

# Light Metals

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## A STUDY OF THE EQUILIBRIUM ADSORPTION OF HYDROGEN

### FLUORIDE ON SMELTER GRADE ALUMINAS

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Equilibrium adsorption isotherm data at 80°C were fitted to the linear form of the Langmuir equation for the reaction of five typical smelter grade aluminas with low concentrations of HF (20-1100 ppm vol.) in dry air. This shows that multilayers of fluoride are adsorbed on the active surface, since a monolayer site area of 3.3 to 5.4 Å<sup>2</sup> is calculated from this procedure, which is not consistent with 11.3 Å<sup>2</sup> found from conventional molecular theory. Heating tests and extractions with water and sodium hydroxide show that at least 95% of the fluoride adsorbed from dry or humid gas is strongly held on the alumina surface. The amount of fluoride adsorbed is at least doubled by the presence of about 5% volume of water vapour in the gas. The effect of water vapour is non-linear, rising rapidly at 1-3% and levelling off at 5-8%. Neither the equilibrium nor the reaction rate is significantly affected by temperature change from 20° to 80°C, suggesting that the adsorption rate is probably controlled by mass transfer of HF to the reacting surface, rather than by chemical reaction. The fluoride concentration adsorbed at equilibrium provides a laboratory method for measuring and comparing alumina reactivities to HF.

## Introduction

For some time, there has been a need to define the reactivity of smelter aluminas used for the dry scrubbing of exhaust gases from the Hall-Heroult aluminum reduction process. The use of specific surface area is quite common and has been referred to by Colpitts (1) and Nasmith and Miller (2). Lobos et al (3) described a method whereby the alumina is equilibrated with the vapours from 50% wt hydrofluoric acid and this procedure has been criticized as being done under conditions non-representative of the dry scrubbing process (1). To overcome these objections, a new procedure has been developed whereby the alumina is equilibrated with low concentrations of HF (20-1000 ppm volume) in air at room temperature. From the adsorption isotherm so developed the maximum HF adsorption can be defined for any alumina and this value can be used as a guide to its suitability for dry scrubbing.

## Theory and Definitions

Adsorption data were fitted to the linear form of the Langmuir isotherm. The normal equilibrium equation is:

$$\theta = \frac{kP}{1 + kP} \quad 1.$$

Where  $\theta$  = fraction of surface covered by adsorbate  
k = equilibrium constant for the adsorption reaction  
P = gas pressure of adsorbate (partial pressure of HF)

If  $\theta$  is replaced by  $v/v_m$ , where v represents volume and  $v_m$  is the volume of gas adsorbed per gram, at the monolayer stage, in cm<sup>3</sup> at 1 atmosphere and 0°C, then the equation becomes:

$$v = \frac{v_m kP}{1 + kP} \quad 2.$$

Expressing this equation in the linear form, we have:

$$\frac{P}{v} = \frac{P}{v_m} + \frac{1}{kv_m} \quad 3.$$

Thus a plot of P/v as ordinate against P as abscissa, will give a straight line of slope 1/v<sub>m</sub> and with an intercept 1/kv<sub>m</sub> on the vertical axis. The P values were expressed as ppm volume of HF (c<sub>HF</sub>) and the ordinate values were calculated from (c<sub>HF</sub> ÷ %F adsorbed on the alumina), since this is proportional to P/v.

The value of v<sub>m</sub> can thus be found from the slope of the linear plot, but will be expressed as a concentration (%F<sub>m</sub>) in the alumina. To convert to volume (cm<sup>3</sup> at 0°C and 1 atm), the following formula was used:

$$v_m = \frac{\%F_m \times 22,400}{100 \times 20} \quad 4.$$

From  $v$ ; the area,  $a$ , of a site occupied by an HF molecule, in the monolayer can be found from:

$$a = \frac{A \times 22,400 \times 10^4}{v_m \times N} \text{ cm}^2$$

$$= \frac{20A \times 10^{22}}{\%F_m \times N} \frac{\text{g}^2}{\text{g}} \quad 5.$$

Where  $A$  = surface area of alumina ( $\text{m}^2 \text{g}^{-1}$ )  
 $N$  = Avogadro's number,  $6.023 \times 10^{23}$

For comparison, the area,  $s$ , covered by an HF molecule (assumed spherical) can be calculated from molecular theory using the relation:

$$s = 1.53 (M^2 V_{sp}^2)^{1/3} \quad 6.$$

Where  $M$  = molecular weight  
 $V_{sp}$  = specific volume (=1 for HF in liquid state)

$$\text{Thus } s_{\text{HF}} = 1.53 (20^2 \times 1)^{1/3} = 11.27 \text{ \AA}^2$$

Equipment

(a) Description

The equipment used is shown in Figure 1. A supply of 5% HF in nitrogen from a cylinder is mixed with a flow of nitrogen from a second cylinder using a mixing coil.

The flows of both gases are adjusted to give the concentration desired at a total flow rate of 5 l/min using the metering valves  $V_1$ ,  $V_4$  and  $V_5$ . The HF/ $N_2$  gas flow is measured continuously with a linear mass flow meter, whereas the total gas flow is adjusted at the outset of our experiment, by using a wet test meter. The gas can be supplied dry or humidified by appropriate setting of the valves  $V_2$  and  $V_3$ . The humidifier is simply a flask containing water at a controlled temperature through which the nitrogen bubbles. The humidity is measured with a wet/dry bulb hygrometer. The gas lines after the humidification are lagged and electrically trace heated, as is the mixing coil, to avoid condensation and to set the desired gas temperature. All gas lines and Swagelok connections are of copper. After mixing, the gas enters or by-passes a small monel reactor containing 0.5g of alumina, by setting the two-way valves  $V_6$  and  $V_7$ . Immediately after  $V_7$ , a flow of buffer solution is supplied by a peristaltic pump at 8 ml/min to mix with the gas through a second coil. The buffer solution is 2% hexamethylene tetramine, 0.02M NaCl, adjusted to pH 5.7 with HCl before use. Measurements have shown that the absorption of HF by the buffer solution is >99% efficient and with the above flows, this produces fluoride solutions in the range  $5.6 \times 10^{-4}$  to  $3.7 \times 10^{-2} \text{M}$ , for which the fluoride electrode has a linear response. The electrode is calibrated with suitable known standards of NaF dissolved in buffer

