

THE INFLUENCE OF PHYSICAL AND CHEMICAL PROPERTIES OF ALUMINA ON  
HYDROGEN FLUORIDE ADSORPTION

J.F. Coyne, M.S. Wainwright, M.P. Brungs

School of Chemical Engineering and Industrial Chemistry

The University of New South Wales

P.O. Box 1, Kensington, N.S.W., 2033 Australia.

A.N. Bagshaw

Research and Development Department

Alcoa of Australia Ltd.

P.O. Box 161, Kwinana, W.A., 6167 Australia.

Hydrogen fluoride adsorption was studied on a series of aluminas having a wide range of physical and chemical properties. There was significant deviation from the linear relationship between adsorptive capacity and BET surface area for commercial aluminas with similar surface areas but from different Bayer processing plants. However, when aluminas of different surface areas were produced by laboratory calcination of a single trihydrate sample the linear relationship was very exact. The deviation from linearity in the case of the commercial samples could not be accounted for by differences in any one of the following properties: phase composition, surface acidity, moisture on ignition, or loss on ignition. When four commercial samples were fractionated to study the effect of particle size, HF adsorption was shown to have a significant maximum for particles in the range 106-125 microns. The presence of adsorbed moisture was found to account for the observed maximum.

### INTRODUCTION

The Hall-Heroult process for producing aluminium relies heavily on the use of fluorine compounds and consequently fumes containing fluorides are inevitable. Since the 1970's dry scrubbing systems using alumina have been employed to remove these fluorides and other unwanted impurities from smelter emissions. A number of investigations (1-4) into the adsorption of hydrogen fluoride on alumina have been conducted since the majority of fluorine in emissions is present as hydrogen fluoride. These investigations have focused mainly on the types of adsorption and the effect of BET surface area on the adsorptive capacity of alumina.

The type of adsorption has been the subject of several papers (1-4). Cochran (1,2) concluded that hydrogen fluoride adsorption on alumina follows classical adsorption theory, with a chemisorbed monolayer first being formed, followed by subsequent physisorption of HF, which was easily desorbed. On the basis of HF adsorption (as wt%F) on a range of aluminas having widely different BET surface areas Cochran determined the amount of HF chemisorbed as a monolayer to be 0.033% F<sup>-</sup>/m<sup>2</sup>. Unlike Cochran, Lamb (3)

found that the adsorption of HF on alumina followed a Langmuir isotherm. Furthermore Lamb calculated that 0.028%F<sup>-</sup>/m<sup>2</sup> was the adsorptive capacity of the alumina surface. On this basis he postulated that 2 to 3 layers of HF were adsorbed and that the adsorption was strong. More recently Baverez and De Marco (4) reported that HF was adsorbed as two "bimolecular layers", each containing 0.053%F<sup>-</sup>/m<sup>2</sup>. They reported that the efficiency of HF adsorption was essentially 100% as long as the first bimolecular layer was incomplete and the rate of adsorption became much slower as the second bimolecular layer formed.

Most of the investigations of HF adsorption have related sorptive capacity to the BET surface area of the aluminas (2-4). In general a linear relationship of the form

$$\% F^{-} = a + b S_{BET} \quad (1)$$

has been obtained. The coefficient "a" is always positive suggesting that low surface area aluminas have greater capacities for HF adsorption per unit area than those with higher surface areas.

The objective of the present work was to study HF adsorption on well characterized aluminas, which were prepared by different calcination processes. In this way it was hoped that the physical and/or chemical properties of the aluminas that correlated with adsorptive capacity could be identified.

### EXPERIMENTAL

#### Aluminas

In preliminary experiments laboratory calcinations of alumina trihydrate were undertaken to produce aluminas with a wide range of BET surface areas. Alumina trihydrate from Alcoa's Pinjarra Refinery was washed to remove any entrained caustic then heated in a muffle furnace at 600°C for 71 hours to form gamma-alumina (117 m<sup>2</sup>/g S<sub>BET</sub>). Further calcination was carried out at temperatures from 600 to 1000°C for periods from 6 to 65 hours in the muffle furnace, to produce aluminas with surface areas ranging from 16 to 87 m<sup>2</sup>/g. The major part of the

study used 21 aluminas provided by Alcoa of Australia Ltd. They were some of the 34 aluminas used by Bagshaw and Welch (5) to study the influence of alumina properties on dissolution in smelting electrolyte. Four of these aluminas were fractionated by sieving to study the effect of particle size on fluoride adsorptive capacity.

