PYROHYDROLYSIS OF SODIUM FLUORIDE CONTAINING SILICATE SLAG FROM SPENT POTLINING

Vladimir Blinov, Tor Grande & Harald A. Øye
Norwegian University of Science and Technology, Norway

ABSTRACT

Due to the toxic nature of spent potlining (SPL), it is becoming one of the major environmental concerns for the aluminium industry, but SPL also represents a major recovery potential because of its energy and fluoride content. The ELKEM SPL recycling process is one of several technically feasible alternatives for treatment and recycling of SPL. In this process fluorides are proposed recovered by pyrohydrolysis of a silicate slag remaining from the first step which produces pig iron by carbothermal reduction. A proposed reaction of the pyrohydrolysis is

$$2\ NaF(slag) + H_2O(g) = Na_2O\ (slag) + 2\ HF(g)$$

In the present paper the thermodynamics of the pyrohydrolysis is discussed. The discussion is based on thermodynamics modelling coupled with high temperature mass spectrometry and vapour pressure determination by Knudsen effusion. The main vaporization of the fluorides is not found to be due to the above reaction forming HF, but due to species as $Si(OH)_xF_y$ *or* $NaAl(OH)_xF_y$ *,* $(x + y = 4)$*. Such vapour species have not been identified earlier.*

INTRODUCTION

As world production capacity of aluminium has increased, so has the amount of waste from failed cathodes. The total spent potlining (SPL) generation in the world is estimated to be about 1.7 M ton per year, which is added to existing piles containing several million ton. Due to the toxic nature of SPL this is becoming one of the major environmental concerns for the aluminium industry. The major environmental problems related to SPL are the content of cyanides in addition to the considerable fluoride content. These compounds are water soluble and leachate from SPL inventories may contaminate ground water or water run-offs. On the other hand, SPL also represents a major recovery potential because of its fluoride and energy content [1].

In recent years governmental regulations or taxations are major factors creating a market for SPL treatment. A future transition from storage to treatment is therefore expected. The ELKEM SPL recycling process is one of the promising processes for treatment of SPL, which also has been tested in a pilot scale 600 kW furnace [2]. A demonstration production is planned for 2. and 3. quarter of 2008 in a former ferrosilicon plant in Ålvik, Norway. In this process, the energy is applied to produce pig iron in an electric furnace and at the same time the toxic cyanides are oxidized. A slag from this process contains 10-15 wt% fluorine which originates from the SPL. However, the fluorides are not present as pure phases but are dissolved in amorphous sodium aluminium silicates which are the major part of the slag. An estimate of the average composition of the slag from the pig iron process is given in Table 1 [2]. The three major components are sodium, aluminium and silicon oxides together with the fluorine which is most probably bonded to sodium.

Table 1: Average composition of the silicate slag from the ELKEM spent potlining process [2]

Element	Composition (wt%)
Na	15-20
Al	5-15
Si	15-25
Fe	2-5
Ca	2-3
K	<0.5
Mg	<1
Mn	<0.3
Other cations	<0.1
F	10-15
∑	68

Presently it is planned to produce a non-leachable glassy slag, but the next step is to recover the fluorides in a separate pyrohydrolysis process. The crushed residual SPL (slag) is hydrolyzed by steam at high temperatures in a fluidized bed reactor [2]. The proposed principle chemical reaction of the pyrohydrolysis is

$$H_2O(g) + 2\ NaF(slag) = 2\ HF(g) + Na_2O\ (slag) \tag{1}$$

The thermodynamics of the pyrohydrolysis of NaF are unfavorable due to the strong endothermic nature of reaction (1). The enthalpy of the reaction at 1500 K is 417 kJ [3]. The equilibrium constant for the reactions is small at the relevant temperature of the process. The purpose of the present work is to investigate the thermodynamics of the pyrohydrolysis process for a thorough discussion of the potential for fluorine recovery. The objective is to enable a calculation of equilibrium pressures of HF(g) at a given pressure of H_2O (g) which demands that both the chemical activity of NaF and Na_2O dissolved in the slag must be determined simultaneously. The activity data of sodium oxide in various sodium aluminium silicates can be estimated from literature data [4]. The experimental challenge left was then to determine the chemical activity of NaF in some fluoride containing silicate melts relevant to SPL. Both high temperature mass spectroscopy and Knudsen effusion measurements have been performed to determine the thermodynamic activity of NaF. Based on these new data the thermodynamic aspects of the pyrohydrolysis of SPL are discussed.

