

SOME STUDIES IN ALUMINA TRIHYDRATE PRECIPITATION KINETICS

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Abstract

From measurements of the growth rate of single gibbsite (alumina trihydrate) crystals in pure NaAlO_2 - NaOH solutions at 80°C , it was possible to derive a growth rate formula which fits the data. This equation is $dI/dt = k[(A - A_\infty)/FC]^2$, where dI/dt is the linear growth rate, k is the rate constant, A is the Al_2O_3 concentration, A_∞ is the final equilibrium Al_2O_3 concentration, and FC is the free caustic concentration. A similar equation may also be derived theoretically from the equilibria involving the formation of the bialuminate ion, $\text{Al}_2(\text{OH})_7^-$, and the assumption that this ion loses OH^- in a rate-determining step to form gibbsite. Starting with the equation for dI/dt , an equation relating the change in Al_2O_3 concentration with time, dA/dt , was derived for gibbsite-seeded precipitation of NaAlO_2 - NaOH solutions. It was possible to numerically integrate this equation provided the surface area of the seed as a function of time or A were known. For seeded batch precipitations where the surface behavior was measured, the integrated equation correctly predicted the fall in Al_2O_3 concentration as a function of time for the temperature range 50 to 80°C with an appropriate choice of the temperature-dependent rate constant k . An apparent activation energy of 12.7 kcal was found.

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1.0 INTRODUCTION

Knowledge of the various rate processes occurring in the crystallization (precipitation) step of the Bayer process is necessary in order to optimize and control this step effectively. Among the most important rate processes here are the linear growth rate of the gibbsite crystals, the rate of deposition of dissolved alumina in seeded crystallization, the rate of nucleation, and the rate of agglomeration of gibbsite crystals. In this paper only the first two rates mentioned will be considered.

The kinetics of crystallization of alumina trihydrate (gibbsite) has been the subject of a number of published papers (1 - 9). There is no general agreement on either the mechanism or the functional dependence of the rate on such parameters as the alumina and caustic concentrations. In the case of those papers where experimental work was performed in order to derive a rate equation, observations were made on seeded caustic aluminate solutions in which a large number (ca. $10^3/\ell$) of gibbsite crystals were present. Due to the difficulty in controlling nucleation and agglomeration in such systems, there is some doubt that the effects of surface and concentration changes could be unequivocally distinguished from each other. One way around these difficulties is to measure the linear growth rate of single gibbsite crystals directly in a fixed concentration environment. Measurement of the gibbsite linear growth rates in caustic aluminate solutions of a variety of concentrations should then allow the formulation of a linear growth rate equation. This is precisely the approach which was taken in the work presented in this paper.

Once having established a linear growth rate equation, it is possible to derive an equation for the time rate of change of the alumina concentration in a seeded supersaturated solution of alumina in caustic by taking into additional account the seed surface and liquor volume changes which occur during crystallization. This has been done, and the resulting equation has been checked against the measured time rate of decrease in alumina concentration for seeded batch crystallization of caustic aluminate liquors where the change in surface area of seed with time was also measured.

2.0 EXPERIMENTAL2.1 Methods Used in Measurement of Growth Rate of Single Gibbsite Crystals2.1.1 Solution Preparation and Analysis

Solutions of NaOH - NaAlO_2 in water were prepared by dissolving 99.99% Al metal, in the form of strips ca. $1 \times 3 \times 0.1$ cm, in 50 wt % NaOH (A. R. grade) contained in a Teflon bottle. When the rather energetic dissolution of the metal was complete and the solution had cooled somewhat, it was filtered through a Whatman No. 5 filter paper and diluted to volume with boiled deionized water.

These solutions were analyzed for their alumina, caustic (sodium hydroxide plus sodium aluminate), and soda (caustic plus sodium carbonate) concentrations by a modified gluconate method, originally due to Watts and Utley (10). The alumina, caustic, and soda concentrations are designated A, C, and S, and are expressed as grams, g, of Al_2O_3 /liter, l , g of Na_2CO_3 / l , and g of Na_2CO_3 / l , respectively, all at 20°C. The NaOH- $NaAlO_2$ solutions had C/S values in the range 0.988 to 0.994. The composition of solutions is generally given by stating the ratio of alumina to caustic concentrations, A/C, and the caustic concentration, C. The free caustic, FC, i.e., the NaOH, concentration is also expressed as equivalent g Na_2CO_3 / l and is given by the relation $FC = C - A \cdot 106/102$.

