REMOVAL OF FLUORINE FROM MOLTEN SLAGS

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ABSTRACT

The use of CaF_2 in steelmaking slags and fluxes is being discouraged or banned in some countries; however no substitute has proven to be as effective. The existing stockpile of slags and other fluorine containing residues need to be treated to extract useful products such F and Fe and then convert the rest into by-products such as man-made sand or cement.

In this study, the rate of F removal from a $CaO\text{-}MgO\text{-}FeO\text{-}SiO_2\text{-}Al_2O_3\text{-}Na_2O$ slag was determined at 1175 to 1250°C. The fluorine containing slag was prepared from a mixture of Electric Arc Furnace slag, fluorine containing waste and calcium carbonate and silica fluxes. The slag chemistry was adjusted so that the slag would be fluid at 1150-1200°C. Fluorine removal was encouraged by the injection of a nitrogen-steam mixture into the slag phase via a stainless steel lance. Fluorine was removed by the formation of gaseous HF and was scrubbed using NaOH. In industrial processing, the F may be recovered for reuse.

Nitrogen gas containing 20% steam was injected at flow rates of 2 and 4 l min^{-1} into 500 g of slag at 1250°C with an initial fluorine content of 6 wt%. The rate of loss of fluorine expressed as wt%min^{-1} did not show any significant change with time and approximately doubled when the flow rate was increased from 2 l min^{-1} to 4 l min^{-1}. The removal rate was found to increase by a further 50% when the steam content was increased to 40% at 4 min^{-1}. These results may be described by the following empirical rate law:

F rate of removal $\propto Q \bullet p_{H_2O}^{1/2}$

where Q is the total gas flow rate and p is the partial pressure of water vapour in the reaction gas.

Temperature was found to have a strong influence on the rate of F removal, with the rate at 1250°C double the rate at 1175°C.

Key Words: *Fluorine, steelmaking slags, kinetics, wastes, residues.*

INTRODUCTION

There are several processes exploiting the properties of fluorine chemistry in the metallurgical industry, especially in aluminium and steel production. There has been significant effort in the aluminium industry to minimize the impact of fluorine containing wastes such as pot room scrubber waste and spent pot lining (SPL) by developing processes that reduce the environmental impact and recycle the fluorine [1, 4, 7, 8, 10, 11]. In the steel industry the use of CaF_2 in steelmaking slags is being discouraged or banned in some countries because of the possibility of reaction with moisture to produce HF [5, 16]. However no substitute has proven to be as effective as CaF_2 to lower liquidus or viscosity and still produce a mold slag with the appropriate properties for use in the continuous steel caster. The existing stockpile of slags and other fluorine containing residues need to be treated to extract useful products such as F and Fe and then convert the rest into by-products like man-made sand or cement.

Slags from smelting processes have been demonstrated as being suitable for handling fluorine containing wastes like waste fluorosilic acid (H_2SiF_6) [9] and producing stable product slags. In the case of fluorosilic acid treatment, the fluorine could be captured in a CaO-CaF_2-SiO_2 slag and used as a replacement for CaF_2 in mold flux powders.

In this study, the rate of F removal from a CaO-MgO-FeO-SiO_2-Al_2O_3-Na2O slag was examined using nitrogen/steam mixtures at 1175 to 1250°C. Fluorine was removed by the formation of gaseous HF and was scrubbed using NaOH. In industrial processing, the HF may be recovered for reuse or converted into other reagents.

EXPERIMENTAL

Equipment

A schematic of the furnace and the crucible assembly in the induction coil of a 400 kHz induction furnace is shown in Figure 1. Recrystallised magnesia crucibles (60 mm O.D., 50 mm I.D. and 200 mm high) were used in this study. A lid used to cover the crucible had a central hole, into which a Pythagoras tube (30 mm O.D. and 60 mm long) was cemented to form a flue. The flue allowed a lance to be passed down into the crucible and into the slag, and let exhaust gasses exit and be collected in the gas off take. A magnesia sheathed thermocouple was used to control the slag temperature. The crucible was heated by two susceptors, one inverted over the other, which were heated by the radio frequency induction.

