J. Sustain. Metall. (2017) 3:515–527
DOI 10.1007/s40831-017-0119-3

RESEARCH ARTICLE

Development of a Suitable Slag Practice for Valorization of Fluorine-Containing Slags

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Abstract A submerged N_2–H_2O gas-injection technique was used to measure the rates of F and Na removal from complex industrial slags containing Al_2O_3, CaO, FeO_x, MgO, MnO, Na_2O, SiO_2, and F at temperatures between 1125 and 1250 °C. The results show that for a given slag chemistry, the rate of F removal is proportional to the gas flow rate and the square root of the water vapor partial pressure. The rate of F removal was also found to increase with silica concentration in the slag. The Na loss was generally low (<1%) and decreased as the silica content increased. There were no detectable losses of Si and Al. To test the environmental soundness of the slag, a series of fluxed slags were melted at 1250 °C and then water granulated. The slags contained 4% F, between 13 and 17% Na_2O, and SiO_2 varying from 16 to 45%. The granulated slags were crushed and subjected to the Australian Standard Bottle Leaching Procedure. With less than 20% SiO_2 in the slag, the leachate contained over 10 ppm F. Increasing SiO_2 above 20% in the slag produced a dramatic reduction of the F content in the leachate, to <2 ppm, and the F content decreased further as the SiO_2 content in the slag increased. The slags containing 25% SiO_2 or more passed the leaching procedure and were classified as nonhazardous.

Keywords Valorization · Slag · Wastes · Byproducts · Kinetics · Fluorine · Leaching

Introduction

Spent pot lining (SPL) is a byproduct of the aluminum smelting process. It contains soluble fluorides and cyanides in a matrix of carbon and oxide refractory materials. Because of its hazardous nature, there has been increased environmental pressure to discontinue landfill of this product and to treat the SPL to destroy the cyanide and to transform it into an environmentally benign product. There are many technical papers in the literature and patents, which have used a range of processes and technologies to recover the values from SPL. However, most of these processes are difficult, do not recover all the values, have doubtful economics, and still produce hazardous wastes.

Portland Aluminium (in Victoria, Australia) selected Ausmelt technology [1] for the treatment of SPL, and an R&D-scale plant was in trial operation at the Portland works at the beginning of 1998. In this process, the SPL together with various fluxing materials is fed into a top submerged lance (TSL) furnace and smelted by blowing oxygen-enriched air and natural gas. The cyanide is destroyed in the high-temperature process and part of the fluorine volatilizes as hydrogen fluoride (HF). The HF is subsequently converted to aluminum fluoride in a fluidized bed of alumina, which is recycled as part of the feed to the Hall–Heroult process. The objective is to lock the remaining fluorine in the slag ($\approx$4 wt% F) which has a

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The contributing editor for this article was I. Sohn.

Electronic supplementary material The online version of this article (doi:10.1007/s40831-017-0119-3) contains supplementary material, which is available to authorized users.

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"fluorine leachability value" of less than 10 ppm by the Australian Standard-Leaching Bottle Test [2, 3].

The plant tests had shown great promise in reaching process goals. However, a number of factors were restricting the process from achieving the optimal outcome. During the trial operation, high rate of sodium volatilization as NaF occurred. This was collected and recycled back into the smelting furnace. A need to improve the rate of fluorine removal from the slag as HF and to inhibit the rate of sodium volatilization and enhance its retention in the slag phase was identified.

The design of the optimal slag chemistry was a key element in the successful operation of the process. The slag had to meet the following requirements:

- A liquidus temperature of less than 1200 °C.
- A slag chemistry where the F removal with steam injection was close to optimal.
- A slag chemistry where volatilization of NaF was minimal.
- A slag chemistry that was close to saturation with MgO-rich phases so as to enhance the refractory life.
- In the solidified state, the slag ought to be nonhazardous to human health and the environment.
- The solidified slag was suitable for further processing or applications, e.g., thermal insulation, cement aggregate, road base.

This paper reports on two aspects of the R&D program, namely:

- Development of optimal slag chemistries with respect to F and Na removal, using kilogram-scale batch TSL smelting tests. Through these TSL smelting tests, the effects of slag chemistry, temperature, and gas-injection rate on the volatilization rates of F and Na were evaluated.
- The second aspect examined was the stability of the slag to environmental leaching tests. For these tests, fluxed slags containing a maximal 4% F were melted and water granulated. The granulated slags were crushed and subjected to the Australian Standard Bottle Leaching Procedure to determine the F content of the leachate [4] and to determine the chemistry where the F content was very low, so that the slag could be classified as nonhazardous.

This study helped Alcoa Portland to optimize the slag chemistry at their demonstration plant at Portland. This study aided in maximizing HF removal from the furnace and minimizing Na in the AlF_3 product. The refractory life was also extended significantly. The granulated vitreous slag product conformed to Victorian EPA criteria to permit its use for unrestricted purposes and consequently avoid the slag being disposed of in landfill.

Experimental

Materials

Certain quantity of slag (D0) collected from the TSL furnace at Portland Aluminium prior to fluorine removal and identified as having a chemistry typical of normal operation was crushed to <5 mm for the smelting tests and analyzed by a standard XRF method. Slag D3 was collected after fluorine stripping in the TSL furnace and was blended with Slag D0 for the granulation and leaching studies. The chemistries of the slags and the commercially supplied fluxes used in the study are given in Table 1.

The liquidus temperature of slag D0 was estimated to be less than 1175 °C using the CSIRO MPE thermodynamic package and a database for $CaO–MgO–FeO_x–SiO_2–Al_2O_3–Na_2O–F$ slags [5].

Smelting Studies

Kilogram-Scale Smelting

A schematic of the furnace and the crucible assembly in the induction coil of a 400-kHz induction furnace is shown in Fig. 1. Recrystallized magnesia crucibles (60 mm O.D., 50 mm I.D., and 200 mm height) were used. The 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 gases exit and be collected in the gas offtake. 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 means of 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 means of 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 mL^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 a burette via a fine silicone hose. The volume of water delivered from the burette was used to calibrate and monitor the water flow rate.