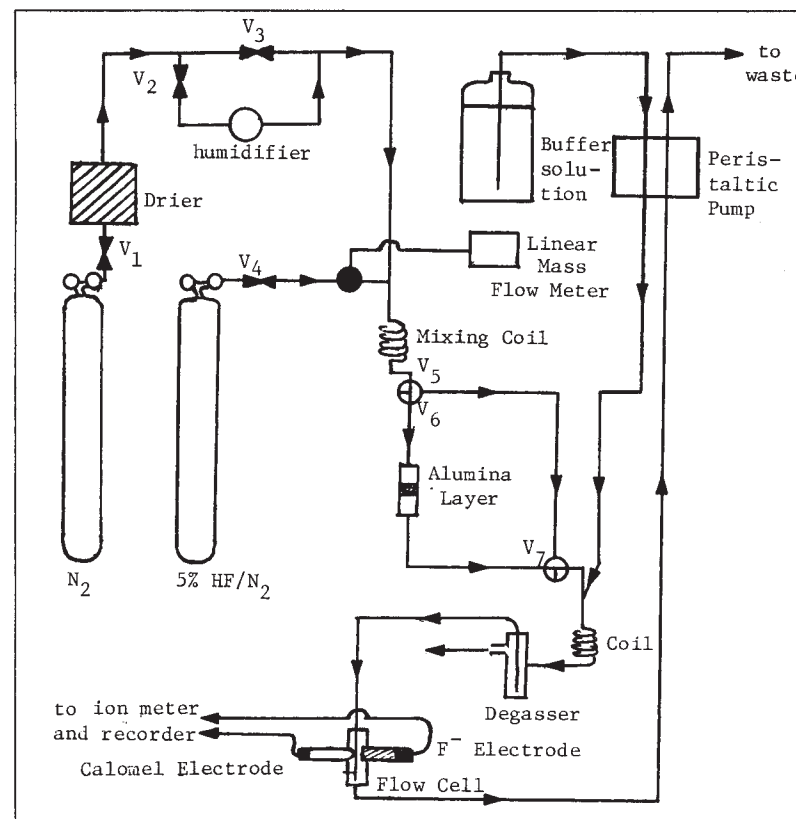


Fig. 1 - HF Adsorption Apparatus

solution.

After degassing, the solution is pumped via the same peristaltic pump through a flow cell containing a calomel reference and fluoride-ion sensitive electrode, and thence to waste. The electrical output of the electrodes is fed via an ion-meter to a strip chart recorder, which thus provides either (a) the entering gas concentration or (b) the exit gas concentration from the monel reactor, depending on the settings of  $V_6$  and  $V_7$ . Thus a continuous record of the reaction can be obtained on the semi-logarithmic chart. Since the electrode signal is proportional to log (concentration) this permits direct reading of HF concentration. A typical curve for Alcan alumina using dry gas at 120 ppm HF, transposed to a linear scale is shown in Figure 2.

(b) Application

1. Equilibrium Data

Reaction curves at 80°C were measured for 5 aluminas, identified below in Table I, together with their surface areas

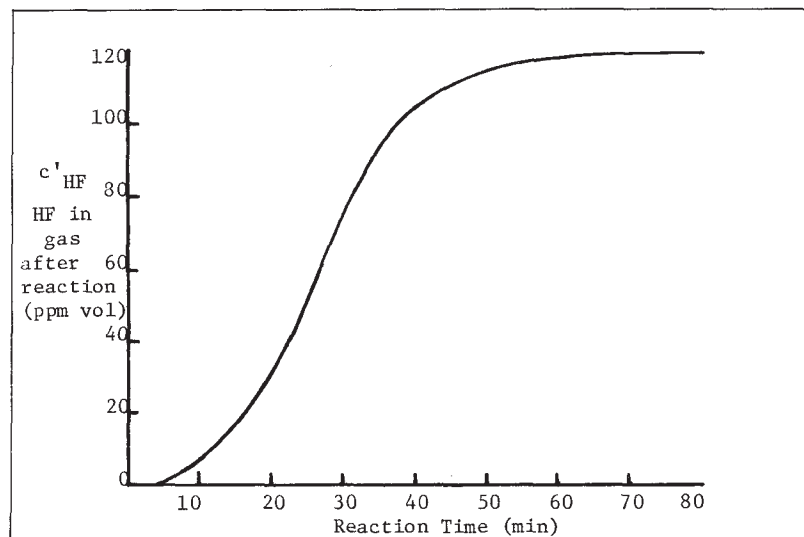


Fig. 2 - Reaction Curve for HF and an Alcan Alumina at 80°C and alpha-alumina concentrations.

Table I

Properties of Aluminas Used

Alumina	Surface Area (m <sup>2</sup> g <sup>-1</sup> )	Alpha-Alumina (%wt)
Alcan	41	27
A	42	21
B	46	11
C	81	17
D	60	28

Concentrations of HF ( $c_{HF}$ ) from 20 to 1100 ppm volume were used in dry gas. For each test, the reaction was taken to equilibrium, i.e. the stage where the exit gas after reaction was equal in concentration to the inlet gas. The alumina was then removed from the apparatus and analyzed for total fluoride. The latter concentration was also found from the reaction by measuring the surface fraction on the graph corresponding to the adsorbed HF, using a planimeter. The entire concentration range was explored for Alcan Arvida alumina at 80°C and at room temperature (about 20°C). Alumina A was tested the same way at 80°C

with two 20°C repeats at high and low concentrations (500 and 120 ppm). For aluminas B, C and D, the procedure was reversed, using the lower temperature for the whole concentration range and 80°C for the two concentrations above. The reason for this will become clear later.