A lance (5 mm O.D. and 3 mm I.D.) was used for injecting nitrogen/water mixtures into the slag and stirring the bath. Water was introduced into the lance by a small capillary that delivered a fine mist high up the lance. Nitrogen flow rates of 1.6, 2.4 and 3.2 l min^{-1} (STP) were used together with water flow rates of 0.32, 1.3 and 0.64 cm^3 min^{-1} giving total gas flows of 2 and 4 l min-1 respectively. The flow rate of nitrogen was maintained by a mass-flow controller and a variable speed peristaltic pump was used to deliver a constant flow rate of water. Water was delivered to the pump from burettes via a fine silicone hose. The volume of water delivered from the burettes was used to calibrate and monitor the water flow rates.

A stainless steel cover over the crucible and steel ducting above the crucible mouth collected the hot acidic off gas from the furnace, which was then drawn through ducting under a slightly reduced pressure. The rest of the fume collection system comprised steel pipe with a dropout box at the end of the pipe approximately 1.5 m from the ingress air point. The gases were then drawn into a scrubbing column packed with Teflon telluretes and washed with 2 M NaOH solution. After the scrubbing column, the gases passed through a halogen indicator trap and then vented to atmosphere.

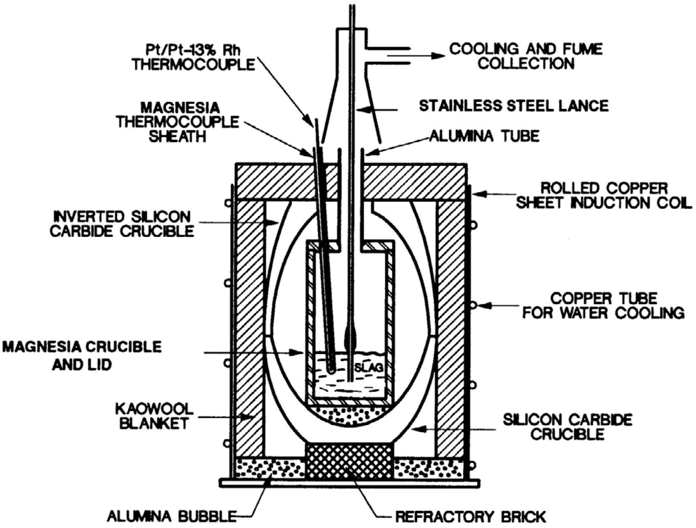

Figure 1: Schematic of the kilogram scale crucible and apparatus used for the test work

Materials

A master slag was prepared from a mixture of Electric Arc Furnace slag, a fluorine-containing waste and calcium carbonate and silica fluxes and the chemistry was targeted so the slag liquidus was below 1175°C. The liquidus temperature was estimated using the MPE thermodynamic package using a special database developed for $CaO-MgO-FeO-SiO_2-Al_2O_3-Na_2O-F$ slags [17]. The composition of the master slag is given in Table 1.

Table 1: Initial and final compositions of the slags used in this study. The basicity (B ratio) is the ratio of $(CaO+MgO+Na_2O)/SiO_2$

		Al_2O_3 (wt%)	Fe_t (wt%)	F (wt%)	B ratio
F1	Initial	21.8	20.3	6.05	2.04
	Final (174 min)	28.8	19.1	4.46	2.02
F2	Initial	21.7	20.4	6.02	2.06
	Final (90 min)	21.5	20.7	4.81	2.06
F3	Initial	21.0	21.9	6.08	2.14
	Final (270 min)	22.3	21.4	2.11	1.94
F4	Initial	17.8	16.5	5.19	1.00
	Final (110 min)	18.6	17.5	3.35	1.20
F8	Initial	21.5	20.1	6.36	2.06
	Final (120 min)	21.7	20.6	5.46	2.06
F11	Initial	18.4	15.3	5.46	1.05
	Final (120 min)	18.9	17.5	3.81	1.18
F12	Initial	18.5	16.4	5.4	1.10
	Final (100 min)	18.9	17.2	2.96	1.16

