3. DIGESTION

Digestion is the operating heart of alumina refineries that use the Bayer process. The papers in this section concern the part of the Bayer process that

- prepares the bauxite to enter the process as a slurry in caustic liquor;

- attacks the alumina hydrate with caustic soda solution (liquor) at elevated temperature, putting the bauxite alumina in solution; and

- recuperates a large part of the heat energy used to elevate the temperature of the attack liquor.

Most alumina refineries use the Bayer process and, consequently, use bauxite that has its recoverable alumina in the form of alumina trihydrate mineral (Gibbsitic bauxite), or as a mixture of alumina trihydrate and alumina monohydrate mineral (Boehmitic bauxite). Only a few refineries use the Bayer process for bauxites containing a significant amount of Diaspore (Diasporic bauxite), where the chemical fomula is the same as Boehmite but the form of the monohydrate crystal is different.

Diasporic bauxite is seldom used in the Bayer process because the digestion conditions required are more severe and less productive than with Boemitic bauxite. Also, many Diasporic types of bauxite contain prohibitively high silica content, resulting in costly losses of caustic soda in processing by the Bayer process.

China has considerable amounts of Diasporic bauxite, usually with relatively high silica content, and uses the Sinter Process to recover alumina. The process sinters the bauxite with (1) soda ash to attack the alumina and (2) limestone to react with and tie up the silica. There have been efforts in China to use the Bayer process in combination with the Sinter process to improve efficiency and reduce energy.

Don Donaldson

Light Metals

BAYER DIGESTION AND PREDIGESTION DESILICATION REACTOR DESIGN

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The presentation comprises a literature survey of the major chemical reaction processes in digestion and slurry holding and a derivation of reactor design based on these studies as well as on plant tests. It contains calculation methods to equate laboratory bomb and container reaction results with those of full-size continuous reactors.

Introduction

This study was done to clarify some of the differences of opinion on the subject of reactions under actual continuous digestion operation, in particular:

1. The possibility of conversion of gibbsite to boehmite under intermediate temperature digestion conditions.

2. The discrepancy between the extent of the goethite to hematite conversion and the subsequent release of lattice bound alumina in the laboratory bomb as compared with actual digestion experience.

3. The controversy of agitated, compartmented digester vessels versus unstirred reactors.

4. Whether or not boehmite dissolution and goethite conversion can be economically accomplished in a tube digester with low residence time at high temperature.

While doing this study it was found that some of the developed theory and calculations also apply to other facets of the Bayer process such as predesilication and precipitation.

Summary

The extraction and conversion reactions that take place during digestion in the Bayer process are discussed in this paper. This is done in a manner that the process design engineer, using simple reactor design theory, can evaluate the type and size of the reactor vessel(s) that will result in optimum digestion conditions for the bauxite in question.

Generalized conclusions are:

1. Pure gibbsitic bauxites are best digested in a series of unstirred reactors at temperatures around 150°C.

2. Boehmitic bauxite may be economically digested in tube digester, providing the boehmite is finely divided, a high velocity (>2 m/sec.) is maintained and at temperatures of 250°C or more, while other boehmitic bauxites are digested better in large unstirred reactors at temperatures between 230 and 250°C at extended residence time.

3. Reactions in which solids are formed and that are controlled by seed surface, such as desilication and goethite to hematite conversion, are best performed in large fully mixed vessels.

4. Conversion from gibbsite to boehmite in liquor that is stable with respect to gibbsite but not to boehmite, will proceed more rapidly in large backmixing vessels.

The Reactions

General

The reactions that govern Bayer alumina extraction are:

1. The dissolution of gibbsite.

2. The dissolution of boehmite.

3. The dissolution of diaspore.

4. The conversion of alumino-goethite to hematite and dissolved alumina.

5. The conversion of gibbsite to boehmite.

6. The conversion of boehmite to diaspore.

7. The desilication reactions.

These will be discussed in two groups, namely the dissolution reactions (1, 2, 3) and the reaction with solid end products (4, 5, 6, 7).

The Dissolution Reactions(1, 2, 3). The minerals gibbsite, boehmite, and diaspore, given enough time, dissolve in caustic liquor to defined equilibria depending on temperature and other solutes.

