

Effects of Additives and Temperature on Dissolution Rate and Diffusivity of Lime in Al_2O_3 -CaO- SiO_2 Based Slags

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The dissolution rate of dense lime specimens in calcium aluminosilicate based melts was measured at 1430 °C to 1600 °C in air, using a rotating disk/cylinder technique. The measured dissolution rates were strongly dependent on the rotation speed with the results indicating mass transfer in the slag phase to be a rate-limiting step. At a given rotation speed, the slag chemistry and temperature had strong effects on the dissolution rate. The diffusivity of CaO in the slag was calculated from the dissolution rate and solubility data, using known mass-transfer correlations. Addition of CaF_2 , MnO_x , FeO_x , and TiO_2 to the slag increased the CaO diffusivity, while SiO_2 had an opposite effect. Addition of CaF_2 had the strongest effect and increased the diffusivity by a factor of 3 to 5 in the temperature range of 1500 °C to 1600 °C. The deduced activation energy for diffusion of CaO in these slags ranged from about 53 to 246 kJ/mole, depending on the concentration of additives used.

I. INTRODUCTION

IN secondary steelmaking, synthetic slag is used to influence the final chemistry and residual oxide inclusions in the steel. The most important functions of the ladle slag are to prevent direct contact between the liquid steel and oxidizing atmosphere, desulfurize the liquid steel, and absorb oxide inclusions formed as the result of deoxidation reactions. Lime based slags are used for aluminum-killed steels, to absorb the alumina and silicate inclusions and form a calcium aluminosilicate slag with a low level of other oxides. Fluorspar (CaF_2) is commonly used as an additive to increase the dissolution rate of calcined lime into this ladle slag as well as to reduce the slag viscosity. While fluorspar is known to be an effective fluxing agent, there are some drawbacks associated with its use. These include volatilization of fluorine containing species into the atmosphere, leaching of the residual fluorine from the discard slag, higher refractory wear rate, and relatively high cost of fluorspar. Therefore, an alternative flux or slag practice, which will promote rapid and complete dissolution of lime into slag without adverse technical and environmental effects, is highly desirable.

The effects of additives on the dissolution rate of lime in the slags have been investigated by a number of researchers. Matsushima *et al.*^[1] used a rotating disk technique to measure the dissolution of lime in calcium silicate based slags with a CaO/ SiO_2 ratio of 1 containing about 20 wt pct Al_2O_3 or FeO_x at temperatures between 1450 °C and 1600 °C. They found that the dissolution rate was several times

greater in slags containing FeO_x . Hamano *et al.*^[2] also used the rotating disc technique to study the effects of various additives (CaF_2 , CaCl_2 , Al_2O_3 , and B_2O_3) on the dissolution of lime in calcium-iron silicate slags with CaO/ SiO_2 ratio of 1 and 40 wt pct FeO_x at temperatures between 1300 °C and 1400 °C. The dissolution rate was found to vary with the sample size. Hamano *et al.*^[2] found that while addition of CaF_2 and CaCl_2 resulted in a higher dissolution rate of lime in the slag, the rate decreased with increasing slag basicity. They also found that the addition of FeO_x increased the dissolution rate of CaO in the slag.

While these findings suggest that additives such as iron oxide and calcium fluoride could increase the dissolution rate, they do not explain the reason(s) for the enhanced dissolution rate of lime by such additives. These and other additives could influence both the thermodynamic driving force for dissolution of lime and the change of transport properties (*e.g.*, diffusivity and viscosity) of the slag.

Published phase equilibria data and models describing the thermodynamics and viscosity of multicomponent slags allow reasonably accurate prediction of the effect of various fluxes on the solubility of lime in slags as well as on the slag viscosity.^[3–13] However, there are limited published studies on the diffusivity of lime or calcium in slags and they generally deal with self-diffusivity, which has been deduced from experiments using the tracer technique. Keller *et al.*^[14] measured the tracer diffusivity of Ca^{45} in CaO- SiO_2 (SiO_2 mole fraction was 0.448 to 0.634) melts over a temperature range of 1500 °C to 1700 °C. Their diffusivity data are of the order of 10^{-6} cm²/s and decrease with increasing silica content of the slag. They showed that Ca^{45} had a lower diffusivity than Fe^{59} and higher than Si^{31} . Their findings are in accord with the data by Towers and Chipman,^[15] who found the tracer diffusivity of calcium and silicon in calcium aluminosilicate slag (CaO/ $\text{SiO}_2 \sim 1$ and 12 wt pct Al_2O_3) to have the same order of magnitude. Subsequent study by Johnston *et al.*^[16] showed that the addition of CaF_2 to calcium aluminosilicate slag has a marked effect on increasing the diffusivity by a factor of 2 or more. Hara *et al.*^[17] showed that addition of 7 wt pct CaO to iron-silicate based slag resulted in higher values of self-diffusivity of Ca^{45} over a temperature range of 1270 °C

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to 1450 °C. The activation energy of diffusion, deduced from their data, shows that increasing the silica concentration of slag increased the activation energy from 117 to 146 kJ/mole.^[14] The activation energy deduced from data by Johnston *et al.*^[16] shows a decrease from 125 to 67 kJ/mole with addition of CaF₂ to the melt.