The equilibrium isotherm data are given in Appendix A, Tables IA to E, covering all five aluminas. Each set of data can be plotted in the form shown below for Alcan alumina, in Figure 3, or in the linear form as in Figure 4.

The straight line shown in Figure 4 was obtained by a linear regression analysis. The regression equation is shown on the graph. The data for all the aluminas were treated in the same way and the slope and intercept for each plot are shown in Table II together with the surface area. The correlation coefficient for every line was  $\geq 0.99$ . Also shown, calculated from these data, are the values for  $\%F_m$ , k and a.

2. Effect of Water Vapour

This was investigated with Alcan and D aluminas at 300 ppm HF and 80°C. Equilibrium tests were done in which the water vapour partial pressure was varied from 0 to about 60 torr for each alumina. The results are plotted in Figure 5.

3. Stability of Adsorbed Fluoride

Heating Tests

Alumina D was reacted in dry and humid gas at 80°C containing 50 ppm of HF and the reaction was stopped shortly before equilibrium. There were two tests with humid gas (40 torr H<sub>2</sub>O) and one with dry gas. The reaction product was analyzed for fluoride. Using a tube furnace at temperatures of 300, 400, 500, 700 and 900°C, 0.5g portions of the products were heated in a platinum boat for 45 minutes. The furnace was continuously purged with dry N<sub>2</sub> at 30 ml min<sup>-1</sup>. The fluoride was determined again after each heating test. Results are shown in Table III.

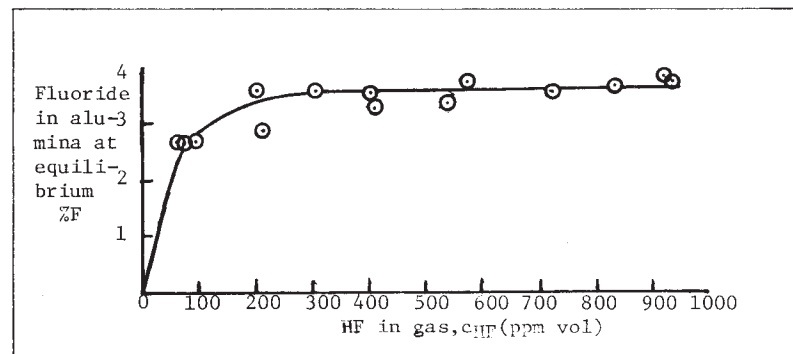


Fig. 3 - Equilibrium Isotherm for Alcan Alumina at 80°C

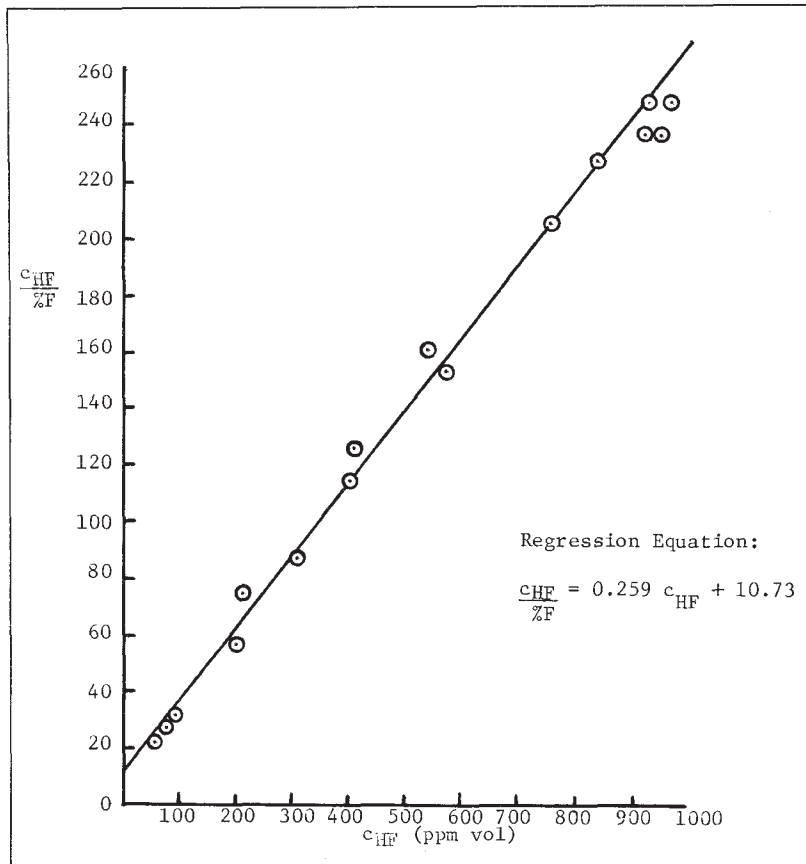


Fig. 4 - Linear Isotherm Plot for Alcan Alumina at 80°C

Table II

Results Derived from Linear Isotherms for all Aluminas

Alumina	Surface Area (m <sup>2</sup> g <sup>-1</sup> )	Properties of Linear Plots		%F <sub>m</sub>	k (x10 <sup>2</sup> )	a <sub>2</sub> (Å <sup>2</sup> )
		Intercept = $\frac{1}{k \times \%F_m}$	Slope = $\frac{1}{\%F_m}$			
Alcan 80°C	41	10.73	0.259	3.86	2.4	3.53
Alcan 20°C	41	5.13	0.255	3.92	5.0	3.47
A 80°C	42	7.55	0.317	3.16	4.2	4.41
B 20°C	46	6.06	0.293	3.41	4.8	4.48
C 20°C	81	1.82	0.194	5.16	11.0	5.21
D 20°C	60	11.09	0.274	3.65	2.5	5.46

