Fluoride Evaporation from CaF_2-SiO_2-CaO Slags and Mold Fluxes in Dry and Humid Atmospheres

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ABSTRACT

The evaporation of fluorine containing gases from metallurgical operations is a significant issue in the industrial use of slags. Experimental studies, undertaken to measure the evaporation rate of fluorine containing gases from liquid slags and from some industrial mold slags in both dry and humid atmospheres, have shown that fluorine evaporation rates were found to be significant in all conditions but were highest under humid conditions.

1. INTRODUCTION

The evaporation of fluorine containing gases from metallurgical operations is a significant issue in the industrial use of slags. Most current developments are towards fluorine minimized or free slag use; however, such advances are not easily accomplished as an obvious fluorine replacement is not currently available. Fluoride addition to slag forming materials have a number of benefits in that it allows fast liquid formation, reduces viscosity over a large temperature range and significantly decreases slag liquidus temperatures. These three benefits account for the wide use of fluoride additions during steelmaking and casting and while there are solutions in ladle and tundish operation that can minimize or eliminate fluoride use, this is not true in the mold of the continuous caster where truly fluorine free mold fluxes are not currently in widespread application.

A better understanding of fluoride evaporation phenomena is a prerequisite for improving both environmental safety and metallurgical efficiency.

2. BACKGROUND

2.1. Thermodynamic Issues

Extensive studies of CaO-SiO_2-CaF_2 slag systems were made by many researchers to examine phase equilibria /1-9/, the activities of the various components /6-9/, and the vapour pressures of gases in equilibrium with the slags /2/. It was reported that off-gas from this slag system at high temperatures consists of primarily SiF_4 (g) and the postulated reaction is:

$$(SiO_2) + 2(CaF_2) \rightarrow SiF_4(g) + 2(CaO) \qquad (1)$$

where the ( ) brackets denote dissolved in a slag and for which the equilibrium constant is expressed as:

$$K = \frac{P_{SiF_4} \cdot (a_{CaO})^2}{a_{SiO_2} \cdot (a_{CaF_2})^2} \qquad (2)$$

Activities of SiO_2 in this system were evaluated by Sommerville and Kay /6/, Hsu *et al.* /7/, Isaksson and Oberg /8/, and Zaitsev *et al.* /9/ with a variety of experimental techniques. Activities of CaO were deduced by Sommerville and Kay /6/ and Zaitsev *et al.* /9/. Activities of CaF_2 have been measured by Zaitsev *et al.* /9/ with the mass-spectral Knudsen effusion technique. Substitution of those activity data and the equilibrium constant value taken from a thermodynamic data source into Eq. 2 provides a method of calculation of equilibrium pressures of SiF_4 as a function of composition. Shinmei *et al.* /2/, using Sievert's method, have carried out a direct measurement of the vapor pressures of SiF_4 at 1450°C as a function of slag composition. A comparison between the estimated pressures and the directly measured pressures by Shinmei *et al.* revealed that there is a significant variation between calculated and measured results. Vaporization of SiF_4 as well as CaF_2, especially when an open system was used, may have lead to significant errors in the calculation of the various activity values previously measured.

Recent work by Simizu *et al* /10/ is summarized in Fig. 1 where significant partial pressures of SiF_4 were measured in the CaO-SiO_2-CaF_2 system. In Fig. 2 the effect of alumina and magnesia addition to the slag were shown to significantly decrease these pressures.

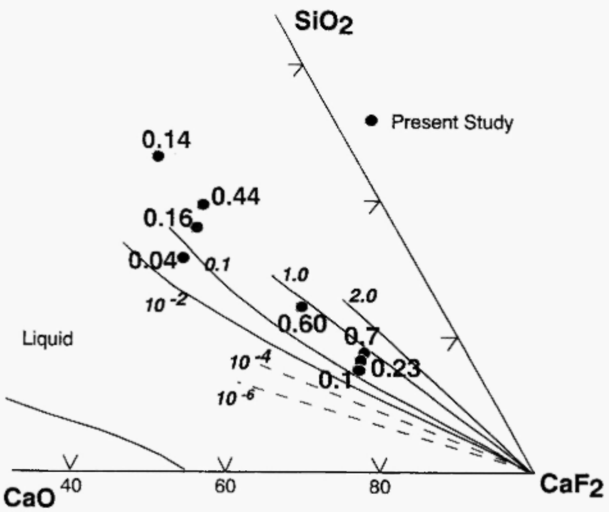

Fig. 1: Plot of experimentally measured equilibrium pressures of SiF_4 over CaO-SiO_2-CaF_2 ternary diagram along with iso-pressure curves of SiF_4 obtained theoretically by Shinmei *et al* /2/, from /10/.