The limited information on self-diffusivity of Ca in slags suggests that additives such as CaF₂ and FeO_x enhance the rate of diffusion of Ca in slags. However, the data cannot be used to estimate the effects of such factors on chemical diffusivity and hence dissolution rate of lime. Furthermore, there are no measurements of CaO diffusivity in calcium aluminosilicate slags with composition close to the industrial ladle slags. Thus, in order to extend our knowledge and understanding of the behavior of some additives to ladle-type slags, the present work was aimed at quantifying the effects of CaF₂, FeO_x, MnO_x, TiO₂, and SiO₂ on the dissolution rate and diffusivity of lime in low silica calcium aluminosilicate slags, using a rotating disk/cylinder method. The forced convection created by this technique is under well-defined hydrodynamic conditions, which minimizes the effect of natural convection that normally occurs in the conventional tracer-diffusivity measurements. Furthermore, the experimental conditions, including slag dynamics, are exactly reproducible and the slag is agitated to a sufficient degree to render a comparison with conditions in the steelmaking process, which provides dissolution rate data.

II. EXPERIMENTAL

A master slag A was prepared from mixtures of reagent grade calcium carbonate, silica, and alumina. The targeted slag composition was CaO-42 wt pct Al₂O₃-8 wt pct SiO₂. The mixture was melted in a graphite crucible (90-mm o.d. and 300-mm height) contained in a clay bonded graphite susceptor, which was heated by a 15-kW induction furnace to about 1550 °C. The slag was cooled in the crucible and then crushed in a jaw crusher to a particle size of <2 mm. Other slags (B-F) were prepared by mixing about 5 wt pct of reagent grade additives (CaF₂, Fe₂O₃, TiO₂, Mn₃O₄, and SiO₂) with an appropriate amount of the master slag (A) and melting the mixture in a platinum crucible in air, followed by quenching on a copper plate. The compositions of the premelted slags used in this study are listed in Table I.

Cylindrical lime crucibles (20-mm o.d., 16-mm i.d., and 30-mm height) were used as specimens in the dissolution experiments. These dense high-purity crucibles with an apparent porosity of 1 wt pct contained less than 3.5 pct

impurities (SiO₂, Al₂O₃, and MgO) and were supplied by Rojan Ceramics (Perth, Australia).

The dissolution experiments were conducted with the rotating disk apparatus shown schematically in Figure 1. In each experiment, about 60 g of premelted slag was placed in a Pt-13 pct Rh crucible, 4 cm in diameter and 5-cm deep. The platinum crucible was placed in the hot zone of a tube furnace and rested on an alumina platform, which had an alumina thermocouple sheath inserted in its center. Temperature measurements were made with a Pt/Pt-13 pct Rh thermocouple located in the alumina sheath with the tip in thermal contact with the crucible bottom. The tube furnace was heated by six MoSi₂ elements in a vertical tube furnace. A Eurotherm programmable temperature controller maintained temperature to ±1 °C. The temperature in the hot zone of the furnace was kept constant to within ±4 °C along a 9-cm vertical length.

The lime specimens were cemented to an 8-mm-diameter alumina tube using an alumina-zirconia cement and then connected to a steel shaft, which was driven by a variable speed motor. The rotation speed was varied with a speed controller and monitored with a digital tachometer, which was accurate to within 1 rpm. In each experiment, the specimen was positioned and aligned in the hot zone of the furnace. The melt was held about 1 cm below the specimen, and the furnace was heated at a rate of 90 °C/h to the desired temperatures (1430 °C to 1600 °C). The specimen and the melt were held at experimental temperature for about 1 hour to ensure the thermal equilibrium. At the start of the run, the crucible was raised until the lime specimen was fully immersed and touched the crucible bottom; the crucible was then lowered 10 mm. After commencing the rotation, the melt was sampled through the top of the furnace at regular time intervals using a cold 2-mm-diameter Pt rod attached to a stainless steel rod. The Pt rod was dipped into the melt and quickly removed from the furnace and quenched in water. This enabled slag samples (0.3 to 0.5 g) to be collected with each dip. The samples were then dried and crushed in a tungsten-carbide ring mill for X-ray fluorescence (XRF) chemical analysis.

Solubility of lime in various slags was also determined by reacting about 0.6 g of lime (a piece from the lime specimen used in the rotating experiments) with about 0.5 g of slag in a platinum capsule located in a muffle furnace under static conditions. After the required reaction time, the capsule with its contents was withdrawn rapidly from the furnace and air quenched. The capsule was cut in half along its length and both sections were mounted in a resin mixture and then polished. The compositions in the frozen slag specimens were analyzed quantitatively with an electron

Table I. Chemical Composition of Master Slags (Weight Percent) Used in the Present Study

Master Slag	CaO	Al ₂ O ₃	SiO ₂	CaF ₂	FeO _x	TiO ₂	MnO _x
A	50	42	8	—	—	—	—
B = A + 5 pct CaF ₂	47.79	39.8	8.09	4.82	—	—	—
C = A + 5 pct FeO _x	47.3	40.3	7.52	—	5.09	—	—
D = A + 5 pct TiO ₂	47.5	40.3	7.76	—	—	4.93	—
E = A + 5 pct MnO _x	47.6	40.3	7.84	—	—	—	4.6
F = A + 5 pct SiO ₂	47.4	40.2	12.8	—	—	—	—

