Dissolution of Dense Lime in Molten Slags under Static Conditions

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Static dissolution of CaO into a CaO–SiO₂–Al₂O₃ slag with fluxing agents (fluorspar, ilmenite and nepheline syenite) was studied using two experimental techniques. In one method, the slag was packed into dense CaO crucibles, and heated to 1500°C/1600°C. After reaction, the crucible was air cooled and cross-sectioned. In the second technique, slag with a piece of lime was heated in a platinum capsule. The development of the Ca₂SiO₄ phase at the lime/slag interface and the CaO dissolved in the slag from the lime specimen were examined by Electron Probe Micro Analysis and Scanning Electron Microscopy. Ilmenite and nepheline syenite were found to be effective substitutes for fluorspar, increasing the CaO dissolution rate in the slag.

KEY WORDS: lime; dissolution; slag; fluorspar; nepheline syenite; ilmenite.

1. Introduction

Product quality and efficiency in the steelmaking industry are influenced by the chemical and rheological properties of the slag produced as an integral part of the operation. The chemistry of the slag is controlled by the addition of lime and other fluxes. Fluxes are required in steelmaking basically for two purposes. Firstly, to lower the melting point of slags so that slags of higher basicity can be used to reduce the level of residuals in steel. Secondly, to decrease the viscosity of slags and thus speed up refining reactions. BOF steelmaking and ladle refining operations are normally run with slag of high basicity, which is achieved by introduction of high volumes of lime. Efficient steelmaking practice requires rapid assimilation of lime by slag, which is influenced strongly by temperature and slag composition. Mechanisms of lime dissolution into slag under different conditions have been studied previously.^{1–9)}

Umakoshi *et al.*²⁾ studied the dissolution of a rotating burnt dolomite cylinder in Fe₇O–CaO–SiO₂ slag as a function of temperature (1350–1400°C) and rotational speed. They found a film of Ca₂SiO₄ at a short distance from the CaO interface which hindered the dissolution of CaO. They also concluded that the dissolution rate was affected by the (Fe, Mg)O solid solution, which was formed on the surface of the burnt lime. Matsushima *et al.*⁶⁾ investigated the dissolution of solid lime by dipping a crystalline lime cylinder into the static CaO–SiO₂–Al₂O₃ and FeO–CaO–SiO₂ slag bath at 1400°C and 1500°C and measured the concentration profile in the vicinity of interface. It was shown that

Ca₂SiO₄ precipitated slightly apart from the interface and the slag near the interface was enriched in Al₂O₃ or FeO, which indicated silica depletion due to the formation of the Ca₂SiO₄ film. These results seemed to confirm the long held belief that when lime is immersed in slag; a layer of di-calcium silicate is formed that slows down the dissolution process.

Fluxes such as fluorspar are usually added to increase the rate of lime dissolution. However, fluorspar causes emission of hazardous fluoride species, leaching of fluoride from generated slag, and refractory wear. These factors and dwindling accessible supplies of fluorspar have stimulated a search for alternative fluxes. The possibility of fluorspar substitution has been previously examined by a number of researchers.^{10–17)} Tribe *et al.*¹³⁾ presented a series of laboratory and industrial tests in which fluorspar in steelmaking slag was partially or fully replaced with feldspathoid mineral (a group of sodium and potassium aluminosilicate). They found that nepheline syenite tailing (NST) can be a suitable substitute for the fluorspar. NST slag exhibited a similar rheological behaviour to the CaF₂ slag. Also, when using NST, the steel chemistry was not affected and adequate desulphurisation was achieved. Singh *et al.*¹⁶⁾ conducted extensive industrial trials to show that the fluidity of slag with ilmenite (FeTiO₃) is very close to the fluidity of the fluorspar-containing slag, and concluded that ilmenite can be used as a fluorspar replacement in open hearth steelmaking. Poggi *et al.*¹⁷⁾ also found that the fluorspar and ilmenite have close melting points and both are very fluid when molten.