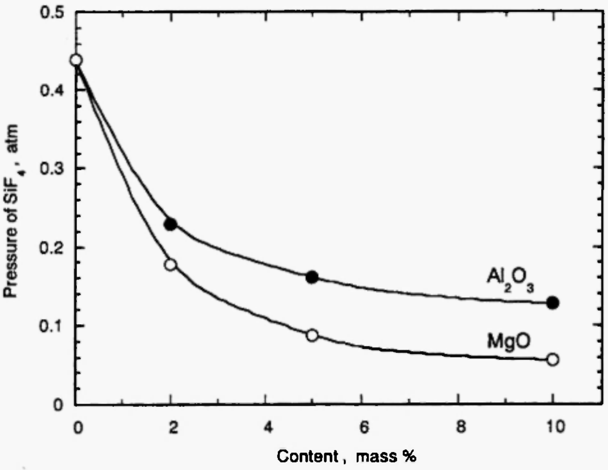

Fig. 2: Effects of Al_2O_3 / MgO addition on the equilibrium pressure of SiF_4, /10/.

3. TRANSPORT ISSUES

3.1. Dry Atmospheres

As far as the transport aspects of fluoride evaporation in a dry atmosphere are concerned, only a few studies have been reported to date. Schwerdrfeger *et al.* /11/, conducted thermogravimetric experiments that showed that $SiF_4(g)$, $AlF_3(g)$, and $TiF_4(g)$ can be formed by adding SiO_2, Al_2O_3, and TiO_2 into CaF_2-CaO slag melts, respectively. The amount of evaporated fluorides decreased with increasing CaO content, indicating that the evaporation rate depended on slag composition. Zaitsev *et al.* /12/ carried out mass spectrometric experiments and suggested that industrial mold fluxes can evaporate significant amounts of KF, NaF, SiF_4, and AlF_3 at elevated temperatures. Again evaporation rates depended on temperature and flux chemistry.

More recently Shimizu has studied the evaporation rates in dry and humid atmospheres /13, 14/ and has shown that the rates of evaporation were sensitive to the gas atmosphere as shown in Fig. 3. Shimizu's work suggests that the rate of evaporation is in a mixed control regime in his experiment where the rate of SiF_4 or NaF evaporation appears to be in a mixed control regime where gaseous diffusion and gas phase mass transport are both important in addition to temperature and flux chemistry. The effect of gaseous diffusion rate is clearly seen in Fig. 3.

If gaseous diffusion is important then the diffusivity of SiF_4 in various gaseous species must be known. The diffusivity of NaF in argon, nitrogen, helium and SiF_4

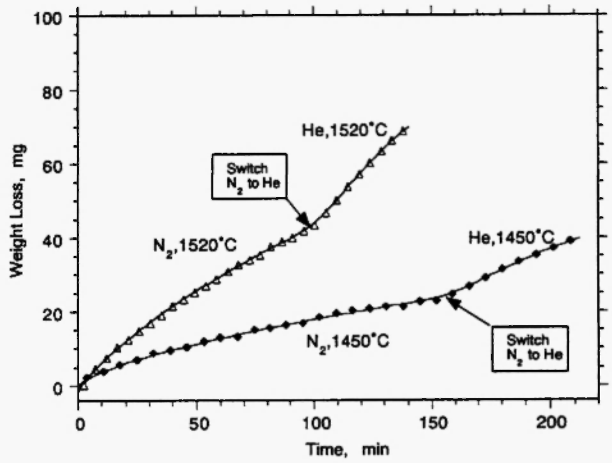

Fig. 3: Weight loss of a mold flux in a dry atmosphere /13/.

was measured by Kashiwaya /15,16/. Examples of calculated binary and ternary diffusion coefficients from Kashiwaya's work are given in Tables 1 and 2.