2.1.2 Method of Attaching Gibbsite Crystals to Slides

The first-tried method of gluing gibbsite crystals to a partly wet acrylic polymer enamel (Sherwin-Williams, decorator clear B9 V 38) coating on a glass slide gave rather variable results in growth rate determinations and was not satisfactory.

It was discovered that glass slides coated with air-dried acrylic enamel and immersed in a 0.75 A/C ratio liquor (180 g/ l caustic concentration) at 80°C would become coated with some particles of gibbsite when the solution spontaneously nucleated. Such solutions would nucleate in 15 to 45 minutes when stirred in a stainless steel beaker. By experience it was found that single particles of 2 to 6 μm size would attach to the slide within a few minutes after the solution became cloudy. If one waited too long, the slide would be too densely covered or agglomerates would form on the slide. Properly prepared slides were then washed and carefully air-dried at room temperature. It was found that drying at 105°C seemed to deactivate the crystals for further growth.

The gibbsite crystals attached to the slides were generally in one of two orientations, either attached on a basal plane or on a hexagonal prism face. Although gibbsite is monoclinic, the crystal habit is pseudo-hexagonal. Most of the crystals formed on the slides appeared to be hexagonal prisms, although occasionally some crystals with pyramidal faces could be seen.

2.1.3 Rate of Growth Determinations

The 25 x 76 mm slides with attached gibbsite crystals were photographed in selected areas with the Leitz microscope fitted with a mechanical stage which allowed precise relocation of the area of interest. To make a rate determination, the slide was fitted into a slit in a rubber stopper and placed into a 250-ml flask containing the liquor at temperature. The flask was maintained at temperature to within 0.1% in a large (90 l) water bath. After a certain time of growth the slide was removed, washed, dried, and rephotographed in the original areas. Measurements of selected crystals on photographic enlargements, which gave an overall magnification of 745x, were made with a precision micrometer caliper.

The magnification factor was determined by photographing a plate ruled at 0.01 mm intervals. Usually 10 to 15 crystals in each of the two orientations were measured on the "before" and "after" photographs for each area of the several areas examined on each slide. For crystals attached to a prism face, the average increases in dimensions in the c-axis direction and perpendicular to it were obtained. For crystals attached by a basal plane, the average increase in dimension perpendicular to the c-axis and normal to a prism face was obtained. One-half the average increase in a crystal dimension divided by the time of immersion in the NaOH- $NaAlO_2$ liquor was taken as the radial linear growth rate. The measurements along the c-axis of the crystals are more precise than those perpendicular to it due to the greater difficulty in discerning the crystal prism boundaries because of optical diffraction effects. The growth rates, expressed in $\mu m/hr$, along the c-axis are probably precise to $\pm 0.2 \mu m/hr$. The rates perpendicular to the c-axis are probably no better than $\pm 0.3 \mu m/hr$.

2.2 Methods Used in Obtaining Precipitation Curves from Seeded NaOH- $NaAlO_2$ Solutions

Sodium hydroxide solutions were prepared by dilution of 50 wt % NaOH (A. R. grade) with deionized water. These solutions were then analyzed and their densities determined. To prepare the NaOH- $NaAlO_2$ solution, weighed amounts of NaOH solution and gibbsite (Alcoa C-31) were digested in gas-fired 240-ml Monel bombs at 240°C for 15 minutes. The bombs were then cooled to the temperature of the precipitation run to be conducted. The bombs were then opened, the desired amount of washed, dried gibbsite seed was added, and the bombs were closed and placed in the constant-temperature bath where they were rotated end-over-end. At the end of a given time the bombs were opened, and the mixture was filtered through a No. 54 Whatman paper on a Buchner funnel. The filtrate was analyzed for A, C, and S and its density was measured. The gibbsite solids were washed with deionized water until caustic-free by phenolphthalein test, dried at 110°C, and weighed. The specific surface of the solids was measured by an air-permeability method (Fisher Sub-Sieve Sizer). This procedure was repeated for various precipitation times ranging from 0.5 to 140 hr, using the same amounts and starting materials in each case of a precipitation condition.