EXPERIMENTAL

Sample Preparation

The samples used were prepared from pure NaF, Al_2O_3, SiO_2 and a Na_2SiO_3 glass made from SiO_2 and Na_2SiO_3 (all chemicals supplied from Merck, Germany). NaF, SiO_2 and Al_2O_3 were dried in vacuum at 400, 1200 and 1200°C, respectively. Na_2SiO_3 glass was made from SiO_2 and Na_2SiO_3 by heat treatment at 1000°C for 24 hours. Samples of about 1.0 -2.0 g were prepared in a glove-box under N_2-atmosphere (< 10 ppm O_2 and H_2O). The salts were transferred into a Pt cylinder (diameter 5 mm, cylinder-wall thickness 0.15 mm) which was sealed in one end by welding. The open end was closed using a stop cock, and the Pt-tube with the stop cock was transferred from the glove-box, mounted on a vacuum-line and evacuated to pressures < 10^{-4} mbar. The Pt-tube with the sample was then sealed by welding. The sealed Pt-capsules were heat treated at 1250°C for 24 hours before they were quenched to room temperature to form a homogeneous glass which was further used in the present studies.

High Temperature Mass Spectroscopy

High temperature mass spectroscopy was performed using a quadrupole mass spectrometer (Extranuclear Laboratories, Inc., USA). A Mo-wound furnace which was connected to the mass spectrometer was applied. Vacuum conditions ($P < 10^{-4}$ mbar) were obtained by using two diffusion pumps, one evacuating the mass spectrometer and the other evacuating the furnace. Liquid nitrogen cooled traps were used in order to prevent pump fluid vapor entering the vacuum system and to provide an additional pumping capacity for vapors involved during the measurements.

About 0.5 g of the samples was contained in a platinum Knudsen effusion cell (0.4 mm effusion orifice). The mass spectrometer was evacuated for 24 hours at 600°C before each measurement. Relative intensities of ions were measured as function of time at constant temperature. Before each measurement the molecular beam into the mass spectrometer was shut off to measure the background level of the spectrometer for each mass to charge ratio. Experiments with pure NaF(l) were performed in order to verify the experimental procedure.

Knudsen Effusion Measurements

Vapour pressure measurements by the Knudsen effusion method were performed in a high temperature graphite furnace described elsewhere [5]. Vacuum conditions

($P < 10^{-4}$ mbar) were obtained by using a diffusion pump. The samples were contained in a Pt-crucible which was placed inside a graphite Knudsen effusion cell with an effusion orifice of 0.4 mm. The cell was attached to a thermobalance which measured the mass loss from the sample assembly as function of time and temperature. The temperature was measured using a Pt/Pt10%Rh thermocouple which was located 3 mm below the bottom of the effusion cell. The vapor pressure of NaF was calculated by the equation

$$P = \frac{\sqrt{T/M}}{44.331(aL)} \frac{\Delta q}{\Delta t} \tag{2}$$

where $\Delta q/\Delta t$ is the weight loss rate, (aL) is the effective orifice area, T is the temperature and M is the molecular mass of NaF. Calibration of the effusion orifice was performed by using pure MgF_2 [6].