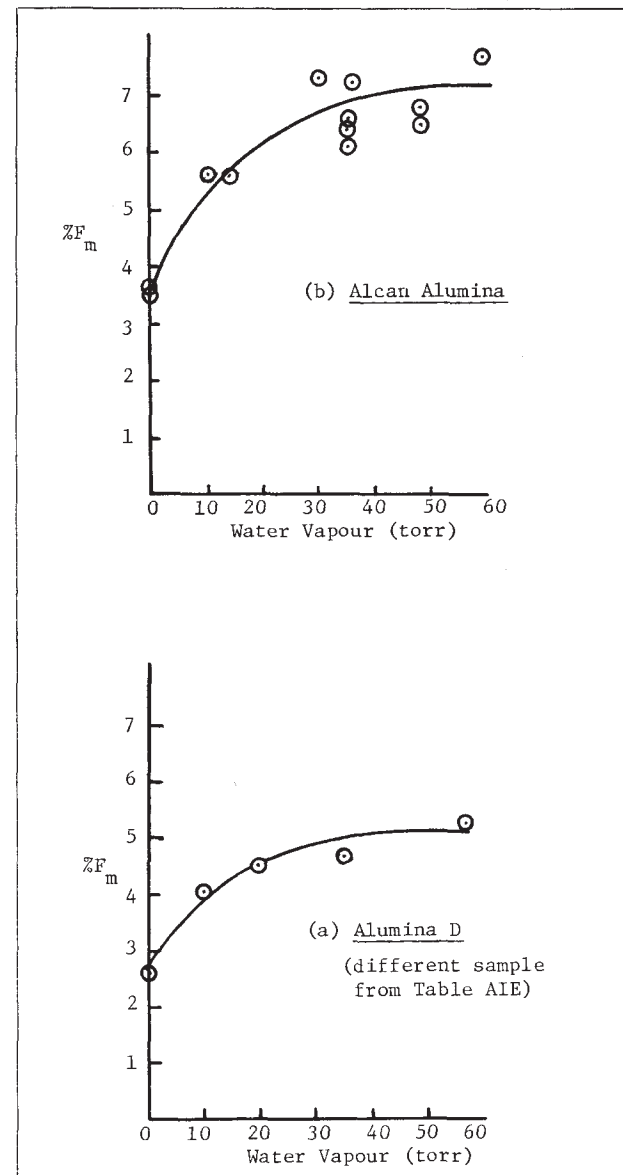


Fig. 5 - Effect of Water Vapour on Equilibrium Fluoride Concentration at 80°C, with c<sub>HF</sub> = 300 ppm

Table III

Heating Tests on Hydrofluorinated Alumina D

Test No.	%F Before Heating	%F After Heating at (°C)				
		300	400	500	700	900
1	1.89 <sup>(1)</sup>	1.93	1.96	1.77	1.65	0.99
2	3.4 <sup>(2)</sup>	3.49	3.38	3.23	3.12	1.66
3	5.9 <sup>(2)</sup>	6.2	6.4	5.7	5.8	2.55

(1) Dry gas (2) Humid gas (40 torr H<sub>2</sub>O)

Extraction with Water and Sodium Hydroxide Solution

One treatment with water and four with 0.1M NaOH were used on Alcan alumina, which had been hydrofluorinated to equilibrium. The water treatment was done at the boiling point, in this case using a Soxhlet tube with 3g of sample. All other extractions were done with 25 ml of liquid and 1g of sample. Of the NaOH extractions, 3 were done at 20°C and the fourth at boiling point in a beaker. After extraction, the mixtures were filtered and washed and the alumina and solutions were analyzed for fluoride, the latter using the fluoride specific ion electrode, by titration and with an automated distillation/colorimetric procedure (Technicon). Results are given in Table IV.

Table IV

Treatment of Hydrofluorinated Alcan Alumina with Water and 0.1M NaOH

Treatment	Fluoride Concentration %					
	Alumina		Solution extract <sup>(1)</sup>			
	Original	After Extraction	By Difference	By Titration <sup>(2)</sup>	By Technicon	By Electrode
Water, 100°C, 24 hr	3.71	3.39	0.32	0.18	-	0.18
NaOH, 20°C, 30 min	4.25	0.68	3.57	3.37	3.40	1.03
NaOH, 20°C, 90 min	4.25	0.58	3.67	3.56	3.50	1.15
NaOH, 20°C, 5 hr	4.25	0.75	3.50	3.99	3.53	1.42
NaOH, 100°C, 30 min	4.25	0.55	3.70	3.59	3.70	1.39

Notes: (1) based on alumina (2) back titration of excess NaOH

4. Temperature and Reaction Rate

The reaction curves for aluminas A and B were compared at 80°C and 20°C for 120 ppm of HF in dry gas. These curves are shown in Figure 6.

5. Measurement of Maximum HF Adsorption (%F<sub>m</sub>)

It will be noted from Figure 3 that the isotherm for Alcan alumina levels off above approximately 200 ppm of HF in the gas. This is also a characteristic of the isotherms of all 5 aluminas. The concentration of fluoride in the alumina corresponding to this level part is equivalent to %F<sub>m</sub>, the maximum adsorption. This provides a method of measuring %F<sub>m</sub>, without determination of the entire isotherm. Thus, a variety of different alumina samples aside from the five specifically mentioned herein, were reacted at 80°C to equilibrium with 300 ppm of HF. The %F<sub>m</sub> value found in each case was plotted against the surface area of each alumina to give the correlation in Figure 7.