### Characterization Methods

The BET surface areas were measured using a Micromeritics Model 2200 High Speed Surface Area Analyzer, which uses  $N_2$  adsorption at  $-195^\circ\text{C}$  to determine  $S_{\text{BET}}$  from a single point measurement. Pore size distributions were determined using a Micromeritics Auto-Pore 9200 automated mercury intrusion porosimeter. The phase composition was determined by the procedure described by Bagshaw and Welch (5). The proportions of the intermediate phases gamma, theta, delta, and chi alumina were determined using the diffraction peaks at 0.197, 0.280, 0.271 and 0.231 nm respectively.

The moisture on ignition (M.O.I.) and loss on ignition (L.O.I.) were determined by heating pre-weighed samples from 25 to  $300^\circ\text{C}$  and from 300 to  $700^\circ\text{C}$  respectively, and allowing samples to cool in a moisture-free environment before re-weighing.

An attempt was made to characterise the surface of the aluminas by measuring the rates of the dehydration of methanol to dimethyl ether. This reaction which is acid-catalysed has been used to measure the surface acidities of alumina supports prepared by the calcination of  $\gamma$ -alumina (6). Methanol conversions were measured over samples of alumina in a flow reactor using the procedure described in detail elsewhere (6). The second rate constant for the dehydration reaction was used as an indicator of the surface acidity of the alumina sample.

The soda contents of the fractionated aluminas were determined using a variation of Ingamill's method for siliceous material. A weighed sample (0.1g) was fused with lithium metaborate (1.4g) in a platinum/gold crucible at  $1000^\circ\text{C}$  for 14 minutes using an electric furnace. The resulting sample was dissolved in a ionization suppressant solution and the soda content was measured using a Varian atomic absorption Spectrometer. The suppressant solution was prepared by dissolving 6.34g caesium chloride in 100 ml concentrated nitric acid and making up the volume to 2 litres.

### HF Adsorption Measurements

A schematic of the apparatus is shown in Figure 1. Water was delivered by a syringe pump to a vaporizer/preheater where it mixed with a flow of dry nitrogen. A calibrated mixture of 0.8 mol % HF in dry nitrogen (Commonwealth Industrial Gases Ltd.) was preheated and mixed with the  $N_2$ /water mixture before passing through a fixed bed of alumina. The exit gas was scrubbed of any residual HF in aqueous sodium hydroxide solution prior to venting. The conditions used for adsorption were:

Mass of alumina	: 0.8g
Temperature	: $120^\circ\text{C}$
Gas flow rate	: 1.6 L/min
HF level	: 1271 ppm (155 mg/Nm <sup>3</sup> )
Water level	: 4.9 vol %
Reaction time	: 1 hour

The volume of HF passed was more than twice that required for equilibrium adsorption.

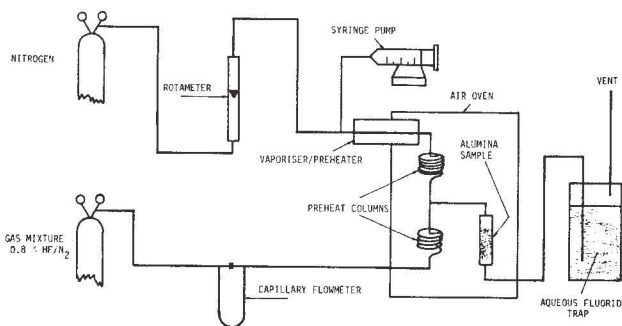


Figure 1 - Schematic of Apparatus used to make HF Adsorption Measurements.