A stainless steel cover over the crucible and steel ducting above the crucible mouth collected the hot off-gas, 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

Table 1 XRF analysis of the materials for use in this study and reported analyses from manufactures for limestone, silica, alumina

Sample	SiO_2 (wt%)	CaO (wt%)	Al_2O_3 (wt%)	FeO_x (wt%)	Na_2O (wt%)	K_2O (wt%)	MgO (wt%)	Cr_2O_3 (wt%)	Mn_3O_4 (wt%)	TiO_2 (wt%)	P_2O_5 (wt%)	F (wt%)
D0 [A]	16.5	13.9	21.4	20.3	16.8	0.6	3.2	0.6	2.5	0.5	0.3	6.0
D0 [B]	16.6	13.9	21.4	20.3	17.1	0.6	3.1	0.6	2.5	0.5	0.3	6.0
D3 (1)	16.2	15.3	27.3	24.8	9.4	0.2	3.6	0.6	2.8	0.4	0.4	1.0
D3 (2)	16.3	15.4	27.2	24.8	9.5	0.2	3.6	0.6	2.8	0.5	0.4	1.0
Limestone	2.23	53.0	0.595	0.545	0.013	0.051	1.05	<0.005	0.004	0.038	0.024	0.19
Silica	99.5	0.243	0.389	0.166	<0.005	0.070	<0.05	0.011	<0.005	0.092	0.006	<0.05
Alumina	<0.05	0.041	96.4	0.005	0.274	<0.005	<0.05	<0.005	<0.005	<0.005	<0.005	<0.05

[A], [B], two representative samples submitted for analysis

(1), (2) Duplicate analysis

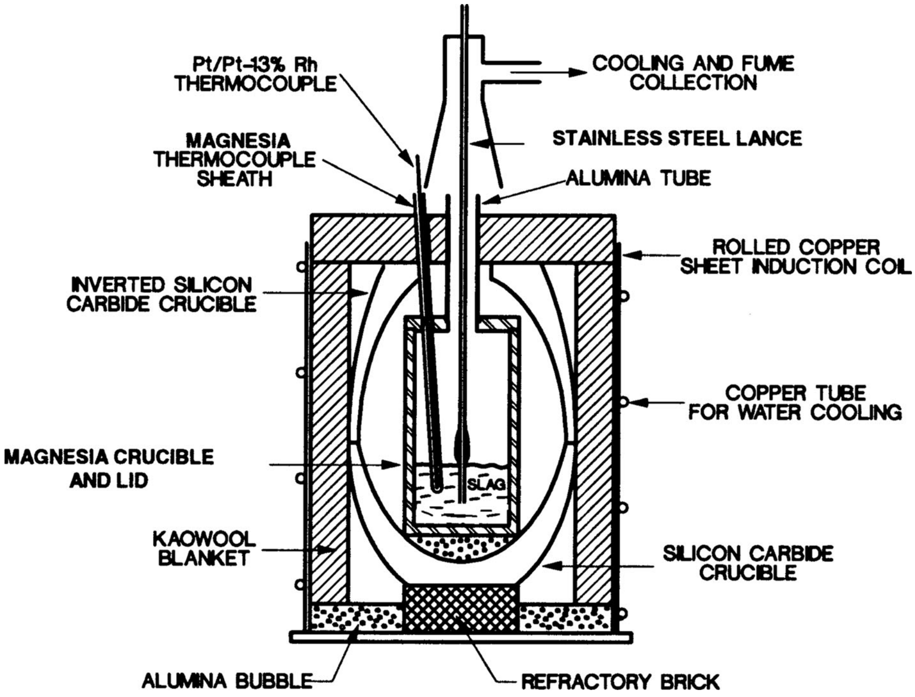

Fig. 1 Schematic of the kilogram-scale crucible and apparatus used for the test work

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 were then vented to atmosphere.

Procedure

The slag and fluxes listed in Table 1 (500 g) were 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 the heat-up process. The furnace was turned on and the crucible heated to the required temperature, typically of 1250 °C in approximately 2 h. The scrubbing tower was turned on, and 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. The hose from the pump was connected to the capillary in the lance and checked for leaks.

When the crucible and contents reached 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 min to ensure homogenization, 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 timer started.

After the required time interval (usually between 10 and 30 min), the lance was lifted and another slag sample was collected. The lance was then returned, and pump and timer

Table 2 Kilogram-scale experimental program

	Slag	Temp (°C)	Parameter investigated	Q_{H_2O} (L min^{-1})	Q_{N_2} (L min^{-1})	Q_{Total} (L min^{-1})	p_{H_2O} (atm)	Slag (g)	Flux (g)
F 1	D0	1250	Dependence of flow rate	0.41	1.60	2.0	0.2	500	
F 2	D0	1250	"	0.75	3.20	4.0	0.2	500	
F 3	D0	1250	H_2O partial pressure	1.72	2.40	4.1	0.42	500	
F 4	88% D0 + 12% S	1250	Silica content	0.80		4.0	0.2	440	60
F 5	82% D0 + 18% S	1250	"	0.81		4.0	0.2	410	90
F 6	94% D0 + 6% A	1250	Alumina content	0.68		4.0	0.18	468	32
F 7	87% D0 + 13% A	1250	"	0.74		4.0	0.19	436	64
F 8	D0	1175	Temperature	0.75	3.2	4.0	0.19	500	
F 9	82% D0 + 18% S	1175	Silica & temperature	0.77	3.2	4.0	0.19	410	90
F 10	82% D0 + 18% S	1125	"	0.75	3.2	4.0	0.19	410	90
F 11	88% D0 + 12% S	1175	"	0.81	3.2	4.0	0.20	440	60
F 12	88% D0 + 12% S	1250	Silica and H_2O partial pressure	1.58	2.40	4.0	0.40	440	60

S silica, *A* alumina

restarted. The interruption duration was less than 2 min. This procedure was repeated until sufficient time had elapsed to have collected eight 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 was then separated from the crucible, and the quantity of slag determined. The slag samples were individually pulverized in a ring mill to a fine powder, and a 500-mg sample of each was used for XRF elemental analysis including fluorine, using a general major/minor application where the detection limit was less than 0.001 wt%.

The experimental program is listed in Table 2. The key variables studied were temperature, gas flow rate, water partial pressure, silica content, and alumina content. Slag (D0) collected from the TSL furnace at Portland prior to F removal was used as the base case chemistry for the experimental program. This slag had a B ratio, defined as $(CaO + MgO + Na_2O)/SiO_2$ of 2.06 and a CaO/SiO_2 ratio of 0.82.

Fluorine Leachability of Glassy Slags

A series of 6-kg-scale water granulation tests were performed to prepare glassy slags so that the leachability of fluorine from slags with different chemistries could be studied. The method used was according to the Australian Standard AS 4439.3-1997, Part 3: Preparation of leachates—Bottle leaching procedure, and treating the slags as a Class 4 Landfill category material. The Standard requirement *in "Part 7.5, Table 2* is that the leaching fluid for this category shall be reagent water" [4]. As local mains water contained 0.7–1.2 ppm of fluorine, all equipment coming into contact with the leachate was washed with distilled water before drying.

All the slag chemistries were targeted to a fluorine content of 4 wt%, which was regarded as an upper limit after fluorine removal. This was achieved using slag (D0) and slag (D3) in proportions required to yield that value. Apart from the fluorine content, the slag chemistries of D0 and D3 were very similar. The Na_2O content was also aimed at a concentration expected in the slag from normal furnace operation, namely 17%. A small amount of Na_2CO_3 was added to raise the Na_2O content to 17%. When silica or limestone was added, the proportions of D0 and D3 were adjusted to maintain 4 wt % F in the slag. The targeted slag chemistries are given in Table 3.