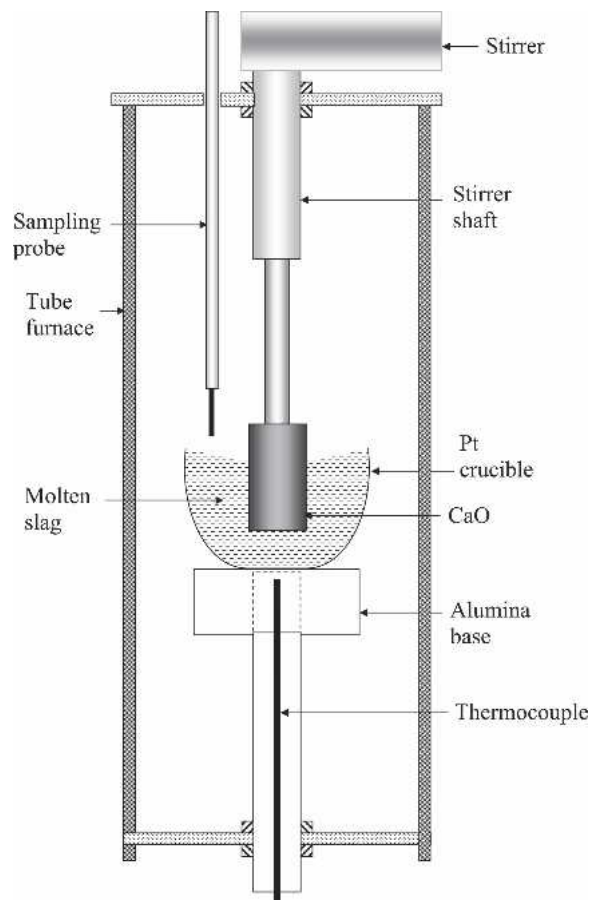


Fig. 1—Schematic of experimental apparatus.

microprobe analyzer (CAMECA* SX50) at The University

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of New South Wales after carbon coating. Examination of the mounted samples for the possible formation of a product layer close to the lime/slag interface was carried out using energy-dispersive spectroscopy with a scanning electron microscope (PHILIPS LS30).*

*PHILIPS is a trademark of Philips Electronics Instruments Corp., Mahwah, NJ.

III. RESULTS

Figure 2 shows the curve-fitted results obtained from a series of experiments on master slag A, at different temperatures and a rotation speed of 90 rpm. The lime concentration of the slag increased with the period of rotation of lime samples in slag. The initial dissolution rate was relatively high and started to slow after 10 to 20 minutes of reaction. Dissolution curves approached a plateau after about an hour of reaction. It is also evident that temperature has a significant effect on the initial rate of lime uptake by the slag.

At 1430 °C, lime dissolution into the slag was quite marginal after 1 hour of reaction. Results obtained from

static experiments at 1430 °C showed formation of a solid $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ layer between the lime specimen and slag. This layer was not apparent in static experiments at temperatures between 1500 °C and 1600 °C. Moreover, in rotating cylinder experiments at higher temperatures, inspection of the lime sample after the end of reaction time revealed that there was either a substantial reduction in the immersed portion of lime specimen or, in some cases, the bottom of the lime sample was fully dissolved in the slag. This happened during the first 10 to 20 minutes of the reaction, after which the dissolution continued from the remaining wall of the lime cylinder. Because the lime sample was attached to the alumina rod with zirconia paste, the complete dissolution of the bottom of the lime sample resulted in the dissolution of zirconia in the slag. The XRF analysis of these samples confirmed the presence of low levels of zirconia in the slag samples after 10 to 20 minutes of reaction; after this, the contact area between the slag and specimen significantly decreased. Thus, the data on the concentration of lime in slag after 10 minutes of rotation is not used in the dissolution rate calculations.

The initial dissolution rate of lime was determined from the linear portion of the curve fitted to the lime concentration data for up to 10 minutes of reaction, where the contact area between the lime specimen and slag could be assumed to be constant. This approximation and the errors from curve fitting resulted in an estimated error bar in the specific rate data of about 20 pct. The effect of rotation speed on the dissolution rate of lime in the master slag A at 1430 °C was measured over a range of rotation speed up to 150 rpm. The results obtained are summarized in Figure 3. They show that the initial rate increased with the rotation speed, implying that mass transfer in the slag played a significant role in the dissolution of lime in the slag phase. Similar results were obtained from the series of experiments performed at 1600 °C and over a range of rotation speed. Formation of a solid layer separating the lime and slag phases was not observed at temperatures between 1500 °C and 1600 °C. It is worth noting that the measured rate at zero rotation speed corresponds to the rate of lime dissolution under natural convection as well as forced convection by agitation of melt due to sampling.

A rotation speed of 90 rpm was chosen as a middle rotation speed within the speed range (where the mass transfer of lime in the liquid phase plays a significant role in the dissolution process) for all subsequent experiments, where the effect of 5 wt pct additives to the slag at various temperatures was investigated. The initial rates determined from the dissolution curves as a function of the experimental temperature are presented in Figure 4. It can be seen that CaF_2 increased the rate of dissolution by a factor of 3, while FeO_x and MnO_x showed comparable effects on increasing the rate by about a factor of 2.

The solubility of lime in the base slag A and slags with additives was determined by reacting the lime samples and static slags at various temperatures, quenching, and analyzing the samples by microprobe analysis. The measured solubility of lime in the slag was found to be about 60 wt pct and within experimental error; it did not show a dependence on temperature or additives used. Thus, the effect of additives on the dissolution rate is unlikely to be related to the driving force for the

transport of lime across the liquid boundary layer adjacent to the lime/slag interface.