### Analytical Procedure

A 0.8g sample of the reacted alumina was weighed into a platinum crucible and 4.0g of sodium carbonate and 2.4g of boric acid were added. The sample was thoroughly mixed and fused in a gas flame after which the fused sample was placed in an electrical furnace at  $1000^\circ\text{C}$  for 15 minutes to obtain a clear solution (complete dissolution). The fused sample was cooled and dissolved in distilled water then mixed with a buffer and the fluoride content of the solution was measured using an Orion selective ion electrode and meter.

### RESULTS AND DISCUSSION

The characterization data for the twenty-one plant grade alumina samples supplied by Alcoa of Australia Ltd. are listed in Table I. These results show that there is no apparent correlation between parameters, in particular between surface area and alpha-alumina content as reported by Raahauge (7), which is largely a result of different calcination techniques.

The linear relationship between adsorptive capacity and BET surface area for the laboratory calcined samples and the plant samples is shown in Figure 2. The laboratory samples which originated from the same trihydrate precursor and calcination technique, show an excellent linear correlation. In contrast the plant aluminas show substantial deviation from linearity. For example at a typical BET surface area of approximately  $65\text{m}^2/\text{g}$  there is an adsorptive capacity range from 7.2 to 8.6 wt%F; this represents a deviation of 17% from the value predicted by the linear model.

Attempts to relate HF adsorption for the plant alumina samples to the alumina phase composition, pore size, pore volume, surface acidity, M.O.I., and L.O.I. revealed no apparent correlations. Plots of HF adsorption residuals (residual = observation - linear model value) against the above parameters showed similar random scatter. This suggests that these properties are not responsible for the deviation from the linear relationship of adsorptive capacity with BET surface area. Although the deviation cannot be explained by the above parameters; it may be attributable to different operating procedures in the precipitation and calcination stages of the refining process. Evidence for this is the work of Puttock et al(8) who reported different particle characteristics, in particular particle size, for products from three different Australian refining plants.

TABLE I

Surface areas, surface acidities and phase compositions (from XRD analysis) of smelter grade aluminas.

Sample	S <sub>BET</sub> m <sup>2</sup> /g	Surface Acidity L/mol.m <sup>2</sup> .s.cm <sup>3</sup>	Phases (wt %)					Code
			Gamma γ	Delta Δ	Theta θ	Chi χ	Alpha α	
1	55	0.51	65	4	14	6	11	F
2	51	0.39	75	5	11	3	6	F
3	46	11.46	63	2	10	3	22	K
4	47	0.57	69	5	12	7	7	F
5	63	1.33	78	5	11	4	2	F
6	98	47.19	73	3	19	4	1	F
7	7	2.24	7	0	4	0	89	K
8	104	55.23	58	9	20	9	4	F
9	75	6.19	83	2	11	3	1	F
10	59	1.22	81	3	10	4	2	F
11	35	0.23	59	5	11	5	20	F
12	72	8.49	88	2	8	2	0	P
13	67	11.63	63	3	11	3	20	K
14	65	10.77	64	2	10	3	21	K
15	53	20.42	64	3	9	2	22	K
16	67	10.57	72	2	9	2	15	K
17	68	80.24	73	6	13	5	3	F
18	71	1.12	76	3	14	2	5	A
19	130	21.82	68	2	19	5	6	A
20	13	0.45	14	2	7	0	77	K
21	64	68.44	47	3	19	6	25	K

**Legend**  
 F - Flash calcination  
 K - Kiln calcination  
 P - Pressure calcination  
 L - Alcoa pilot flash calcination.

