Fluoride Desorption of Secondary Alumina at High Temperatures[†]

Yujuan YANG, Bingliang GAO,* Jiangyu YU, Zhaowen WANG,
 Zhongning SHI, and Xianwei HU

School of Materials & Metallurgy, Northeastern University, Shenyang 110004, China

* Corresponding author: gaobl@smm.neu.edu.cn

ABSTRACT

Primary alumina is used as the raw material as well as the sorbent for fluoride in aluminum electrolysis. Secondary alumina is the product of primary alumina after absorbing fluoride in exhaust pot gas. The fluorine and mass loss during heating secondary alumina was measured to study the fluoride desorption process of alumina. It was found that during the heating of secondary alumina, HF emission was always combined with H₂O escape at approximately 740°C or below. 47% fluorine in secondary alumina desorbed in the form of HF at 30–740°C, while the rest 53% desorbed in the form of chiolite at 740–1100°C.

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1. Introduction

Due to the vaporization and hydrolysis of the aluminum bath, aluminum smelting cells produce fluoride emissions consisting of sodium aluminum fluoride and hydrogen fluoride.¹ Considering environmental and economic aspects, primary alumina (manufactured/fresh alumina) is widely used as sorbent in the dry scrubbing system for the capture of gaseous and particulate fluoride, with an efficiency of 98% (Fig. 1). Secondary alumina, which is the corresponding byproduct of this process, is also added into the smelting cell to reduce fluorine loss.

Smelter-based fluoride evolution and recovery chemistry was first addressed at Alcoa in 1971.² Many researchers have studied the effects of physical and chemical properties of alumina on the adsorption capacity for gaseous HF and solid dust. Several mechanisms of HF adsorption have been proposed to reconcile the results of XRD, XPS, NMR, TGA, and DSC and so on.^{3,4} The chemical and physical adsorption of HF at room temperature may correspond to desorption of fluoride during feeding. This paper is mainly focused on the desorption reaction, reaction rate, desorption composition and quantity. Combined with adsorption mechanism, the mechanism of fluorine desorption is discussed in this paper.

2. Experimental

Primary alumina and its corresponding byproduct—secondary alumina samples used in this study were taken from aluminum smelting plant. After reaction in the dry scrubber, secondary alumina contains a bit more fine particles than primary alumina as can be observed from size distribution measurement. Since it doesn't affect the results of fluorine content and TGA analysis, it is neglected.

2.1 Fluorine content determination

Secondary alumina samples were preheated at different temperatures respectively for 2 h, and then extracted with 0.01 mol·L⁻¹ NaOH solution to free its fluorine ion and a fluorine ion selective electrode (PF-1 style from INESA Scientific Instrument Co., Ltd.) was used to determine the fluorine content of the solution. The fluorine concentration of each sample was measured for three times to check the

Figure 1. Traditional co-current dry scrubber.⁵

reproducibility. The results turned out to be of good reproducibility and the final data was taken as the average value of three determinations.

2.2 TGA measurement

The weight loss of primary alumina and its corresponding secondary alumina samples during heating was measured by the using of NETZSCH STA 409C/CD equipment from 30 to 1100°C with a rate of 10°C·min⁻¹ in high purity corundum cells, with 50 ml·min⁻¹ argon protection. The results were calculated based on the same mass of samples.

2.3 XRD measurement

Diffraction data of the volatilization of aluminum bath was collected by the using of Cu-Kα radiation equipped on PANalytical PW3040/60 X' Pert Pro MPD diffractometer. The total scan time was 1020 s with an angular range of 5–90° (2θ).

3. Results and Discussion

3.1 Fluorine loss of heated secondary alumina

The fluorine contents of secondary alumina heated at different temperatures are shown in Fig. 2.

As is shown in Fig. 2, the fluorine content of secondary alumina decreased linearly from 110 to 800°C. Then it showed a sharper decrease from 800 to 1100°C where fluorine content went to zero. The faster desorption rate of latter interval suggests a different desorption modality of fluorine.

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Figure 2. (Color online) Fluorine content of heated secondary alumina.

Figure 3. (Color online) TGA curves of primary alumina and secondary alumina.