Contamination of water in the samples gave significant experimental problems (see Figure 1). As long as the vapour pressure of volatile OH-containing species dominated, accurate measurement of vapor pressure of fluorides could not be obtained. To minimize the influence of water contamination, the samples were first annealed at 1400°C for 18-20 hours at 500 mbar N_2-pressure. The furnace was then evacuated. However, a stable weight loss versus time was not obtained before 10- 20 hours after the evacuation had started. This is shown for sample 4 in Figure 2. A considerable weight loss (~ 0.5- 1 wt%) was observed during the first period of annealing at 500 mbar N_2. The weight loss decreased considerably during the next 20 hours at reduced pressure, Pressures below 10^{-4} mbar were only obtained after a stable weight loss versus time had been achieved. Based on the mass spectroscopy data the initial high weight loss during the first 20-40 hours was mainly due to water containing species and these data were therefore not applied to calculate the vapor pressure of NaF. The compositions of the melts reported were not corrected for the weight loss during the Knudsen effusion experiments.

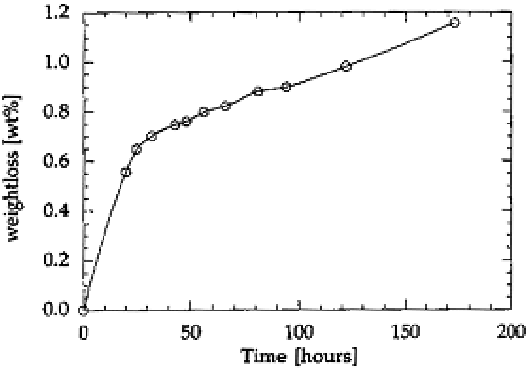

Figure 1: The weight loss of sample 4 as function of time. After this initial period of annealing in 500 mbar N_2 for 18-20 hours and successive evacuation, the weight loss rate became stable and the vapour pressure of NaF was determined at various temperatures.

RESULTS

The compositions of the fluoride containing silicate melts investigated are given in Table 2. The compositions were chosen based on an average composition of the SPL slag given in Table 1 when neglecting all other elements except Na, Al, Si, O and F. This corresponds to a melt consisting of 1.1 mole SiO_2, 0.3 mole Al_2O_3 and 1.00 mole Na^+.

Samples 1 - 5 are then determined by substituting 2 mole NaF with 1 mole Na_2O. Samples 6 - 8 are based on sample 2 but with different SiO_2/ Al_2O_3 ratio. Only samples 1, 2 and 4 were investigated by mass spectroscopy.

Table 2: The composition of the samples examined by mass spectroscopy and Knudsen effusion method

	Composition [mol]				**Composition [mol fraction]**			
Sample	**NaF**	**Na_2O**	**Al_2O_3**	**SiO_2**	**NaF**	**Na_2O**	**Al_2O_3**	**SiO_2**
1	0.60	0.20	0.30	1.10	0.273	0.091	0.136	0.500
2	0.40	0.30	0.30	1.10	0.190	0.143	0.143	0.524
3	0.20	0.40	0.30	1.10	0.100	0.200	0.150	0.550
4	0.10	0.45	0.30	1.10	0.051	0.231	0.154	0.564
5	0.05	0.475	0.30	1.10	0.026	0.247	0.156	0.571
6	0.40	0.30	0.50	1.10	0.174	0.130	0.217	0.478
7	0.40	0.30	0.30	1.40	0.167	0.125	0.125	0.583
8	0.40	0.33	0.10	1.10	0.207	0.171	0.052	0.570

