Kinetics of Dissolution of Alumina in Acidic Solution

The dissolution kinetics of alumina in aqueous solution was studied in batch and continuous systems. Data were correlated by the kinetic equation $C(t) = 1 - \exp(-kt^{\alpha})$. The parameter k was a function of temperature and acid concentration, while the parameter α remained constant.

The temperature variation of k was accurately represented by an Arrhenius-type equation with a temperature coefficient, 18,200 kJ/kmol. The data obtained in batch experiments were free of mass transport and mixing effects. Adsorption-desorption equilibrium of hydrogen ion at the alumina surface was observed. The results supported postulated reactions reported in the literature for alumina dissolution. The basic features of the mechanism include hydration of the aluminum oxide surface, hydrogen ion adsorption followed by reaction to form a positively charged surface species [$Al(OH)_2^+$], formation of stable surface species [$AlOOH$ and $(Al(OH)_2)_2\,SO_4$], and desorption of products.

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Introduction

The interaction of alumina with acids is encountered in the preparation and regeneration of certain types of catalysts. For example, in studies of the preparation of Pt/Al_2O_3 catalysts, the interaction of hexachloroplatinic acid with alumina supports, and the influence of adding inorganic acids as coingredients to hexachloroplatinic acid impregnating solution have been investigated (Maatman et al., 1971; Santacesaria et al., 1977; Shyr and Ernst, 1980). Methods have been proposed for the removal of nickel and vanadium from contaminated $Co/Mo/Al_2O_3$ hydrodesulfurization catalysts (Hernandez, 1982; Ganguli, 1984; Myerson and Ernst, 1985). Each of these processes employs at least one step in which the catalyst is contacted with an acidic solution.

One purpose of this work was to examine the dissolution of alumina in aqueous acid solutions. Such data may aid in the further development of catalyst preparation and catalyst regeneration procedures.

Often dissolution processes can be described by mass transfer theories (Nernst, 1904), which predict that the instantaneous dissolution rate varies in proportion to a driving force—usually a difference between dissolved species concentration at the solid surface and that in the bulk solution. The rate follows an equation of the form:

$$dc/dt = k''a^*(c_\infty - c) \qquad (1)$$

which, for constant a^*, has the solution:

$$c/c_\infty = 1 - \exp(-k''a^*t) \qquad (2)$$

Several authors, including Hulbert and Huff (1970) and Kabai (1973), have found that Eq. 2 often does not adequately describe dissolution processes involving metals and metal oxides. Kabai grouped dissolution processes into three basic classifications. In type I, the initial rate of dissolution is finite. Type I processes would include those described by Eq. 2. Type II dissolution exhibits an initial rate approaching zero, or an induction period (Diggle, 1973). As the process proceeds, the rate increases and rises to a maximum until equilibrium, or a decreasing amount of undissolved solid, slows the rate. In Type III dissolution, the initial rate is infinite. The rate continually decreases with increasing time (Kabai, 1973).

Hulbert and Huff studied the kinetics of alumina removal from calcined kaolin by acids in a batch system. They screened power law reaction models as well as numerous diffusion-reaction models and found that none was adequate for describing the data; however, the nucleation equation (Christian, 1965) of the

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general form:

$$C(t) = 1 - \exp(-kt^{\alpha}) \quad (3)$$

produced a good fit of their data. Kabai used this model to correlate data for the batch dissolution of 50 substances consisting of metal oxides and metal oxide hydrates. Data obtained in these experiments on systems that exhibited type I ($\alpha = 1$), II ($\alpha > 1$), and III ($\alpha < 1$) behavior could be accurately represented by Eq. 3. Although Eq. 3 has been used extensively for correlating dissolution data (Hulbert and Huff, 1970; Kabai, 1973; Gorichev et al., 1976), the connection between a dissolution process and a nucleation process, for which Eq. 3 was developed, has never been clearly established. Hulbert and Huff reasoned that dissolution data should fit a nucleation equation if the dissolution process involves:

1. Diffusion of hydronium ions to active sites
2. Nucleation of products at active sites
3. Hydration of products and diffusion of products into solution

Kabai showed that the rate parameter k varies with temperature and initial acid concentration. The parameter α is independent of these variables, but is a function of the substance that is being dissolved.

Another purpose of this work was to experimentally examine the dissolution of alumina in aqueous sulfuric acid solutions at a variety of experimental conditions and correlate the results with one of the above equations.