3.2 TGA analysis

Both primary alumina and secondary alumina processes the loss of moisture and hydroxyl when heated to 1100°C. The fluorine desorption of secondary alumina also occurred in this period. The TGA curves of primary and secondary alumina are shown together in Fig. 3.

As is shown in Fig. 3, TGA curve of primary alumina showed a gradual loss of weight as the temperature increased. While the secondary alumina showed a multistage weight loss compared to primary alumina, which corresponds to different desorption reactions and desorption rates. Subtract the weight loss of primary alumina from that of secondary alumina, the difference value (D-value) curve demonstrated an apparent multistage fluorine loss of secondary alumina as shown in Fig. 4. Figure 2 is overlapped into Fig. 4 for easy understanding.

According to the slope of D-value curve, the fluorine desorption can generally be divided into four stages: 30–170°C, 170–350°C, 350–740°C, and 740–1100°C. The data variations in D-value curve were caused by fluoride loss and excessive dehydration of secondary alumina at each stage compared to primary alumina. Desorption of the fluoride in these four stages are discussed separately as follows.

Fluoride desorption from 740 to 1100°C: Since secondary alumina adsorbed emissions generated by bath evaporation from the aluminum cell, the fluoride will volatilize again when it is heated to a high temperature. In order to make sure the contents of the emissions, the volatile dust of aluminum bath was collected with an iron plate and its XRD patterns is shown in Fig. 5.

As can be seen in Fig. 5, the solid volatile of aluminum bath was mainly consisted of chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$)⁶ and Fe_3O_4 ⁷ which comes from the iron baseplate of the collection unit.

According to Fig. 4, the weight loss from 740 to 1100°C was 0.5100%. Correspondingly, the fluorine loss was 0.2888%. Supposing that the volatile matter was some kind of fluoride, then the fluorine content of the fluoride is $0.2888\% / 0.5100\% = 56.6\%$, which is very close to that of chiolite (%F = 57.6%).

Figure 4. (Color online) D-value curve of weight loss of secondary alumina during heating.

Figure 5. XRD patterns of collected dust from bath emissions.

Figure 6. (Color online) Binary phase diagram of NaF- AlF_3 .⁸

Figure 6 shows the binary phase diagram of NaF- AlF_3 .⁸ Chiolite, with 37.5 mol% AlF_3 , reaches up to peritectic point when heated to 725°C. As the temperature goes up, liquid phase appears, following with fluoride volatile emissions. When it reaches up to liquids temperature (860°C), all chiolite turns into liquid phase.

Some agglomerates which may be caused by the reaction of alumina with sodium aluminum fluoride were observed in secondary alumina samples heated at 800°C or higher.

Results of XRD analysis, fluorine content of lost fluoride and the NaF- AlF_3 phase diagram all lead to a conclusion: the emissions of secondary alumina from 740 to 1100°C are consisted of sodium aluminum fluoride dust (mainly chiolite).

Fluoride desorption from 30 to 740°C: According to Fig. 3, from 30–1000°C, the overall mass and fluorine loss was 0.8388% and 0.5987% separately. Since in the temperature range of 740–1100°C, chiolite went out with fluorine loss of $0.5100\% \times 57.6\%$ (%F of chiolite) = 0.2938%, so fluorine loss during this period should be modified as $0.5987\% - 0.2938\% = 0.3049\%$ and mass

Table 1. Fluorine loss and its corresponding fluoride during heating.

Temperature, °C	%F (HF)	%F (Chiolite)
30–170	4.60	0
170–350	14.38	0
350–740	27.63	0
740–1100	0	53.39
Overall	46.61	53.39
	100.00	

loss should be $0.8388 - 0.5100 = 0.3288\%$. Supposing that the fluorine went out in some form of fluoride, the fluorine content of this assumptive fluoride should be 0.3099% (fluorine change)/ 0.3288% (mass change) = 94.25% , which is very close to that of HF component (%F = 95%).