The current study examines the dissolution of lime at steelmaking temperatures in calcium aluminosilicate slags with basicity of 1. The aim of this study is to examine the effect of addition of 10 wt% fluxing agents: fluorspar, nepheline syenite and ilmenite on the rate of lime dissolution in the slag. While acknowledging that in industry, the burnt lime is porous (more than 50% porosity for soft-burnt lime and about 25% porosity for hard-burnt), it was decided to use a low porosity lime (8.4%). This was to ensure a sharp lime/slag boundary and consequently better control of experimental conditions.

2. Experimental

Static dissolution of CaO into slag was studied by two experimental techniques. Firstly, holding slag in a dense lime crucible, varying reaction time, temperature and slag chemistry. Secondly, by reacting a piece of lime with slag in a small platinum crucible, varying temperature.

2.1. Materials

Manufacture of the lime crucibles included the following operations. The limestone powder with 50–70 μm particle size was milled with alumina balls producing 0.8–1 μm particles that were then calcined to CaO and pressed in a mould and subsequently fired to provide the necessary density and strength. This technique allowed a close control of bulk density and apparent porosity by precisely varying compacting pressure, sintering temperature, rate of heating and cooling and sintering time.

The experimental slags were prepared in a platinum crucible by melting a mixture of slag components, quenching the melt and then re-melting to ensure slags' homogeneity. The master slag was a three component CaO–SiO₂–Al₂O₃ system with 45 wt% CaO, 45 wt% SiO₂, and 10 wt% Al₂O₃. Flux additions were made by adding 10 wt% of fluorspar and fluorspar replacement candidates to the master slag. The flux compositions used in the present work are presented in **Table 1** and the chemical composition of slags studied in the present work are tabulated in **Table 2**. In the case of the CaF₂ addition, subsequent analysis revealed that

the CaF₂ content of the resultant slag was only 5.7 wt% indicating a loss of fluorine. The fluorine loss and oxidation of calcium of fluorspar was previously reported by Shimizu *et al.*¹⁸⁾

2.2. Experimental Procedure

The dissolution of dense lime in molten slag was studied at 1 500 and 1 600°C as a function of time and slag composition. After cooling the samples the chemical composition of various elements in the liquid slag and also phase identification were quantitatively performed by EPMA mapping and SEM analysis.

In the first experimental technique performed at The University of New South Wales, the CaO crucible was filled with slag and charged to the muffle furnace. A sample was heated slowly at 100°C/h up to 1 250°C which is below the melting point of slag studied in this work, in order to minimize the risk of thermal shock in the crucible and then heated quickly at 600°C/h up to 1 500°C/1 600°C. Zero reaction time was defined as the time when the furnace first reached the desired temperature. After the required reaction times of 30 and 60 min, the crucible and slag were taken out of the furnace and quickly quenched in air. Due to the severe thermal shock, in most cases and especially experiments at 1 600°C, the lime crucible was shattered into pieces after air quenching, making it difficult to prepare a sample of lime with attached slag for further analysis. The recovered crucible with its slag content was cross-sectioned and mounted in resin.

Samples were prepared with a flat and well-polished surface, finished to (0–1) μm and then coated with a carbon layer (thickness ~ 200 Å) for electron probe microanalysis (EPMA). A CAMECA SX50 EPMA at The University of New South Wales was used in quantitative analysis of samples. All samples were examined using an accelerating voltage of 15 kV, a beam current of 20 nA and a beam size of 1 μm . Point analysis was performed for each distinct phase identified using back-scattered electron mode. A MATLAB¹⁹⁾ program was developed to convert the concentration profile of each element in the matrix to the mole percentage of various oxides and determined the phase locations in the ternary phase diagram. The phase diagrams at different temperatures were obtained from FactSage.²⁰⁾ The elemental distribution in the slag adjacent to the lime/slag interface was mapped by 2 μm step size stage movement in an area of 512 by 512 μm size and at a 256 by 256 image resolution. A MATLAB program was also developed to analyze the results from mapping. The program enabled recognition of Ca₂SiO₄ and Ca₃SiO₅ phases in the mapped area.