3.0 GIBBSITE SINGLE CRYSTALS GROWTH RATE RESULTS AND FORMULATION OF A RATE EQUATION

3.1 Results

The average linear growth rates of single gibbsite crystals, 2 to 10 μm in size and attached to a polyacrylate film on a glass slide, in contact with various NaOH- $NaAlO_2$ solutions at 80°C are presented in Table I. In almost all cases the rates were obtained at two times differing by a factor of about 2. There is no indication of an induction effect, as

TABLE I. GIBBSITE LINEAR (RADIAL) GROWTH RATE DATA AT 80°C IN NaAlO₂-NaOH SOLUTIONS

NaAlO ₂ -NaOH solution composition		Radial growth rate of gibbsite crystals in μm/hr as determined on			Average rates, μm/hr		Rate ratio, along/perpend.
A/C	g/l C	Crystals attached on prism face		Crystals attached on basal plane perpend. to c-axis	Along c-axis	Perpend. to c-axis	
		Along c-axis	Perpend. to c-axis				
0.745	182.0	9.2 (.33) ^a , 9.2 (.5)	7.6 (.33), 7.3 (.5)	6.9 (.33), 6.1 (.5)	9.2	7.0	1.3
0.691	183.1	4.7 (1), 4.5 (2)	3.6 (1), 2.6 (2)	3.9 (1), 4.0 (2)	4.5	3.5	1.3
0.660	119.5	4.1 (1)	3.5 (1)	3.5 (1)	4.1	3.5	1.2
0.649	220.2	1.9 (1), 1.9 (3)	1.7 (1), 1.8 (3)	1.7 (1), 1.7 (3)	1.9	1.7	1.1
0.648	182.0	2.7 (1), 2.6 (2)	2.2 (1), 1.9 (2)	2.2 (1), 2.3 (2)	2.7	2.2	1.2
0.600	182.0	1.3 (2), 1.4 (4)	0.9 (2), 1.2 (4)	0.8 (2)	1.4	1.1	1.3

a. Numbers in parentheses are duration of crystallization runs in hours.

evidenced by the closely agreeing values for the rate along the c-axis at the two times, except, perhaps, in the case of the 0.600 A/C solution.

The smaller variability of the results obtained on measurements made along the c-axis of the crystals can be seen from the table.

Within the limits of the estimated experimental error, the ratios of the growth rates along to the rates perpendicular to the c-axis of the crystals are constant.

3.2 Formulation of a Rate Equation

The present work and previous work on the rate of gibbsite precipitation from caustic aluminate solutions clearly indicated that the rate is some function of the aluminate ion concentration. Further, as the rate must fall to zero at the saturation value for alumina in the caustic solution, the rate must be some function of the supersaturation, i.e., of (A - A_∞).

For a NaOH-NaAlO₂ solution of a certain composition at some temperature t, it was concluded that there is associated with the solution in contact with solid gibbsite a single valued A_∞ corresponding to a real

attainable state of the closed system. This A_∞ would be the intersection, on a plot of alumina concentration vs. caustic concentration, of the equilibrium solubility curve for gibbsite in caustic solutions with the curve representing possible compositions for a given starting NaOH-NaAlO₂ solution composition. If A₀ and C₀ are the starting values for the alumina and caustic concentrations for the NaOH-NaAlO₂ solution, then the relation between A and C, the other possible composition parameters, is given by

$$C(1 - \frac{\partial V}{\partial W} A_0) = C_0(1 - \frac{\partial V}{\partial W} A),$$

where ∂V/∂W is the volume change in the solution attendant on the dissolution of a certain weight of gibbsite. The units of ∂V/∂W are l/g of Al₂O₃ for A units being g of Al₂O₃/l. From the specific volume of Al₂O₃ in solution as given by Adamson, Bloore, and Carr (12), the value of 0.00092 ml/g of Al₂O₃ may be calculated for ∂V/∂W.

Values for A_∞ and C_∞ for each of the NaOH-NaAlO₂ solutions used in the growth rate experiments have been calculated by the method outlined above and are included in Table II. Values for A, FC, and FC_∞ can be derived from the other parameters listed in the table.