Experimental

Alcoa Fl alumina, which has a BET surface area of 2.5×10^5 m^2/kg and pore volume of 4×10^{-4} m^3/kg, was used throughout this work for both batch and flow experiments. This large surface area is due primarily to the internal pores of the alumina. The external surface area is insignificant compared to the total. The majority of experiments were run in a well-stirred and heated 1×10^{-3} m^3 Pyrex beaker. At the beginning of most experiments, 8×10^{-4} m^3 of acidic solution was added to the beaker. The range of acid concentrations was 0.1 to 10% H_2SO_4 (i.e., volume of concentrated H_2SO_4 per 100 volumes of solution). The temperature and agitation rates were established and a weighed amount of alumina quickly added (usually 2 to 10 kg/m^3). A timer was started at the instant the alumina was added. At various points in time, samples of the contents (solid-liquid mixture) were taken from the vessel and filtered. The filtrate was analyzed by a Perkin Elmer model 2380 atomic absorption spectrophotometer for dissolved aluminum content and the solid was stored for characterization of the surface or for further processing. The pH of the filtrate was monitored by a Fisher Accumet model 230 pH/ion meter. Preliminary experiments (Franke, 1985) established that the rate of dissolution was independent of stirring speed (in the range of 250 to 500 rpm), particle size (for particles 140 to 170 mesh or smaller), and volume change due to removal of samples (up to 1.75×10^{-4} m^3 removed). Because the system was well mixed the sampling did not significantly change the solids-to-liquid ratio of materials in the beaker. Unless otherwise specified, all batch experiments in this work were conducted with 140 to 170 mesh particles at an approximate stirring speed of 300 rpm.

The pH measurements could not be converted directly to hydrogen ion concentration because of the complex nature of the system: species H^+, HSO_4^-, H_2SO_4, as well as various ions containing aluminum can have an influence on pH measurements. A calibration curve was constructed that related the total concentration of hydrogen in species H^+, HSO_4^-, and H_2SO_4 or ($[H^+] + [HSO_4^-] + 2[H_2SO_4]$) to pH. This total concentration of hydrogen species will be referred to as THS. This curve was prepared simply by measuring the pH of a series of H_2SO_4 solutions of known concentration and plotting the calculated THS values vs. measured pH. The influence of dissolved aluminum species on pH at a given THS could not be directly determined: any introduction of Al^{3+} ions to an acid solution would change the THS because of complex interactions of Al^{3+} with the various hydrogen-containing species. Instead, the influence of adding Na^+ ions to acid solution on pH was investigated. By inference, conclusions regarding the influence of Al^{3+} on pH were drawn. Adding Na^+ in the range of Al^{3+} concentration encountered in dissolution experiments did not influence the relationship between THS vs. pH (Franke, 1985). Because of the negligible influence of Na^+ on pH at very low Na^+ concentration, it was assumed that the influence of the dissolved aluminum was also negligible.

Packed-bed flow experiments were conducted in which acid solution was passed through 1×10^{-3} kg of 16–20 mesh alumina particles supported by glass wool in a 2×10^{-2} m dia. Pyrex tube. Effluent from the tube could be sampled and analyzed at various times or accumulated and analyzed for average aluminum concentration over the total time period.

Results and Discussion

Typical dissolution curves for the batch experiments are shown in Figure 1. These curves are characterized by a very fast initial rate and continually decreasing rate as time proceeds. This trend corresponds to the type III dissolution described previously. Figure 1 shows how the concentration profile changes as a function of temperature. Throughout all experiments, the fraction of the total (initial) alumina that is in solution and defined by C was much less than 1. Under those conditions, Eq. 3 can be written in the approximate form:

$$C(t) = kt^{\alpha} \quad (3a)$$

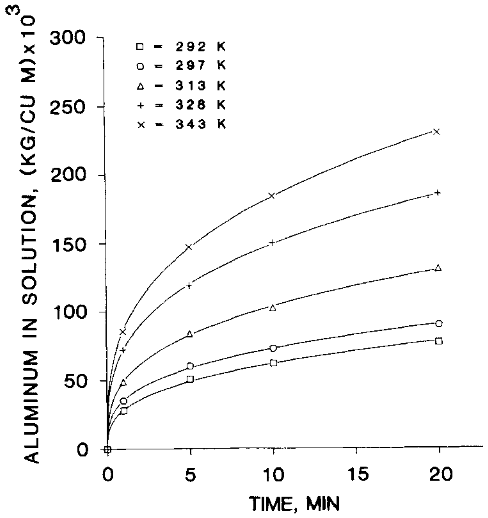

Figure 1. Effect of temperature on batch dissolution of alumina.