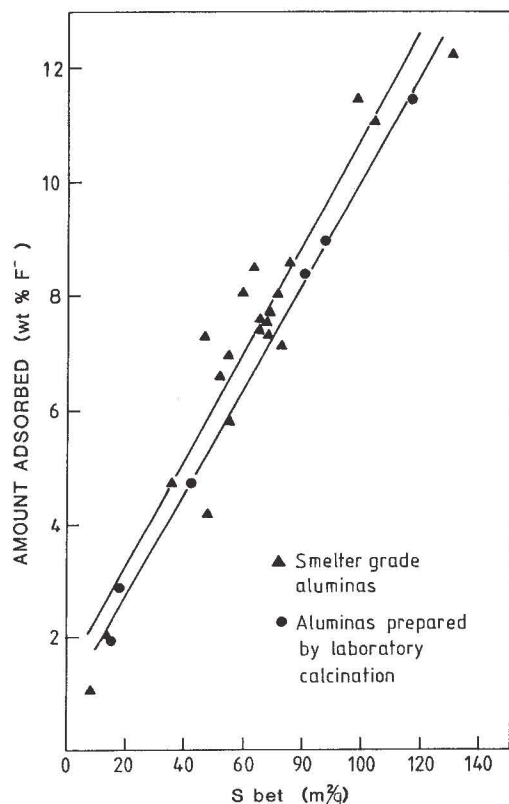


Figure 2 - HF Adsorption (wt % F) versus BET Surface Area.

The influence of particle size on HF adsorptive capacity was studied on fractioned samples of four smelter-grade aluminas from different Bayer Plants. Three of these aluminas were calcined by the Alcoa flash calcination process and the other by kiln calcination. The fractioned samples were characterised in terms of BET surface area, alumina phases ( $\gamma$ ,  $\theta$ ,  $\Delta$ ,  $\chi$ , and  $\alpha$ ), surface acidity, M.O.I., L.O.I., and soda content. The data for two aluminas prepared by the different calcination procedures are presented in Table II. Hydrogen fluoride adsorptive capacities for these two fractioned samples are presented as a function of particle size in Figures 3 and 4. All four of the fractioned samples exhibited similar strong adsorption maxima for the 106-125 $\mu$ m fraction. Figure 3 is typical of the plots obtained for the three flash calcined aluminas. Their maxima were more pronounced than for kiln calcined alumina [Figure 4], the reason being that with flash calcination there is a narrower spread of property variation with particle size. Plots of wt % F/S<sub>BET</sub> versus particle size also exhibited strong maxima in the 106-125 $\mu$ m range, which indicates the phenomena is not due to a surface area effect.

It is apparent from the characterization data in Table II that BET surface area increases with increasing particle size where as alpha-alumina content decreases. These relationships are consistent with smaller particles being calcined to a greater extent than the larger particles. However, the amounts of intermediate alumina phases, (gamma, delta, theta and chi) showed no definite relationship with particle size. Similarly there was no correlation between soda content or surface acidity and particle size, even

TABLE II  
Physical and Chemical Properties of Fractioned Aluminas.

	$S_{BET}$ $m^2/g$	Surface Acidity $L/mol.m^2.s.cm^3$	$Na_2O$ wt %	M.O.I. wt %	Gamma $\gamma$	Phases (wt %) Delta $\Delta$	Theta $\theta$	Chi $\chi$	Alpha $\alpha$
<b>SAMPLE A (Flash Calcined)</b>									
+150 $\mu m$	56	0.63	0.47	2.82	78	4	11	3	4
-150+125 $\mu m$	54	0.62	0.47	2.73	79	2	13	2	4
-125+106 $\mu m$	53	0.77	0.44	2.93	76	3	15	2	4
-106+75 $\mu m$	56	0.91	0.47	2.65	81	3	10	1	5
-75+45 $\mu m$	48	1.57	0.50	2.55	77	3	10	1	9
-45+20 $\mu m$	46	3.24	0.51	2.34	69	2	8	0	21
<b>SAMPLE B (Kiln Calcined)</b>									
+150 $\mu m$	52	14.1	0.54	2.47	72	4	11	1	12
-150+125 $\mu m$	53	11.2	0.44	2.59	73	2	10	1	14
-125+106 $\mu m$	50	11.4	0.58	2.75	74	3	7	0	6
-106+75 $\mu m$	49	12.6	-	-	61	4	14	0	21
-75+45 $\mu m$	47	15.0	0.46	2.76	53	3	14	0	30
-45+20 $\mu m$	41	9.6	0.59	2.32	29	4	19	0	48