Table 1
Binary diffusion coefficient calculated /14, 15/.

Temp. K	$De_{NaF\text{-}Ar}$ (cm^2/s)	$De_{NaF\text{-}SiF4}$ (cm^2/s)	$De_{SiF4\text{-}Ar}$ (cm^2/s)
1473	2.1879	1.1426	1.5233
1573	2.4577	1.2884	1.6989
1673	2.7394	1.4410	1.8819
1773	3.0326	1.6001	2.0721

Table 2
Calculation examples for the ternary diffusion coefficient /15/.

	$x_{NaF}=0.06, x_{SiF4}=0.70, x_{Ar}=0.24$			
Temp. K	D_{11}	D_{12}	D_{22}	D_{21}
1473	1.34	-0.04	1.5	-0.31
1573	1.51	-0.05	1.68	-0.33
1673	1.6	-0.05	1.86	-0.36
1773	1.86	-0.06	2.05	-0.38

3.2. Humid Atmospheres

Fluorine-containing slag melts have the potential to evaporate a significant amount of fluoride containing gaseous species at a high rate in dry atmospheres /1/. Those species include SiF_4, CaF_2, and NaF. When slag melts are exposed to a humid atmosphere, it is expected that the presence of water vapour will change the fluoride vaporization behaviour. For example, SiF_4 (g) reacts with water vapour in the following manner:

$$SiF_4(g) + 2H_2O(g) \rightarrow 4HF(g) + SiO_2(s) \qquad (3)$$

Fluorine in the slag melt can also react with H_2O at the interface by the reaction:

$$2F^- + H_2O(g) \rightarrow 2HF(g) + O^{2-} \qquad (4)$$

Both reactions produce HF, which is harmful to the environment. Water vapour in a gas atmosphere is thus expected to have a substantial effect on the rate of fluoride evaporation from liquid slags.

The kinetics of the fluoride evaporation in humid atmospheres was investigated by several researchers. Klein and Schwerdfegar /18/ conducted weight loss studies by means of a high temperature balance and documented that (1) H_2O vapour reacts with the fluorine contained in CaF_2-SiO_2-CaO slag melts to emit a significant amount of HF at 1600°C and (2) the rate of evaporation increased with increasing humidity. They also found that the rate of HF evaporation was primarily controlled by the gaseous diffusion of HF and of H_2O. Kumar *et al.* /19/ carried out similar thermogravimetric experiments between 970°C and 1350°C. An interesting phenomenon that they observed was that the rate of fluorine loss from SiO_2 CaO + CaF_2 melts was found to be much faster than that from SiO_2·2CaO + CaF_2 melts in water-saturated air stream. Zaitsev *et al.* /1/ found that HF evaporation from multi-component mold fluxes in humid atmosphere was increased by a factor of 10 compared to that in dry atmosphere.

An example of the effect of humidity on the weight loss of a mold flux is given in Fig. 4, where the rate of evaporation was found to be a function of temperature and the level of the humidity /14/. Slag compositions are given in Table 3.

There are 2 possible processes to account for the effect of humidity: 1) $H_2O(g)$ reaction with gaseous fluorides (i.e., SiF_4) represented by Eq. 3; and, 2) $H_2O(g)$ reacting with fluorine at the slag melt interface as represented by Eq. 4. When the amount of SiF_4 (g) is small (in the case of slag TS-2) or 0 (in the case of slag BS-1), HF is assumed to be generated primarily by the latter process. The possible rate-controlling processes involved in the HF formation by Eq. 4 can be summarized as follows:

(1) Transport of H_2O from bulk gas towards the interface through gaseous boundary layer.
(2) Transport of fluorine from bulk liquid towards the interface through liquid boundary layer.
(3) Chemical reaction at the interface.
(4) Transport of HF from the interface towards the bulk gas flow in gaseous boundary layer.

These processes are schematically illustrated in Fig. 5.

