |
| | | | | Ti ⁽⁴⁾ | | n.f. | 8.5 x 10 ⁻⁷ | |
| | | | | Fe ⁽¹⁾ | | t.m. | 1.2 x 10 ⁻⁵ | 2.1 x 10 ⁻⁵ |
| | | | CaF ₂ (trace) | Fe ⁽¹⁾ | | t.m. | 2.5 x 10 ⁻⁵ | 4.0 x 10 ⁻⁵ |
| | | | | Mn | | t.m. | 1.1 x 10 ⁻⁵ | 3.2 x 10 ⁻⁵ |
| | | | | Zn ⁽⁵⁾ | | | 1.0 x 10 ⁻⁵ | 1.8 x 10 ⁻⁵ |
| | | | | Ca ⁽¹⁾ | | n.m. | 5.0 x 10 ⁻⁶ | 9.0 x 10 ⁻⁶ |
| | | | CaF ₂ (trace) | Ca ⁽¹⁾ | | n.m. | 1.5 x 10 ⁻⁵ | 2.0 x 10 ⁻⁵ |
| | | | | Mg | | n.m. | 3.8 x 10 ⁻⁵ | |
| | | | | | F ⁽¹⁾ | | 2.8 x 10 ⁻⁵ | 3.5 x 10 ⁻⁵ |
| | | | | | O ⁽⁵⁾ | | 7.5 x 10 ⁻⁶ | 1.8 x 10 ⁻⁵ |
| | | | | | P ⁽⁴⁾ | | 1.2 x 10 ⁻⁶ | 2.3 x 10 ⁻⁶ |
| | | | 1.5% S | | S ⁽⁶⁾ | | 7.8 x 10 ⁻⁷ | 5.2 x 10 ⁻⁶ |
| 23 | 14 | 62 | | Si ⁽³⁾ | | | 1.8 x 10 ⁻⁶ | |
| | | | | Ca ⁽¹⁾ | | | 5.3 x 10 ⁻⁶ | 9.0 x 10 ⁻⁶ |
| 43 | 10 | 47 | | Al ⁽²⁾ | | | 6.2 x 10 ⁻⁷ | 2.0 x 10 ⁻⁶ |

Table 1: Diffusion in ternary slags of the approximate composition indicated (n.f. indicates network forming, t.m., transition metal and n.m., network modifying).

the slag network, might be expected to diffuse at a different rate from the network modifying, highly ionic species, such as the alkaline earth metals calcium and magnesium. This effect is demonstrated in the paper. The behaviour of transition metals, however, is of considerable interest because these metals are the very ones that much of extractive metallurgy seeks to extract.

Transition metals are characterised by a variable valency and the valency depends on the chemical environment in which the metals are present. Thus in an acidic environment the ions may be expected to form anionic complexes as the valency increases while in the more basic slags the transition metal ions may be expected to remain as simple cations. Diffusivities would reflect this trend with the simple cationic species diffusing more rapidly than the higher valency ions that have strong

interactions with their respective anion complexes. This trend is demonstrated for manganese in calcium silicate slags.

2. TERNARY CaO Al₂O₃ SiO₂ SLAGS

Table 1 below lists diffusivities of various species in a ternary slag of approximate composition 40 wt% CaO, 20 wt% Al₂O₃, 40 wt% SiO₂ at two chosen temperatures of 1450°C and 1600°C. For ease of analysis the cations have been grouped into network forming (n.f.), transition metals (t.m.) and network modifying (n.m.) species. No attempt has been made to classify the anions in a like manner but fluorine is the only ion that cannot participate in the silicate network so that in this sense it may be likened to the network modifying species.

The network forming species Al³⁺, Si⁴⁺ and Ti⁴⁺ are characterised by relatively low diffusivities and the implication is that this reflects a strong interaction with the silicate network. If they are more securely bound to the network then the driving force for diffusion is correspondingly diminished. Silicon is, of course the main network forming element and silicon oxygen bridging forms the main network skeleton. Titanium has similar characteristics to silicon and, being also tetravalent, it can probably replace the silicon without too much disruption to the network. The similarity in the two diffusivities reflects this.

The very low diffusivity of aluminium is somewhat puzzling because it cannot replace silicon so easily as titanium and network distortion would be greater. Nevertheless aluminosilicate networks are common in minerals and therefore probably also in slags so that aluminium does certainly have a strong network forming characteristic. Thus the general trend in diffusivities is as would be expected. The reduction of the aluminium content from 20 to 10% does not appear to affect greatly the diffusivity of aluminium.

Transition metal (and zinc) diffusivities are remarkably similar at both 1450°C and 1600°C and the values are relatively high. This reflects the network modifying nature of these transition metals and the fact that their participation in the silicate network is only minimal. The results of diffusion measurements on manganese are preliminary at this stage but they are supported by previous work reported by Nagata et al⁽⁴⁾. It is interesting to note that the presence of a fast diffusing species such as fluorine⁽¹⁾ or sodium⁽⁴⁾ can influence the rate of diffusion at least of iron. In the presence of a trace of CaF₂ the diffusivity of iron increases by more than 50% at 1600°C. This may be partly explained by considerations of electrical neutrality since a fast diffusing ion such as the fluoride ion will carry with it a net charge. This will, in turn develop a charge gradient opposing the ionic diffusion. Considerations of electrical neutrality therefore suggest that to negate this effect diffusing ions must be accompanied by an ion or ions of opposite charge. The effect is therefore to speed up the entire diffusion of all species in the slag. A secondary effect is that the presence of even small amounts of fluoride ion tends to break up the silicate network as can be seen by the effect of fluoride additions on viscosity⁽⁸⁾. The relative contributions of the two effects are difficult to gauge.