Procedure

The experimental procedure used was as follows:

Crushed slag and fluxes (500g) was added to the magnesia crucible which was then placed in the graphite susceptors and the insulation and thermocouple put in place. The gas train was assembled. The lance was positioned above the slag and a blanket cover of N_2 was maintained during heat up. The furnace was turned on and the crucible heated to 1250°C in approximately 2 hours. The scrubbing tower was turned on and any off-gases were then drawn into the gas train.

The water reservoirs were filled and the flow of water from the peristaltic pump was checked to see if the required flow was being delivered. The silicone hose from the pump was connected to the stainless steel capillary in the lance and checked for leaks.

When the crucible and contents had attained the required temperature, the nitrogen flow rate was set to the required rate and then the lance was lowered into the slag and positioned 10 mm from the crucible bottom. The slag was stirred for 2 minutes to ensure homogenisation and then the lance was withdrawn and a small slag sample was collected on a steel dip rod. The lance was then returned to the melt, the water pump turned on and the stopwatch started.

After the required time interval had elapsed (usually between 10 and 30 minutes) the lance was lifted and another slag sample was collected. The lance was then returned, pump and watch restarted. The interruption duration was less than two minutes. This procedure was repeated until sufficient time had elapsed to have collected 8 slag samples. The furnace was then turned off and the crucible was allowed to cool. When the crucible was cold, it was weighed, the slag separated from the crucible and the quantity of slag determined.

The compositions of the slags collected during the experiments were determined by XRF analysis.

RESULTS

The initial and final chemistries of the slags used in the test work are given in 1. The basicity (B) ratio of the slags is defined by the weight ratio of $(CaO+MgO+Na_2O)/SiO_2$. The variation of the fluorine content with time for experiments F1, F2 and F3 are shown in Figure 2. In this study, as tracked by both the Na_2O/CaO ratio and CaO/SiO_2 ratio in the slag, less than 1% of the Na and Si present in the slag volatilised and reported to the gas phase, and therefore the loss of F by NaF(g) or SiF_4(g) formation was negligible. The fluorine lost from the slag was predominantly due to the formation of HF(g).

It was found that a simple linear equation could be used to fit the variation of the fluorine content with time as shown in Figure 2. A summary of the test results is presented in Table. The data of most interest are:

- The initial fluorine content (F_0).
- The initial rate of F loss expressed as % min^{-1} calculated from a linear least squares fit of the F content in the slag over 90 or 120 minutes of smelting.
- The rate expressed as mol s^{-1}, rate from above using mass of slag and gas flow rate.
- The average partial pressure of HF calculated from the rate data and the gas flow rate.
- The relative rate, where the base case is at 1250°C, the total gas flow rate 4 l min^{-1} and the H_2O partial pressure 0.2 atm.

- The rate data are summarised in Table 2. The observed rate varies between 0.007 and 0.024 wt% F min^{-1}. The estimated partial pressure of HF in the exit gas is 0.02 to 0.035 atm at 1250°C.

Effect of Gas Flow Rate and Water Partial Pressure on F Removal

The effect of gas flow rate was examined in tests 1 and 2 at 1250°C, where 80%N_2-20% H_2O gas mixtures were used to generate HF. The rates of F loss from the two experiments where the injecting gas rates were 2 and 4 l min^{-1} are compared in Figure 2 and the rates of F loss are given in Table 2. The rate of F removal approximately doubled when the gas flow rate doubled.