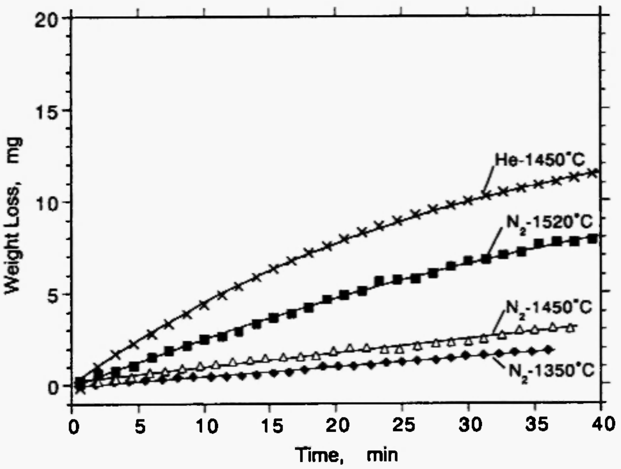

Fig. 4: Rate of weight loss of mold flux B in N_2 with a variation in humidity.

Table 3

Composition of CaF_2-SiO_2-CaO slags and mold fluxes (in wt%)/14/.

Name	CaF_2	SiO_2	CaO	Al_2O_3	MgO	Na_2O
TS-1	39	39	22	-	-	-
TS-2	40	31	29	-	-	-
BS-1	90	-	10	-	-	-
Flux-	31	28	22	5	-	14
Flux-	33	28	26	6	3	4

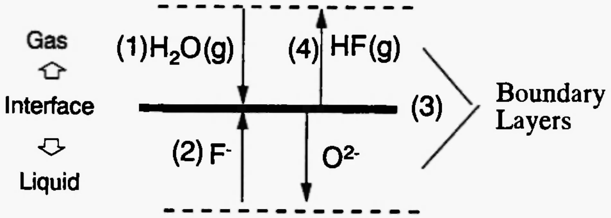

Fig. 5: Possible rate-controlling processes involved in fluoride evaporation in a humid atmosphere.

Among these 4 processes, the gaseous transport, i.e., (1) and (4), is considered to be a primary rate-controlling process, since the experimental results showed that the rates of weight loss were several times larger for He than for N_2. To construct a theoretical formulation it was assumed that the mass transport of fluorine in the liquid phase and the chemical reaction at the interface were fast. Consequently, the overall rate of weight loss should be determined by gas phase mass transfer of H_2O and HF. The molar fluxes of H_2O and HF can be given, respectively, by:

$$N_{H2O} = \frac{D_{H_2O-N_2/He}}{L \cdot RT} \left(P_{H2O}{}^{i} - P_{H2O}{}^{b}\right) \tag{5}$$

$$N_{HF} = \frac{D_{HF-N_2/He}}{L \cdot RT} \left(P_{HF}{}^{i} - P_{HF}{}^{b}\right) \tag{6}$$

At steady states, the chemical reaction at the interface:

$$CaF_2 + H_2O(g) \rightarrow CaO + 2HF(g) \qquad (7)$$

requires that the molar fluxes of H_2O and HF satisfy the stoichiometric relationship:

$$2NH_2O \rightarrow NHF \qquad (8)$$

Substitution of Eqs.(5) and (6) into Eq.(8), assuming $PHF^b = 0$, leads to

$$2DH_2O\,(PH_2O^i - PH_2O^b) = -\,DHF\,PHF^i \qquad (9)$$

In this equation, there are two unknowns: PH_2O^i and PHF^i. Assuming the chemical reaction, Eq. 6, is in equilibrium at steady state, the equilibrium constant can be given by:

$$K_1 = \frac{a_{CaO} \cdot P_{HF}^{i\,2}}{a_{CaF_2} \cdot P_{H_2O}^{i}} \qquad (10)$$

which provides us with another relation for PH_2O^i and PHF^i. K_1 was calculated based on thermodynamic data /10/. Solving the simultaneous equations of (9) and (10) for PH_2O^i and PHF^i, this can be reduced to an evaluation of a_{CaO}/a_{CaF_2} in Eq. 10.