The network modifying ions calcium and magnesium show a marked increase in diffusivity over the network forming ions as would be expected. It is noteworthy, however that it is not until traces of fluoride ion are introduced that calcium diffusivities reach the levels of the transition metals or of magnesium. This effect is more apparent as the temperature increases⁽¹⁾ reflecting the higher activation energy involved. The calcium diffusivity increases by about 45% at 1600°C.

The behaviour of the anions is to some extent analogous to that of the cations.

| Components | | | Ratio CaO/SiO ₂ | Diffusing ion | Diffusivity; Dcm ² sec ⁻¹ | |
|------------|--------------------------------|--|-------------------------------|-------------------|---|-------------------------|
| | | | | | 1450°C | 1600°C |
| CaO | SiO ₂ | | 1:2 | Si ⁽⁴⁾ | 8.5 x 10 ⁻⁷ | 3.8 x 10 ⁻⁶ |
| | | | 1:1 | Si ⁽⁴⁾ | | 1.5 x 10 ⁻⁵ |
| | | | 1:2 | Ca ⁽⁴⁾ | | 1.75 x 10 ⁻⁵ |
| | | | 1:1 | Ca ⁽⁴⁾ | | 3.14 x 10 ⁻⁵ |
| CaO | Al ₂ O ₃ | | 1:1 | Ca ⁽¹⁾ | 1.9 x 10 ⁻⁵ | 3.92 x 10 ⁻⁵ |
| CaO | SiO ₂ | | 1:2 | Mn | | 2.6 x 10 ⁻⁵ |
| | | | 1:1 | Mn | | 3.7 x 10 ⁻⁵ |

Table 2: Diffusion in binary slags of varying compositions as indicated.

Apart from oxygen, anions which could be expected to participate in the silicate network are sulfur and phosphorous. Fluorine has a strong modifying effect on the network and this is reflected in its high diffusivity. The net effect of this is on the diffusion of cations is noted above. The relatively high value for the diffusivity of oxygen suggests that 'free' oxygen anions play an important role in this diffusion.

For comparison some diffusivities for Ca²⁺ and Si⁴⁺ are included for a ternary slag with a much higher silica content. The diffusivities do not appear to vary greatly leading to the conclusion that the diffusion mechanism is similar in the two slags. It would appear that the presence of an aluminosilicate network is the main feature influencing the diffusivities as measured.

3. BINARY SYSTEMS

Table 2 shows some selected values for the diffusion of ions in systems containing CaO, SiO₂ and Al₂O₃. The data available for these systems are very sparse and some of the diffusivities which have been published conflict. The approach taken is therefore one of 'best guess' and, in some cases, diffusivities have been calculated from

graphical or other information using the Arrhenius plot

$$D = D_0 \exp(Q/RT).$$

Using 1600°C as the main temperature for comparison it can be seen that the diffusivity of silicon has actually decreased in the binary CaO/SiO₂ system when the lime silica ratio is 1:2, the diffusivity of calcium has increased marginally. The effects are only small for this lime silica ratio but as the lime content increases the silicon diffusivity increases significantly from a value of approximately 3.8 x 10⁻⁶ to 1.5 x 10⁻⁵ cm²sec⁻¹. The effect on the calcium diffusivity is relatively much weaker but the same trend is evident. Thus the influence of alumina in the ternary system is to contribute to the break up of the silica lattice and to help to mobilise the silicon allowing it to diffuse more easily.

The effect of removing the silicate network completely can be seen in the increased diffusivity of calcium in the binary lime alumina slag to 3.9 x 10⁻⁵ cm²sec⁻¹.

The diffusivity of the transition metal manganese is recorded for binary silicate slags of two lime silica ratios at a temperature of 1600°C. Both sets of data

show increased mobility over the network forming species. There is not, however the marked distinction that is found in the ternary slags. Although the data is sparse and comparison between the binary and the ternary slag is tentative the diffusion of manganese appears to be measurably lower in the slag of lime silica ratio of 1:2 than in that of the two slags of lime silica ratio 1:1. This may be simply a result of the varying silica content leading to indirect comparisons. The lack of good quality data precludes too much comment on this and there is a clear need for more measurements to be made in relevant systems before the mechanisms of diffusion can be objectively assessed.

4.CONCLUSIONS

The mechanisms of diffusion in silicate and aluminosilicate slags is closely associated with the structure of the slags and nature of the ions themselves. It is well accepted that the network forming ions are closely bound to the silicate lattice and this has a measurable effect on the diffusivities of these species.

In general transition metals seem to have similar diffusivities and these are of the same order as other network modifying ions.

However indications are emerging that diffusivities of these ions are dependent of composition and in particular on the slag basicity. A measure of this is the lime silica ratio of the slag.

Network modifying ions are relatively mobile in the slags but the difference between the diffusivities of calcium and of silicon diminishes as the temperature increases. This no doubt reflects the increased mobility of silica as the temperature effects break up the silicate network. The effect of fluorine may be expected to be similar.

The behaviour of anions is as would be expected in that the network interactions predicted for these species seem to reflect in their diffusivities. More data is required to confirm this and to see the effect of composition on the diffusion of the anions. This is particularly the case for the diffusion of oxygen in slags.

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