TABLE II. COMPARISON OF LINEAR GROWTH RATE ALONG THE c-AXIS OF GIBBSITE CRYSTALS IN CONTACT WITH NaOH-NaAlO₂ SOLUTIONS AT 80°C WITH RATES CALCULATED FROM VARIOUS EQUATIONS

NaAlO ₂ -NaOH solution composition		Measured growth rate, along c-axis of prism, μm/hr	Calculated growth rate from various equations (R), normalized to the 0.691 A/C run value, μm/hr								Cal'd. A _∞ /C _∞ , g/l
A/C	g/l C		R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	
0.745	182.0	9.2	6.0	5.2	6.0	6.9	6.7	9.5	9.5	6.0	67.3 195.1
0.691	183.1	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	67.0 194.4
0.660	119.5	4.1	5.3	3.1	2.2	1.6	5.7	3.4	4.1	4.7	37.8 124.4
0.649	220.2	1.9	2.8	4.3	4.0	3.8	2.2	2.3	2.1	3.1	86.9 233.3
0.648	182.0	2.7	3.6	4.0	3.5	3.0	3.1	2.6	2.6	3.5	65.8 191.8
0.600	182.1	1.4	2.6	3.4	2.5	1.8	1.9	1.4	1.4	2.6	65.1 190.3

Various rate equations, listed in Table III, were tested for their ability to predict the measured average growth rate along the c-axis of the gibbsite crystals. To do this, the eight equations listed were assumed to express the rate for the 0.691 A/C, 183.1 g/l caustic solution

case, i.e., 4.5 μm/hr. The rates predicted for each of the other solutions by each of the equations were then calculated.

As can be seen by examination of Table II, the equation which best fits the data is R₇. Thus, the linear growth rate, dl/dt, is best represented by

$$\frac{dl}{dt} = k_7 \left(\frac{A - A_{\infty}}{FC_{\infty}} \right)^2.$$

TABLE III. VARIOUS EQUATIONS TESTED

R₁ = k₁ $\left(\frac{A - A_{\infty}}{C_{\infty}} \right)^2$, linear form of Pearson's (1) equation

R₂ = k₂ (A - A_∞)

R₃ = k₃ (A - A_∞)²

R₄ = k₄ (A - A_∞)³

R₅ = k₅ $\left(\frac{A - A_{\infty}}{C_{\infty}} \right)^3$

R₆ = k₆ $\left(\frac{A}{FC} - \frac{A_{\infty}}{FC_{\infty}} \right)^2$

R₇ = k₇ $\left(\frac{A - A_{\infty}}{FC} \right)^2$ + Best fit to data!

R₈ = k₈ $\left(\frac{A - A_{\infty}}{FC_{\infty}} \right)^2$

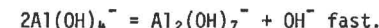
4.0 CHEMICAL AND SURFACE REACTION MECHANISMS WHICH LEAD TO THE SAME RATE EQUATION EMPIRICALLY FOUND

By consideration of certain equilibria which are known to exist in NaOH-NaAlO₂ solutions and by postulating a two-step surface event, it has been possible to derive the rate equation for the growth of gibbsite in contact with NaOH-NaAlO₂ solutions which was found empirically.

J. R. Glastonbury (12) in his paper on the nature of sodium aluminate solutions has reviewed the work of others. The aluminate ion in solution is concluded to be mainly in the forms AlO₂⁻ and Al(OH)₄⁻, the relative amounts depending on the NaOH concentration. E. T. Allen and H. F. Rogers (13) and D. Prociw (14) have demonstrated the existence of the bialuminate ion in aluminate solutions. D. Prociw has estimated the equilibrium constant for its formation from aluminate ions to be 10⁻⁴ at 25°C.

Considering the growth of gibbsite in contact with NaOH-NaAlO₂ solutions to be surface-controlled, it may be postulated that the rate-controlling events are the adsorption of the bialuminate ion onto the

gibbsite surface and the loss of a hydroxyl ion from the adsorbed bialuminate ion to form gibbsite. Thus, one may write



Probability of adsorption of Al₂(OH)₇⁻ on gibbsite surface = P_{abs} = k_{abs}(Al₂(OH)₇⁻). Probability of loss of OH⁻ from adsorbed Al₂(OH)₇⁻ will be influenced by concentration of OH⁻ in solution, the probability being less the higher the (OH⁻). P_{loss OH⁻} = k_{loss OH⁻} / (OH⁻). The rate of formation of gibbsite from Al₂(OH)₇⁻ is then proportional to the product of the two probabilities above, i.e.:

$$\text{growth rate} = k \frac{(Al_2(OH)_7^-)}{(OH^-)}.$$

Substituting the expression for (Al₂(OH)₇⁻) from

$$(Al_2(OH)_7^-) = \frac{K(Al(OH)_4^-)^2}{(OH^-)},$$

the equilibrium expression for the formation of Al₂(OH)₇⁻ from Al(OH)₄⁻, into the growth rate equation, one obtains