Attempts made to measure the concentration of Fe^{2+} in slag samples containing FeO_x produced results with a low level of Fe^{2+} and relatively high degree of uncertainty (*i.e.*, $<0.2 \text{ wt pct} \pm 0.2 \text{ wt pct}$). This is thought to be due to relatively low concentrations of Fe^{2+} in these samples, which contain 5 wt pct FeO_x and were pre-equilibrated in air. Based on these data and a review of published data on redox equilibria in basic slags under oxidizing atmosphere,^[18] the authors concluded that the predominate oxidation state of iron in these slags is Fe^{3+} with very low levels of Fe^{2+} , Mn^{3+} and Mn^{4+} are not very stable at high temperatures, and according to the published redox equilibria data,^[19] the $\text{Mn}^{3+}/\text{Mn}^{2+}$ should be about 0.2 in the slags studied at about 1500 °C in air. Similarly, based on analysis of published redox equilibria data,^[20] Ti^{2+} and Ti^{3+} are less stable under such oxidizing conditions and the expected $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio in the slags studied should be greater than 500.

IV. DISCUSSION

The observed dependence of the dissolution rate on rotation speed at 1600 °C (Figure 5) suggests that, in this case, mass transfer in the liquid phase could be controlling the dissolution rate of lime. It is expected that when the dissolution is controlled by mass transfer in the liquid slag, the dissolution rate of a disk would increase linearly with the square root of rotation speed^[21] and, in the case of a rotating cylinder, the increase in rate would be proportional to the rotation speed raised to the power of 3/4.^[22] Accordingly, for the rotating specimen used in the present work, the dependence of dissolution rate on rotation speed should lay between the expected dependence for a disk and cylinder, with the total mass transfer being a sum of the two components; *i.e.*,

$$\text{Rate}_{\text{total}} \propto A\omega^{1/2} + B\omega^{3/4} \quad [1]$$

where ω is the rotating speed in rad/s, and the terms A and B are dependent on the physical properties of the slag and contact area between the disc and cylinder with the slag.*

*The terms A and B are coefficients in the calculation of mass transfer of lime into the slag from the disk and cylinder, respectively, and will be explained in Eqs. [6] through [8]. They are calculated from the kinematic viscosity of slag and the geometry of the wetted area of the rotating sample in the melt.

The apparent linear dependence of the initial rate on $A\omega^{1/2} + B\omega^{3/4}$, as shown in Figure 5, provides further evidence that liquid-phase mass transfer played a significant role in controlling the dissolution of these samples over the rotation speed of 30 to 150 rpm. As mentioned earlier, in static experiments at 1430 °C, formation and growth of a solid layer on the surface of the lime specimen were observed, while at higher temperatures, this phase was not stable and did not form. It is reasonable to consider that the measured dissolution rates at 1430 °C were in a mixed control regime of liquid-phase mass transfer and diffusion in the solid layer formed. According to the phase diagram for the $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ system,^[3] the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ phase that formed at 1430 °C becomes unstable at 1500 °C and above in slags containing 5 wt pct or

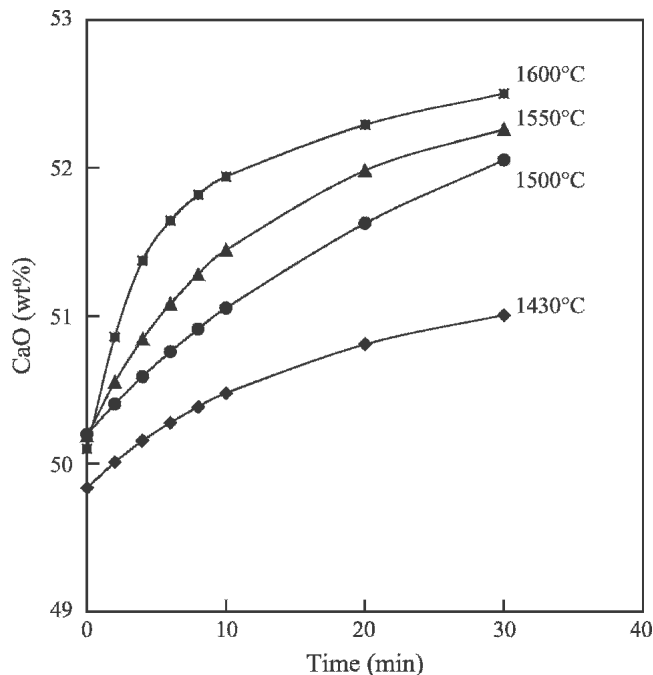


Fig. 2—Measured variation of the CaO concentration in master slag A with reaction time for samples rotated at 90 rpm at different temperatures.

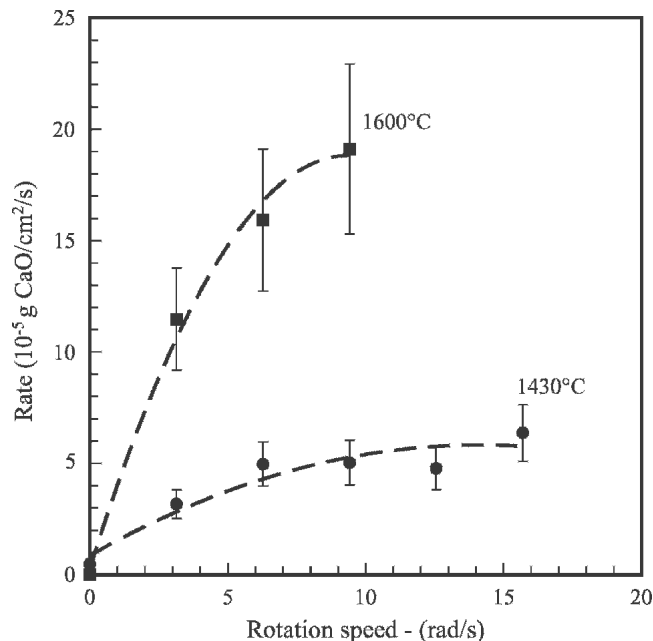


Fig. 3—Variation of the CaO dissolution rate in master slag A with rotation speed for samples at 1430 °C and 1600 °C.

more SiO_2 . The observed effect of temperature on destabilizing the solid layer separating the lime and slag at 1500 °C, 1550 °C, and 1600 °C from the present work is in agreement with the phase diagram data and suggests that the measured rates at these temperatures were most likely controlled by liquid-phase mass transfer only.