Volatile Species Due to Water Contaminations

Contamination of water in the samples gave significant contributions to the initial weight loss of all the samples. This was particularly a problem for some preliminary experiments in which samples with water contaminated raw materials were used. Samples with low water content were obtained by careful drying of the raw materials. The total weight loss during ca 2 hours measurements at 1100°C was reduced from about 5 wt% down to ca 0.5-1.5 wt% by reducing the moisture content. To illustrate the effect of the water contamination the distribution of observed intensities of ionic fragments for *best and worst* case for sample 4 are shown in Figure 2. The intensity of the ionic fragments with mass to charge ratio (m/e) 46, 47, 48, 64, 66, 81 and 85 was observed to decrease rapidly with time at isothermal conditions for all the samples. After about 1 hour heat treatment of the samples at 1100°C the intensity of these species was approaching the background level for the spectrometer . These ionic fragments do not correspond to any known ionic fragment pattern of fluorides. The mass spectra were therefore attributed to evaporation of OH^--containing species. Based on the ionic fragment pattern shown in Figure 3 compared with Table 3, $NaAl(OH)_xF_y$ or $Si(OH\}_xF_y$ ($x + y= 4$) are proposed as possible volatile species due to moisture. Possible species are also $Al(OH)_xF_y$ ($x + y= 3$). Suggested ionic fragments of the first two species are summarized in Table 3. The ionic fragments with mass to charge ratio (m/e) 46, 47, 48, 64, 66, 81 and 85 can all be attributed to the two suggested volatile species. The dominant ionic fragments reported for $NaAlF_4$(g) and SiF_4(g) are 23 and 85 m/e corresponding to Na^+ and SiF^{3+} [7]. The relatively low intensity of Na^+ shown in Figure 3a indicates that $NaAl(OH)_xF_y$ is probably not major volatile species. By comparing Figure 3a and Table 3 the silicon containing species $Si(OH)_xF_y$ is probably the dominant volatile species for sodium aluminium silicate melts containing sodium fluoride and water contaminations. This type of gas species has previously not been reported.

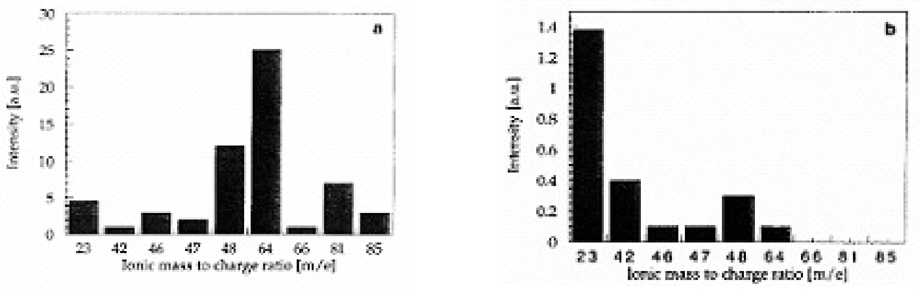

Figure 2: The intensity distribution of ionic fragments observed for sample 4 a) *worst* case with considerable water contaminations (1000°C) and b) *best* case with low water contaminations in the sample (1100°C)

Table 3: Possible ionic fragments from the suggested volatile species $Si(OH)_xF_y$ and $NaAl(OH)_xF_y$. On1y ionic fragments corresponding to observed mass to charge ratios are given

Species	**Mass to charge ratio**	**Ionic fragments**
$Si(OH\}_xF_y$	46	$Si(OH)H^+$
	47	SiF^+
	48	$SiFH^+$
	64	$Si(OH)F^+$
	66	$SiF_2{}^+$
	81	$Si(OH)_2F^+$
	85	$SiF_3{}^+$
$NaAl(OH)_xF_y$	23	Na^+
	46	AlF^+
	47	$AlFH^+$
	48	$AlFH_2{}^+$
	64	$Al(OH)FH^+$
	66	AlF_2H^+
	81	$Al(OH)_2FH^+$
	85	AlF_3H^+

Volatile Fluoride Species in Dry Silicate Melts

Samples with low content of moisture were prepared after considerable effort, and in the following only results obtained for these samples are reported. A typical isothermal development of the intensity of the observed ionic fragments versus time for sample 4 is given in Figure 3. The intensity of the ionic fragments with mass to charge ratio (m/e) 46, 47, 66 and 85 decreased rapidly approaching the background level intensity during the first period of 50-100 min. Only the ions with m/e 23 (Na^+) and 42 (NaF^+) have significant intensities after this first period. Corresponding trends were also observed for sample 1 and 2. The total weight loss was less than 1 wt% for all the mass spectroscopy experiments which means that no major changes in composition had occurred during the experiments.