$$\text{growth rate} = kK \frac{(Al(OH)_4^-)^2}{(OH^-)^2}.$$

For gibbsite in contact with a NaOH-NaAlO₂ solution saturated with alumina there is an (Al(OH)₄⁻)_∞ or equilibrium concentration. There is no net deposition of gibbsite here and the growth rate is zero. Including this in the growth rate equation gives

$$\text{growth rate} = kK \left[\frac{(Al(OH)_4^-)}{(OH^-)} - \frac{(Al(OH)_4^-)_{\infty}}{(OH^-)} \right]^2$$

which is the same equation found empirically except for the constant term which differs because the units for concentration chosen differ.

This postulated mechanism for the rate of precipitation of gibbsite provides a qualitative explanation for the slowness of gibbsite formation also. Thus, in a solution of 0.65 A/C ratio at 180 g/l caustic concentration the (Al(OH)₄⁻) is 2.3 moles/l, the (OH⁻) is 1.1 moles/l, but the (Al₂(OH)₇⁻) is only 5 x 10⁻⁴ moles/l (based on the equilibrium constant for its formation of 10⁻⁴ at 25°C).

5.0 DERIVATION OF EQUATION FOR TIME RATE OF CHANGE OF ALUMINA CONCENTRATION AND TEST AGAINST BATCH GIBBSITE-SEEDED PRECIPITATIONS OF NaOH-NaAlO₂ SOLUTIONS

5.1 Derivation of Equation for dA/dt

In order to test the linear growth rate equation against batch precipitations where the change in alumina concentration A or the ratio A/C with time are determined, it is necessary to derive an equation for dA/dt.

Starting with the linear growth rate equation,

$$\frac{dl}{dt} = k_7 \left(\frac{A - A_{\infty}}{FC} \right)^2,$$

then,
$$\frac{dv}{dt} = S \frac{dl}{dt} = k_7 S \left(\frac{A - A_{\infty}}{FC} \right)^2,$$

where v is the volume of gibbsite and S is its surface area. If ρ is the density of gibbsite and W its mass, then:

$$\frac{dW}{dt} = \rho \frac{dv}{dt} = k_7 \rho S \left(\frac{A - A_{\infty}}{FC} \right)^2.$$

Now,
$$\frac{dW}{dt} = \frac{d(AV)}{dt} = V \frac{dA}{dt} + A \frac{dV}{dt},$$

where A is alumina concentration and V is volume of NaOH-NaAlO₂ solution. One may write further

$$\frac{dW}{dt} = V \frac{dA}{dt} + A \frac{\partial V}{\partial W} \frac{dW}{dt},$$

rearranging,
$$\frac{1}{V} \frac{dW}{dt} = \frac{1}{1 - A \frac{\partial V}{\partial W}} \cdot \frac{dA}{dt}.$$

Therefore,
$$\frac{dA}{dt} = k_7 \rho \frac{S}{V} \left(1 - \frac{\partial V}{\partial W} A \right) \left(\frac{A - A_{\infty}}{FC} \right)^2.$$

If one considers an initial solution volume of V₀ with an alumina concentration initially of A₀, then

$$V = V_0 \frac{\left(1 - \frac{\partial V}{\partial W} A_0 \right)}{\left(1 - \frac{\partial V}{\partial W} A \right)},$$

and writing k for k₇ρ and \bar{S} for S/V₀, then

$$\frac{dA}{dt} = k \bar{S} \frac{\left(1 - \frac{\partial V}{\partial W} A \right)^2}{\left(1 - \frac{\partial V}{\partial W} A_0 \right)} \left(\frac{A - A_{\infty}}{FC} \right)^2.$$

5.2 Test of Equation for dA/dt against Batch Precipitation Data

If the value of \bar{S} is known instantaneously or as a function of A, then the equation for dA/dt may be integrated numerically to give A as a function of time for a given set of starting conditions, i.e., for some A₀, C₀, and temperature. The A_∞ depends on the temperature and on the final C in the completely precipitated (equilibrated) solution. The caustic concentration at any time is given by

$$C = C_0 \left(1 - \frac{\partial V}{\partial W} A \right) / \left(1 - \frac{\partial V}{\partial W} A_0 \right).$$

It is thus possible to obtain A/C vs. time curves for a given precipitation provided the surface behavior is known. Such information was available from the work of M. J. Berger and H. J. Ducote of this laboratory. Their work provided A/C and \bar{S} values as a function of time for numerous batch precipitations at temperatures from 50° to 80°C for pure NaOH-NaAlO₂ solutions seeded with gibbsite.

