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The effect of an applied electrical potential on refractory corrosion by slag

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ABSTRACT

An investigation has been carried out to assess the effects of an applied voltage on the dissolution rate of MgO refractory in a steelmaking like slag. In this study corrosion results obtained from dip tests using a dense direct bonded MgO refractory in a CaO-SiO₂-Fe₂O₃-FeO-MgO slag are presented. These results demonstrate that the application of a voltage across a dense MgO refractory-slag interface can change the rate of refractory dissolution. For the slag composition used and the voltage range tested, it was found that a maximum corrosion rate was obtained at a voltage setting of -0.45V. The results of this investigation have been explained in terms of voltage affects on Marangoni (interfacial tension induced) stirring and its effect on the MgO dissolution reaction that is at least partly controlled by mass transfer in the slag.



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INTRODUCTION

Refractories are the primary containment material used in the metal processing industries. Their service lifetime is often dictated by the rate the refractory dissolves in the liquid slag generated by the metal refining process (1). The dissolution rate is a function of contact area between the slag and refractory which in turn is a function of the area calculated using the macro dimensions of the refractory and the pore structure within the refractory. Recently there have been two separate studies that have shown that the rate of slag penetration into a refractory and hence the rate of dissolution of a refractory into slag may be affected by the application of a small applied voltage across a slag-refractory interface (2,3). The results of these studies were explained using an integrated form of Poiseuille's law (1), shown in Equation 1, for liquid penetration, l , into pores,

$$l^2 = \left(\frac{r\gamma \cos(\theta/2)}{\eta} \right) t \quad (1)$$

where r is the pore radius, γ is the interfacial tension, θ the contact angle between the slag and refractory, η is the dynamic viscosity of the slag and t is time. The authors argue that by application of an electrode potential across the refractory-slag interface the γ and θ change thereby reducing the depth of penetration for a given time.

These (Kazakov et al (2) and Riaz et al (3)) investigations raise a number of important questions,

- a) Why should the interfacial tension and contact angle of a slag-refractory system change with changing applied voltage?
- b) Does this change in interfacial tension and contact angle of the slag-refractory system change the rates of dissolution of refractories with extremely low porosity where increased contact area generated by slag penetration into pores is not an issue?

At present there is no answer to question a) but it is likely that an explanation may be found by considering the application of a number of existing theories that have attempted to explain the composition stratification in other systems such as metal-aqueous (4,5) solutions, metal-polymers (6) and molten salts-metal (5,7,8) systems under an applied voltage and the effects of this change on the interfacial tension of the system. In these systems it has been found that ions/molecules at or near the phase interface order themselves to minimise the voltage affects. This has the effect of changing the interfacial properties of the phase interface. Highly basic slags are ionic in nature (9) and to all intents and purposes can be considered as a molten salt. Acidic slags are more covalent (9) and may not be easily represented as molten salts. It is likely that models, which describe the behaviour of molten salts, will have some applicability to slags in general and basic slags in particular. Unfortunately, Kazakov et al (2) and Riaz et al (3) investigations were on penetration of slag into pores. It is difficult to define the contact

area between a porous refractory and the slag in these experiments. This precludes direct application of molten salt theories and hence an answer to the question why should the interfacial tension and contact angle of a slag-refractory system change with changing applied voltage? The study of a simpler refractory-slag system under an applied voltage with a more dense refractory, (minimal porosity) and therefore a better defined contact area may enable an answer to the question. It may be expected, though it has to be confirmed, that changes in interfacial tension and/or wetting of the slag-refractory system due to an applied voltage would also affect the dissolution rate of more dense refractories. It is known that changing the interfacial tension and/or wetting will also change the interfacial (Marangoni) flow conditions (10) at the slag-refractory-gas interface. Marangoni flows are interfacial tension driven flows and are known to affect corrosion at the slag-refractory-gas interface (1,10). Such a change in local flow conditions would have a significant effect on refractory-slag dissolution systems that are at least in part controlled by mass transport in the slag phase. The confirmation that an applied voltage affects the dissolution behaviour of the simpler dense refractory-slag system is a necessary pre-cursor to addressing more fundamental issues of why the interfacial tension and/or wetting change with applied voltage. In this study the dissolution of a dense MgO refractory in contact with a CaO-SiO₂-Fe₂O₃-FeO-MgO slag under an applied voltage has been studied and reported.

MgO was chosen as the refractory to be studied as

- it is a widely used refractory in the liquid metal processing industry and
- it is known that the dissolution of this refractory in a CaO-SiO₂-Fe₂O₃-FeO-MgO system is at least in part controlled by mass transfer in the slag phase (11) and therefore will be significantly affected by Marangoni flows.