Study on the fluoride desorption of secondary alumina during heating should trace back to the adsorption process of primary alumina for aluminum pot gas. According to Lamb model,⁹ the chemisorption of hydrogen fluoride is a two-step reaction. Firstly the fluorine ion within hydrogen fluoride is adsorbed on alumina, substituting the hydroxyl groups initially chemisorbed on alumina and forming the monolayer (Reaction 1). Secondly the multistage adsorption of HF molecules occurs via the formation of hydrogen bonds (Reaction 2). In the presence of moisture, multilayers are relatively stable [see (3)]. Hydrogen bonds become weaker as they get further away from the chemisorbed layer.¹⁰

On the basis of Lamb model, Neal R. Dando proposed that the chemisorbed HF occurs on chemically active sites of the alumina surface in the formation of $\text{AlF}_3 \cdot n\text{H}_2\text{O}$ and $\text{NaF} \cdot n\text{H}_2\text{O}$ complexes.¹¹ Other researchers concluded that the physical adsorption of HF works through the hydroxyl groups and physically adsorbed moisture with the formation of HF and H_2O layers. Both these conclusions made a point of hydroxyl and moisture in alumina.¹² When secondary alumina is added into smelting cells, a sudden heating up is unavoidable, accompanied with the loss of most hydroxyl and moisture.

As the loss of hydroxyl and moisture during heating, hydrogen bonds get weaker. Bonds broken first take place on the further hydrogen from the chemisorbed layer (Reaction 4). In the present paper, samples heated at 1100°C for 2 h contained no fluorine, which means the generated AlF_x combined with chiolite and formed eutectic fluoride.

Fluorine loss of secondary alumina during heating is listed in Table 1.

Fluoride desorption from 30 to 170°C : According to data in Fig. 4, the mass and fluorine lost during this period was 0.1738% and 0.0327% respectively. The fluorine content of the volatile is 0.0327% (fluorine change)/ 0.1738% (mass change) = 18.83% . Supposing that all the fluorine escaped as HF, the content of HF was $18.83\%/95\%$ (%F of HF gas) = 19.82% , and the H_2O percentage in the volatile was $100\% - 19.82\% = 80.18\%$. Since the moisture and hydroxyl has been deducted from D-value curve, this part of excessive dehydration directly caused an over glissade of the

Table 2. The composition of emissions from secondary alumina in different temperature intervals.

T °C	%F (HF)	% H_2O	%F (Chiolite)	Overall %
30–170	19.82	80.18	0	100.00
170–350	28.45	71.55	0	100.00
350–740	59.37	58.38	0	100.00
740–1100	0	0	100	100.00

following mass data. The mass data from D-value curve is modified with excessive dehydrated water in the next stages.

Fluoride desorption from 170 to 350°C : During this period, the mass and fluorine loss was 0.1326% and 0.0876% respectively. But this mass change did not include the premature water loss below 170°C as mentioned above. H_2O escaped (Reaction 4) below 170°C was 0.2388% (D-value at 170°C) $\times$ 80.18% (H_2O percentage of volatile at $30\text{--}170^\circ\text{C}$) = 0.1915% . So the calibrated mass decreased at $170\text{--}350^\circ\text{C}$ was 0.1326% (mass loss) + 0.1915% (calibration) = 0.3241% . It was calculated that HF and H_2O takes proportion of 28.45% and 71.55% respectively.

Fluoride desorption from 350 to 740°C : With the same method as above, the mass and fluorine loss of this period from Fig. 3 was -0.1451% and 0.1587% . The amount of H_2O lost during $170\text{--}350^\circ\text{C}$ was 0.3241% (D-value at 350°C) $\times$ 71.55% (H_2O percentage of volatile at $350\text{--}740^\circ\text{C}$) = 0.2319% . The mass loss of this period should be calibrated as -0.1451% (mass change) + 0.2319% (over lost water at $170\text{--}350^\circ\text{C}$) + 0.1915% (over lost water at below 170°C) = 0.2814% . As a result, HF and H_2O take up to 59.37% and 58.38% respectively.

Overall, the approximately composition of emissions from $30\text{--}1100^\circ\text{C}$ is shown in Table 2.

4. Conclusions

Fluoride desorption occurred during the preheating of secondary alumina. At the temperature of $30\text{--}740^\circ\text{C}$, the emission of hydrogen fluoride and H_2O was dominant. Desorption of HF was always combined with H_2O lost. As the temperature increased to 740°C , HF ratio in desorption rose from 19.82 to 59.37% . At the temperature of $740\text{--}1100^\circ\text{C}$, the volatilization of sodium aluminum fluoride (mainly chiolite) dust gained in importance. In this period, the residual 53.39% fluorine in secondary alumina got lost.

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