Table 1. Influence of Temperature on Dissolution Rate Parameters

Temp. K	$k \times 10^3$ $\min^{-\alpha}$	α
292	5.5	0.33
297	6.7	0.32
313	9.2	0.33
328	13.7	0.32
343	16.3	0.34

Initial acid concentration, 0.5%; total solids concentration, 10 kg/m^3

The linearized form is:

$$\ln C(t) = \ln k + \alpha \ln t \tag{3b}$$

Table 1 shows the results of fitting the data of Figure 1 to Eq. 3b. The parameter k increases with increasing temperature while α remains constant (0.33 ± 0.007) over the entire temperature range.

Plotting k in accordance with an Arrhenius-type equation,

$$k = A \exp(-E/RT) \tag{4}$$

yields a preexponential factor, $A = 9.8$, for experiments in which initial acid concentration was 0.5% vol/vol, and a temperature coefficient, $E = 18{,}200$ kJ/kmol.

Data obtained in similar experiments conducted at other initial acid concentrations also exhibited an excellent fit to Eq. 3, Figure 2. Deviation in α for nine experiments was $\pm 3.7\%$ about the average. The acid concentration in each experiment was well in excess with respect to the extent of dissolution, assuming the stoichiometry of 3 mol hydrogen ion consumed for each mole aluminum dissolved. Table 2 shows the values of k and α that resulted from fitting the data to Eq. 3b. The parameter k shows a weak dependence on the initial acid concentration, Figure 3, while the value of α is constant. The model that accurately fits the batch dissolution data is therefore:

$$k = 11.1 \times [H_2SO_4]^{0.18} \exp(-18{,}200/RT) \tag{5}$$

where $[H_2SO_4]$ is the initial volume percent acid in solution.

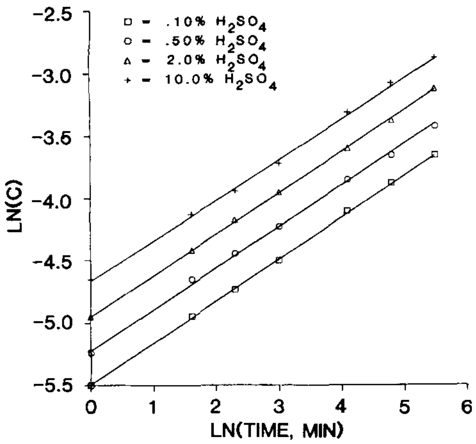

Figure 2. Batch dissolution data at 292 K Plotted according to Eq. 3b: effect of initial acid concentration.

Table 2. Influence of Initial Acid Concentration on Dissolution Parameters

Acid Conc. % H_2SO_4	$k \times 10^3$ $\min^{-\alpha}$	α
0.10	4.1	0.34
0.50	5.5	0.33
2.00	7.1	0.33
10.00	9.4	0.33

Temperature, 292 K; total solids concentration, 5 kg/m^3

Attempts were made to explain the type III behavior in terms of physical processes in the initial seconds of an experiment. Several tests were conducted that deviated from the standard experimental procedure. In the standard dissolution experiment, the dry alumina was introduced into the agitated acid solution. In one variation of this procedure, additions of acid and alumina were reversed: Alumina was agitated in distilled water. To begin the dissolution process, enough concentrated acid was quickly added to this agitated mixture to produce an acid concentration equivalent to the initial concentration in the standard experiment. In another variation, prewetted instead of dry alumina was added to agitated acid solution. The resulting profiles of dissolved aluminum vs. time and k and α parameter values were nearly identical for the three experiments, Table 3. These results show that

1. The initial fast rate is not the result of any transient physical interaction between solid and liquid phases.
2. The hydration of the alumina surface that occurs when dry alumina is introduced into a solution is very rapid and does not influence the rate of alumina dissolution.

This result is in agreement with Diggle et al. (1970) and Warren and Devuyst (1974), who suggested that fast hydration of the oxide surface is the initial step in the dissolution process. Uvarov (1962) has shown by infrared investigation that upon contacting aluminum with an aqueous environment, a hydroxide layer, $Al(OH)_3$, always forms.

Experiments were run to determine whether the decline in dissolution rate with time in Figure 1 was caused by the increase

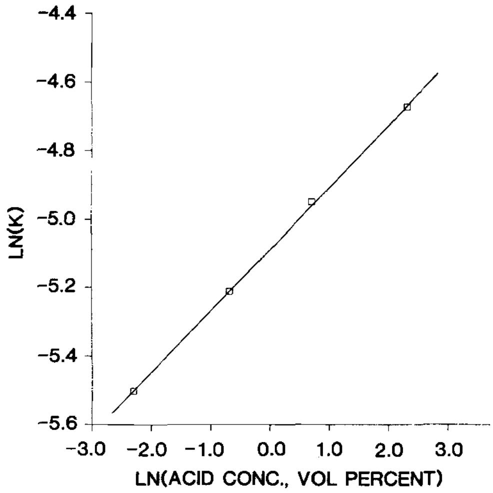

Figure 3. Dependence of rate Parameter on initial acid concentration.