Kilogram-Scale Slag Melting and Granulation

For the granulated slag preparation, a tilting induction furnace was used. A magnesia crucible of 70 mm O.D. × 60 mm I.D. × 240 mm H was placed in a susceptor located in the induction coil. The space between the crucible and susceptor was filled with graphite flakes to ensure an even heat distribution. Alumina cement was used to secure the crucible in the susceptor for pouring. An R-type thermocouple was positioned outside the magnesia crucible and a K-type thermocouple enclosed in a stainless steel sheath was positioned inside the crucible for temperature measurement.

Approximately 750 g of the mixed slags and fluxes were added to the crucible and then heated to 1250 °C in 2 h. The remaining mixture was then gradually added over 30 min. The melt was then stirred with nitrogen at 3.5 L min^{-1} with a stainless steel lance for 10 min prior to pouring.

The melt was poured onto an inclined copper plate with a 1 cm deep by 10 cm wide channel. Water flowing at 20 L min^{-1} was sprayed onto the surface of the channel. When the slag was poured into the channel, it quenched rapidly, granulated, and washed down to a recovery tank.

Table 3 Targeted slag compositions

	SiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	CaO (wt%)	Na_2O (wt%)	F (wt%)	MgO (wt%)	Mn_3O_4 (wt%)	Cr_2O_3 (wt%)	P_2O_5 (wt%)
Q 1	16.0	23.0	21.0	14.0	17.0	4.0	3.0	2.5	0.5	0.3
Q 2	26.0	19.0	18.0	12.0	16.0	4.0	3.0	2.0	0.5	0.3
Q 3	31.0	18.0	17.0	11.0	16.0	4.0	3.0	2.0	0.4	0.2
Q 4	45.0	13.0	13.0	9.0	14.0	4.0	2.0	1.5	0.3	0.2
Q 5	15.0	21.0	19.0	18.0	13.0	4.0	3.0	2.0	0.5	0.3
Q 6	20.0	21.0	20.0	13.0	17.0	4.0	3.0	2.0	0.5	0.3

Table 4 Granulated slag compositions

	SiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	CaO (wt%)	Na_2O (wt%)	F (wt%)	MgO (wt%)	Mn_3O_4 (wt%)	Cr_2O_3 (wt%)	P_2O_5 (wt%)
Q 1	16.3	22.8	21.1	14.0	16.9	3.94	3.6	2.5	0.5	0.3
Q 2	25.9	18.7	17.5	12.0	16.0	4.1	3.2	2.1	0.5	0.3
Q 3	31.9	18.4	17.4	11.8	16.3	4.21	3.5	2.1	0.5	0.3
Q 4	46.2	13.4	13.0	9.0	14.4	3.9	3.1	1.6	0.4	0.2
Q 5	15.5	20.8	17.1	20.6	16.2	4.15	4.7	2.2	0.5	0.3
Q 6	19.9	21.4	20.0	13.4	16.5	4.7	3.6	2.3	0.5	0.3

After decanting the water, the recovered slag was dried at 80 °C in an air-forced oven. A small amount was removed and submitted for XRF and XRD analysis. The remaining sample was used to study the leaching behavior. The chemical analysis of the slags is shown in Table 4, and the powder pattern in the XRD spectra was of the form of a typical quenched glass with some small peaks indicative of some crystallinity [6].

Leaching Tests

2 L Nalgene bottles were used as leaching vessels. The device employed for agitation was designed to hold four bottles and was capable of rotating them in an end-over manner at the prescribed rate of 30 ± 2 rev/min. A 142-mm hazardous waste filtration unit supplied by Gelman Sciences was used for separating the leach liquors. It was designed to meet the requirements of the US EPA SW-846 1311 toxicity characteristic leaching procedure (TCLP) [7] and uses a 0.6-µm glass fiber filter.

The granulated slags were friable glass with a particle size of approximately <8 mm. A representative sample of each slag was crushed using a mortar and pestle until it passed a 2.4-mm screen. Each of the six slags was tested in duplicate.

A sample of 100 g of slag was placed in the extraction bottle and two liters of distilled water added. The bottle was capped and placed in the agitator and the samples were rotated for 18 h, after which the leachate was filtered and a liquid sample collected for analysis.

The fluorine was analyzed by ion chromatography using a Dionex DX300 chromatography system. The standards for calibration were prepared from A.R. grade sodium fluoride. A reference slag with an independently determined value for F leachability of 20 ppm was tested using the above procedure. The F leachability obtained was 20.5 ppm, in excellent agreement with the established value of 20 ppm.

Results

Smelting Studies

The chemical analyses of the slag samples collected as a function of time are given in Appendix, Tables A1 to A12 in Supplementary Material. In test F 1, an alumina lance was used and the results showed a steady increase in alumina content with time as shown in Fig. 2a. The fluorine content (Fig. 3) shows a linear decrease with time. The fluorine analysis was corrected for the dilution by alumina, which reduced the apparent rate of removal. This correction for increase in slag volume/dilution was not required in all the other tests as stainless steel lances were used

(Fig. 2b) and changes in slag compositions due to lance dissolution (i.e., the iron and chromium content) were not evident.

Linear equations were used to fit the variation of the fluorine content with time for experiments F 1 to F 12, as typified in Fig. 3. A summary of the test results is presented in Table 5. The data of most interest are

- Initial fluorine content (F_0);
- 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 min of smelting);
- Rate of F loss expressed as mol s^{-1} (calculated from above using mass of slag and gas flow rate);
- Average partial pressure of HF (calculated from the rate data and the gas flow rate); and
- The relative rates of F loss using the base cases, i.e., 1250 °C, DO slag, total gas flow rate of 4 L min^{-1}, and partial pressure of water of 0.2 atm.

The rate data are summarized in Table 5. The observed rate varies between 0.007 and 0.024 wt% F min^{-1}. The estimated partial pressure of HF in the exit gas ranges from 0.02 to 0.035 atm at 1250 °C.

Fluorine Leachability of Glassy Slags

The results of two samples of each of the six water granulated slags subjected to the Australian Standard Bottle Leaching Procedure are given in Table 6. There was good reproducibility between the A and B samples for each slag, but significant variation with slag composition. This will be discussed in the next section.