Interpretation of Data

The evidence of Table II and the data in Appendix A, Table AI, show that the equilibrium between the active alumina surface and low concentrations of HF, is not significantly affected by temperature change from 20 to 80°C. This explains why the isotherm measurement was changed to 20°C for aluminas C and D, since measurement is easier at room temperature. Thus measurement of %F at room temperature provides an appropriate estimate of fluoride adsorption capacity. Figure 7 shows good correlation of %F<sub>m</sub> with surface area, confirming the latter also as an appropriate method. However, the 5% standard deviation of %F<sub>m</sub> values predicted from surface area, using the correlation of Figure 7, implies that surface area is not a particularly accurate measure of fluoride adsorption. Thus when a rough measure of the latter is required, surface area is quite satisfactory, but for an accurate, more reliable value, the %F should be determined by reacting the alumina directly with HF between 200 and 1000 ppm concentration. Although the correlation shown was obtained with %F values found at 80°C, the measurement can be made equally well and more conveniently at 20°C. It is interesting to note also, from Figure 6, that the rate of adsorption is not affected by this temperature change, which suggests that the rate-controlling step is not chemical but could be the rate of mass transfer of HF to the reacting surface.

It is clear from the evidence of Figure 4 and Table II, that each of the aluminas produces equilibrium data to fit the linear Langmuir model extremely well. This model is obtained by equating the rates of evaporation and condensation of the adsorbate at equilibrium. The maximum equilibrium concentration obtained in this way, i.e. v<sub>m</sub>, or in our case %F<sub>m</sub>, is taken to mean that the surface is covered with a monolayer of adsorbate at this point. Although it is essentially a physical model it can be used to represent chemisorption, where the completion of a monolayer implies that the chemical reaction with the available surface sites

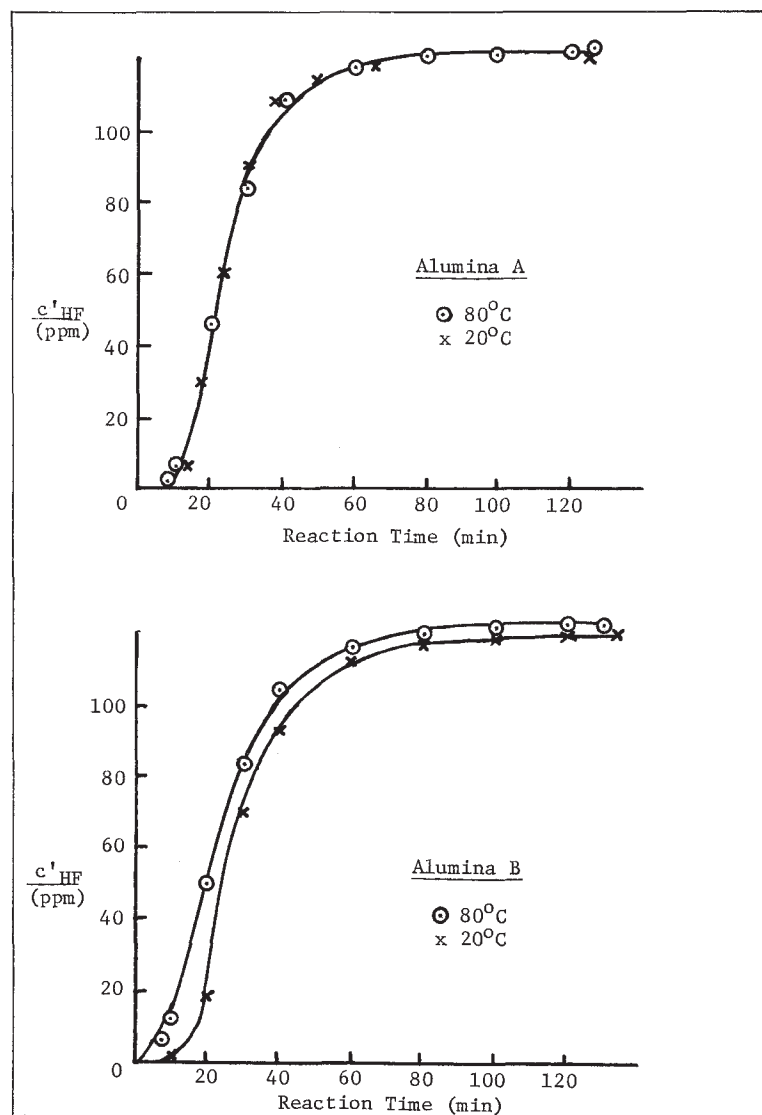


Fig. 6 - Effect of Temperature on Reaction Rate for 2 Aluminas

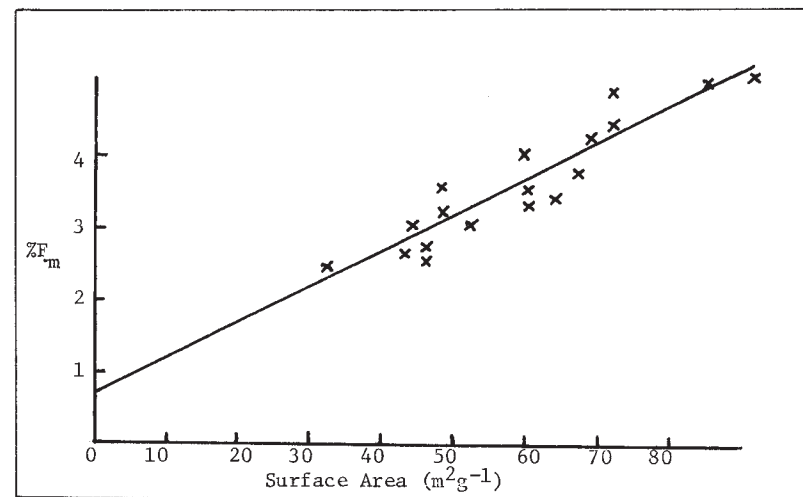


Fig. 7 - Correlation of Surface Area with Maximum Fluoride Adsorption ( $\%F_m$ ) for a Variety of Aluminas