Table 3. Influence of Contacting Conditions on Dissolution Parameters

Method	$k \times 10^3$ $\text{min}^{-\alpha}$	α
Standard	6.7	0.32
Prewetted alumina addition	6.5	0.33
Concentrated acid addition	6.5	0.33
Preaddition of aluminum ions	6.6	0.32

Initial acid concentration, 0.5%; total solids concentration, 10 kg/m^3; temperature, 297–298 K

in dissolved aluminum concentration. In one experiment aluminum sulfate, equivalent to 0.1 kg/m^3 (100 ppm) of Al^{3+}, was added to the acid solution prior to the addition of the dry alumina. The resulting profile of net increase in dissolved aluminum vs. time and k and α parameter values were nearly identical to those for the standard experiment, Table 3. In another set of experiments, the solutions from initial dissolution runs at standard conditions were recovered after 20 min of contact with the alumina. These solutions were reacidified to the initial pH by the addition of H_2SO_4 solution. The alumina dissolution experiments were then rerun using the reacidified solutions. At the end of 20 min of contact the solutions were recovered and analyzed for dissolved aluminum. Table 4 shows that the net increase in dissolved aluminum after 20 min of contact in the repeat runs was similar to the dissolved aluminum after 20 min in the initial runs. These results rule out any inhibition of the dissolution process by dissolved aluminum at the concentration levels encountered in these experiments. These results also rule out the use of Eq. 2 for describing the dissolution data in this study. Since the higher Al^{3+} levels did not influence the rate of dissolution, the value of c in Eq. 2 must be much smaller than c_∞. For very small values of c, Eq. 2 becomes:

$$\frac{dc}{dt} = k''a^*c_\infty \tag{1a}$$

which for constant a^* has the solution

$$c = [k''a^*c_\infty]t \tag{2a}$$

If Eq. 2a applied, a plot of C vs. t would produce a straight line. Figure 1 shows that the data from these experiments cannot be represented by this equation.

Table 4. Influence of Dissolved Aluminum on Rate of Dissolution*

Init. Acid Conc.	Aluminum Concentration, kg/m^3 × 10^3				
	Initial Run		Repeat Run		Net Increase**
	0 min	20 min	0 min	20 min	
0.05	0	60	27	88	61
0.10	0	101	52	153	101
0.25	0	118	59	180	121
0.50	0	132	66	200	134

*T = 297°C; slurry concentration = 20 kg/m^3

**Aluminum concentration at t = 20 min in repeat run minus aluminum concentration at t = 0 min in repeat run

The role of acid in the dissolution process was investigated as follows. The pH meter readings taken before and during a dissolution experiment were converted to concentrations of THS by means of calibration curves. These data are shown in Table 5 for experiments at three different initial acid concentrations. The loss of THS equals the difference between THS concentration initially and at the times of sampling. In accord with reported mechanisms for alumina dissolution (Diggle et al., 1970; Warren and Devuyst, 1974), hydrogen ion was assumed to be the species that attacked the alumina. Thus the loss of THS during an experiment was attributed to the consumption of hydrogen ions. Figure 4 shows graphically the hydrogen ion consumption vs. time. Three aspects of the curves are important. First, the extremely fast initial rate of hydrogen ion consumption; second, the greatly reduced rate of hydrogen ion consumption at later times (the corresponding reduction in alumina dissolution rate in Figure 1 is much slower); and third, the increase in hydrogen ion consumption (as well as dissolved alumina). This behavior suggests that some of the hydrogen ion may initially undergo a rapid adsorption on the alumina surface before any alumina dissolves. The range of the experimental data in Figure 4 was limited by the inability to accurately read the differences between pH meter outputs for samples taken at different times. The accuracy was poorest at high acid concentration. Thus only one data point for the experiment at 2% initial acid concentration could be determined accurately.