It was shown that addition of CaF_2 , and transition metal oxides (FeO_x , MnO_x , and TiO_2) increased the rate of lime dissolution in slag. Given that measured solubility of lime in

these slags did not show a significant dependence on temperature and levels of additives used, the observed effect of these additives is most likely through modifying the transport properties of the slag. This would be in accord with the findings of Hamano *et al.*^[2] and Lee *et al.*,^[23] where the addition of CaF₂ and transition metal oxides to their slags enhanced the transport properties of slag and subsequently increased the rate of dissolution of lime and alumina in their slags.

A number of researchers^[23–26] have deduced the chemical diffusivity in slags from dissolution rate data under forced-convection using the rotating disk/cylinder technique. They used the well-established Levich equation,^[21] which relates the mass-transfer coefficient (k_{disk} , cm/s) to the angular velocity of the disk (ω , rad/s) and physical properties of the liquid phase (kinematic viscosity, ν and diffusivity, D); *i.e.*,

$$k_{\text{disk}} = 0.621 D^{2/3} \omega^{1/2} \nu^{-1/6} \quad [2]$$

For the cylinder side of the rotating sample in liquid solvent, the hydrodynamic condition is also well researched and correlations between the mass-transfer coefficient (k_{cylinder}), peripheral velocity (V , cm/s), and Schmidt number (Sc) were expressed as a function of Reynolds number (Re).^[22] Kosaka and Minowa^[27] derived the following modified correlation from analysis of dissolution of rotating cylinders in various molten metallic systems:

$$k_{\text{cylinder}} = 0.065 Re^{-1/4} Sc^{-2/3} V \quad [3]$$

where $Re = \frac{\rho V d}{\mu}$, $Sc = \frac{\mu}{\rho D}$ and ρ , μ , and D are slag density, slag viscosity, and diffusivity of solute in the melt, respectively. This correlation was selected by the present authors for the analysis of experimental data obtained at high temperature.

It follows that the total mass flux from the rotating lime sample (j_{total}) to the liquid slag could be expressed as the sum of the mass fluxes from the disk (j_{disk}) and cylinder (j_{cylinder}); *i.e.*,

$$j_{\text{total}} = j_{\text{disk}} + j_{\text{cylinder}} \quad [4]$$

Equation [4] can be written as

$$k_{\text{total}} \cdot A_{\text{total}} \cdot \Delta C = k_{\text{disk}} \cdot A_{\text{disk}} \cdot \Delta C + k_{\text{cylinder}} \cdot A_{\text{cylinder}} \cdot \Delta C \quad [5]$$

where K , A , and ΔC represent the mass-transfer coefficient (cm/s), the surface area in contact with the melt (cm²), and the chemical driving force for dissolution (mole/cm³), respectively.

By substituting Eqs. [3] and [4] into Eq. [5] and rearranging terms, it can be shown that

$$k_{\text{total}} = \frac{r}{r+2h} 0.621 D^{2/3} \omega^{1/2} \left(\frac{\rho}{\mu}\right)^{1/6} + \frac{2h}{r+2h} 0.055 D^{2/3} r^{1/2} \omega^{3/4} \left(\frac{\rho}{\mu}\right)^{5/12} \quad [6]$$

$$k_{\text{total}} = D^{2/3} (A\omega^{1/2} + B\omega^{3/4}) \quad [7]$$

where D , R , and H are the chemical diffusivity, the radius of rotating sample, and the depth of immersion of the sample in the melt, respectively.

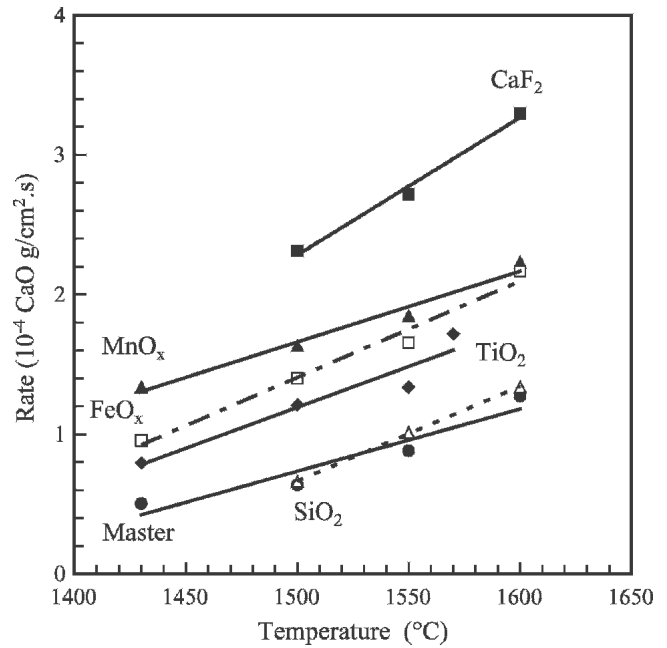


Fig. 4—Variation of dissolution rate of lime sample in slags with temperature for slags containing up to 5 wt pct of different additives (CaF₂, MnO_x, FeO_x, TiO₂, SiO₂).