In this study, to evaluate a_{CaO}/a_{CaF_2} of the slags, experimental data obtained in previous studies /20,21/ were utilized. a_{CaO}/a_{CaF_2} for the binary CaF_2-CaO slag melt was derived from the reliable data of the activities /20/. a_{CaO}/a_{CaF_2} for the ternary CaF_2-SiO_2-CaO slag melt, on the other hand, was calculated by using the equilibrium constant for the reaction:

$$2CaF_2 + SiO_2 \rightarrow SiF_4\,(g) + 2CaO \qquad (11)$$

That is:

$$\frac{a_{CaO}}{a_{CaF_2}} = \sqrt{\frac{K_2 \cdot a_{SiO_2}}{P_{SiF_4}}} \qquad (12)$$

Here, $PSiF_4$ has been already obtained in a previous study as a function of temperature and slag composition; K_2 was calculated by referring to thermodynamic data /10/; and a_{SiO_2} was extrapolated from the experimental data of Sommerville and Kay /6/. It should be noted that the activity of SiO_2 was assumed to be less dependent on temperature than K_2 and $PSiF_4$ in Eq. 10.

Adding a_{CaO}/a_{CaF_2} to Eq. 10 finally P_{HF}^i can be calculated by means of Eq. 9 and Eq. 8. The weight loss rate due to HF evaporation is then derived as:

$$-\frac{dW}{dt} = \frac{1}{L \cdot RT}\left((MHF - 1/2MH_2O)\,DHF\,P\,HF^i\right) \qquad (13)$$

If HF evaporation is assumed to occur without interfering with other volatile fluorides such as $SiF_4(g)$ and $CaF_2(g)$, the rate of total weight loss can be formulated as follows:

$$-\frac{dW}{dt} = \frac{1}{L \cdot RT}\left((MHF - 1/2MH_2O)\,DHF\,PHF^i + MSiF_4\,DSiF_4\,PSiF_4^i + MCaF_2\,DCaF_2\,P\,CaF_2^i\right) \qquad (14)$$

3.3. Diffusion Model vs. Experimental

In order to calculate the weight loss of the slag melts based on Eq. 14, the gaseous diffusivity values must be specified. Estimated DH_2O and DHF are shown in Table 4.

Table 4

Estimated diffusion coefficients D_{AB} in cm^2/s.

(a) in N_2			(b) in He		
T °C	H_2O	HF	T °C	H_2O	HF
1350	4.8	4.0	1350	15.4	12.3
1450	5.3	4.4	1450	17.0	13.5
1520	5.7	4.6	1520	18.2	14.5

Fig. 8 shows a plot of the weight loss rate against the pressure of $H_2O(g)$ (i.e.; H_2O content of the bulk flow). The experimentally obtained values are compared with the theoretical relationships in the figure. The experimental values used are those at the holding time of 30 minutes. The theoretical rates were derived by adding the experimental rates in the dry experiments to those calculated by means of Eq. 12. It can be clearly seen that the theoretical curves are in good agreement with the experimental values. This proves the validity of the theoretical formulas. In either kind of slag melt the contribution of HF evaporation due to surface reaction to the total weight loss is found to be significant (Fig. 6).

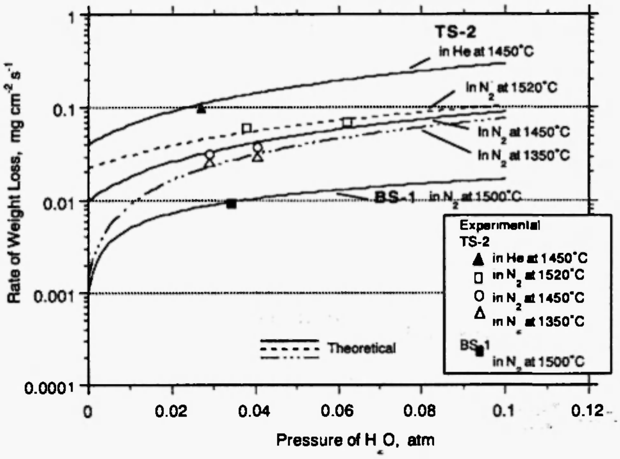

Fig. 6: Relationship between humidity and the rate of weight loss for CaF_2-SiO_2-CaO slags of low $PSiF_4$ /14/.