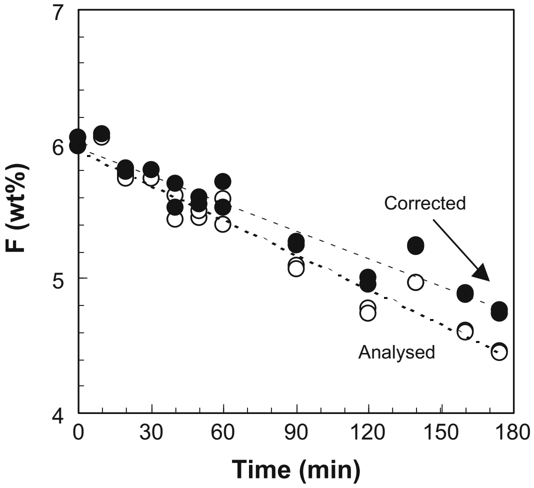

Fig. 3 Changes in fluorine composition with time for experiment F 1. The analyzed fluorine content was corrected for dilution with alumina, due to dissolution into the slag

Discussion

Volatilization of Na, Si, and Al from Slag

Co-volatilization of species other than fluorine from the slag is of concern in producing a high-purity AlF_3 product after scrubbing the fluorine from the furnace off gas. Of particular concern is the transfer of Na and Si from the slag to the AlF_3 product. The amount of solid fume collected in the present study was negligible, typically less than a gram and this was mainly scale generated by the acidic off-gas reacting with the mild steel ducting. The small amount of fume collected was not sufficient for chemical analysis and

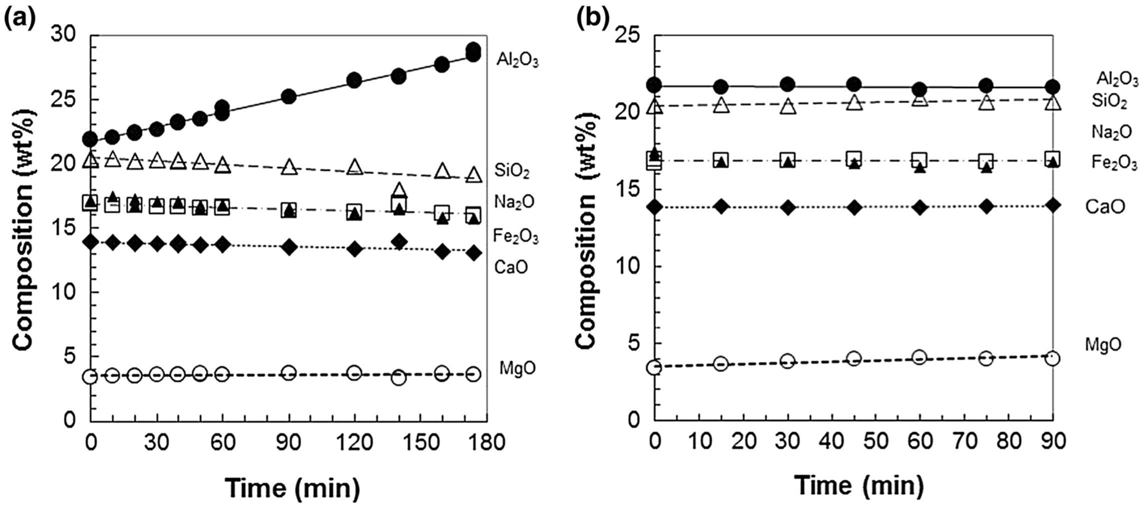

Fig. 2 **a** Changes in slag composition with time for experiment F 1 where an alumina lance was used. **b** Experiment F 2 with a stainless steel lance

Table 5 Summary of results from kilogram-scale smelting tests

	Slag	Temp (°C)	Q_{Total} (L min^{-1})	p_{H_2O} (atm)	F_0	F_{60}	Rate of F loss		Rel. rate	p_{HF}
							% min^{-1}	Mol s^{-1}		
F 1	D0	1250	2.0	0.2	6.13	5.59	0.0069	3.0×10^{-5}	0.53	0.020
F 2	D0	1250	4.0	0.2	6.02	5.03	0.0135	5.9×10^{-5}	**1.0**	0.020
F 3	D0	1250	4.1	0.42	6.5	5.01	0.020	8.9×10^{-5}	1.51	0.030
F 4	88%D0 + 12%S	1250	4.0	0.2	5.2	4.09	0.0186	8.0×10^{-5}	1.38	0.027
F 5	82%D0 + 18%S	1250	4.0	0.2	5.0	3.53	0.021	9.3×10^{-5}	1.64	0.031
F 6	94%D0 + 6%A	1250	4.0	0.18	5.85	5.06	0.012	5.1×10^{-5}	0.95	0.017
F 7	87%D0 + 13%A	1250	4.0	0.19	5.52	4.50	0.0144	6.3×10^{-5}	1.10	0.021
F 8	D0	1175	4.0	0.19	6.36	5.94	0.0067	2.8×10^{-5}	0.51	0.010
F 9	82%D0 + 18%S	1175	4.0	0.19	5.0	4.15	0.0145	6.4×10^{-5}	1.11	0.021
F 10	82%D0 + 18%S	1125	4.0	0.19	4.90	4.18	0.0121	5.3×10^{-5}	0.90	0.018
F 11	88%D0 + 12%S	1175	4.0	0.20	5.46	4.48	0.0135	5.9×10^{-5}	1.0	0.020
F 12	88%D0 + 12%S	1250	4.0	0.40	5.44	3.58	0.0242	1.1×10^{-4}	1.8	0.035

Table 6 Fluorine leachate analysis of the granulated slags

Granulated slag	Fluorine in leach liquor (ppm)	
	A sample	B sample
Q 1	12.1	11.8
Q 2	1.6	1.3
Q 3	0.96	1.16
Q 4	0.32	0.21
Q 5	11.7	12.9
Q 6	11.1	11.1

the approach taken to examine the loss of volatiles was to track composition changes in the slag. Figure 4 shows the changes in the Na_2O/CaO ratio with time and the effect of basicity (CaO/SiO_2 ratio) on sodium loss.

As CaO/SiO_2 ratio decreased, sodium volatilization from the slag decreased. Reducing temperature also significantly reduced sodium loss, to the extent that for a slag with a CaO/SiO_2 ratio of 0.36, the loss of Na was calculated to be <2 g per kilogram of slag at 1175 °C.

Alumina addition (Fig. 5) had little effect on reducing sodium vaporization. The slope of the Na_2O/CaO ratio with time for three experiments at different alumina contents and constant CaO/SiO_2 ratio was effectively constant. The potential for Si and Al to volatilize was also studied in a similar manner to Na, with changes in the Al_2O_3/CaO and SiO_2/CaO ratios with time examined. When the natural scatter in the chemical analysis was considered, the amount of Si and Al deporting to the fume was insignificant.

Fluorine Removal from Slag

The effect of gas flow rate on the removal of fluorine was examined in two tests at 1250 °C, where 80% N_2–20% H_2O gas mixtures were used to generate HF. The rate of F loss from the two experiments where the injecting gas rates were 2 and 4 L min^{-1}, respectively, is compared in Fig. 6 and the rates of F loss are given in Table 5. The rate of F removal nearly doubled when the gas flow rate doubled.

