Adsorption of Hydrogen Fluoride on Alumina

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The investigations of Cochran et al. (1970) show that hydrogen fluoride emitted from aluminum smelters may be recovered by adsorption on alumina. This alumina may be used as feed to the smelters—recycling the fluoride and helping maintain the fluorine inventory. Their work shows the HF to be chemisorbed on the alumina in an amorphous form which forms AlF_3 on heating; an adsorption isotherm for HF on alumina at 121°C is given.

This work was extended by Cook et al. (1971) when they developed the Alcoa 398 system for contacting smelter fumes with incoming alumina feed. The system operates at temperatures around 125°C.

In this study we have looked at the low temperature adsorption of HF on alumina (20 to 25°C), tested a technique for extrapolating the isotherm data of Cochran et al. (1970), and attempted to build a kinetic model of the adsorption process.

The single adsorption isotherm for HF on alumina, developed experimentally by Cochran et al. (1970) is used to predict the isotherm for the system at 25°C, by using a Berenyi (1923) modified Polanyi potential adsorption theory.

The potential theory assumes a compressed multilayer film of adsorbate and defines an adsorption potential ϵ and a volume of adsorption ϕ. The adsorption potential is the work done by adsorption forces to bring a molecule from the gas phase to a point near the adsorbent. The adsorption volume is that volume enclosed by the Polanyi potential surface and the surface of the adsorbent. This theory derives a characteristic curve which represents the potential distribution in adsorption volume space for all temperatures.

The characteristic curve is generated from a plot of ϵ versus ϕ. For temperatures below the critical temperature this relationship is described as follows:

$$\epsilon = RT \ln (P_v/P_0) \tag{1}$$

$$\phi = \frac{x}{f_T} / \rho \tag{2}$$

The characteristic curve was constructed by using these definitions of ϵ and ϕ, and values from the known isotherms. Then ϵ was calculated at 25°C and at the pressure of interest. The characteristic curve was used to obtain ϕ, and with the proper value of Berenyi correction factor f_T, the specific adsorption was calculated and compared with experimental data.

To establish a kinetic model, Michaels (1962) adsorption zone theory was used to describe absorption in a packed bed.

The equation for the exchange zone height is

$$Za = N_T \frac{G}{k_g a} \tag{3}$$

The value of the number of theoretical units (N_T) (assuming constant driving force), can be expressed as

$$N_T = \frac{2\,Y_0\,X_u}{Y_B\,X_T} \tag{4}$$

The value of N_T depends on the limits imposed for breakthrough and exhaustion of the bed. The value for the mass transfer coefficient depends upon the controlling kinetic mechanism for the rate of adsorption. The obvious transport mechanisms for physical adsorption processes are external mass transport and internal mass transport or pore diffusion.

The mass transfer coefficients for external transport and pore diffusion may be calculated (Perry, 1964) and Equation (3) evaluated to find the theoretical exchange zone height.

The zone height can also be determined from experimental results by a careful interpretation of breakthrough curves.

Treybal (1955), by considering an idealized break-

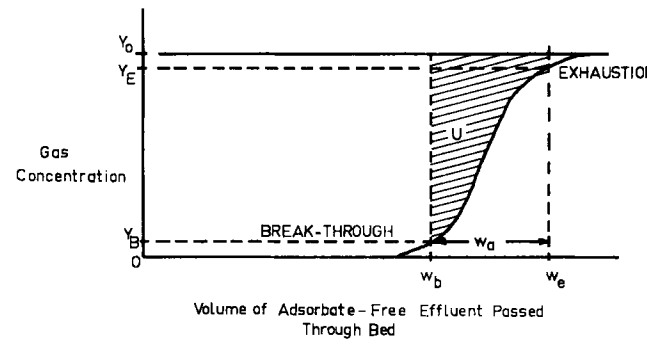

Fig 1. Idealized breakthrough curve for adsorption in a packed bed.

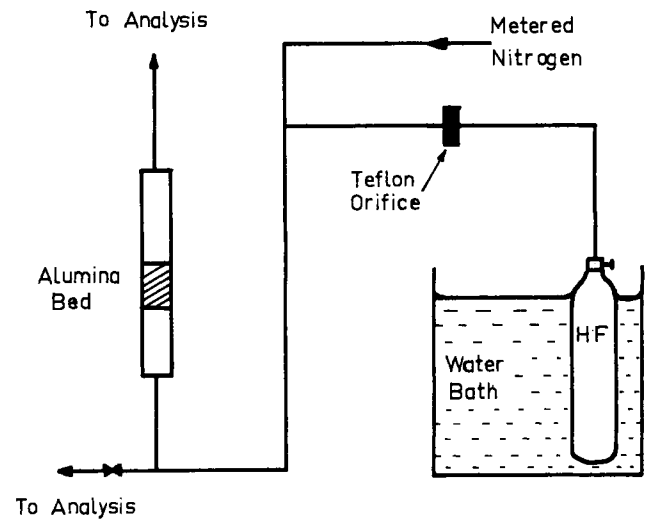

Fig. 2. Schematic layout of apparatus.