The formation of solid phases formed at the CaO crucible/slag interface was further investigated by carrying out another series of static experiments at Commonwealth Sci-

Table 1. Chemical compositions of fluxes.

(a) nepheline syenite		(b) ilmenite	
Oxides	Wt%	Oxides	Wt%
SiO ₂	59.30	TiO ₂	55.3
Al ₂ O ₃	19.28	Fe ₂ O ₃	24.1
Fe ₂ O ₃	2.25	FeO	16
CaO	0.91	Al ₂ O ₃	0.58
MgO	0.09	SiO ₂	0.93
Na ₂ O	8.33	MnO	1.48
K ₂ O	5.32	P ₂ O ₅	0.03
FeO	2.27	Cr ₂ O ₃	0.045

Table 2. Chemical compositions of slags.

Slag	CaO	SiO ₂	Al ₂ O ₃	CaF ₂	Na ₂ O	K ₂ O	Fe ₂ O ₃	TiO ₂
master slag	45.3	45	9.7	-	-	-	-	-
slag + CaF ₂	44.4	40.7	9.1	5.7	-	-	-	-
slag + nepheline syenite	41	46.2	10.5	-	0.9	0.6	0.9	-
slag + ilmenite	40.5	41.1	8.7	-	-	-	3.9	5.9

entific and Industrial Research Organization (CSIRO) division of Minerals, in which a platinum capsule was used to contain the slag and a piece of lime. The small platinum capsules (15 mm ID by 32 mm height) were made by welding two sides of a thin platinum foil. About 0.5 g of slag and 0.6–0.7 g of dense chipped CaO from crucible pieces were contained in the platinum capsule and were held vertically by shallow holes drilled in a refractory brick. The muffle furnace was ramped up to 1000°C at the rate of 100°C/h and then to the target temperature at the rate of 800°C/h. After reaching the temperatures of 1500 and 1600°C and exposure at temperature for the required reaction time, the platinum capsules were taken out of the muffle furnace and rapidly quenched on a brass plate, which was also cooled by an air flow on its back surface. The use of thin and small platinum foil in this technique provided a very fast cooling rate compared to the previous technique. The samples from the reaction experiments were cut, mounted in resin and coated with a carbon layer. These samples were analyzed using a Philips XL30 Scanning Electron Microscope at University of Melbourne. The electron optical system accelerating voltage was 20 kV.

3. Experimental Results and Discussion

Electron Micrographs of the sample at 1500°C from the lime crucible experiment (Fig. 1(a)) show formation of a Ca_2SiO_4 layer, which was also observed by Matsushima *et al.*⁶⁾ However at 1600°C, no discrete layer of Ca_2SiO_4 was detected (Fig. 1(b)). The dendritic appearance of the crys-

tallites indicates that they were not present in the liquid phase but crystallised out during cooling. Although a layer of Ca_2SiO_4 was not observed at 1600°C, it does not mean that it was not formed at this temperature. The loss of materials at the lime/slag interface because of the lime crucible shattering on air quenching or the loss of the layer in sample preparation cannot be excluded. “Slag composition” is the composition of the slag at experimental temperatures determined by analysis of quenched samples that consisted of both crystalline and glassy phases. Where the composition of these phases has been determined, it will be referred to as the crystalline or glassy phase composition.