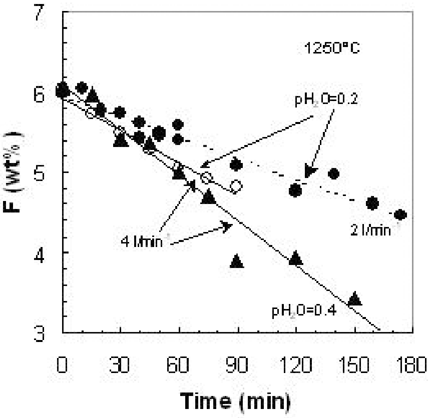

Figure 2: The effect of gas flow rate and partial pressure of H_2O on F removal from slag with a B ratio of 2.05 at 1250°C

Table 2: Summary of kilogram scale test results

	Temp (°C)	Q Total (l min^{-1})	p_{H_2O} (atm)	F_0 (wt%)	F_{60} (wt%)	Rate of F loss (% min-1)	Rate of F loss (Mol s^{-1})	Rel. Rate	P_{HF} (atm)
F1	1250	2.0	0.2	6.13	5.59	0.0069	3.0x10^{-5}	0.53	0.020
F2	1250	4.0	0.2	6.02	5.03	0.0135	5.9x10^{-5}	1.0	0.020
F3	1250	4.1	0.42	6.5	5.01	0.020	8.9x10^{-5}	1.51	0.030
F4	1250	4.0	0.2	5.19	4.09	0.0186	8.0x10^{-5}	1.38	0.027
F12	1250	4.0	0.4	5.44	3.58	0.0242	1.1x10^{-4}	1.8	0.035
F8	1175	4.0	0.19	6.36	5.94	0.0067	2.8x10^{-5}	0.51	0.01
F11	1175	4.0	0.2	5.46	4.48	0.0135	5.9x10^{-5}	1.0	0.02

The one to one correspondence of the F removal rate with injecting gas flow rate suggests that under the flow rate and injection conditions (gentle bubbling) the reaction is fast enough that the rate is controlled by gas supply and the gas and slag may be close to equilibrium. The water vapour pressure was also varied at two levels, i.e., 0.2 and 0.4 atm. The rate of F removal was found to increase with increasing p_{H_2O} in the reaction gas. Quantitatively, the rate was proportional to the square root of p_{H_2O}. Combining these two observations, it was found that the rate of F removal followed the following relationship:

$$rate \propto Q \bullet p_{H_2O}^{1/2} \tag{1}$$

as shown in Figure 3, where Q is the total gas flow rate.

Effect of Slag Basicity

Two basicity levels of the slag were tested in the experiments. The basicity ratio is defined by the ratio of the basic oxides (CaO, MgO, Na_2O) in weight percent over the acidic oxides (SiO_2), $(CaO+MgO+Na_2O)/SiO_2$

Figure 3 shows that as the basicity of the slag decreased, the rate of F removal increased.

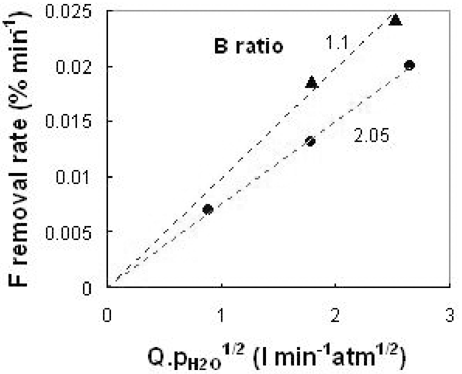

Figure 3: Rate of F removal at 1250°C from slags with a B ratio of 2.05 and 1.1 as a function of gas flow rate and p_{H_2O}

Effect of Temperature on the F Removal Rate

The rate of fluorine removal from the slag was also studied at a temperature of 1175°C, just above the estimated liquidus temperature. A comparison of the changes in the fluorine removal rate with temperature and slag basicity is shown in Figure 4. For a given slag basicity, the rate of fluorine removal at 1175°C was about half of that determined upon the same injection conditions at 1250°C.