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Table 1. Results from a Series of Runs at an Inlet Concentration of 1000 ppm HF

	1	2	3	4	5	Predicted value
Specific total capacity ccHF @ 25°C	47.58	47.33	45.86	44.90	45.60	52.2
Fraction ability for further adsorption-f	0.601	0.535	0.560	0.531	0.606	
Zone heights-Za, cm	0.242	0.252	0.262	0.269	0.242	0.096

Table 2. Results for a Series of Runs at Inlet Concentrations of 2000 ppm HF

	1	2	3	4	Predicted value
Specific total capacity ccHF @ 25°C	52.53	47.82	53.71	56.14	54.6
Fraction ability for further adsorption-f	0.556	0.554	0.581	0.508	
Zone heights-Za, cm	0.261	0.336	0.313	0.481	0.096

through curve (Figure 1) and using Michaels (1962) theory develops the equation

$$Za = Z\left(\frac{w_a}{w_e - (1-f)\,w_a}\right) \tag{5}$$

In this expression, the bed height (Z) may be directly measured and w_e and w_a may be taken from the breakthrough curve (Figure 1).

The fractional ability of the alumina in the absorbing zone to absorb HF (f) is given by

$$f = \frac{U}{Y_0\, w_a} \tag{6}$$

U, Y_0 and w_a may be obtained from the breakthrough curves. Thus the right-hand side of Equation (5) may be evaluated from experimental breakthrough curves and the result compared with the predicted value from Equation (3).

EXPERIMENT

A schematic diagram of the apparatus is shown in Figure 2. The apparatus was constructed entirely from copper, with teflon gaskets and packings. This was found to be quite resistant to HF attack.

A cylinder of liquified HF was maintained at constant temperature, and gas from the cylinder was metered through an orifice in a teflon disk. The flow rate of HF could be adjusted by altering the temperature of the gas cylinder. The metered HF was diluted with nitrogen and passed to a column containing the alumina sorbent.

Sampling points located before and after the column were used to continually analyse for HF. This analysis was based on the electro chemical method of Baker and Morrison (1955).

The alumina, supplied by Alcan Australia Ltd., was the standard material which is fed to their aluminum smelters. The material is predominantly alumina, between 100 and 325 mesh, with a BET surface area of 48.6 m^2/g.

An analysis supplied by Alcan shows the major impurities to be sodium (0.22% NaO), iron (0.024% FeO), and silica (0.017% SiO_2).

Several runs were made and breakthrough curves prepared for HF inlet concentrations in the range 1000 to 2000 ppm. These relatively high concentrations were used so that the time for a run could be limited to less than 14 hours.

RESULTS

Typical breakthrough curves (outlet gas concentration versus time) are shown in Figure 3, for inlet gas compositions of 1000 ppm and 2000 ppm HF. From curves such as these, the specific capacity of the sorbent and the height of the adsorption zone were determined. Results from runs at 1000 and 2000 ppm are listed in Tables 1 and 2, along with values predicted by the techniques discussed above.

The specific adsorption capacities predicted from Cochran's (1970) isotherm compare favorably with our experimental results. However, the predicted exchange zone height, based on pore diffusion control, was three to four times lower than the experimental values.

DISCUSSION

The experimental results cannot be explained by considering any of the mass transfer steps to be controlling.

It is possible that the silica impurity in the alumina could react with HF forming silicon tetrafluoride which would escape. This could cause the collapse of the structure of the adsorbent and result in pore diffusion control. However, the silica content of the sorbent is very low (0.017%), and it is unlikely that the leaching of this small quantity from the alumina would seriously disrupt the particle structure.

It is thus most likely that the chemisorption reaction rate is slow, controlling the rate process and resulting in the large exchange zone heights found in the experiment.