Change in the slag chemical and phase composition in the process of lime dissolution measured by EPMA at 1500°C is shown in the CaO–SiO₂–Al₂O₃ phase diagram in Fig. 2. After achieving 1500°C (zero time), CaO concentration in the slag increased from the initial 45 to 48 wt%. After 30 min reaction, it reached 52 wt% and increased further to 54 wt% after 60 min. In the CaO–SiO₂–Al₂O₃ phase diagram, these compositions are within the liquid area (Fig. 2). At zero reaction time, the observed presence of the Ca_2SiO_4 phase at the slag crucible boundary (Fig. 1(a)) is the result of local non equilibrium conditions. The growth rate of di-calcium layer at 1500°C was measured by line scan with EPMA. The thickness of the layer is shown in Table 3. The measurement shows that at zero reaction time, the Ca_2SiO_4 layer has already been formed with a thickness of 164 μm , although the CaO content in the liquid slag was outside the Ca_2SiO_4 –liquid equilibrium curve. This means

(a)

(b)

Fig. 1. SEM of base slag in the lime crucible experiments for time=0 with 1000 magnification at (a) 1500°C, (b) 1600°C.

Fig. 2. The composition of bulk slag at various reaction times (min) in phase diagram for basic slag at 1500°C.

Table 3. Growth of Ca_2SiO_4 layer at 1500°C when the slag is reacted with CaO in the lime crucible and platinum capsule.

Reaction time (minutes)	Thickness of Ca_2SiO_4 layer (μm) at 1500 °C	
	CaO Crucible	Platinum Crucible
0	164	94
30	192	191
60	321	199

Fig. 3. The composition of bulk slag at various reaction times (min) in phase diagram for basic slag at 1 600°C.

that dissolution of lime into the slag occurred through the di-calcium silicate layer. The liquid phase composition achieved the equilibrium with Ca_2SiO_4 (Ca_2SiO_4 -liquid curve on the phase diagram) in 30 min. Slag CaO concentration increased slightly further with 1 h exposure. Obviously the dissolution of lime has been hindered by the formation of the Ca_2SiO_4 layer, and the rate of the Ca_2SiO_4 layer growth was greater than its dissolution rate. The growth of the Ca_2SiO_4 layer was accompanied by a change in the chemistry of the liquid slag along the Ca_2SiO_4 -liquid curve in accordance with the phase diagram in Fig. 2; the liquid slag was depleted of SiO_2 and enriched with Al_2O_3 , while the CaO concentration in liquid phase changed slightly, although its total concentration increased as a result of increasing thickness of the Ca_2SiO_4 layer.

At 1 600°C the change in slag chemical and phase composition in process of lime dissolution measured by EPMA is shown in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ phase diagram in Fig. 3. The initial dissolution rate of CaO into the slag was much faster than at 1 500°C. By “zero” reaction time, CaO concentration in the slag increased from 45 to 53 wt%, which is very close to the Ca_2SiO_4 -liquid equilibrium curve. Change in the slag’s CaO content with increasing reaction time was small (to 54–55 wt%) indicating that dissolution of lime had slowed dramatically and at this CaO content, the slag is saturated with di-calcium silicate. The composition of liquid slag analyzed by EPMA revealed an increase in alumina and a decrease in silica in the slag which indicates formation of the di-calcium silicate phase. Total content of CaO in the slag was about the same at 1 500°C and 1 600°C after dissolution for 30 min (52–54 wt%) and 60 min (53–55 wt%). The fact that the CaO content of slag has not been increased at 1 600°C and after 1 h of reaction shows that a layer of di-calcium was formed on the lime and slag interface.

In experiments, conducted in platinum capsule, a solid phase product layer was formed between the lime particles and the slag at both temperatures, which was identified by EDS analysis as Ca_2SiO_4 . At 1 500°C, the formation of reaction layer at the lime/slag interface at 1 500°C for the reaction times of 0, 30 and 60 min was in agreement with the

Fig. 4. Identified layer of Ca_2SiO_4 on the lime/slag interface by SEM when lime was reacted with slag in a platinum capsule at 1 500°C for reaction times of (a) 0, (b) 30 min and (c) 60 min.

observation from the previous experimental series. The micrographs of the reaction layer at 1 500°C and its growth is illustrated in Fig. 4. The average growth rate of the di-calcium layer as shown in Table 3 differs from the result of the experiments conducted in lime crucible. This could be due to the different slag to lime specimen ratio and also different cooling rate in both experimental techniques.