The overall stoichiometry for alumina dissolution has been reported (Diggle et al., 1970) to be:

$$Al_2O_3 + 6\,H^+ = 2Al^{3+} + 3H_2O \tag{4}$$

The stoichiometry shows that the dissolution of one aluminum ion consumes three hydrogen ions. Thus, by comparing the aluminum in solution to the hydrogen consumed in the reaction the amount of hydrogen ion adsorbed on the solid surface can be determined. The following equation describes the relation:

$$H^+ \text{ adsorbed} = H^+ \text{ consumed} - 3\,(Al^{3+} \text{ dissolved}) \tag{5}$$

Table 5 shows that the amount of hydrogen ion adsorption remains essentially constant over the duration of each experiment and the magnitude of the amount adsorbed is related to the acid concentration in solution. The amount of hydrogen ion adsorbed on the solid surface should correspond to the number of aluminum atoms exposed to the solvent phase. The approximate concentration of aluminum atoms on the surface of the alumina is 8.5×10^{18} atoms/m^2 (Anderson, 1975; Gates et al., 1979). Table 5 shows that the surface coverage of adsorbed hydrogen ion ranges from about 60% of the surface aluminum atoms for the 2.0% acid to about 20% coverage for the 0.1% acid solution. (Note: The 60% figure for the 2.0% acid was based on the one data point at 5 min; however, more extensive data for 0.1 and 0.5% acid, Table 5, show that surface coverage did not change between 5 and 20 min. It was assumed therefore that surface coverage for the 2.0% acid case also did not change over this time period.)

The data suggest that adsorption-desorption equilibrium is established for the hydrogen ion. Figure 5 shows the parameter k as a function of the equilibrium hydrogen ion adsorption on the alumina surface. The figure shows that k is proportional to the apparent equilibrium concentration of hydrogen ion adsorbed on the alumina surface raised to the 0.5 power. Thus, the

Table 5. Consumption of Hydrogen Species

Init. H_2SO_4 Conc. vol. %	Time, min	Total Hydrogen Species Conc., kmol/m^3		Aluminum Conc. kmol/m^3	Adsorbed Hydrogen Ion		Ratio of Adsorbed Hydrogen Ions to Surface Aluminum Atoms × 100
		Initial	Consumed		kmol/m^3	ion/m^2 × 10^{-18}	
0.10	0	0.034	0	0	—	—	—
	1	0.016	0.018	0.002	0.012	1.6	19
	5	0.013	0.021	0.003	0.012	1.6	19
	10	0.011	0.023	0.003	0.014	1.8	21
	20	0.010	0.024	0.004	0.012	1.6	19
0.50	0	0.188	0	0	—	—	—
	1	0.156	0.031	0.002	0.025	3.1	35
	5	0.152	0.035	0.004	0.023	2.9	34
	20	0.148	0.040	0.005	0.025	3.1	35
2.00	0	0.750	0	0	—	—	—
	5	0.694	0.056	0.005	0.041	5.1	60

Temperature, 298 K; total solids concentration, 20 kg/m^3

k values for the dissolution experiments as shown in Figure 5 can be written:

$$k = k'([H+]_{ads})^{0.5} \qquad (6)$$

where $[H+]_{ads}$ is the concentration of adsorbed hydrogen ions on the alumina surface in kmol/m^3, and $k' = 0.038$. It can be concluded that *k* is not a mass transfer coefficient but a reaction rate constant. Because of the initial fast adsorption and the apparent equilibrium concentration of hydrogen ion on the surface, it follows that transport of hydrogen ion to, and adsorption of hydrogen ion on, the surface are not the rate-controlling processes in these dissolution experiments. This finding suggests that the surface reaction, desorption of reaction products from the surface, or transport of products away from the surface controls the overall dissolution rate.

Another type of study involved multiple dissolution experiments on the same alumina sample. Figure 6 and Table 6 show the results of these experiments. Each experiment consisted of a 40 min dissolution run with 0.5% H_2SO_4. Between runs, the alumina was washed in copious amounts of distilled water, followed by drying in an oven at 120°C. Table 6 shows that the value of alpha remained constant but the rate constant decreased with each run. Figure 6 clearly shows that the rate of dissolution and the amount of aluminum removed decreased in each subsequent run. The greatest decrease occurred between runs 1 and 2. The magnitude of the decrease became less in subsequent runs.

Figures 7 and 8 represent the behavior shown in pulse flow experiments. Alternating pulses of the acid solution and distilled water separated by small air gaps were passed through the flow apparatus. Figure 7 shows the instantaneous aluminum concentration in the outlet solution. Figure 8 shows the integrated area under each pulse curve of Figure 7, which is the average concentration of aluminum in each pulse. In agreement with the batch results, Figure 6, the instantaneous concentration within each acid pulse and the average concentration in each subsequent acid pulse decreased with time. After a few minutes the aluminum concentration profile leveled off. Unexpectedly, the first few distilled water pulses showed higher concentrations of aluminum than the corresponding acid pulses, while later pairs of acid and distilled water pulses showed very similar concentration profiles. The distilled water pulses also showed a slightly steeper aluminum concentration change with time over the length of the pulse than did the corresponding acid pulses.