The one-to-one correspondence of the F removal rate with injecting gas flow rate suggests that the reactions summarized in Eq. (1) are fast enough that the gas and slag may be close to equilibrium:

$$H_2O + (0.5\ SiF_4,\ CaF_2,\ 2\ NaF)_{slag} \rightleftharpoons 2HF + (0.5\ SiO_2,\ CaO,\ Na_2O)_{slag} \qquad (1)$$

The possible reactions have the same form of relationship between the water and HF partial pressure:

$$p_{HF}^2 = p_{H_2O} \cdot a_{CaF_2}/a_{CaO} \cdot K_1, \qquad (2)$$

$$p_{HF}^2 = p_{H_2O} \cdot a_{NaF}^2/a_{Na_2O} \cdot K_2, \qquad (3)$$

$$p_{HF}^2 = p_{H_2O} \cdot a_{SiF_4}^{0.5}\Big/a_{SiO_2}^{0.5} \cdot K_3, \qquad (4)$$

where a is the activity of the species in the slag and K_1, K_2, K_3 refer to the respective equilibrium constants (Eq. 1).

Dominant F Species in the Gas Phase

The previous sections show that there is a strong association between water injection and loss of fluorine from the slag, and the volatilization of other cations which may form volatile fluorides species is at least a magnitude smaller than the removal of fluorine. In dry atmospheres, fluorine

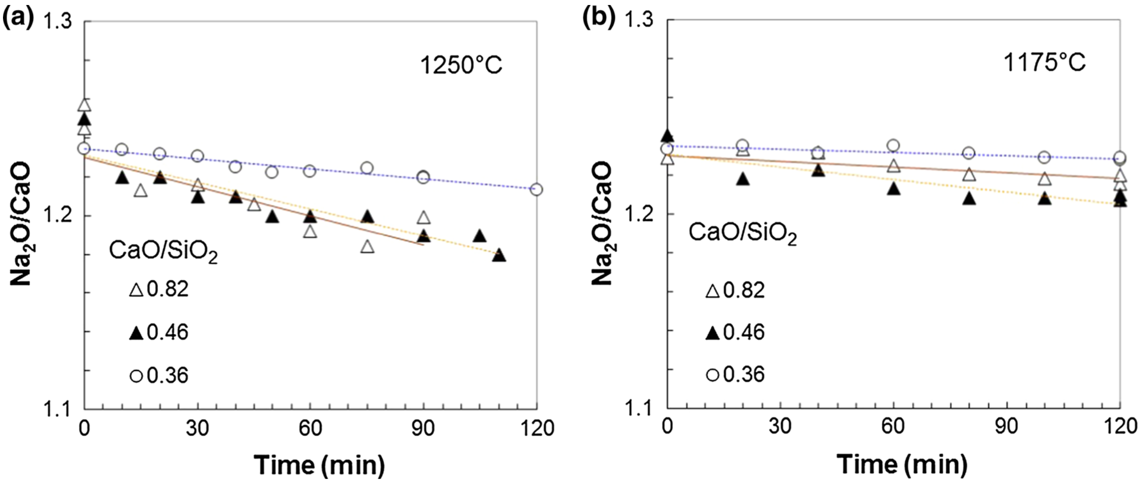

Fig. 4 Effect of CaO/SiO$_2$ ratio on sodium loss from the slag at **a** 1250 °C and **b** 1175 °C. *Symbols* represent the constant CaO/SiO$_2$ ratio

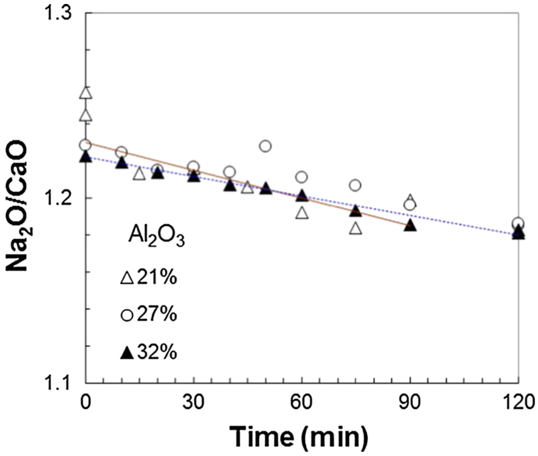

Fig. 5 Loss of sodium from slag fluxed with alumina (CaO/SiO$_2$ = 0.82) at 1250 °C

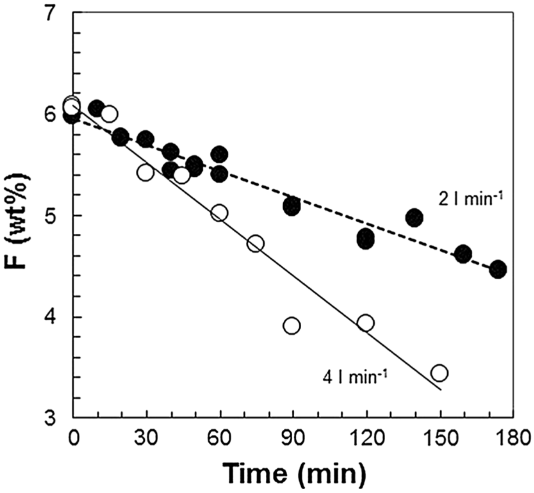

Fig. 6 The effect of gas flow rate with $p_{H_2O} = 0.2$ atm. on F removal from slag with a B ratio of 2.06 at 1250 °C

can be lost from complex slags as gaseous CaF$_2$, SiF$_4$, TiF, NaF, and KF [8–10]. Fluorine is lost from CaO–CaF$_2$–SiO$_2$ slags as CaF$_2$(g) and SiF$_4$(g) with the latter species having the higher partial pressure. The SiF$_4$ partial pressure above the slag decreases as the CaO/SiO$_2$ ratio increases [11, 12]. For sodium- and fluorine-containing slags such as mold powder slags [12], NaF volatilizes from the slag and condenses in the cold zones of the furnace. In this study, as tracked by the Na$_2$O/CaO ratio and the CaO/SiO$_2$ ratio, less than 1% of Na and Si present in the slags volatilized 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 5, and the nominal cross-sectional area of the crucible, the rate of F lost from the crucible was 1.5 to 5.6 × 10^{-6} mol cm^{-2} s^{-1}, the higher value at 1250 °C. Shimizu and Cramb [10] 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$_2$O, 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 rates of weight loss from the mold flux slag were 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 the rate of F loss of 1 × 10^{-7} mol cm^2 s^{-1}, 55 times smaller than the current 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 vapor and steam as given by Eq. (1).