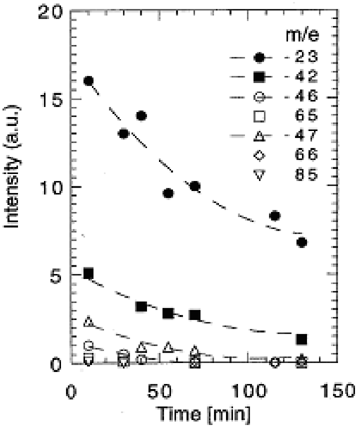

Figure 3: Intensity pattern of ionic fragments observed for sample 4 at 1100°C.
The mass to charge ratio (m/e) is given for each ion in the figure

The ionic fragments with m/e 23 (Na^+) and 42 (NaF^+) are proposed to correspond to the equilibrium vapour above the melts when the contribution from water contamination is neglected. This is based on the fact that the intensity of all other ionic fragments decreased to the background level after the first period. The possible volatile fluoride species from the present melts are NaF(g), $NaAlF_4$(g) and SiF_4(g). The following ionization fragment patterns for these gas species have previously been reported; 23,42 and 65 for NaF, 23,46 and 107 for $NaAlF_4$ and 47, 66 and 85 for SiF_4 [7]. The absence of ionic fragments with mass charge ratio 85 and 107 exclude the possibility of a significant vapor pressure of SiF_4 and $NaAlF_4$. It could therefore be concluded that the composition of the equilibrium vapour above the melts was essentially pure NaF(g). The activity of NaF(g) could therefore directly be determined by measuring the total vapor pressure above the melts by Knudsen effusion measurements.

Determination of the Vapor Pressure of NaF

The measured vapor pressure of NaF for samples 2 - 8 is shown versus inverse temperature in Figure 4. Sample 1 is not included as the melt wetted the platinum crucible and the melt came in contact with the graphite cell which caused carbothermal reduction of the oxides in the melt.

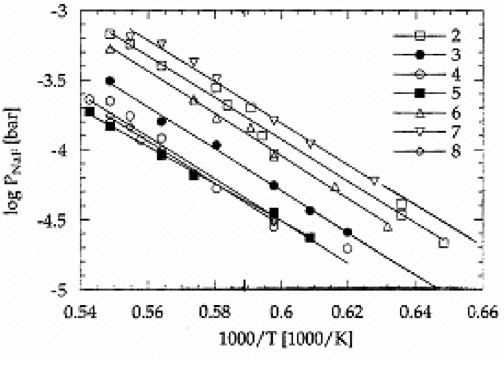

Figure 4: The vapor pressure of NaF for samples 2 -8 as function of inverse temperature

The enthalpy of evaporation of NaF is directly determined by slope of the curves since at these reduced pressures the vapor is composed of nearly pure NaF(g) (Na_2F_2(g) molecules can be neglected). For all the samples, except sample 5, the enthalpy of evaporation is in the interval 285-289 kJ/mol. This is 53-57 kJ/mol higher than for pure NaF(l) which indicates a negative interaction energy between NaF and the sodium aluminium silicate melts. For sample 5, that has the lowest content of NaF, the enthalpy of evaporation is 254 kJ/mol. The content of NaF in sample 5 is very low, and a low evaporation energy is therefore highly unexpected and probably reflects a higher uncertainty of the data for this particular sample.

The temperature dependence of the activity of NaF in the melts is shown in Figure 5. The activity of NaF in all the melts increases with increasing temperature. The temperature dependence of the activity is relatively weak due to the moderate difference in the heat of evaporation of NaF from the melts compared to pure NaF(l).