EXPERIMENTAL

A series of experiments was carried out to study the effect of an applied voltage across a refractory-slag interface on the dissolution of MgO in a synthetic steelmaking slag. A cylindrical piece of high density MgO refractory was dipped in liquid slag for 90 minutes, removed and water quenched. The resulting corroded refractory sample was then sectioned, ground and polished for microscopy using standard ceramographic methods. The refractory dissolution was measured by evaluating the corroded area of the sample using digital analysis. A schematic of a MgO sample is given in Figure 1. The "before" represents the sample prior to the dissolution experiment, the "after" represents a sectioned sample after exposure to the slag. The hatched area represents the corroded area of the sample as a result of the dissolution process.

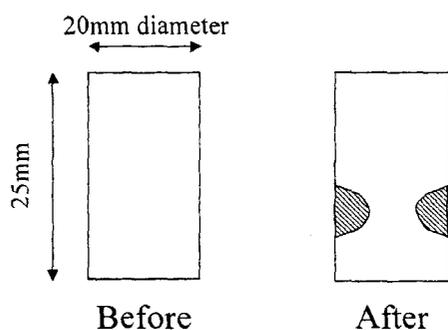


Figure 1-A schematic showing the MgO sample before and after the dissolution experiment. The hatched area represents the corroded area of the sample.

The experiments were carried out in a dried air atmosphere and heated to 1540°C in a molybdenum di-silicide vertical tube furnace. A schematic of the furnace set-up is given in Figure 2. A schematic of the electrical circuit used to apply the voltage is given in Figure 3. The cylindrical MgO test samples were supplied by Rojan Advanced Ceramics, Henderson, Western Australia. They are greater than 97% pure and had a density of in excess of 96% theoretical.

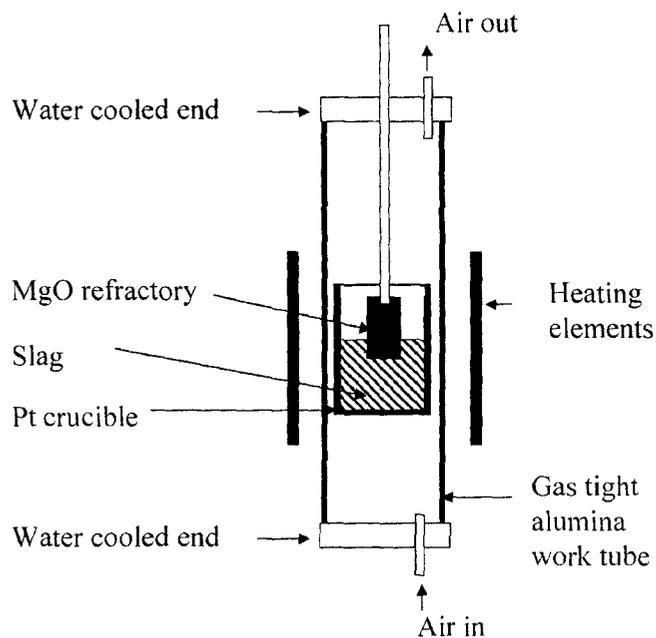


Figure 2-A schematic of the furnace set-up.

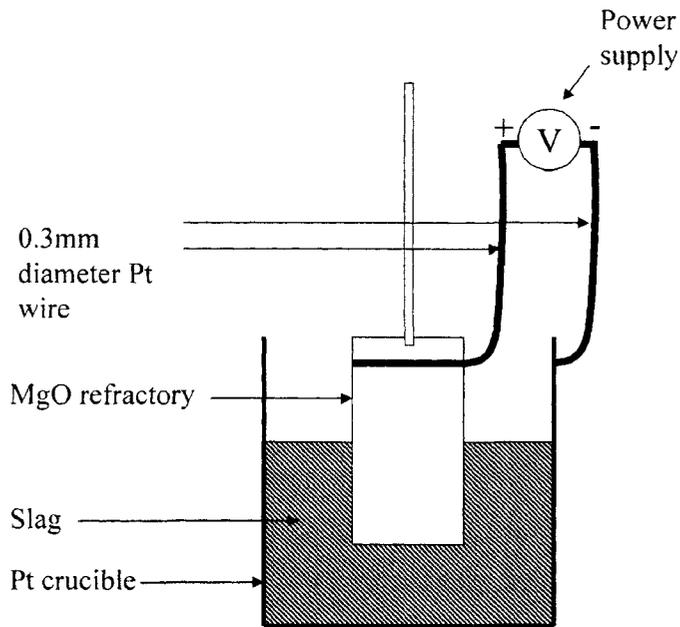


Figure 3-A schematic of the electrical circuit used to apply a voltage.