The existence of acid-insoluble surface species was supported

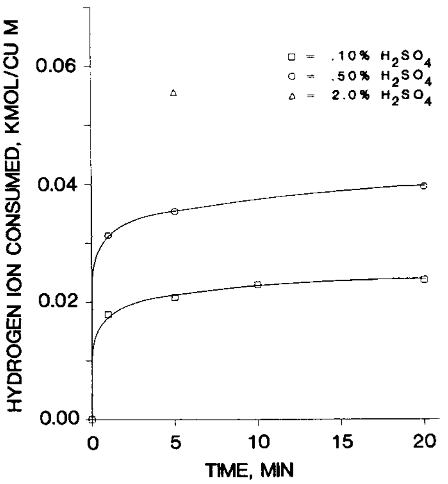

Figure 4. Consumption of hydrogen ions during batch dissolution of alumina.

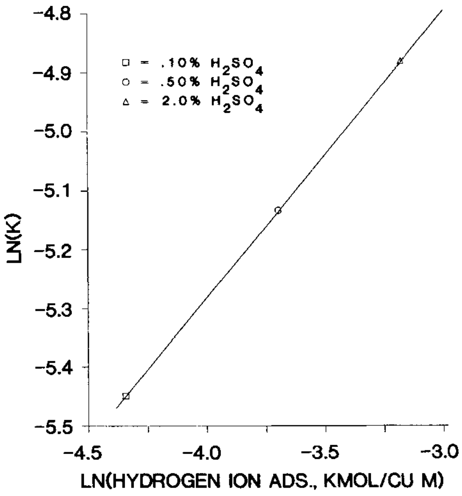

Figure 5. Effect of adsorbed hydrogen ions on rate parameter.

Table 6. Dissolution Rate Parameters for Multiple Experiments on a Single Alumina Sample

Run No.	$k \times 10^{-3}$ $\text{min}^{-\alpha}$	α
1	$k = 5.9$	0.33
2	$k = 3.9$	0.34
3	$k = 2.8$	0.34
4	$k = 2.0$	0.34

Initial acid concentration, 0.5%; total solids concentration, 2.5 kg/m^3; temperature, 292 K

by results of the pulse experiments. It appears that the aqueous acid pulse contacted the alumina surface and reacted to form surface products; some of these surface products desorbed and entered the solution while others remained undissolved on the alumina surface. The distilled water pulse then contacted the surface and removed some of the acid-insoluble surface species. The reason that these latter species dissolved in water can be explained as follows: After the surface had been contacted with acid solution there was an abundance of positively charged species on the outer layer of the solid phase. When the distilled water, which is essentially neutral, contacted the surface, the surface species immediately began to desorb and enter the solution to equilibrate the electronic charge between the two phases.

The batch and flow experiment results indicate a change in the makeup of the surface as dissolution proceeded. A number of possibilities exist as to how the surface could be altered during dissolution, such as a changing surface area, deposited reaction products, or a phase change in the alumina. BET surface area changes during dissolution did not account for the decrease in dissolution rate. Table 7, for example, shows BET surface area for four samples that had been contacted with acid solution in the batch apparatus for various lengths of time. There is no significant trend in these data. The variation in these areas about an average of 263,000 m^2/kg was only ±1.8%. X-ray diffraction patterns also showed no significant change in bulk phase as a result of the dissolution process. Previous workers (Diggle et al., 1970) have suggested that both a change in phase on the alumina surface and the deposition of a hydroxyaluminum sulfate can cause a decrease in dissolution rate.

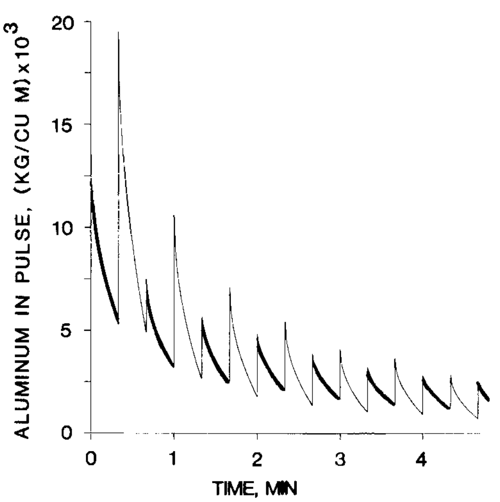

Figure 7. Outlet aluminum concentration in pulse flow experiments.