3.4. Effect of Humidity on the Rate of HF Evaporation

To see the effect of humidity on the rate of HF evaporation (i.e.; excluding SiF_4 evaporation), the difference between the rate of weight loss in humid flow and that in dry flow (i.e., the rate of weight loss due to HF evolution) was plotted versus H_2O content in Fig. 7. The vertical axis of Fig. 7 is in a linear scale, while that of Fig. 6 is in a logarithmic scale. Again, agreement between the calculated and the measured can be seen more clearly. A notable finding is that the rate is distinctively dependent on slag composition and bulk gas species but comparatively independent of temperature. It is also found that the rate is a linear function of H_2O content of bulk gas within the indicated range of H_2O content.

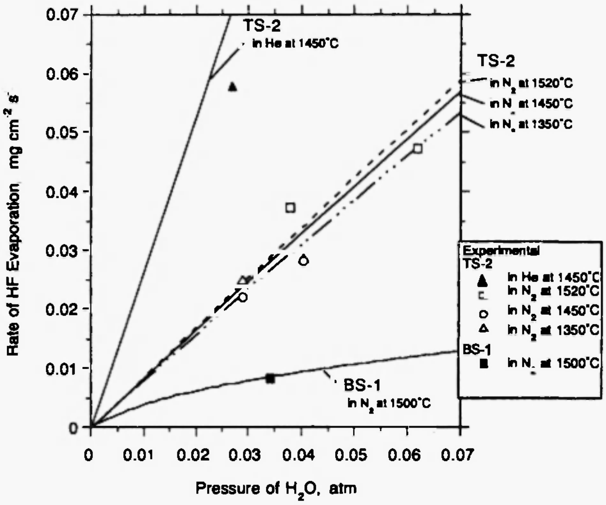

Fig. 7: Effect of humidity on the rate of weight loss due to HF evaporation (i.e.; rate of HF evaporation) for CaF_2-SiO_2-CaO slags of low $PSiF_4$ /14/.

3.5. Effect of Slag Composition on the Rate of HF Evaporation

The dependence of the rate on the slag composition is considered to be associated with changing values of a_{CaO}/a_{CaF_2} in Eq. 10. The relationship between a_{CaO}/a_{CaF_2} and the rate of HF evaporation is then shown in Fig. 8. This figure presents several interesting findings. One is the presence of upper limits of the rate of HF evaporation when decreasing a_{CaO}/a_{CaF_2}. One explanation for this may be that a finite amount of H_2O transport from the bulk flow to the interface prevents the overall rate of weight loss from rising continuously. Another finding is that the rate of HF evaporation tends to decrease significantly with increasing a_{CaO}/a_{CaF_2}. Decreasing PHF', caused by increasing a_{CaO}/a_{CaF_2} through Eq. 8, can account for this phenomenon. The other feature on this graph is again the small temperature dependence of the HF evaporation rate. It can be clearly seen that the experimental data in both studies (i.e., the present study and Schwerdtfeger *et al.*'s study) fit the theoretical relationship well.

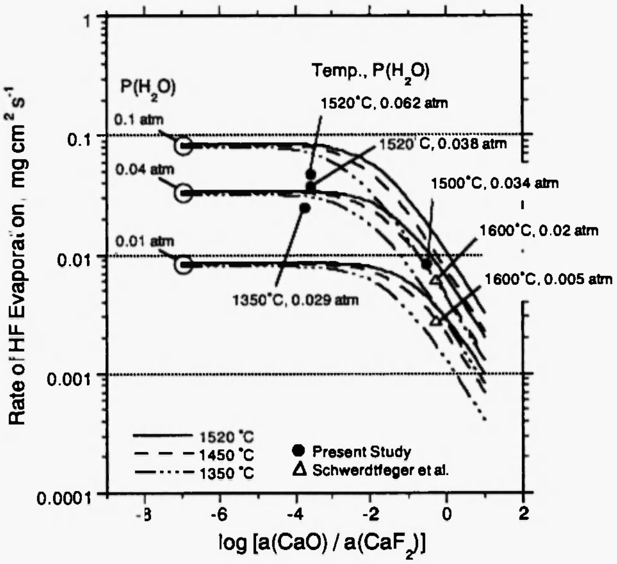

Fig. 8: Variations in the rate of weight loss due to HF evaporation (i.e.; rate of HF evaporation) in N_2 with a_{CaO}/a_{CaF_2} of CaF_2-SiO_2-CaO slags of low $PSiF_4$ /14/.