The composition of the slag used in this study was 45.79% CaO, 45.79% SiO₂, 4.55% Fe₂O₃, 0.89% FeO and 2.98% MgO. The reported slag composition is based on ICP measurements for CaO, SiO₂, MgO and total Fe. A back titration method was used to establish the FeO content. The rest of the iron was assumed to be Fe₂O₃. The slag was prepared by pre-melting appropriate mixtures of CaO, SiO₂, Fe₂O₃ and MgO in air, quenching the slag and then crushing the resultant glass. This process was repeated to obtain a homogenous slag. The crushed oxide was then melted in-situ in the Platinum crucible prior to running an experiment.

RESULTS/DISCUSSION

The results of the effect of an applied voltage on the dissolution experiments are given in Figure 4. It can be seen that an applied voltage does affect the amount of corrosion and therefore refractory dissolution observed in these experiments. The corroded area reported in this study takes place at the refractory-slag-gas interface. At approximately -0.45 V the amount of MgO corrosion and hence dissolution rate is at a

maximum. There also appears to be less corrosion at voltages between -0.75 and -0.6 V than at voltages between -0.3 V and 0 V, though more data are required to confirm this trend.

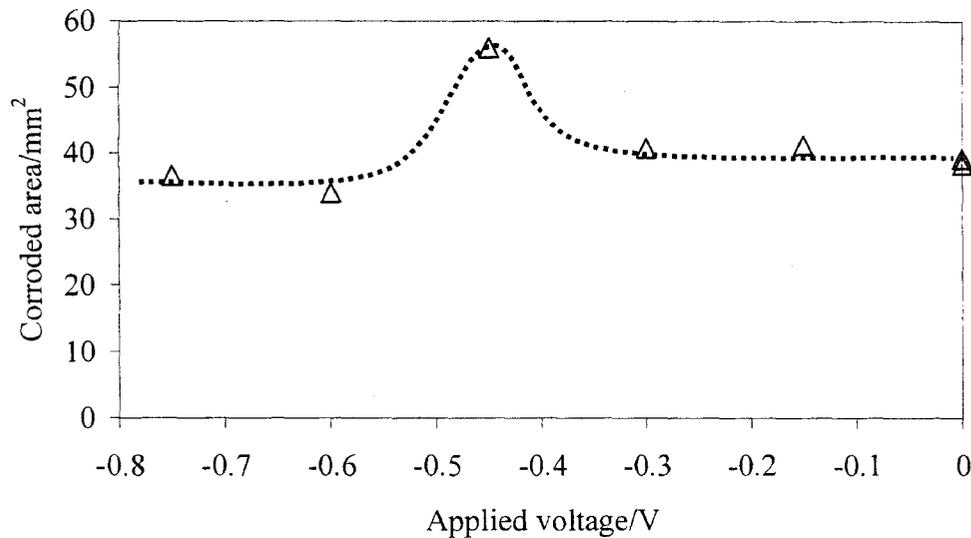
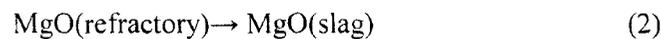


Figure 4-A plot showing the affects of an applied voltage on the corrosion of MgO in a slag of composition 45.79% CaO, 45.79% SiO₂, 4.55% Fe₂O₃, 0.89% FeO and 2.98% MgO at 1540°C. The corroded area is as shown in Figure 1.

Why should an applied voltage across the refractory-slag interface affect the dissolution rate of the MgO refractory? It is known that MgO dissolution in the slag used in this study is at least in part controlled by mass transfer in the slag phase (11). To discuss the effects of an applied voltage on a mass transfer controlled process it is instructive to consider a simple mass transfer model for steady state refractory corrosion, as shown in Figure 5. In this figure A and B represent the MgO in the refractory and slag phase respectively, C is the molar concentration and *i* represents interface. On the assumption that the dissolution process, as describe by Equation 2, is controlled purely by mass transfer in the slag



then the MgO dissolution flux, *J*, into the slag can be obtained from an application of Fick's law (Equation 3) to the refractory-slag system

$$J = -\frac{D}{\delta} (C_{\text{MgO}} - C'_{\text{MgO}}) \quad \text{mole.cm}^{-2}.\text{s}^{-1} \quad (3)$$

where D is the interdiffusion coefficient, δ is the stagnant (boundary) layer as defined in Figure 5, C_{MgO} is the MgO concentration in the bulk of the slag and C_{MgO}^i is the MgO concentration in the slag at reaction interface.