Bold lines, acid pulse; fine lines, water pulse
Temp. 295 K; initial H_2SO_4 conc., 2.0%; solution flow rate, 5×10^{-4} m^3/min; alumina particle size, 16 to 20 mesh; weight of alumina, 10^{-3} kg

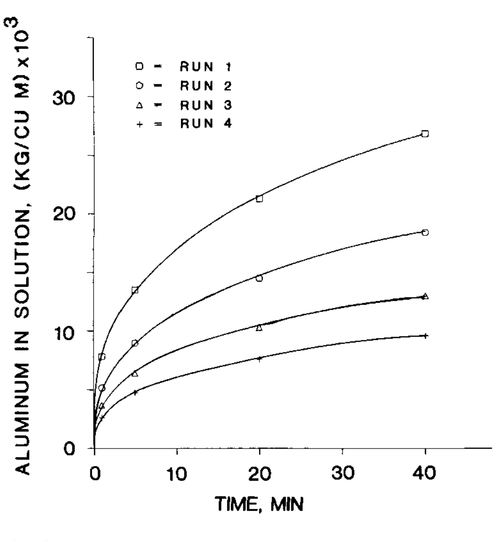

Figure 6. Multiple dissolution experiments on a single alumina sample at 292 K.

It should also be noted that the results shown in Figure 6 rule out the possibility that fines in the alumina sample caused the initial fast rate of dissolution that characterized all dissolution experiments. If fines had been the cause, the fast initial dissolution rate would have occurred only in run 1. The initial rate of run 2 would have equaled the rate of run 1 at 40 min. Similarly the initial rates of runs 3 and 4 would have equaled respectively the rates of runs 2 and 3 at 40 min.

Conclusions

The results of this work support postulated reactions reported in the literature for alumina dissolution (Diggle et al., 1970; Uvarov, 1962; Warren et al., 1974). These reactions can be sum-

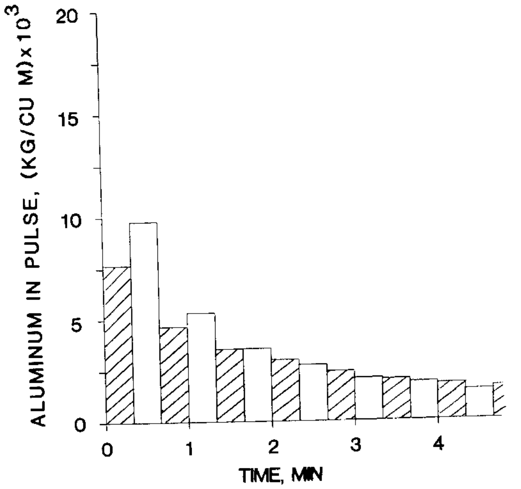

Figure 8. Average aluminum concentration in each pulse shown in Figure 7.

Shaded area, acid pulse; open area, water pulse.

Table 7. Surface Areas of Alumina Samples Contacted by Acid Solution in a Batch System

Time min	BET Surface Area $m^2/kg \times 10^{-3}$
0	254
1	265
10	261
60	272
120	261
Avg	263

marized as follows:

Hydration

$$Al_2O_3 + 3\,H_2O = 2\,Al(OH)_3 \qquad (7)$$

$$Al_2O_3 + H_2O = 2\,AlOOH \qquad (8)$$

Hydrogen ion adsorption

$$AlOOH + H^+ = Al(OH)_2^+ \qquad (9)$$

$$Al(OH)_3 + H^+ = Al(OH)_2^+ + H_2O \qquad (10)$$

Product formation

$$Al(OH)_2^+ + 2\,H^+ = Al^{3+} + 2\,H_2O \qquad (11)$$

$$2\,Al(OH)_2^+ + SO_4^{-2} = [Al(OH)_2]_2SO_4 \qquad (12)$$

$$Al(OH)_2^+ = AlOOH + H^+ \qquad (13)$$

The first two reactions show the hydration steps in the mechanism. Two different types of hydration products, AlOOH and $Al(OH)_3$, are generated during the surface reactions. Equations 9 and 10 show that after adsorption, the hydrogen ion reacts with the hydroxide surface to produce a positively charged surface species, possibly $Al(OH)_2^+$. The species AlOOH is much less soluble than $Al(OH)_3$, so that reaction 9 is probably the predominant pathway in the formation of the positively charged surface species.