The equilibria can be described as:

$$[\text{Mineral}] + (\text{OH}^-) \xrightleftharpoons{} (\text{Al ion}^-) \pm (1,2)\ H_2O \qquad (1)$$
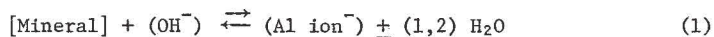
The activity of the mineral [mineral] = 1 by definition (single solid phase). For very dilute liquor the activity of the solutes is equal to their concentration and the activity of water (H_2O) = 1. Two moles of (Al ion$^-$) represent one mole of (Al_2O_3) and two moles of (OH$^-$) can be represented by one mole of (Na_2CO_3). Therefore the equilibrium is simplified to:

$$K = f(T) = \frac{(Al_2O_3)}{(Na_2CO_3)} \qquad (2)$$

The actual equilibria have been determined by many researchers.[1,3,6,11,16] The deviation from the simple relation above is caused by the interactions of the ions in solution, reducing their activity below the level their concentration would indicate and by the reduced activity of water.

A summary of equilibria data in synthetic ("pure") liquors has been presented in Figure I.

The dissolution rates of gibbsite, boehmite, and diaspore differ greatly. Because of this, three distinctly different types of Bayer digestion conditions can be found.
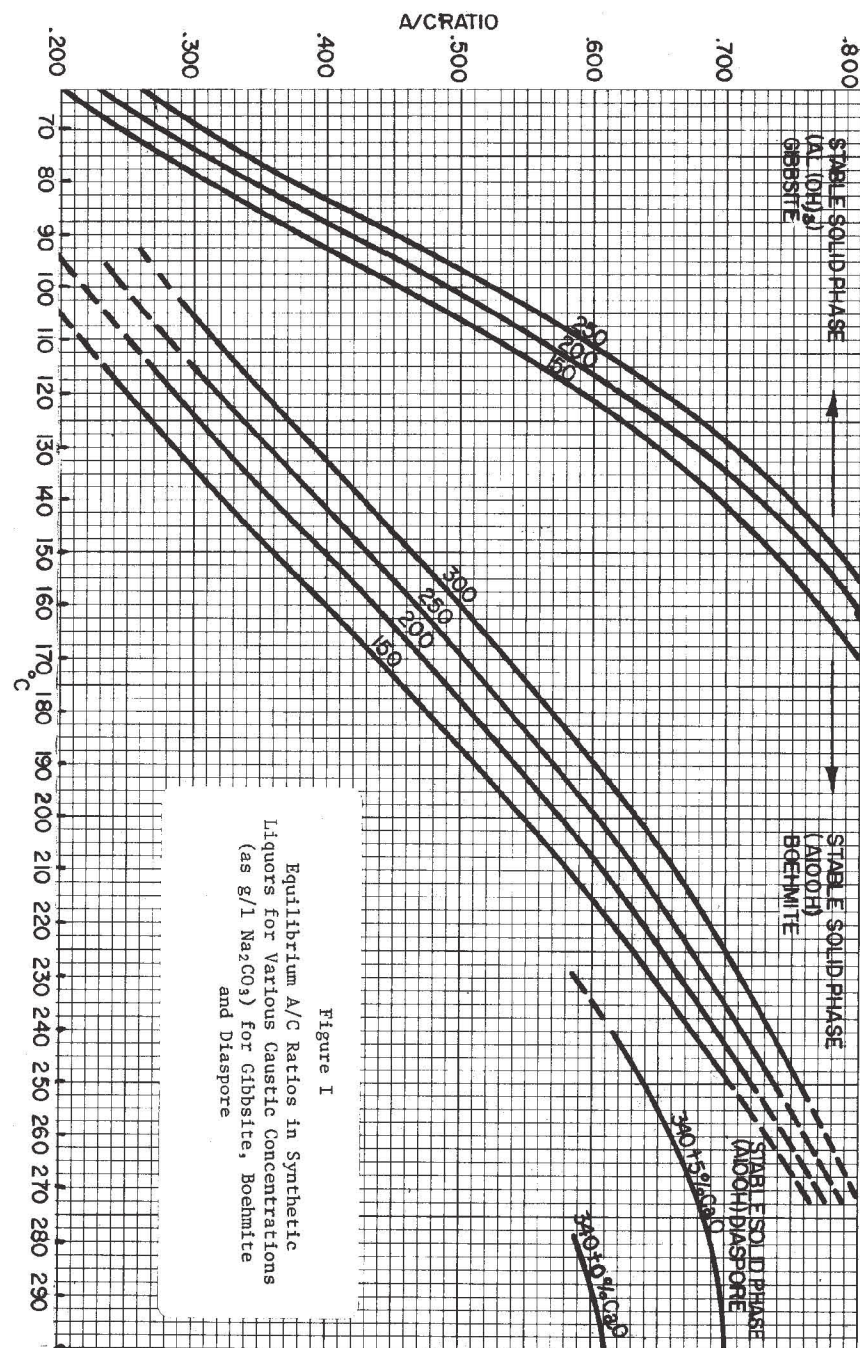