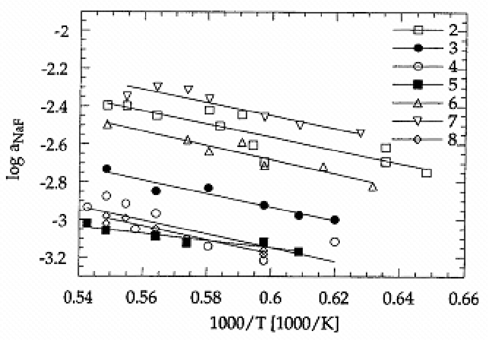

Figure 5: The chemical activity of NaF in samples 2 -8 as function of inverse temperature. The standard state is pure NaF(l)

The activity of NaF(l) as function of molfraction NaF at 1600 K is illustrated by the series 2, 3, 4, 5 (Figure 6, Symbol o, lower scale). The amount of Al_2O_3 and SiO_2 is kept constant for this series. The activity of NaF is found to increase exponentially with increasing amount of NaF. The activity for sample 5 is extrapolated from the four low temperature values using the same slope as the other samples.

The influence of the Al_2O_3/SiO_2 ratio on the chemical activity of NaF(l) is illustrated by the series 2, 6, 7, 8 (Figure 6). The amount of NaF is kept constant for this series. The activity of NaF is only moderately dependent on the Al_2O_3/SiO_2 ratio except for sample 8 where a low value is found. The ratio Al_2O_3/SiO_2 is, however, only 0.091, and the phase field is no longer in the nepheline region but in the albite region [8]. The conclusion from these results is that there are no significant improvements of the thermodynamics for reaction (1) by moderate additions of SiO_2 or Al_2O_3 to the SPL slag. Most favorable is, however, to add SiO_2 to SPL to obtain a high activity of SiO_2 and thereby a low activity of Na_2O.

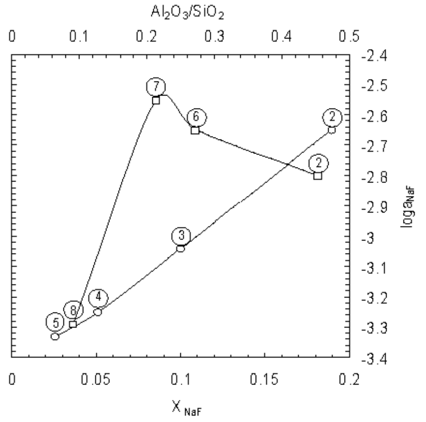

Figure 6: Activity of NaF as function of mol fraction of NaF (2, 3, 4, 5) and activity of NaF as function of the molar Al_2O_3/SiO_2 ratio (2, 6, 7, 8)

Sample 7 with the highest value for a_{NaF} is chosen to illustrate vaporization of HF due to Reaction 1. Sample 7 contains 58.3 mol% SiO_2, 12.5 mol% Al_2O_3, 12.5 mol% Na_2O and 16.7 mol% NaF. Log $a_{NaF} = -2.44$ at 1700 K (Figure 6). Pelton [4] has recently done a critical reevaluation of the thermodynamics of the system Na_2O-SiO_2-Al_2O_3 including recent data. This model will be incorporated in the FACT data base. He calculated activity of Na_2O in a slag containing 12.5 mol Na_2O, 12.5 mol% Al_2O_3 and 58.3 mol% SiO_2 (no NaF) to be $1.58 \cdot 10^{-10}$. It is difficult to estimate the effect of NaF on this activity, but it would certainly cause it to increase. Just to give an idea, Pelton calculated the activity of Na_2O to $4.06 \cdot 10^{-8}$ at 1700 K in a slag containing ((16.7/2 + 12.5) = 20.85) mol Na_2O, 12.5 mol Al_2O_3 and 58.3 mol SiO_2. The activity of Na_2O in sample 7 at 1700 K is probably between these values. A reasonable estimate is $a_{Na_2O} = 10^{-9}$.