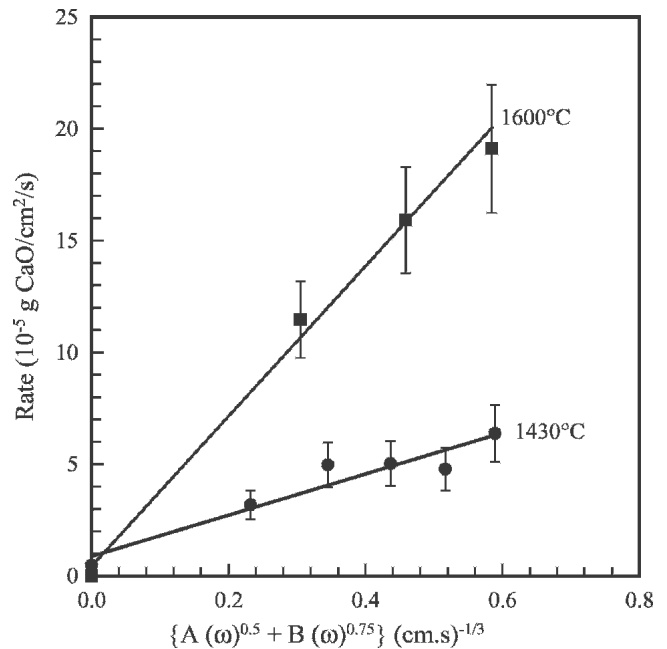


Fig. 5—Dependence of dissolution rate of lime in master slag A on $A(\omega)^{0.5} + B(\omega)^{0.75}$.

It should be noted from the relationship between the mass-transfer coefficient and viscosity that the dependence of mass transfer on slag viscosity is small; thus, changes to viscosity are unlikely to be the main cause of the increase in the lime dissolution. On the other hand, the dependence of mass transfer on diffusivity is stronger; thus, the marked increase in dissolution rate and mass transfer is likely to be caused by the increase in the diffusivity of lime in the slag.

The total mass-transfer coefficient (k_{total}) was calculated from the experimental dissolution rate shown in Figure 4 and the concentration gradient of lime between the lime-slag interface (C_s) and the bulk slag (C_b) according to the following equation:

$$k_{\text{total}} = \frac{\text{Rate}_{\text{total}}}{(C_s - C_b) \cdot \rho_{\text{slag}}} \quad [8]$$

The physical properties of the slag were estimated using Urbain's viscosity model,^[28] where, according to the *Slag Atlas*,^[3] the discrepancies between the experimental values and the predicted data by this model are about 25 to 30 pct, which is similar to the uncertainties in the experimental data on the slag viscosity. The slag density was estimated from the method proposed by Mills *et al.*,^[29] where the standard deviation of data predicted by the model compared to the experimental values was reported to be about ± 2 to 3 pct.

By equating Eqs. [6] and [8], the diffusivity of lime in the slag could be deduced. The uncertainty in calculation of the slope of initial dissolution rate, weight of molten slag bath, immersed area of lime sample in the slag, and dissolution rate data would result in about ± 33 pct uncertainty in estimation of diffusivity data. Figure 6 shows the variation of the diffusivity with the reciprocal of absolute temperature for the slags studied.

The diffusivity of lime in the master slag A was found to increase with temperature from 1.32×10^{-5} to 3×10^{-5} cm²/s as the temperature was increased from 1500 °C to 1600 °C. Addition of 5 wt pct CaF₂ to the master slag A increased the diffusivity by factors of 3 and 5 at 1600 °C and 1500 °C, respectively. Additions of MnO_x, FeO_x, and TiO₂ also showed marked effects on the diffusivity, and the diffusivity increased by 2 to 4 times depending on the additive and temperature, while addition of SiO₂ reduced the diffusivity of lime.

The observed effects of additives such as FeO_x and CaF₂ on the diffusivity of lime in the slag are in good accord with published data on self-tracer diffusivity in calcium silicate based slags containing transition metal oxides at comparable temperatures.^[14,16,17,30] The chemical diffusivity data from the present work for the master slag A are higher than the published self-diffusivity data and comparable with the apparent chemical diffusivity of magnesia and alumina in similar slags.^[23-26] Given that self-diffusivity is a measure of random movement of atoms in the melt, while the diffusion of CaO in the present work (chemical diffusivity) is affected by chemical gradient across the concentration boundary layer, it is reasonable to expect chemical diffusivity to be greater than self-diffusivity in melts.

The relationship between the structure of melts and their transport properties is believed to be a key to the fundamental understanding of the mechanism of diffusion in silicate melts and the effect of additives on the diffusivities. It has been postulated by Zhang and Jahanshahi^[8,9] that bond strength between ionic species should influence the structure and, hence, viscosity of such melts. Thus, apart from the differences in bond strength between cations (Ca²⁺, Mg²⁺, and Fe²⁺) and oxygen ions (O²⁻), the influence of various cations on the bonding environment of the silicate anions is

different. For a given silica content, when a small fraction of a cation is replaced by another in the melts, the changes in the structure of silicate anions are not expected to be great. Therefore, the variation in viscosity and diffusivity caused by such replacement may be attributed mainly to the difference in the strength of M²⁺-oxygen ion interaction; *i.e.*, the stronger the interaction between the ions in the melt, the more difficult the movement of ionic species and the slower the diffusion. Therefore, higher viscosity and lower diffusivity values are expected for melts with stronger M-O bond.