At 1 600°C, the experiments with platinum capsule were performed at the reaction times of 15, 30 and 60 min. The sample recovery during these experiments was more difficult than the experiments done at 1 500°C. The results for experiments at 15 and 60 min of reaction time shown in Fig. 5 clearly indicate the formation of Ca_2SiO_4 , which grows with time. For the experiment at reaction time of 30 min, the Ca_2SiO_4 was not recovered; it was presumably lost during quenching.

Mass balance calculations, based on the EPMA analysis of a glassy phase, were used to estimate the quantity of calcium oxide transferred to the slag at 1 600°C with addition of various fluxes in the lime crucible experiments (Table 4). The underlying assumption was that the increased alumina

Fig. 5. Identified layer of Ca_2SiO_4 on the lime/slag interface by SEM when lime was reacted with slag in a platinum capsule at 1600°C for reaction times of (a) 15 min, (b) 60 min, (c) overview of platinum capsule with slag and reaction layer after 60 min of reaction.

Table 4. Mass (g) of CaO dissolved in the slags (per 100 g of slag) at 1600°C .

Reaction time (minutes)	0	30	60
Master slag	17	19.5	19.9
Slag + CaF_2	15	16	20
Slag + N.S	18.7	23.3	26.3
Slag + ilmenite	29.4	30.8	30

content of the glassy phase had to be the result of precipitation of Ca_2SiO_4 . The mass of the glassy phase was calculated from the Al_2O_3 mass balance and the mass of di-calcium silicate from the SiO_2 mass balance, and finally the CaO transferred to the slag was estimated by mass balance of CaO. It is acknowledged that the accuracy of the EPMA results will have a significant effect on the accuracy and thus value of the resulting mass balances. At the same time, the results obtained (Table 4) are reasonably self consistent. They indicate that loss of fluoride from the fluorspar flux with consequent increase in slag CaO content has actually

decreased the lime dissolution. With both the ilmenite and nepheline syenite fluxes, there has been an increase in dissolution of CaO with time and flux addition. This is in accord with the data in the literature where addition of ilmenite and nepheline syenite has reduced the viscosity of slag with comparable effects with CaF_2 .^{10–13,16,17)}

With the addition of the fluorspar, ilmenite and nepheline syenite fluxes to the slag, no Ca_2SiO_4 layer was observed in the experiments, and CaO content of slag increased more rapidly with time (Table 4). Consequently, it would appear that flux addition might either prevent the formation of Ca_2SiO_4 layer or if a Ca_2SiO_4 layer is formed, dissolve the layer with the net effect of an increased lime dissolution rate.

Quaternary $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-(FeO}_x\text{, TiO}_2\text{, Na}_2\text{O)}$ phase diagrams constructed using FactSage,²⁰⁾ show that addition of nepheline syenite and ilmenite does not prevent formation of di-calcium silicate at 1600°C . However, it is known,²¹⁾ that addition of FeO_x , TiO_2 , Na_2O and K_2O decreases the viscosity of the slag. Decrease in the slag viscosity with addition of nepheline syenite and ilmenite accelerated the dissolution of Ca_2SiO_4 into the molten slag.

4. Conclusions

The dissolution of dense lime in molten $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slags was studied at temperatures of 1500°C and 1600°C by reaction of slags with a lime crucible. The effects of different fluxing agents and time of reaction were investigated. Ilmenite was the most effective flux and nepheline syenite was comparable to fluorspar, increasing the lime dissolution. When slag was reacted in the lime crucible at 1500°C , a di-calcium silicate layer was formed between the slag and CaO crucible, however at 1600°C no di-calcium silicate layer was evident. The formation of Ca_2SiO_4 layer was experimentally verified at 1600°C by reaction of lime and slag in a thin platinum capsule. No Ca_2SiO_4 layer was observed in experiments with flux addition; it was either not formed or dissolved in the slag. This is a major factor in explaining the increased rate of lime dissolution in the slag.

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