Effects of Slag Chemistry and Temperature on F Removal

Silica Content

In the previous section, it is argued that the reaction between water vapor and the slag may be close to equilibrium, and therefore from Eqs. (2) and (3), decreasing the ratio of a_{CaO}/a_{CaF_2} and a_{Na_2O}/a^2_{NaF} will increase the HF partial pressure. Addition of an acidic oxide such as silica will decrease the activity of Na_2O and CaO in the slag, and to a lesser degree reduce the activity of NaF and CaF_2 [5]. Figure 7 shows that the rate of fluorine removal increased as the silica content increased and the CaO/SiO_2 ratio decreased. Over the composition range covered, there appears to be a linear relationship between silica content (expressed as basicity) and F removal rate. The rate of F removal increased as the basicity of the slag decreased, i.e., the activity of CaO decreased.

As shown in Fig. 7b, within the temperature range studied, the fluorine removal rate increased as temperature increased. The rate of F removal from slag at a constant basicity ratio doubled over a 75 °C temperature increase from 1175 to 1250 °C.

Alumina Content

The effect of alumina addition to the as-received slag was studied at two higher concentrations, 27 and 32% Al_2O_3. The effect of the alumina addition on the rate of F removal is shown in Fig. 8, with the F removal rate constant when fluxed to 32% Al_2O_3.

When the effect of alumina addition was compared with silica, silica was found to be a more effective flux in increasing the fluorine removal rate.

The Rate Law and the Rate-Limiting Step

The one-to-one correspondence of the F removal rate with injecting gas flow rate, shown in Fig. 6, suggests that the reaction between water vapor and F in the slag was fast enough that the gas and slag may be close to equilibrium. Figure 6 shows a zero order rate with respect to F concentration in the melt. Thus, the possibility of mixed mass transfer-controlled regime could be ruled out.

The apparent dependence of the rate on the slag chemistry could be explained in terms of the effect of slag chemistry on the activities of fluoride species and hence the driving force for the volatilization of F from the melt, when one considers the following rate equation:

$$\text{rate} = k_g\left(p^e_{HF} - p^b_{HF}\right)$$

where k_g is the gas mass transfer coefficient and p^e_{HF} and p^b_{HF} are the partial pressures of HF at the slag–gas interface and in bulk gas.

The rate equations derived from Eqs. (2) to (4) all have the same form:

$$\text{rate} = Q_m \cdot p^e_{HF}/p_T \quad \propto \quad Q \cdot (p_{H_2O})^{1/2}, \tag{5}$$

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 total pressure. Keeping the gas flow rate at 4 L min^{-1} and doubling the water partial pressure increased the rate by about 50% as

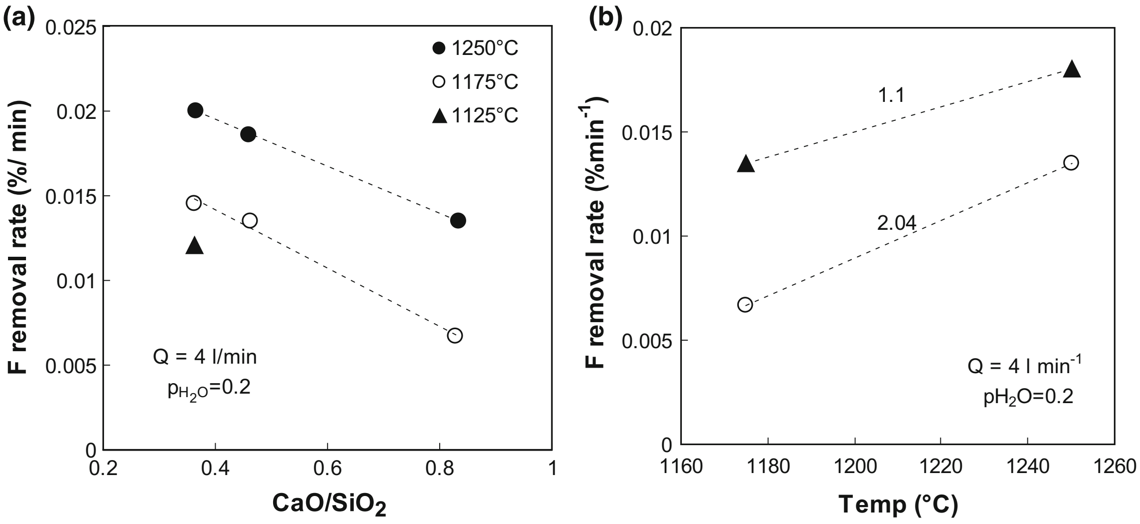

Fig. 7 Effect of silica expressed as CaO/SiO_2 ratio and temperature on the F removal rate. **a** CaO/SiO_2 ratio. **b** Temperature

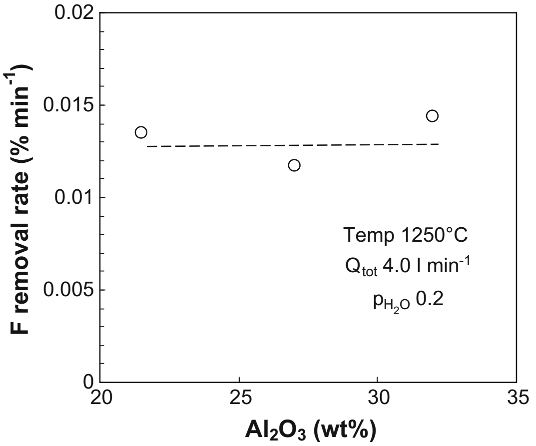

Fig. 8 Effect of fluxing with alumina ($CaO/SiO_2 = 0.82$) on the F removal rate

shown in Table 5 (AF3). The rate of F removal for the slags with a constant basicity ratio (B ratio = $(CaO + MgO + Na_2O)/SiO_2$), where flow rate and/or partial pressure of H_2O was varied, was plotted against the right-hand side of Eq. (4) and is shown in Fig. 9. In addition, the figure shows a straight line passing through the origin that could be plotted for the rate data for slags where the basicity was fixed.

Breaking down the reaction (Eq. 1), the sequence of the reaction may involve the following steps:

$$H_2O \rightarrow H_{(ad)} + OH_{(ad)}, \tag{6}$$

$$OH_{(ad)} \rightarrow O_{(ad)} + H_{(ad)}, \tag{7}$$

$$H_{(ad)} + F_{(ad)} \rightarrow HF. \tag{8}$$

In essence, the reaction sequence includes steps of H_2O dissociation and HF formation. As discussed above, the formation of HF far exceeds the volatilization of F as SiF_4 (and the sub-fluorides) or NaF, etc. There is no experimental kinetic information regarding the HF formation step (Eq. 8).