Zhang *et al.*^[8] considered the melting point of the oxide of divalent cations as an indication of the strength of the interaction between that cation and oxygen ions and showed that, for a number of divalent cations (Ca²⁺, Mg²⁺, Mn²⁺, Fe²⁺, Pb²⁺, *etc.*), there is strong correlation between the melting point of the oxides and their effect on lowering the slag viscosity of silicate melts. An alternative measure of bond strength between cations and oxygen anions is the enthalpy of formation of the oxides per g-atom of oxygen. According to the thermochemistry data on oxides,^[31] the enthalpies of formation of TiO₂, MnO, and FeO are about -472, -385, and -272 kJ/g atom of oxygen. This trend in the heat of formation is similar to the observed effects of additives on the diffusivity in the present work and tends to reflect the interaction between the oxygen anions and the cations introduced to the melt.

Given the fact that the slag considered in this study is very basic, the silicate anions are mostly in the form of nonchained anions, *i.e.*, SiO₄⁴⁻. Thus, when CaF₂ is added to the slag, a portion of the F⁻ ions (ionic radii of 1.33 Å) could replace some of the oxygen ions with a similar ionic radii of (1.32 Å) in the SiO₄⁴⁻ anion. Then, the existing Ca²⁺ cations and the ones introduced to

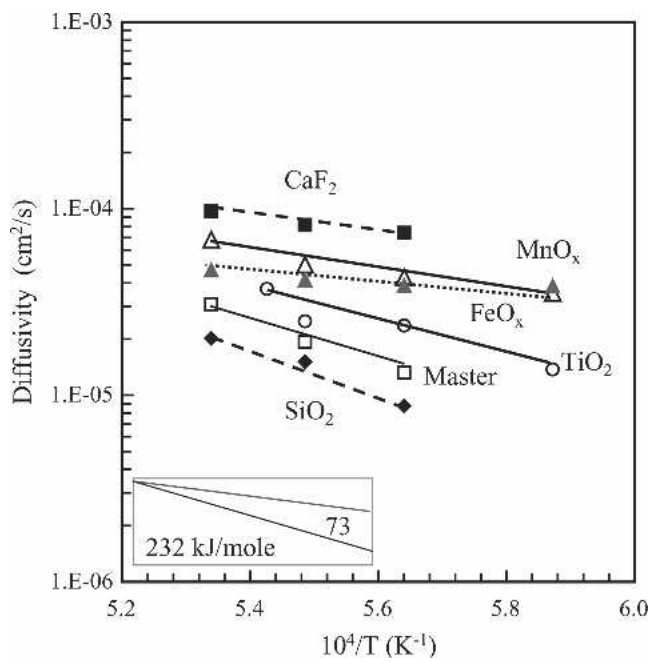


Fig. 6—Variation of the diffusivity of lime in the slags with reciprocal of temperature for slags with up to 5 wt pct of additives. The activation energy of diffusion for master slag is 231 kJ/mole, which is decreased to 73 kJ/mole by addition of CaF₂ to the melt.

the melt by addition of CaF₂ have weaker bonding with F⁻ compared to oxygen. The remainder of F⁻ ions in the slag could influence the interdiffusivity of other species in the slag and hence increase the diffusivity of CaO. However, the exact split of the F between SiO₃F³⁻ and F⁻ cannot be readily quantified. It was noted that addition of 5 pct CaF₂ to slag resulted in considerable increase in the diffusivity of CaO. It is likely that the observed effect is partly due to the introduction charge gradient caused by the fast diffusing F⁻ ions and partly due to weaker interactions between the cations and anions such as F⁻. Given that fast diffusing species could have a marked effect on the interdiffusivity of other species in slag, one would expect this mechanism to be primarily responsible for the observed effect of CaF₂ addition.

The effect of temperature on the diffusivity was investigated by deducing the activation energy of diffusion (*Q*) in the slags studied using the Arrhenius equation:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad [9]$$

where *D*₀ = a constant for a given solute and is independent of temperature (cm²/s), *D* = the diffusivity (cm²/s), *Q* = activation energy for the diffusion process (J · mole⁻¹), and *R* = 8.3144 = the universal gas constant (J · mole⁻¹ · K⁻¹).

The deduced activation energies are presented in Table II. The uncertainty of the estimation of activation energy data is about 33 pct. The results in Table II show that the activation energy of the master slag (232 kJ/mole) decreased markedly with the addition of 5 wt pct FeO_x, CaF₂, MnO_x, and TiO₂ but increased with the addition of 5 wt pct SiO₂ to the slag. The relatively high effect of FeO_x as compared with CaF₂ on reducing the activation energy for diffusion is a little surprising, and at this stage, no firm explanation can be offered. This may be due to the possible errors in the calculated effect of temperature on the viscosity of these slags. The activation energy for diffusion (*Q*) is generally regarded as the energy required for a species to diffuse in the melt. In the master slag, the energy barrier for the diffusion of CaO is the movement of anions. Therefore, with the addition of additives and CaF₂, the interaction of cations and anions would become weaker; thus, the silicate anions move more easily, which leads to a lower energy barrier for diffusion of CaO. On the other hand, by addition of SiO₂ to the melt, the movement of silicate anions becomes more restricted and slow; thus, the energy barrier for diffusion would increase.

The relationship between diffusivity and viscosity could be expressed according to Eyring's relation,^[32] where the diffusion of species in the melt is claimed to be controlled by the mobility of large anions. According to Eyring,^[32] the diffusivity (*D*) and viscosity (*η*) are related according to

$$D = \frac{kT}{\eta\lambda} \quad [10]$$

where *k* is the Boltzman constant and *λ* is the jump distance of diffusing species.