The above equation for dA/dt was tested against a given set of batch data by first finding a function which allowed the calculation of \bar{S} in terms of A. The equation for dA/dt was then integrated numerically (with the aid of a computer) after choosing a value for k. The value for k was then changed until the best fit to the A/C-vs.-time data was found. In general, very good reproduction of the batch data was possible with the equation in the absence of induction effects and when the scatter of the surface data was small. By changing the value of k, it was possible to fit the batch data at 80°, 70°, 60°, and 50°C. This is shown in Table IV where some representative precipitation runs are presented. The precipitation conditions in Table IV are for four temperatures, three caustic concentrations, two seed types, and two initial seed surfaces. The measured (data) and calculated A/C values at various times and the difference (Δ) in the two values are presented. The estimated error in the analytical determination of A/C is ±0.006. The Δ values are approximately of this size.

The values of k so obtained are:

k	Temperature, °C
5.85	80
3.25	70
2.08	60
1.09	50

A plot of log k vs. 1/T, where T is absolute temperature, gives a straight line from which an apparent activation energy of 12.7 kcal is calculated.

TABLE IV. COMPARISON OF CALCULATED AND MEASURED A/C VS. TIME POINTS FOR VARIOUS BATCH PRECIPITATIONS

Precipitation Conditions:														
				a			b			c			d	
Temp., °C:				50			60			70			80	
A ₀ , g/l				123.59			140.66			104.0			141.85	
C ₀ , g/l				190.52			220.3			160.0			223.27	
A _∞ , g/l				36.96			59.45			45.35			88.31	
Seed type				TT			ST			TT			ST	
Seed specific surface, cm ² /g				1956			716			1956			716	
Seed surface, S ₀ , m ² /l				12.5			12.4			12.5			6.1	
Time, hr	A/C Ratio													
	a			b			c			d				
	Data	Calc'd	Δ	Data	Calc'd	Δ	Data	Calc'd	Δ	Data	Calc'd	Δ		
0.5	0.641	0.623	0.018				0.558	0.553	0.005					
0.75							0.522	0.526	-0.004					
1.00	0.599	0.576	0.023	0.564	0.564	0	0.500	0.505	-0.005	0.575	0.579	-0.004		
3.00	0.485	0.479	0.006	0.485	0.480	0.005				0.514	0.522	-0.008		
5.00	0.434	0.425	0.009				0.375	0.387	-0.012					
6.00				0.427	0.422	0.005								
8.00	0.387	0.379	0.008				0.352	0.358	-0.006	0.466	0.466	0		
10.00							0.344	0.347	-0.003					
11.0				0.383	0.377	0.006								
15.0	0.327	0.324	0.003											
15.50							0.329	0.326	0.003					
16.00										0.437	0.433	0.004		
18.50				0.346	0.342	0.004								
20.00							0.321	0.316	0.005					
23.00	0.289	0.289	0											
28.00	0.279	0.281	-0.002				0.315	0.306	0.009					
30.00										0.412	0.411	0.001		
40.00	0.258	0.255	0.003											
40.50							0.306	0.296	0.010					
41.00										0.405	0.403	0.002		
72.00				0.289	0.283	0.006								
140.00				0.274	0.269	0.005								

6.0 CONCLUDING REMARKS

For the linear growth rate measurements, the average of the growth rates along and perpendicular to the c-axis of gibbsite for the 0.745 A/C at 182 g/l caustic solution case at 80°C is 8.1 μm/hr. From this it is possible to calculate k₇ and thus k (= ρk₇) directly. The value is 7.10. This is to be compared with the value 5.85 obtained from fitting the batch precipitation data using Fisher air-permeability surface areas. The difference in these numbers may be interpreted in several ways: the Fisher area is too large; only part of the surface area is active for growth; the simple average of growth rate in two directions is incorrect. In any case, the form of the rate equation appears to be correct.

The prediction of the surface area (or the particle-size distribution) at any time remains the biggest problem in the development of a mathematical model for precipitation. It is hoped that the present work will aid in the ultimate solution to this problem.

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