At 1700 K the equilibrium constant for Reaction 1 is $10^{-6.60}$ [3]. Hence,

$$\frac{P_{HF}^2 \cdot a_{Na_2O}}{P_{H_2O} \cdot (a_{NaF})^2} = \frac{P_{HF}^2 \cdot 10^{-9.00}}{P_{H_2O} \cdot (10^{-2.44})} = 10^{-6.60}$$

$$\frac{P_{HF}^2}{P_{H_2O}} = 10^{-2.41}$$

At 1 atmosphere pressure $P_{HF} = 0.056$ atm. If sample 5 is chosen, $P_{HF} = 0.009$ atm at 1700 K.

Vaporization of Fluorides According to Reaction 1 is Hence Expected to be Small

E.Q. Dahl used an induction furnace to melt 12 kg of a Si-Al-Na-Fe-O-F slag in a graphite crucible [9]. Steam was introduced through an immersed lance at temperatures between 1280 and 1420°C. A typical result showing the change in slag composition during the blowing period is shown in Figure 7.

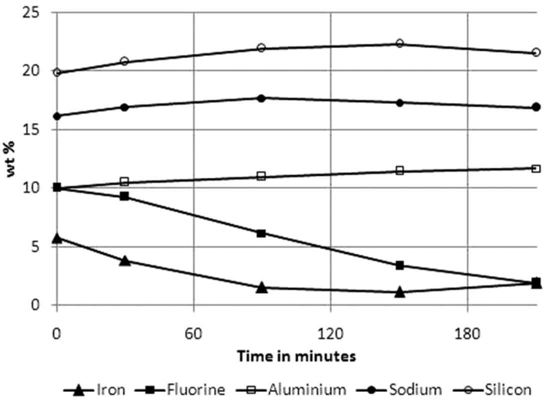

Figure 7: Change in slag composition by blowing with steam. Redrawn from Dahl [9]

It can be seen from Figure 7 that the reaction was rather slow and not very dependant of the temperature. The utilization of steam turned out to be low, less than 20% in the initial tests. Optimal conditions were, however, not obtained. The crucible is rather small and the lance penetrates approximately 15 cm into the slag. The bubbles, therefore, have a short retention time before they leave the bath. An efficient removal of fluorides is expected by optimal conditions. These results are in strong contrast to the calculated vaporization of HF from Reaction 1 where a maximum yield between 0.5 and 5.6% is predicted.

Although the objective of the present investigation was the thermodynamics of Reaction 1, the observation of volatile fluorine containing species in presence of water might be the most important findings of this study. Based on the ionic fragment pattern shown in Figure3, $NaAl(OH)_xF_y$ or Si $(OH)_xF_y$ ($x+y=4$) were proposed as possible volatile species in sodium aluminium silicate melts containing NaF and water contaminations. $Si(OH)_xF_y$ is probably the dominant species due to the relatively low intensity of ionic fragments corresponding to Na^+ and since the ionic fragments with mass to charge ratio 48, 64, 81 and 85 are most probably due to $SiFH^+$, $Si(OH)^-$, $Si(OH)_2F^+$ and SiF^{3+}. The exact molecular composition of the volatile species could not be determined by mass spectroscopy. These types of species have previously not been reported.

The accurate vapor pressure of the OH-containing species was not determined. However, the present results indicate a considerable vapor pressure of these gas species. High vapor pressure of the species in presence of water will have a large impact on the performance of the pyrohydrolysis of SPL. In fact, based on the present findings it is expected that HF(g) is not a major product in the reaction between the oxyfluoride silicate slag and steam. The effect of these gas species will be studied in future work. It is particularly important to determine the fluoride content in these gas species to evaluate the potential in relation to fluoride recovery.

ACKNOWLEDGEMENTS

The authors appreciate A. D. Pelton's recalculation of the activity of Na_2O, using most recent data.

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