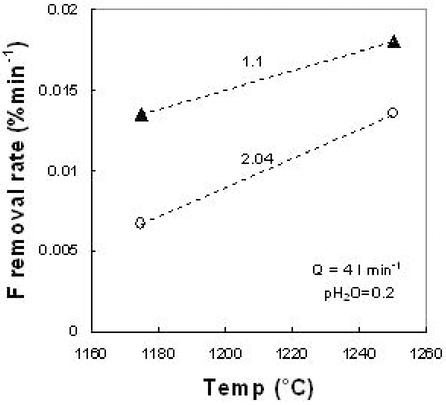

Figure 4: Effect of temperature on the rate of F removal from slags with a B ratio of 2.05 and 1.1 for injection conditions of 4 l min^{-1} and H_2O partial pressure of 0.2 atm

DISCUSSION

Dominant F Species in the Removal Reaction

In dry atmospheres, fluorine can be lost from complex slags as gaseous CaF_2, SiF_4, TiF, NaF and KF [12, 13, 16]. Fluorine is lost from CaO-CaF_2-SiO_2 slags as $CaF_2(g)$ and $SiF_4(g)$ with the latter specie having the higher partial pressure. The SiF_4 partial pressure above the slag decreases as the CaO/SiO_2 ratio increases [15, 14,]. For sodium and fluorine containing slags such as mold powder slags [14], NaF volatilises from the slag and condenses in the cold zones of the furnace. In this study, as tracked by the Na_2O/CaO and CaO/SiO_2 ratios, less than 1% of Na and Si present in the slags may be accounted as volatilised and reported to the gas phase, whereas the F content decreased to be between 86 and 35% of the initial concentration.

Using the data presented in Table 2R, and the nominal cross sectional area of the crucible, the rate of F lost from the crucible in the present study was 1.5 - 5.6 $\text{x}10^{-6}$ mol cm^{-2} s^{-1}, with the higher value at 1250°C. Shimizu & Cramb [13] determined that for mold flux slags, the major volatile species when dry N_2 or He was blown onto the surface of the slag were NaF and SiF_4. They did not directly determine which was the predominant species but estimated the proportions of NaF and SiF_4 in the gas phase from slag composition changes. For a mold flux slag containing 14% Na_2O, 27% SiO_2 and 15%F, NaF was identified as the major volatile fluoride species. Under conditions where the supply of carrier gas was more than 10 times the calculated gaseous mass transfer rate, the rate of weight loss from the mold flux slag was 2.4, 1.5 and 0.06 mg cm^{-2} s^{-1} at 1520, 1450 and 1350°C, respectively. From extrapolation to 1250°C, the estimated weight loss rate is 0.0054 mg $cm^{-2}s^{-1}$, equivalent to rate of F loss of 1 x 10^{-7} mol $cm^{-2}s^{-1}$, 55 times smaller than in this study. Given that the mold flux slag had a fluorine content that was also 2.5 times greater than the slags in this study, it is unlikely that fluorine loss in this study was due to volatilization of species of the metal fluorides but mostly from reaction between water vapour and steam as in Equation 2.

$$H_2O + (0.5\ SiF_4, CaF_2, 2\ NaF)_{slag} \Leftrightarrow 2\ HF + (0.5\ SiO_2, CaO, Na_2O)_{slag} \tag{2}$$

The Rate Law and the Rate Limiting Step

The apparent rate law (Equation 1) could well be accounted for assuming the gas-slag reaction attained an equilibrium state. The rate under such conditions is:

$$rate = Q_m \cdot p^{e}_{HF} / p_T \propto Q \cdot (p_{H2O})^{1/2} \tag{3}$$

where Q_m is the molar gas flow rate, p^{e}_{HF} is the equilibrium partial pressure of HF in the gas and p_T is the total pressure (an assumption is also made that $p_{HF} << p_{H_2O}$)

However, such rate law could also be due to some other kinetic characteristics. Breaking down reaction (2), the sequence of the reaction may involve the following steps:

$$H_2O \rightarrow H(ad) + OH(ad) \tag{4}$$

$$OH(ad) \rightarrow O(ad) + H(ad) \tag{5}$$

$$(ad) + F(ad) \rightarrow HF \tag{6}$$

In essence the reaction sequence includes steps of H_2O dissociation, and HF formation.