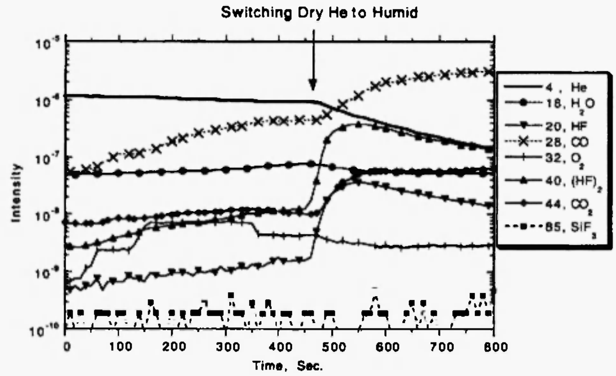

Fig. 9: Mass spectrometric observation of behaviours of gaseous species: Slag B.

3.6. Mold Flux Evaporation

Evaporation of gaseous fluorides from mold fluxes was well documented by Zaitsov /1/ and Shimizu /14/ and is shown in Fig. 4 as a function of temperature and humidity. However in actual casting conditions, evaporation occurs in a temperature gradient and the NaF or HF must diffuse through a bed of unmelted mold powder. This is an important issue as the vapour pressure of NaF(s or l) below 1050°C is negligible (i.e., <<1 atm) according to thermodynamic data /14/; therefore it is considered that virtually all of the NaF evolved from the slag melt will condense on lower temperature sites in the mold powder bed as NaF deposits at moderate temperatures (<1273K). Thus, as long as the mold powder layer surface temperature is lower than 1000^{0}C, NaF will not leave the mold powder.

The effect of humidity in this respect can be profound. A mass spectroscopic study of the off gases from an industrial mold flux can be seen in Fig. 9.

In Fig. 9, changes in intensity are plotted against time for the gaseous species of the mass numbers such as 4, 18, 20, 28, 32, 40, 44, and 85. The arrow in the graph denotes the point when dry He gas was switched to humid He.

In Fig. 9, it can be found that the intensities of 20 and 40 behaved in a substantially similar way, which leads to the conclusion that 20 represents HF and 40 represents $(HF)_2$ resulting from the attachment of HF. This relationship between HF and $(HF)_2$ was also found in the other experiments carried out with the other slag samples. The H_2O addition caused the evolution of HF as well as the additional increase in the amount of CO and CO_2. H_2O intensity slightly declined at the time of the change in humidity. The HF evolution is considered to be due to the reaction of (1). The rapid increase in the intensities of CO and CO_2 due to the H_2O addition can be attributed to those reactions:

$$C + H_2O \rightarrow CO + H_2 \quad (15)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (16)$$

$$2H_2 + O_2 \rightarrow H_2O \quad (17)$$

Another finding is that no significant level of SiF_4 was detected throughout the entire period of the experiment: the intensity level on the order of 10^{-10} was almost equivalent to the minimum for the mass spectrometer.

The rate of fluorine evaporation in mold slags is strongly influenced by gas phase mass transport, i.e. the rate at which a humid gas is blown onto the surface of a slag. This is shown in Fig. 10.