When the "thermodynamic factor," $\left(\frac{\partial \ln a_i}{\partial \ln c_i}\right)$, is introduced to account for the departure from ideal behavior, then Eq. [10] becomes

$$\frac{D_i \eta}{T} = \frac{k}{\lambda} \left(\frac{\partial \ln a_i}{\partial \ln c_i}\right) \quad [11]$$

where *D*_{*i*}, *a*_{*i*}, and *c*_{*i*} are the chemical diffusivity, activity, and concentration of solute *i* in the slag, respectively. This equation is sometimes referred to as the modified Stokes–Einstein relation.^[31] In Figure 7, the variation of log (*D*/*T*) with log (*η*) for slags with various additives is shown. It can be seen that the master slag A and the slags with addition of 5 wt pct SiO₂ or TiO₂ tend to follow the Eyring theory, where the slope from the log (*D*/*T*) vs log (*η*) plot is close to -1, but results for slags with other additives deviate from the Eyring theory. It should be noted that the diffusivity data have the uncertainty of about 33 pct, and the uncertainty of viscosity data is about 30 pct depending on the slag chemistry. Thus, the relationship between the diffusivity and viscosity in the framework of Eyring theory only indicates the general trend of data. According to Eyring theory, the movement of anions in the melt governs the diffusion of cations. The results of the present work show that the relationship between diffusivity and viscosity in the master slag and slag with 5 wt pct addition of SiO₂ closely follow the Eyring correlation. This shows that movement of anions in the melt plays a significant role in controlling the transport of cations. By the addition of additives such as TiO₂, MnO_x, FeO_x, and CaF₂, the diffusivity viscosity relationship deviates from the Eyring

Table II. Activation Energy of Diffusion (kJ/mole)

Slag	Activation Energy (kJ/mole)
A	232
B = A + 5 pct CaF ₂	73
C = A + 5 pct FeO _x	53
D = A + 5 pct MnO _x	98
E = A + 5 pct TiO ₂	162
F = A + 5 pct SiO ₂	246

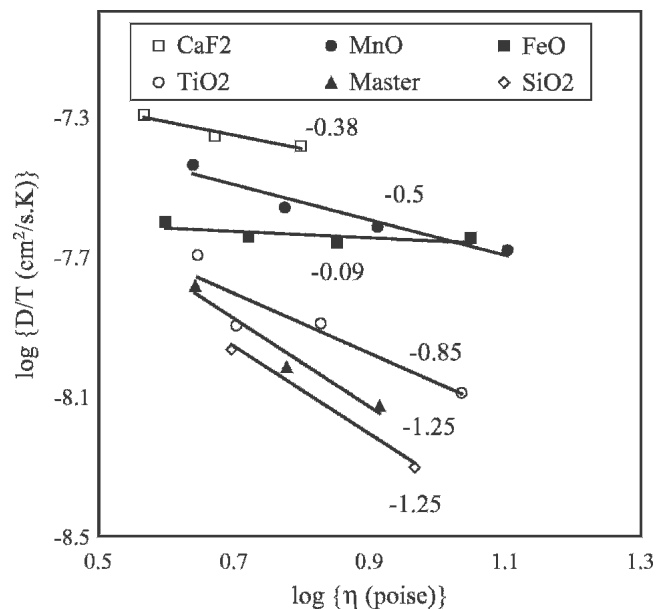


Fig. 7—Investigation on applicability of Eyring's theory for slags with various additives. The numbers on the plot show the slope of the lines.

theory (Figure 7), supporting the theory that movement of anions in the melt is a minor factor in controlling the diffusion of cations in such basic slags. This could be explained on the basis of the weaker interaction of added cations to the melt with oxygen of anions, which would lead to the easier mobility of anions in the melt and consequently faster diffusion of CaO in the slag. This is in agreement with the data in the present work on the effect of additives on the diffusivity of lime in the slag.

V. CONCLUSIONS

The dissolution rate of CaO was measured in CaO-42 wt pct Al₂O₃-8 pct SiO₂ base slag in a temperature range of 1430 °C to 1600 °C under conditions where the liquid slag mass transfer played a significant role in controlling the dissolution. The average dissolution rate of lime in the base slag over a temperature range of 1430 °C to 1550 °C was of the order of magnitude of 10⁻⁵ (g/cm² · s), while at 1600 °C, the dissolution rate was an order of magnitude higher. Addition of CaF₂ increased the dissolution rate by about a factor of 3, while addition of FeO_x and MnO_x doubled the dissolution rate.

The diffusivity of CaO in calcium aluminosilicate slags was deduced from the data on the dissolution rate and solubility of lime in the slag. The diffusivity increased substantially with increasing temperature and concentration of some additives in the slag. Addition of CaF₂ had the strongest effect and increased the diffusivity by a factor of 3 to 5 in the temperature range of 1500 °C to 1600 °C. MnO_x and FeO_x had a comparable effect in increasing the diffusivity by a factor of 2 to 4. TiO₂ also increased the diffusivity by a factor of about 2. However, addition of SiO₂ to the slag decreased the lime diffusivity.

The effects of temperature on the diffusivity of lime in the base slag and slags with additives were examined by calculation of the activation energy of diffusion. The activation energy for diffusion of lime in the base slag was about 232 kJ/mole. Addition of SiO₂ to the melt increased the activation energy to about 246 kJ/mole, while other additives reduced the activation energy. FeO_x showed the strongest effect on reducing the activation to about 53 kJ/mole.

The findings of the present work show that CaF₂ had the strongest effect on the dissolution kinetics of lime in the slag; MnO_x and FeO_x also increased the dissolution rate and diffusivity considerably.

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