is complete. Using this concept, the site area for an HF molecule, calculated from  $\%F_m$ , using equation 5 is in all cases much lower than that obtained from molecular theory, using equation 6, i.e.  $11.27\text{\AA}^2$ . Thus an anomaly exists, which must be explained. The difference between both methods of determining the site area is large, being 2 to 3 times smaller from the Langmuir model. Molecular theory assumes a spherical molecule and that the HF is in the liquid state which is the condition for closest molecular packing. Thus although the HF molecule is not completely spherical, it is virtually impossible to explain this difference by invoking different orientations of the molecule on the surface. Thus if we accept the value of  $11.27\text{\AA}^2$  as the correct area covered by an HF molecule, the fluoride concentrations in Table V below would correspond to a monolayer for each of the five aluminas. The concentrations found at equilibrium ( $\%F_m$ ) are repeated for comparison. The only possible explanation for the differences shown is that at equilibrium there is more than one layer of HF.

Table V

Monolayer Fluoride Concentrations

Alumina	Monolayer	
	$\%F$	$\%F_m$
Alcan	1.15	3.86
A	1.18	3.16
B	1.29	3.41
C	2.27	5.16
D	1.68	3.65

The results suggest that at equilibrium, 2 to 3 layers of HF are adsorbed from dry gas. From humid gas it could be as high as 4 or more layers (see Figure 5). It is probable that other mechanisms than chemisorption may be responsible for the adsorption of HF beyond the monolayer, such as hydrogen bonding. A hypothetical model for the adsorption will be discussed later.

Cochran et al (4) and Colpitts (1) calculated a monolayer by considering the HF molecule as a cube of side  $3.2\text{\AA}$  with a density of  $1\text{g cm}^{-3}$  at  $0^\circ\text{C}$  (liquid state). In terms of concentration, this gives a factor of 0.032%F per  $\text{m}^2$  of surface for a monolayer coverage. The molecular theory approach herein produces a factor of 0.028%F per  $\text{m}^2$ , which is in reasonable agreement. Thus a defined monolayer using the above authors' terms would be only 14% higher than the values in Table V. Cochran et al show that fluoride adsorbed up to the monolayer is strongly held or chemisorbed and not easily released by heating, which is confirmed by our work. However, these investigators state that fluoride adsorbed over and above the monolayer is loosely held or physically adsorbed and will be easily released on heating.

Our results of heating tests in Table III on alumina hydrofluorinated beyond the monolayer stage, show that this is not the case. A temperature of at least  $500^\circ\text{C}$  is required to begin releasing fluoride, whether it has been adsorbed from dry or humid gas. It is quite evident that the fluoride adsorbed over a monolayer behaves in exactly the same way towards heat as "monolayer fluoride". Thus this extra fluoride is either very strongly bound or converted to  $\text{AlF}_3$  on heating.

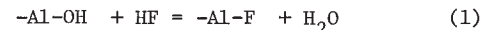
Colpitts (1) claims that fluoride adsorbed beyond a monolayer can be easily washed off with water and measured. However, the extraction tests done with water and NaOH on Alcan alumina hydrofluorinated to equilibrium (Table IV) do not confirm this. Only 5% of the total fluoride can be extracted at  $100^\circ\text{C}$  with water even with a very long extraction period. This proportion of the total adsorbed fluoride could be physically bound but to extract more fluoride, a chemical treatment with NaOH is necessary. In this way, we can remove 82-87% of the fluoride. The fluoride electrode analysis of the extract showed that only 30-40% of the fluoride removed was present as  $\text{F}^-$  ion presumably originating from adsorbed HF. It is well known that the fluoride electrode only responds to free  $\text{F}^-$  in solution and the rest of the fluoride extracted, as found by titration etc, must have been present as a complex ion, probably formed by reaction with the alumina itself. Thus the attack was severe enough to remove some of the alumina matrix and still 10% of the fluoride was not removed. Thus (a) there is very little physically or loosely bound alumina and (b) fluoride adsorbed above the monolayer is also held quite strongly but perhaps involving a different mechanism.

The somewhat low equilibrium constants shown in Table II suggest that at equilibrium, desorption is also occurring to a measurable extent. This does not concur with the concept of fluoride which is strongly bound or chemisorbed to the surface, since it is difficult to desorb such fluoride. The explanation may be

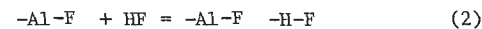
that several processes are occurring, possibly in sequence. Initially a chemisorbed monolayer may form, followed by further strongly bound layers. There would be very little desorption during these stages, but if the last stage is physical adsorption accounting for 5% or so of the fluoride, then it is this reaction equilibrium which is being considered in the Langmuir model. If this is correct, then desorption could be occurring at equilibrium accounting for the low equilibrium constants. The  $k$  values shown, however, should not be regarded as accurate, since the intercept in the regression fit is influenced by all the data and the scatter will produce a fairly large error in the value of  $k$ . A more detailed description of this model is given below.