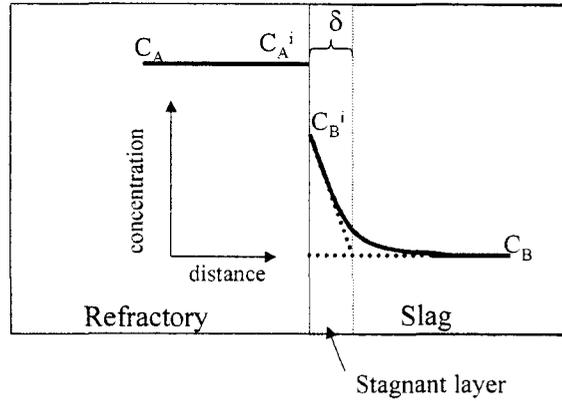


Figure 5-A schematic of the MgO refractory dissolution process showing concentration profiles on either side of the reaction interface.

Any phenomenon that affects the velocity of the slag adjacent the stagnant layer δ , will affect the concentration profile across the stagnant layer and hence the value of δ . Any changes in δ will change the MgO dissolution rate (flux J in Equation 3). At the refractory-slag-gas interface it is known that Marangoni flows are active and play a significant part in the wear/corrosion profiles obtained in the refractory at that interface (12). These flows are a result of shear stresses, τ , caused by interfacial tension gradients and can be described by Equation 4 (12)

$$\tau = \frac{d\gamma}{dx} = \frac{\partial\gamma}{\partial T} \frac{dT}{dx} + \frac{\partial\gamma}{\partial C} \frac{dC}{dx} + \frac{\partial\gamma}{\partial\psi} \frac{d\psi}{dx} \quad (4)$$

where x is distance, T is temperature, C is concentration and ψ voltage. Other symbols are as defined previously. For all other things being equal, a change in the voltage term in Equation 4, as a result the applied voltage to the slag-refractory system will be reflected by a change in the Marangoni flow velocity. This in turn will affect the MgO dissolution flux, as the thickness of the stagnant layer δ in Equation 3 will change. The MgO dissolution data as a function of applied voltage obtained in this study are consistent with, and therefore could be explained by such an argument. The argument that the applied voltage in the dense refractory-slag system studied in this investigation affects the interfacial phenomena, and hence the dissolution rate is consistent with Kazacov et al (2) and Riaz et al (3) explanation of the slag penetration observations of their porous refractory under an applied voltage. Essentially they argued that applying a

voltage to their porous refractory-slag system changed the interfacial characteristics of the slag penetration.

The assertion that changing the interfacial characteristics of a refractory-slag system by applying a voltage will change how the refractory reacts with the slag is an appealing one. It offers the potential to be able to control, among other things, refractory corrosion in liquid metal production, a significant cost to many processes. Unfortunately, at present, it is not possible to predict with any certainty whether the applied voltage to the slag-refractory system will lessen or increase the dissolution rate of the refractory. Nor is it known with any certainty if any of the current models that have been developed to describe the behaviour of a solid-liquid interface when a voltage is applied across the interface (4-8) are applicable to slag-refractory systems. These models describe how the ions stratify at the solid-liquid interface under an applied voltage and that the stratification is a function of temperature, slag composition (principally ion size) and slag capacitance.

Our understanding of ion sizes in slags is primarily limited to basic (depolymerised) slags (9). The ions present in acid slags, for example slags rich in silica, are not well described (9). The lack of knowledge of acid slags is not necessarily a major problem as most slags used in liquid metal processing are basic. What is a problem though is that there are very little capacitance data for slags (13,14,15). This makes direct application of the solid-liquid interface models difficult.

CONCLUSIONS

The dissolution rate of dense MgO refractory in a CaO-SiO₂-Fe₂O₃-FeO-MgO slag can be altered by the application of an applied voltage across the slag-refractory interface. This effect has been explained by considering the consequences of an applied voltage on the rate of Marangoni flow at the slag-refractory-gas interface and in turn, the flow effect on the rate of the mass transfer controlled MgO dissolution reaction.

The fact that the dissolution rate of a refractory can be altered by the application of a voltage across the refractory-slag interface offers a potential new tool to control refractory losses in liquid metal processing.

A maximum dissolution rate of dense MgO in the slag studied was achieved at -0.45V.

The results of this study on dense MgO dissolution in slag are consistent with Kazacov et al (2) and Riaz et al's (3) studies of the effects of an applied voltage on slag penetration into porous refractories.

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