Figure I

Equilibrium A/C Ratios in Synthetic Liquors for Various Caustic Concentrations (as g/l Na_2CO_3) for Gibbsite, Boehmite and Diaspore

(a) Low temperature, low concentration 130 - 150°C, 150 - 160 gpl
    NaOH (as Na₂CO₃), gibbsite only.

(b) High temperature, medium to high concentration 200 - 250°C,
    160 - 380 gpl NaOH (as Na₂CO₃), boehmite and gibbsite.

(c) High temperature, high concentration 230 - 280°C, 230 - 380 gpl
    NaOH (as Na₂CO₃) diaspore (+ boehmite and gibbsite).

Intermediate operating ranges will usually not be found because of
conversion reactions and general economics.

The dissolution reactions are reaction rate controlled up to certain
temperatures, while above these certain temperatures ion diffusion trans-
fer limits the reaction rate. These reactions are represented schematically
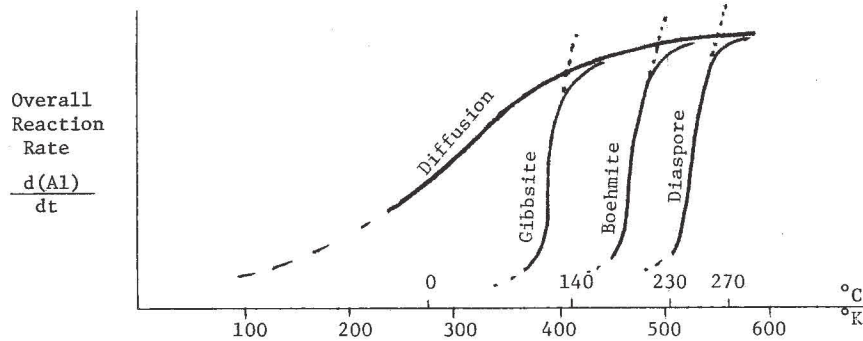in Figure II.

Figure II

Schematic Representation of Reaction Rate vs. Temperature

The temperature at which ion diffusion takes over as the rate con-
trolling process will depend on crystallinity, specific surface, and
liquor concentrations.

The Reactions with Solid End Products(4, 5, 6, 7). The conversion
of goethite to hematite, the alumina conversion reactions, and the desil-
ication reaction are more complicated than the dissolution reactions men-
tioned above. These reactions, where a solid end product is formed, have
in common that the initial reaction rate is dictated by the available seed
surface, probably because nucleation requires high energy levels.

Schematically the two groups of reactions can be presented as in
Figure III, showing the effect of time on the progression of the two types
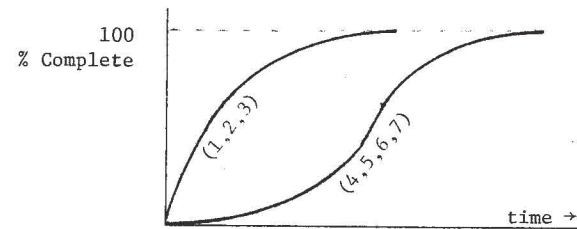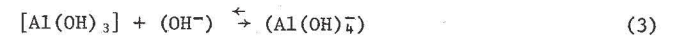of reactions.