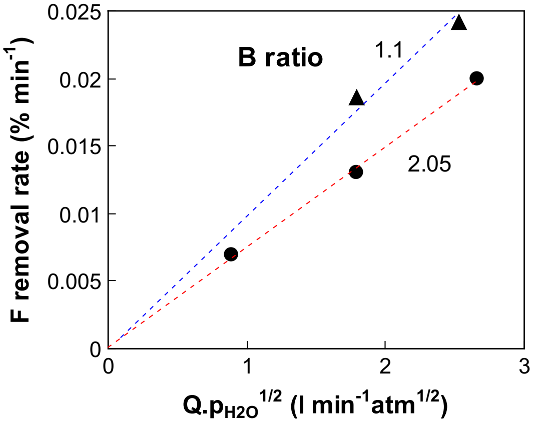

Fig. 9 Rate of F removal at 1250 °C from slags with B ratios of 2.05 and 1.1 as a function of gas flow rate; Q and p_{H_2O}

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 [13] and calcium aluminosilicate slag containing 1% Fe [14]. The reaction includes the same sequence indicated by Eqs. (4) and (5). The rate was found to be proportional to the partial pressure of H_2O. The rate law is shown to be in agreement with Eq. (7) being the rate-limiting step, with Eq. (6), and the reaction

$$2H_{(ad)} \rightarrow H_2 \tag{9}$$

being 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, Glaws and Belton 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 the slag composition 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 (Eq. 8) is the slowest step, therefore rate limiting, the same rate law (Eq. 5) also applies.

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

Returning to the equilibrium consideration, reaction (1) may give rise to the following relationships between H_2O and HF partial pressures, shown in Eqs. (2) to (4). The equilibrium constants of these reactions, K_1, K_2, and K_3 have values of 2.29×10^{-4}, 8.1×10^{-9}, and 4.28 at 1250 °C, respectively [15]. For these reactions, the reference state is solid for CaF_2, NaF, CaO, Na_2O, and SiO_2 with SiF_4 having a gaseous reference state. The equilibrium HF pressure may be estimated from any of the Eqs. (2) to (4).

For the slag with a B ratio of 2.06, which contained 17% SiO_2, and p_{H2O} of 0.2 atm, the calculated equilibrium partial pressure of HF is 0.04 atm, agreeing within a factor of 2 with the partial pressure calculated from the slag composition changes of 0.02 atm. Figure 10 shows the

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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.

relationship between the initial and final partial pressures of HF and the corresponding activity of lime in the slag.

The uncertainties in determining the initial rate of F loss were estimated to be <10%, while the uncertainties at the end of the experiments will be significantly greater. The uncertainties arising from calculating the activity of CaO are estimated to be at least 10%, as the description of the thermodynamic behavior is built up from behavior in binary systems [5, 16]. Figure 10 shows that, when the uncertainties are considered, there is consistent behavior of all the slag compositions studied with respect to fluorine removal. 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.

Effects of Silica and Alumina on Magnesia Solubility

The dissolution of MgO into the slag from the crucible increased as the silica content increased (Fig. 11a). During the progress of the experiment, the slag with a CaO/SiO_2 ratio of 0.82 appeared to reach magnesia saturation at about 4% MgO after an hour. When the slag was fluxed with silica, the initial dissolution rate of MgO was slightly higher, and after 2 h the slags had a MgO content of 5% but appeared not to have yet attained MgO saturation. When alumina was used as a flux (Fig. 11b), the dissolution of MgO was lowered, suggesting that addition of alumina has stabilized a spinel phase and reduced MgO solubility.

Figure 12 shows that reducing the operating temperature to 1175 °C reduced the impact of MgO dissolution and the solubility of MgO in the slag appeared to be lowered by at least 1%. After 60 min, the F content of the slag fluxed to 26% silica was 4.5%, and the slag fluxed to 31% SiO_2 contained 4.1% F, still significantly lower than the F content of the existing fluxed slag at 1250 °C over the same period.

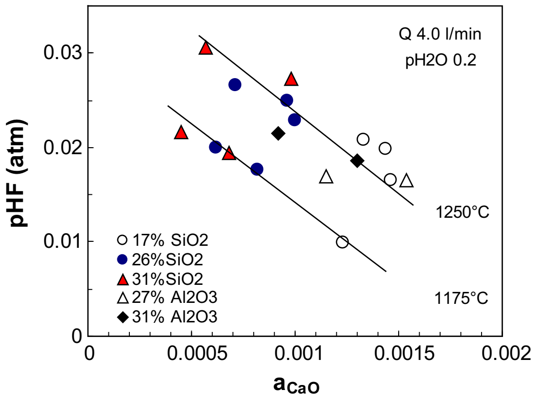

Fig. 10 Relationship between the calculated initial and final HF partial pressures from the experiments and the activities of CaO calculated using the CSIRO MPE software from the corresponding slag compositions [4]

Fluorine Leachability from Quenched Granulated Slag

The concentration of fluorine in the leachate plotted against the silica content in the slag is shown in Fig. 13. The leaching results that for a slag which contained less than 20 wt% SiO_2, the leachate contained over 10 ppm F. Increasing SiO_2 above 20 wt% in the slag produced a dramatic reduction of the F content in the leachate. When slag contains more than 25 wt% SiO_2, fluorine in the leachate was less than 2 ppm and decreased further as the SiO_2 content in the slag increased. Increasing the basicity of the slag by adding lime did not decrease F dissolution.

The low F levels in the leachate of the granulated slags which contain greater than 25% SiO_2 mean that the slags are classified as nonhazardous and can be used for unrestricted purposes. The intended opportunity to use the slag was for road and footpath construction, where the slag would be a replacement for sand, gravel, or aggregate [2, 3].

Practical Issues Regarding Treatment of F-Containing Residues and Wastes

The steel industry produces F-containing wastes, 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 on the liquidus temperature of the slag and the gas-injection conditions. This work shows that a with a carefully designed slag chemistry, F can be 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 have favorable free energies of formation from oxides [15].

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 vapor phase. There was less than 1% change observed for Na_2O/SiO_2, CaO/SiO_2, and CaO/Na_2O ratios of the slag,