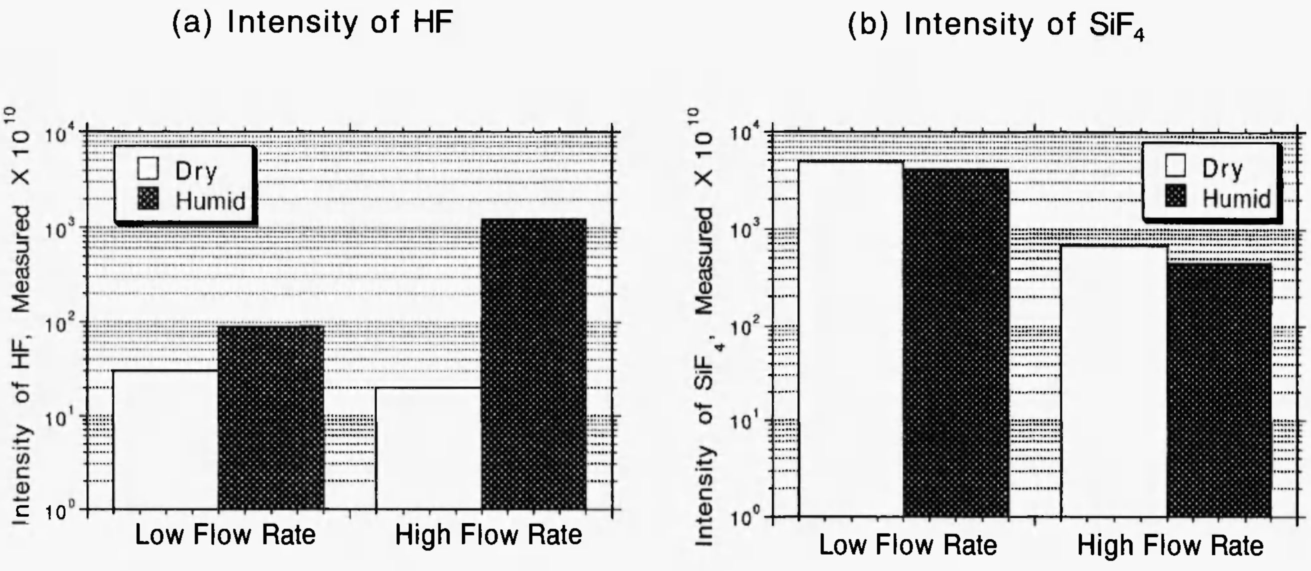

Fig. 10: Effect of the flow rate of carrier gas on the HF and SiF_4 evolution.

The convective mass transfer for the geometry of the crucible set-up that was used to determine the results of Fig. 10 can be expressed as:

$$Sh = 0.0048 \times Re^{1.06}\, Sc^{0.33} (r/d)^{0.09} \tag{18}$$

where

Sh = md/D: m (mass transfer coefficient); D (diffusivity),
Re = ud/ν: u (velocity of carrier gas); ν (kinematic viscosity),

and

Sc = ν /D

In Fig. 10, the flow rate of the carrier gas was increased from 40 to 140 ml/min. From Eq. 16, it is found that an increased velocity of flow almost proportionally increases the mass transfer coefficient for a diffusing species through the boundary layer formed near the interface between slag melt and gas phase. If HF evolution is assumed to be dominated by the reaction between H_2O (g) and slag melt, the mechanism of the reaction will have to involve the gas phase mass transfer of H_2O (g) as well as of HF (g). In contrast, if HF is produced by reaction 4, the reaction will be expected to occur mostly in the bulk phase, as was shown by Schwerdtfeger, Ries and Bruckman /11/. This consideration implies that in theory, increasing the flow rate of the carrier gas would have some effect only on the former case, not on the later case. Of course, the increased mass transfer coefficient may have an impact on increasing the amount of SiF_4 evolution, but in this experiment the quantity of evolved SiF_4 (g) was even smaller in the case of the higher flow rate; thus, it is safe to say that the HF evolution in the present experiment was controlled dominantly by the former case: the reaction between H_2O (g) and fluorine in the slag melt.

4. CONCLUSION

There has been a significant body of work documenting the problem of fluorine evaporation for slags. Although the evaporation rate can be minimized by proper slag design, the effect of humidity is always to increase the formation rate of HF. The rate of fluorine gaseous species evaporation is a function of slag chemistry, temperature, gaseous species diffusivity, humidity and gas phase mass transport. Under dry conditions mold practices that ensure that the flux surface temperature remains below 1000^0C can help minimize off-gassing; however, in he presence of substantial humidity, this effect can be mitigated.

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