As discussed above, the formation of HF far exceeds volatilisation of F as SiF_4 (and the sub-fluorides) or NaF, etc. There is no experimental kinetic information regarding the HF formation step (reaction 6).

Glaws and Belton studied the rate of deuterium isotope exchange, whereby the rate of oxygen transfer from H_2O-H_2 mixtures to molten slags of silica saturated iron silicate [6] and calcium aluminosilicate slag containing 1% Fe [3]. The reaction includes the same sequence indicated by Equations (4) and (5). The rate has been found to be proportional to the partial pressure of H_2O, p_{H_2O} .The rate law is shown to be in agreement with step (5) being the rate limiting step, with reaction (4) and the reaction

$$2H(ad) \rightarrow H_2 \tag{7}$$

sufficiently fast. Through a comparison of the isotope exchange rate and the oxygen transfer from a steady state study of the reaction with H_2O-CO mixtures, it was concluded that the hydrogen exchange and the H_2O dissociation reactions occur in sequence. The rate limiting step was the dissociation of H_2O. The first order rate constant was also found to be inversely proportional to the activity of oxygen, $a_o = p_{H_2O}/p_{H_2}$.

Neglecting the possible effects of the limited changes in slag chemistry, and assuming the effective gas-slag reaction area is dominated by the gas bubbles and this area is proportional to the total gas flow rate [1], the rate law observed in this study would be in agreement with the same reaction scheme determined by Glaws and Belton. In fact, if the HF formation step (6) is the slow step, therefore rate limiting, the same rate law (Equation 3) could also be derived.

The level of control in these experiments may not be sufficient for detailed establishment of the reaction kinetics. Clearly further study on the interfacial reaction will be desirable.

Returning to the equilibrium consideration, reaction (2) may give rise to the following relationships between H_2O and HF partial pressures, i.e., at equilibrium:

$$p_{HF}^2 = \frac{p_{H_2O} \cdot a_{SiF_4}^{0.5}}{a_{SiO_2}^{0.5}} \cdot K_8 \tag{8}$$

$$p_{HF}^2 = \frac{p_{H_2O} \cdot a_{CaF_2}}{a_{CaO}} \cdot K_9 \tag{9}$$

$$p_{HF}^2 = \frac{p_{H_2O} \cdot a_{NaF}^2}{a_{Na_2O}} \cdot K_{10} \tag{10}$$

where a is the activity of the species in the slag, p is the partial pressure in the gas and K_8, K_9 and K_{10} refer to the equilibrium constants of reactions involving Si, Ca and Na in Equations 8 to 10 respectively. K_8 has a value of 4.28 at 1250°C, where a_{SiF_4} is with respect to the gaseous standard state, and a_{SiO_2} is with respect to solid cristobalite. In Equations 9 and 10, the reference state is solid for CaF_2, NaF, CaO and Na_2O. K_9 has a value of 2.29×10^{-4} and K_{10} has a value of 8.1×10^{-9} at 1250°C [2]. The equilibrium HF pressure may be estimated from any of the Equations of (8-10).