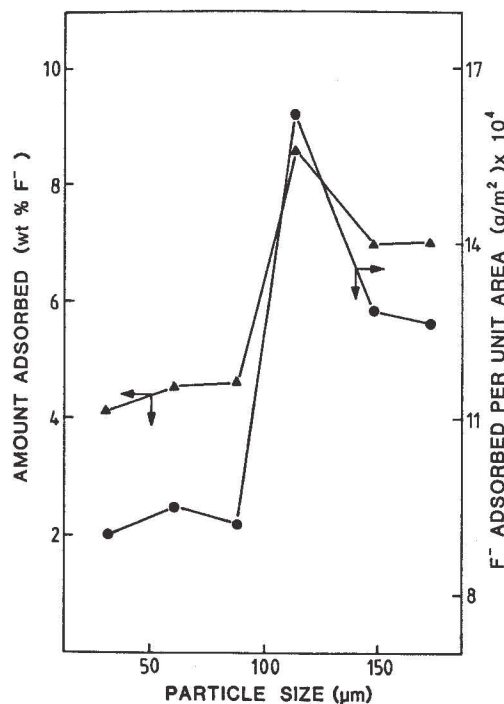


Figure 3 - HF Adsorption versus Particle Size for Flash Calcined Alumina (Sample A).

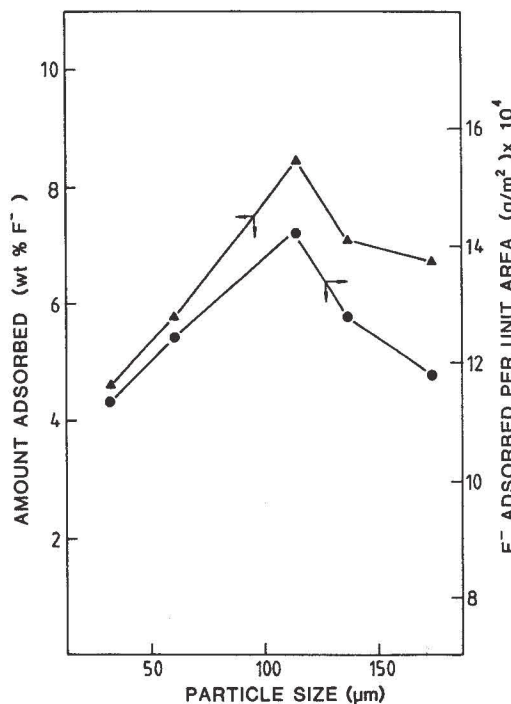


Figure 4 - HF Adsorption versus Particle Size for Kiln Calcined Alumina (Sample B).

though soda levels ranged from 0.42 to 0.59 wt %, and relative acidities varied from 0.6-13.8. Thus none of these properties can explain why the 106-125 $\mu m$  fraction adsorbs substantially more hydrogen fluoride than the other size fractions.

Plots of M.O.I. versus particle size for the fractioned samples [Figure 5] show that, as for HF adsorption, M.O.I. exhibits a distinct maximum for

particles in the 106-125 micron range. Similar plots of L.O.I. versus particle size revealed no such maxima. The results in Figure 5 suggest that the presence of adsorbed moisture is responsible for the observed maxima in HF adsorption. It is evident that weakly bound water which is easily removed by heating to 300°C is of greater importance than the more strongly bound water which is removed by heating from 300 to 700°C.

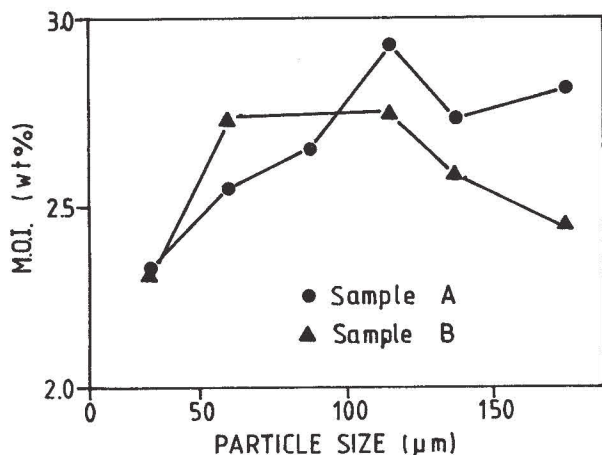


Figure 5 - Moisture Content [M.O.I. (wt %)] versus Particle Size.