A Postulated Model for the HF/ $\text{Al}_2\text{O}_3$  Dry Scrubbing Process

It is most probable that the reaction involves initially (a) sodium and (b) hydroxyl groups on the alumina surface. It is well established that the former exists in Bayer process alumina as leachable and non-leachable soda. The latter is known to be mainly in the form of  $\beta$ -alumina or  $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$  and is very inert, most likely being non-reactive to HF. The former is easily water-soluble existing probably in forms such as  $\text{Na}_2\text{CO}_3$ , which would certainly react with HF. Thus one would expect a portion of the total sodium present to react with HF to form NaF. However, there is not enough sodium present in the alumina to account for all of the HF adsorbed. Thus after the stoichiometry of reaction to NaF has been satisfied, there must be reaction with other active sites on the alumina surface. Peri and Hannan (6) using infrared spectroscopy identified three distinctly different types of hydroxyl groups on the surface of  $\gamma$ -alumina, which are bound differently. Only heat treatment above  $800^\circ\text{C}$  could remove most of these, showing that they are combined chemically to the surface. In further studies (7), Peri found two more types of hydroxyl groups, one of which persisted up to  $700^\circ\text{C}$  and the other up to  $900^\circ\text{C}$ . Thus there are five types of hydroxyl which are strongly combined to the surface, all of which could probably react with HF gas, as shown below:

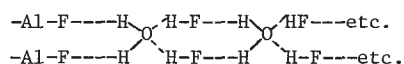


This reaction may occur until all reactive hydroxyl sites are removed. At this point a fluoride "monolayer" has been completed. The extent of this monolayer will depend on the number of hydroxyl sites available and will not necessarily correspond with the surface area found by physical adsorption, although there should be a correlation between the two. Further adsorption has to be via another mechanism. This could be a hydrogen bonding process between the fluoride ions already adsorbed and incoming HF molecules. In fact, this process could be responsible for multilayer formation:



The strength of the H-bonds would probably diminish as they become more remote from the original surface. From studies of the

cyclic hexamer (HF)<sub>6</sub>, Simons and Hildebrand (8) found a value of 6.7 k cal/mole for the enthalpy of formation of the F-H---F H-bond but there is a reason to believe that the bond is stronger than this and this might account for the tenacity with which the adsorbed fluoride is held on the surface. Fyfe (9) gives a value of 10.9 k cal/mole for this bond. The strongest hydrogen bond known is that of the HF<sub>2</sub><sup>-</sup>(g) ion which has an enthalpy of formation of 58 k cal/mole (10). In the presence of water, other possibilities exist, such as below:



Thus molecular chains could be formed up to the point where the pores of the alumina are completely plugged with reaction product. Pauling stated that from studies of the HF<sub>2</sub><sup>-</sup>(aq) ion it can be shown that the O-H---F<sup>-</sup> H-bond can be assigned a value of 13 k cal/mole(11). Thus the introduction of H<sub>2</sub>O into the molecular structure may have a strengthening effect. The alumina also has physically bound water on its surface and in the scrubbing process at about 100°C, most of this is probably released but if any is left, it may participate in the reaction also in a similar fashion to the water vapour from the gas.

Our own attempts to study the surface were confined to electron spectroscopy for chemical analysis (ESCA). No hydroxide groups could be detected by this method in fresh alumina, but the presence of NaF was confirmed in reacted samples.

The above is not intended to be a complete explanation of the process, but it is probably not far from reality. Evidently, with water and HF present in the system there are many possible models which may be postulated similar to the above.

#### Implications in Dry Scrubbing Al Reduction Cell Gases

1. The capacity of smelter aluminas for adsorbing HF in dry scrubbing is not limited by formation of a fluoride monolayer.
2. The suitability of an alumina for dry scrubbing can be estimated by comparing the equilibrium fluoride capacity, measured as described herein, with the expected emission of HF from the process. From published data (5), these emissions will result in certain concentrations of fluoride adsorbed on the alumina, assuming 100% scrubbing efficiency when all the reduction alumina requirement is used for scrubbing. These concentrations are approximately 0.4% F for prebake gas, 0.6% F for HS and 1.1% F for VS Soderberg gas. All the aluminas tested herein, have equilibrium capacities well above these values. Evidently it is unlikely that the alumina could be reacted to equilibrium with no loss of scrubbing efficiency. The proportion of the total fluoride capacity which can be utilized in a dry scrubber will depend on the kinetics of the adsorption process or processes and the extent of gas/solid contact in the system. These are questions which warrant further study.

3. The presence of atmospheric humidity will probably enhance the adsorption capacity measured in dry gas. However, since the effect of water vapour seems to maximise at concentrations normally present in the atmosphere, there would be little gained by adding steam or vapour to the gas, when scrubbing with low reactivity alumina, except where atmospheric humidity is very low, such as in desert areas, or areas with very cold winters.
4. The stability of the adsorbed fluoride is such that little or no fluoride loss will occur while scrubber product rests on the surface of the reduction cell, since the temperature of the cover seldom exceeds 500°C.

#### Conclusions

1. Multilayers of HF can be adsorbed on smelter grade aluminas at equilibrium with low concentrations of HF (20-1100 ppm vol) in dry N<sub>2</sub>. These concentrations are typical of those found in aluminum reduction cell gases.
2. These layers are strongly adsorbed and are only removed by heating above 500°C or by chemical attack (e.g. NaOH solution).
3. The amount of fluoride adsorbed can be doubled by the presence of about 5% vol (40 torr) if water vapour in the gas. This effect is non-linear, approximating an exponential curve which levels off at 5-8%.
4. Temperature change from 20° to 80°C has neither an effect on the amount of fluoride adsorbed at equilibrium, nor upon the rate of adsorption. This suggests that chemical reaction is not the rate controlling step.
5. The fluoride concentration in the alumina at equilibrium can be used as a method for measuring and comparing reactivities to HF in the laboratory, for different aluminas. This can be most conveniently done at 20°C and at concentrations of HF ≥300 ppm volume in the gas. When a less accurate indication is required the surface area is a satisfactory measure.