NOTATION

- a = specific surface of sorbent
- f = fractional ability for further adsorption
- f_t = Berenyi correction factor
- G = mass velocity of absorbate free gas
- k_g = mass transfer coefficient

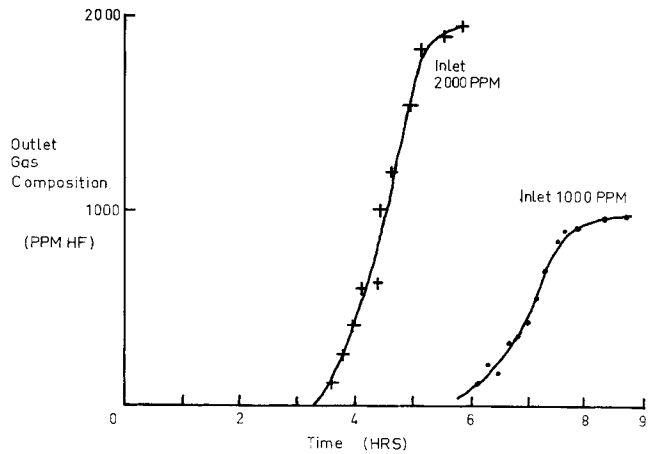

Fig. 3. Typical experimental breakthrough curves for inlet gas compositions of 1000 and 2000 ppm Hf.

N_T = number of theoretical units
P_0 = partial pressure of adsorbate
P_v = vapor pressure of adsorbate
R = gas constant
T = temperature
U = solute adsorbed in adsorption zone
w_a = quantity of effluent from adsorber between breakthrough and exhaustion
w_e = quantity of effluent from adsorber at breakthrough
X_u = adsorbent composition at exhaustion
X_T = adsorbent composition at total saturation
x = volume of HF adsorbed
Y_0 = adsorbate composition of entering gas
Y_B = adsorbate composition of gas at breakthrough
Z = height of adsorbent bed
Z_a = height of exchange zone
ϵ = adsorption potential
ϕ = volume of adsorption
ρ = density at boiling point

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Suboptimal Control of Stochastic Distributed Parameter Systems

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A problem with important process applications is the control of distributed parameter systems subject to boundary and volume disturbances and measurement errors. The optimal control of linear stochastic distributed systems has been studied by Tzafestas and Nightingale (1968), Kushner (1968), Thau (1969), Pell and Aris (1970), Bensoussian (1971), and Sholar and Wiberg (1972), while feedback control of nonlinear stochastic distributed systems was investigated by Yu and Seinfeld (1972). The objective of this communication is to propose a suboptimal scheme for control of nonlinear noisy distributed parameter systems. Briefly, the scheme is based on the extension of the Lyapunov functional method and is designed to be easy to implement in practice.

STATEMENT OF THE PROBLEM

We consider the class of systems governed by the vector nonlinear partial differential equation

$$x_t(r, t) = f[r, t, x, x_r, x_{rr}, v(r, t)] + \xi(r, t) \qquad (1)$$

defined for time $t \geq 0$ on the normalized spatial domain $r\epsilon(0, 1)$. $x(r, t)$ is the n-vector state, x_t, x_r, x_{rr} denote $\partial x/\partial t$, $\partial x/\partial r$ and $\partial^2 x/\partial r^2$, respectively, and $v(r, t)$ is a known p-vector ($p \leq n$) volume control. The boundary conditions for Equation (1) are given by the l-vector ($l \leq n$) functions

$$g_0(t, x, x_r, \omega_0(t)) + \xi_0(t) = 0 \quad r = 0 \qquad (2)$$

$$g_1(t, x, x_r, \omega_1(t)) + \xi_1(t) = 0 \quad r = 1 \qquad (3)$$

where $\omega_0(t)$ and $\omega_1(t)$ are known p_0 and p_1-vector boundary controls, respectively.

Observations of the system are made continuously in time at N discrete spatial positions in the form

$$y(r_i, t) = h(r_i, t, x(r_i,t)) + \eta(r_i, t)$$

$$i = 1, 2, \ldots, N \qquad (4)$$

where $y(r_i, t)$, the observation, is an m-vector ($m \leq n$) and $r_i\epsilon[0, 1]$.

The random disturbances $\xi(r, t)$, $\xi_0(t)$, $\xi_1(t)$ and $\eta(r_i, t)$ are assumed to have unknown statistical properties other than they are independent and have zero mean.

An important general class of control problems is the regulator problem. The general regulator problem for the system (1) to (4) would involve keeping the state $x(r, t)$ as close as possible to some desired state $x^d(r)$ over some period of time $[0, t_f]$ on the basis of the observations $y(r_i, t)$, $i = 1, 2, \ldots, N$. Formally stated, we want to specify the volume control $v(r, t)$ and the boundary controls, $\omega_0(t)$ and $\omega_1(t)$ as functions of the observations, to minimize the performance index