It is of interest to note that the amount of water introduced with the HF in the adsorption experiments was two orders of magnitude greater than that adsorbed on the particles initially. Despite this the adsorption of HF went through a maximum with moisture content (M.O.I.) of sample. This suggests that it is the surface water (pre-adsorbed) which determines the HF adsorptive capacity of alumina rather than gas-phase water.

Since adsorption is a surface phenomenon it is not surprising that HF adsorption exhibited little correlation with the amounts of the various alumina phases present which are bulk properties as determined by X-ray diffraction analysis. Nevertheless it is possible that relative amounts of the transition phases-alumina present on the surface influence water adsorption and hence HF adsorption. The measurement of methanol dehydration was an attempt to provide information about the alumina surface. However, since the reaction is catalysed by the acidity of the surface, the presence of surface soda in addition to the alumina phases complicates the measurement.

In this preliminary investigation we have shown that HF adsorption on aluminas is a complex process and that properties other than the BET surface area influence the amount adsorbed. The results suggest that HF molecules become bound to water molecules adsorbed on the alumina surface. Thus the water acts as a bridge between the alumina surface and the HF molecule, a model which is consistent with the mechanism proposed by Baverez and De Marco (4).

#### CONCLUSIONS

An excellent linear correlation between HF adsorptive capacity and BET surface area was observed for alumina samples calcined in the laboratory using the one precursor trihydrate. In contrast significant deviation was evident for commercial aluminas from different Bayer refining plants. This deviation could not be explained by the physical and chemical properties such as the amounts of different alumina phases, pore size or volume, surface acidity, M.O.I. or L.O.I.

When commercial aluminas were fractionated to different size ranges a significant maximum in HF adsorption was observed for particles in the 106-125 micron range. This effect was explained by greater water adsorption as indicated by the M.O.I. values for this size range.

From this study it is unclear why a particular particle size fraction adsorbs more water and hence more hydrogen fluoride. Work is continuing in this area to further the understanding of hydrogen fluoride adsorption on smelter-grade aluminas.

#### ACKNOWLEDGEMENTS

Support of this research by Alcoa of Australia Ltd. through N. Broad at the Point Henry Smelter is gratefully acknowledged.

#### REFERENCES

1. Cochran, C.N., Sleppy, W.C., Frank, W.B., "Fumes in Aluminium Smelting; Chemistry of Evolution and Recovery.", *J. of Metals* 22, (9) (1970), 54-57.
2. Cochran, C.N., "Recovery of Hydrogen Fluoride Fumes on Alumina in Aluminium Smelting.", *Environ. Sci. Tech.* 8, (1) (1974), 63-66.
3. Lamb, W.D., "A Study of the Equilibrium Adsorption of Hydrogen Fluoride on Smelter Grade Aluminas.", *Light Metals* (1978), 425-444.
4. Baverez, M., DeMarco, R., "A Study of the Adsorption of Hydrogen Fluoride on certain Smelter Grade Aluminas.", *Light Metals* (1979), 891-907.
5. Bagshaw, A.N., Welch, B.J., "The Influence of Alumina Properties on its Dissolution in Smelting Electrolyte.", *Light Metals* (1986), 35-39.
6. Kwan, M.Y.H., et al "Modified Alumina Supports for the Catalytic Oxidation of Benzene to Maleic Anhydride over Vanadia.", *Appl. Catal.* (in press).
7. Raahauge, B.E., Nichelsen, J., "Industrial Prospects and Operational Experience with 32 mtpd Stationary Alumina Calciner.", *Light Metals* (1980), 81-102.
8. Puttock, S.J., et al "Characterization and Dewatering of Australian Alumina Trihydrate." *Int. J. Miner Process* 16 (1986), 263-279.