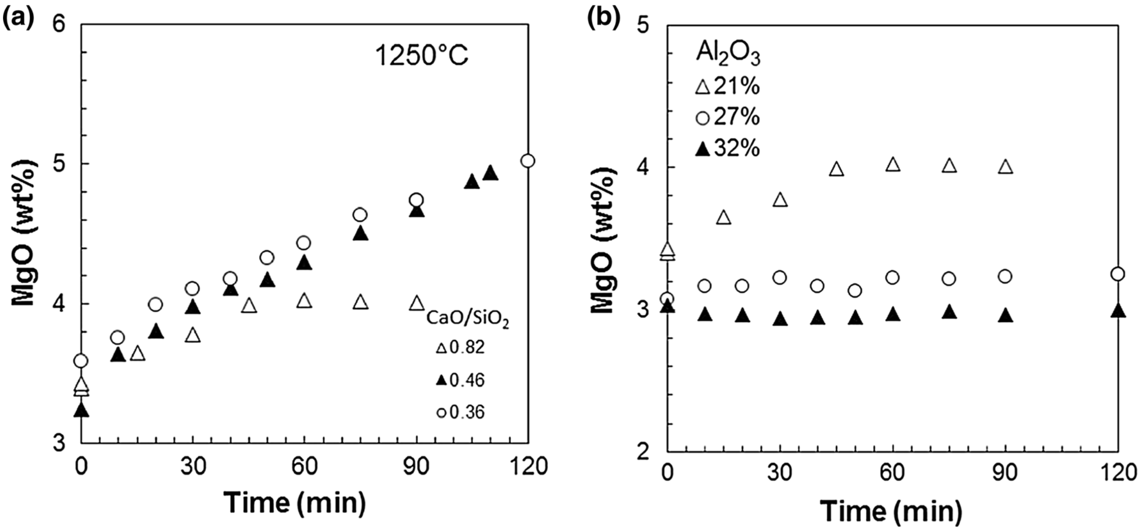

Fig. 11 Effects of **a** silica fluxing and **b** alumina fluxing ($CaO/SiO_2 = 0.82$) on the MgO content at 1250 °C

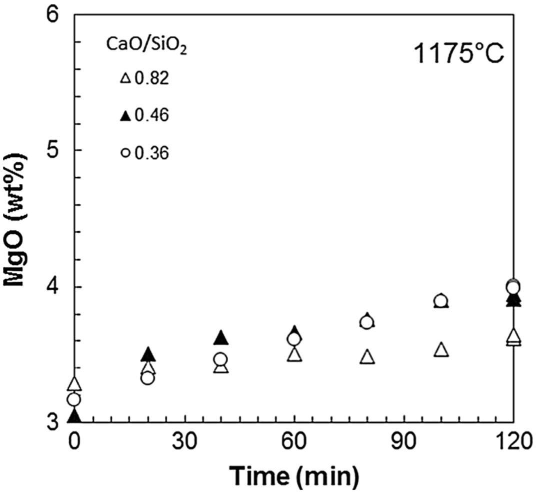

Fig. 12 Effect of silica fluxing on the MgO content at 1175 °C

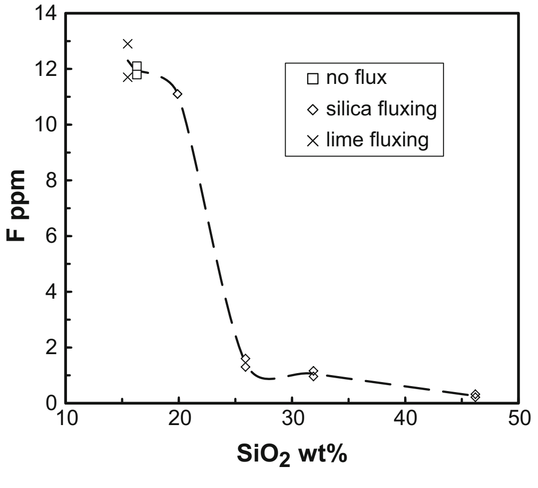

Fig. 13 Fluorine content of the leach liquor from the water granulated slags

confirming that F was lost primarily as HF and not NaF, CaF_2, or SiF_4.

Over the concentration range of 6–3 wt% in the slag, the rate of fluorine removal expressed as % min^{-1} did not show any significant change with time and approximately doubled when the flow rate was increased from 2 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 H_2O partial pressure to the power of 0.5. 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. Under the conditions of this study, the rate of reaction was most likely controlled by gas supply and the reaction between H_2O vapor and F in the slag was close to equilibrium.

The leaching studies showed that for slags with relatively high F content of around 4%, increasing the silica content decreased the leachability of the slags significantly. As lower F content in the slag is expected after fluorine recovery, the F contents in the leachate will be correspondingly lower.

This study aided Alcoa Portland in optimizing the slag chemistry at their demonstration plant at Portland, Victoria. The removal of F from the slag was increased and the sodium concentration in the AlF_3 product reduced. The refractory life in the furnace was also extended significantly. The granulated vitreous slag product conformed to Victorian EPA criteria to permit its use for unrestricted purposes.

Acknowledgements The authors wish to acknowledge the financial support of Alcoa and the valuable discussions with Ken Mansfield, Gavin Swan, and Jim Harpley of Alcoa Portland during the study. The authors also thank Alcoa for permission to publish the work.

References

1. Floyd J, Johnson GA (1999) REWAS'99, 1999 global symposium on recycling, waste treatment and clean technology, San Sebastian, Spain
2. Mansfield K, Swayn G, Harpley J (2002) SPL treatment and fluoride recycling project. In: EPD Congress 2002 and Fundamentals of Advanced Materials for Energy Conversion as held at the 2002 TMS Annual Meeting, pp 315–327
3. Mansfield K, Swayn G, Harpley J (2002) Green Processing 2002, AusIMM, pp 307–314
4. Australian Standard, AS 4439.3—1997, Wastes, sediments and contaminated soils, part 3: preparation of leachates—bottle leaching procedure
5. Zhang L, Jahanshahi S, Sun S, Chen C, Bourke B, Wright S, Somerville M (2002) CSIRO's multiphase reaction models and their industrial applications. JOM 54(11):51–56
6. Wright S, Zhang L, Jahanshahi S (1997) 5th international conference on molten slags, fluxes and salts, '97. Iron and Steel Society, Sydney, pp 231–240
7. US EPA SW-846 1311 Toxicity characteristic leaching procedure
8. Schwerdtfeger K, Ries R, Bruckmann G (1982) In: Proceedings of the 7th ICVM, Tokyo, pp 1204–1220
9. Zaitsev AI, Leites AV, Litvina AD, Mogutnov BM (1994) Investigation of the mould powder volatiles during continuous casting. Steel Res 65:368–374
10. Shimizu K, Cramb AW (2002) The kinetics of fluoride evaporation from CaF_2–SiO_2–CaO slags and mold fluxes in dry atmospheres. Iron Steelmak 29(6):43–53
11. Shinmei M (1979) Properties of slags for electro-slag remelting. Iron and Steel Institute of Japan, Tokyo
12. Shimizu K, Suzuki T, Jimbo I, Cramb AW (2001) An investigation on the vaporization of fluorides from slag melts. Iron Steelmak 28(7):87–93
13. Glaws PC, Belton GR (1990) Deuterium exchange studies of the interfacial rate of reaction of water vapor with silica-saturated iron silicate melts. Metall Trans B 21:511–519
14. Belton GR (1992) In: 4th international symposium on metallurgical slags and fluxes. ISIJ, Sendai, pp 516–524
15. Barin I (1989) Thermochemical data of pure substances. VCH, Weiheim
16. Slag Atlas (1995) Ed: Verein Deutscher Eisenhuttenleutte, 2nd edn. Verlag Stahleisen GmbH, Dusseldorf