Both AlOOH and $[Al(OH)_2]_2SO_4$ are reaction products that remain on the alumina surface. These species are relatively insoluble in the acidic solution and act as poisons to the dissolution process. As the overall process proceeds, more of these species accumulate on the surface to further hinder dissolution.

Reaction 11 represents the final step in the dissolution. The positively charged surface species reacts further with hydrogen ion to form an aluminum cation that desorbs and is then transported into the bulk solution.

The basic features of the mechanism are hydration to form a hydroxide surface, hydrogen ion adsorption followed by reaction to form a positively charged surface species, formation of more stable species on the surface, and desorption of products; they are all supported by experimental results of this work.

Notation

A = preexponential factor, $min^{-\alpha}$
a^* = effective solid surface area per unit solution volume, m^{-1}
C = fraction of initial aluminum in solution phase at time t
c = concentration of aluminum in solution, $kmol/m^3$
E = temperature coefficient, kJ/kmol
k = rate parameter, Eq. 3, $min^{-\alpha}$
k' = rate parameter, $(min^{-\alpha})(kmol/m^3)^{-0.5}$
k'' = intrinsic rate constant, Eq. 1, m/min
t = time, min
α = parameter, Eq. 3
∞ = saturation

Literature cited

Anderson, J. R. *Structure of Metal Catalysts,* Academic Press, New York, 46 (1975).

Christian, J. W., *The Theory of Transformation in Metals and Alloys,* 1st ed., Pergamon, New York, 471 (1965).

Diggle, J. W., *Dissolution of Oxide Phases in Oxides and Oxide Films,* Dekker, New York, **2,** 281 (1973).

Diggle, J. W., T. C. Downie, and C. W. Goulding, "The Dissolution of Porous Oxide Films on Aluminum," *Electrochim. Acta.,* **15,** 1079 (1970).

Franke, M., "An Investigation of the Kinetics and Mechanisms in the Dissolution of Alumina in Aqueous Sulfuric Acid," M.S. Thesis, Georgia Inst. Tech., Atlanta (1985).

Ganguli, P. S., "Catalyst Regeneration Process Including Metal Contaminants Removal," U.S. Pat. No. 4,454,240 (1984).

Gates, B. C., J. R. Katzer, and G. C. Schuit, *Chemistry of Catalytic Processes,* McGraw-Hill, New York, 251 (1979).

Gorichev, I. G., N. G. Klyuchnikov, Z. P. Bibikova, and L. F. Popova, "Kinetics of the Dissolution of Iron (III) Oxide in Sulfuric Acid," *Zhurnal Fizicheskoi Khimii* (Engl. trans.), **50,** 1189 (1976).

Hernandez, J. O. "On the Use of Spent Hydrodesulfurization Catalysts," *Symp. Recovery of Spent Catalysts,* Am. Chem. Soc. Meet. Kansas City, MO, Prepr., 679 (Sept., 1982).

Hulbert, S. F., and D. E. Huff, "Kinetics of Alumina Removal from a Calcined Kaolin with Nitric, Sulfuric, and Hydrochloric Acids," *Clay Minerals,* **8,** 337 (1970).

Kabai, J., "Determination of Specific Activation Energies of Metal Oxides and Metal Oxide Hydrates by Measurement of the Rate of Dissolution," *Acta Chim. Acad. Acad. Sci. Hungaricae,* **78**(1), 57 (1973).

Maatman, R. W., P. Mahaffy, P. Hoekstra, and C. Addink "The Preparation of Pt-Alumina Catalyst and Its Role in Cyclohexane Dehydrogenation," *J. Catal.* **23,** 105 (1971).

Myerson, A. S., and W. R. Ernst, "Removal of Inorganic Contaminants from Catalysts," U.S. Pat. No. 4,559,313 (1985).

Nernst, W., "Theorie der Reaktionsgeschwindigkeit in heterogenen Systemen," *Z. Phys. Chem.,* **47,** 52 (1904).

Santacesaria, E., S. Carra, and I. Adami, "Adsorption of Hexachloroplatinic Acid on γ-Alumina," *Ind. Eng. Chem., Prod. Res. Dev.,* **16**(1), 41 (1977).

Shyr, Y-S., and W. R. Ernst, "Preparation of Nonuniformly Active Catalysts," *J. Catal.,* **63,** 425 (1980).

Uvarov, A. V., "Infrared Investigation of the Interaction between Water and an Aluminum Oxide Surface," *Z. Fiz. Khim.* (Engl. trans.), **36**(6), 717 (1962).

Warren, I. H., and E. A. Devuyst, "Fundamentals of the Leaching of Simple Oxides," *Ind. Chem. Eng. Ser. No. 42,* 7.1 (1974).

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