The measurements of the SiF_4 partial pressure above CaO-CaF_2-SiO_2 slags [14] can be extrapolated to the same temperature and silica content as this study; (17 and 26 %). The p_{SIF_4} may be between 10^{-4} and 10^{-3} atm respectively. However the fluorine content of these slags was 19%, more than 3 times the concentration of the present study which was

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[1] This assumption may not be unreasonable with consideration that the bubble size and the residence time in the study are not likely to change significantly with the flow rate of the bubbling gas.

around 6%, So p_{SIF_4} could be a factor of 3^4 times smaller if we assume that the behaviour of F in the slags is ideal or Henrian. For the experiment F1 identified in Tables 1 and 2, the slag contained 17% SiO_2, and p_{H_2O} was 0.2 atm. The partial pressure of SiF_4 and activity of SiO_2 was estimated from the MPE [17] to be 10^{-6} atm and 0.25 respectively.

The calculated equilibrium partial pressure of HF was 0.04 atm, agreeing within a factor of 2 with the partial pressure of 0.02 atm calculated from the experimentally determined slag composition changes. Similarly the activity ratio of a_{CaO}/a_{CaF_2} may be used and calculated using the MPE. Figure 5 shows the relationship between the initial and final partial pressures of HF from the experiments and the activity of lime at the same time.

The close agreement between the calculated equilibrium HF partial pressure and that determined experimentally suggests that the gas and slag may be close to equilibrium. The rate of F removal may be limited by the supply of reactants (H_2O) to the slag.

Practical Issues Regarding Treatment of F Containing Residues and Wastes

The steel industry produces a couple of F containing wastes as the slags, namely ladle slags fluxed with CaF_2 and the slag derived from casting powders, normally called mold fluxes or slags. The fluorine content in the ladle slags and mold slags could be reduced by steam injection, with similar or higher rates of reaction expected depending upon the gas injection conditions. With well designed slag chemistry, F could be economically recovered and the slag produced can be environmentally stable and useful. The HF recovered could either be captured as acid, or as a useful fluoride species, such as AlF_3 or CaF_2 which also has a favourable free energy of reaction [2].

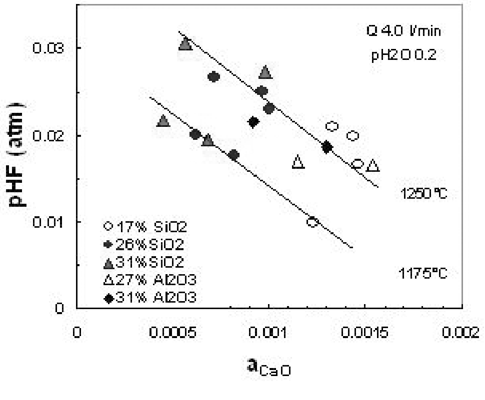

Figure 5: Relationship between the calculated initial and final HF partial pressures from the experiments and the activity of CaO calculated using the MPE from the corresponding initial and final slag compositions [17]

CONCLUSIONS

In this study, the rate of F removal from a $CaO-MgO-FeO-SiO_2-Al_2O_3-Na_2O$ slag containing 6% F was determined at temperatures of 1175 and 1250°C. Fluorine removal was encouraged by the injection of a nitrogen-steam mixture into the slag and HF was generated in the vapour phase. There was less than 1% change observed for Na_2O/SiO_2, CaO/SiO_2 and CaO/Na_2O ratios of the slag, confirming that F was lost primarily as HF and not NaF, or SiF_4.

Over the concentration range of 6 to 3 wt% in the slag, the rate of fluorine removal expressed as wt% min^{-1} did not show any significant change with time and approximately doubled when the flow rate was increased from 2 l min^{-1} to 4 l min^{-1}. The removal rate was found to increase by a further 50% when the steam content was increased to 40% at 4 l min^{-1}.

Under the conditions of this study, the rate of F removal was proportional to the total gas flow multiplied by the square root of the H_2O partial pressure. The rate of F removal from the slag at 1250°C was twice the rate measured at 1175°C. The rate of F removal from the slag increased as the basicity decreased or the silica content increased. The probable rate limiting steps of the H_2O reaction with the slag were discussed. Under the conditions of this study, the rate of reaction was most likely controlled by gas supply and the reaction between H_2O vapour and F in the slag was close to equilibrium.

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