#### Nomenclature

a = site area for an adsorbate molecule (HF); Å<sup>2</sup>  
 A = surface area of alumina; m<sup>2</sup>g<sup>-1</sup>  
 c<sub>HF</sub> = concentration of HF in gas phase (ppm)  
 c'<sub>HF</sub> = concentration of HF (ppm) after reaction with alumina  
 %F = maximum equilibrium fluoride concentration  
 k = equilibrium constant  
 M = molecular weight  
 N = Avogadro's number, 6.023 x 10<sup>23</sup>  
 P = pressure of adsorbate in gas phase  
 v<sub>m</sub> = Langmuir monolayer of adsorbate on 1g of solid  
 (cm<sup>3</sup> at 0°C, 1 atm)  
 V<sub>sp</sub> = specific volume; cm<sup>3</sup>g<sup>-1</sup>



$\theta$  = fraction of surface covered by adsorbate at equilibrium

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Appendix A

Table AI

Dry Gas Equilibrium Isotherm Data

A. Alcan Alumina

HF in gas (ppm)	%F in Al <sub>2</sub> O <sub>3</sub>		ppm HF %F
	Curve	Analyzed Mean	
80°C			
58	2.63	2.67	21.9
60	2.67	2.83	21.8
70	2.74	2.56	26.4
91	2.68	2.64	34.2
200	3.70	3.40	56.3
210	2.77	2.85	74.7
305	3.57	3.49	86.4
400	3.29	3.70	114.3
405	3.19	3.30	124.3
535	3.38	3.30	160.2
570	3.77	3.70	152.4
720	3.71	3.30	205.1
830	3.59	3.70	227.4
915	3.99	3.75	236.4
925	3.50	4.00	246.7
20°C			
14	2.22	2.23	6.3
65	3.33	3.60	18.7
95	3.85	3.60	25.5
185	C.D. <sup>(1)</sup>	3.33	55.6
200	3.47	3.40	58.1
280	3.29	3.25	85.6
297	3.96	3.82	76.4
334	3.85	3.80	87.2
405	3.28	3.39	121.3
495	4.46	4.08	115.9
617	3.94	4.04	154.6
685	3.80	4.30	169.1
712	3.44	3.56	203.4
800	3.60	3.68	219.8
900	3.71	3.76	240.6
1000	3.80	3.77	263.9
1086	4.05	4.10	266.2

Note: (1) C.D. = chart damaged.

B. Alumina A (80°C)

HF in gas (ppm)	%F in Al <sub>2</sub> O <sub>3</sub>			ppm HF %F
	Curve	Analyzed	Mean	
18	2.30	2.10	2.20	8.2
53	2.21	2.20	2.21	24.0
122	2.69	2.75	2.72	44.9
120(1)	3.15	2.70	2.93	41.0(1)
201	2.65	2.56	2.61	77.0
303	3.13	2.99	3.06	99.0
408	3.15	2.64	2.90	140.7
535	3.01	2.65	2.83	189.1
500(1)	2.90	2.60	2.75	181.8(1)
605	3.26	2.90	3.08	196.4
726	3.44	3.06	3.25	223.4
815	-	3.21	3.21	253.9
980	-	3.02	3.02	324.5

(1) 20°C

D. Alumina C (20°C)

HF in gas (ppm)	%F in Al <sub>2</sub> O <sub>3</sub>			ppm HF %F
	Curve	Analyzed	Mean	
23	-	4.75	4.75	4.8
78	4.67	4.68	4.68	16.7
95	4.22	4.50	4.36	21.8
122(1)	4.58	4.63	4.61	26.5(1)
198	4.95	4.93	4.94	40.1
302	5.43	5.15	5.29	57.1
400	-	5.05	5.05	79.2
495	-	5.20	5.20	95.2
515(1)	4.58	4.63	4.61	111.8(1)
700	5.61	5.20	5.41	129.5
800	5.20	4.90	5.05	158.4
915	-	5.05	5.05	181.2
1000	5.25	5.00	5.13	194.9

(1) 80°C

C. Alumina B (20°C)

18	2.32	2.38	2.35	7.7
46	2.61	2.75	2.68	17.2
78	2.86	2.80	2.83	27.6
120	2.48	2.75	2.62	45.9
120(1)	2.54	2.70	2.62	45.9(1)
194	3.21	3.08	3.15	61.6
305	-	3.18	3.18	95.9
403	3.61	3.38	3.50	115.3
503	3.22	3.18	3.20	157.2
503(1)	3.30	2.80	3.05	164.9(1)
510	3.53	3.10	3.32	153.6
605	3.58	3.15	3.37	179.5
710	-	3.35	3.35	211.9
790	-	3.25	3.25	243.1
905	3.46	3.20	3.33	271.8
1000	-	3.38	3.38	295.9

(1) 80°C

E. Alumina D (20°C)

26	-	2.30	2.30	11.3
48	-	2.45	2.45	19.6
85	2.72	2.64	2.68	31.7
119	3.05	2.90	2.98	40.0
112(1)	2.54	2.90	2.72	41.2(1)
194	2.93	3.17	3.05	63.6
198	2.84	2.75	2.80	70.8
205	2.62	2.75	2.69	76.2
328	3.34	2.88	3.11	105.5
405	3.56	2.95	3.26	124.2
520	3.41	3.18	3.30	157.8
515(1)	3.92	3.40	3.66	140.7(1)
528	3.33	3.35	3.34	158.1
598	-	3.17	3.17	188.6
700	-	3.40	3.40	205.9
800	3.60	3.40	3.50	228.6
915	3.84	3.33	3.59	254.9
1000	3.62	3.46	3.54	282.5

(1) 80°C