Figure III

Schematic Reaction Progress

For the Two Types of Reactions

Low Temperature, Low Caustic Concentration

Gibbsite Extraction. This range is chosen to extract gibbsite while
completing desilication of the liquor to an acceptable level. The
equilibrium is described[22] as:

$$[Al(OH)_3] + (OH^-) \rightleftarrows (Al(OH)_4^-) \qquad (3)$$

although no conclusive evidence has been presented that the alumina in sol-
ution is present as (Al(OH)₄⁻). Experimental equilibrium data in synthetic
liquors, summarized in Figure I, are shown as lines above which gibbsite
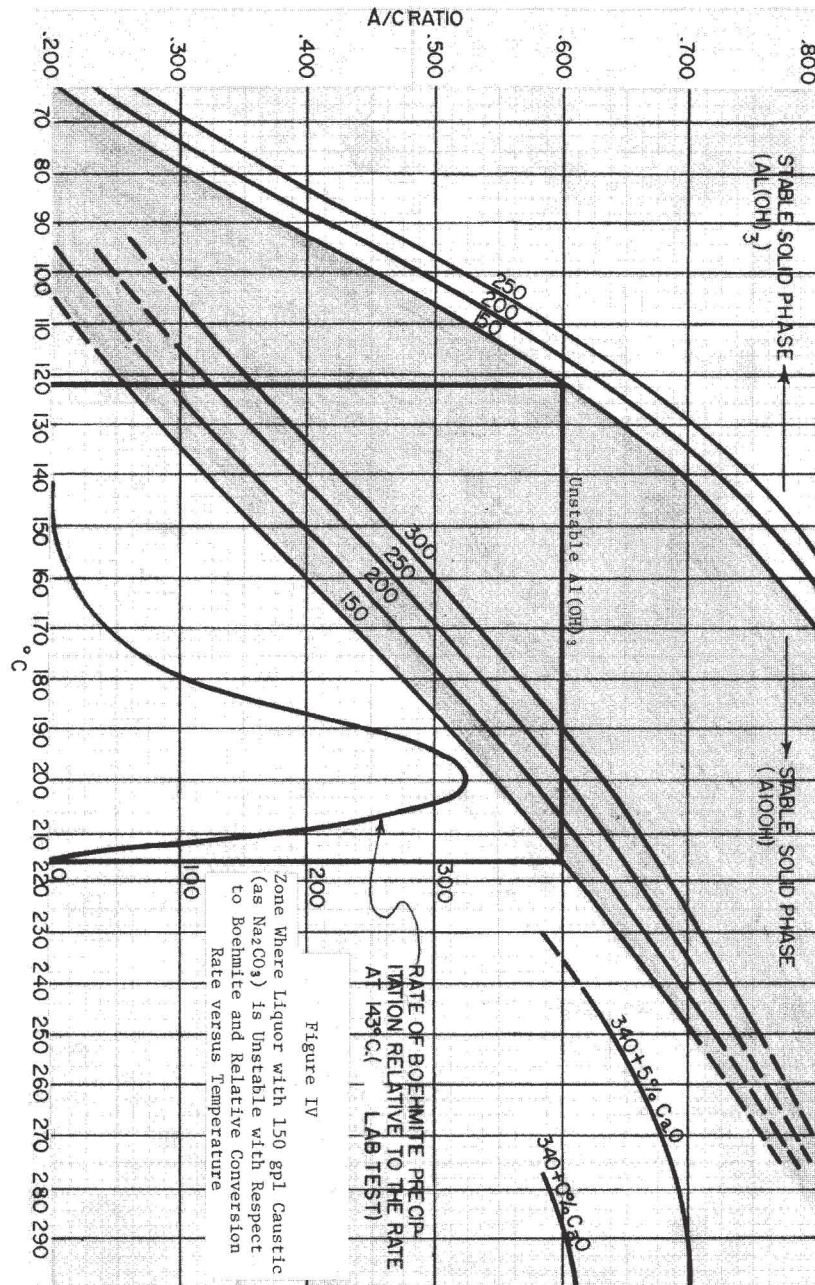is stable.

Providing that the reactor is charged to stay below equilibrium con-
ditions, the dissolution rate can be described as follows:

$$\frac{d(A)}{dt} = f \left[((A_\infty) - (A)), \ Sg, \ e^{-\frac{k}{T}} \right] \qquad (4)$$

Where: (A) = alumina in solution

(A∞) = equilibrium solubility = f(T, (OH⁻))

Sg = specific surface area of the gibbsite

k = measure of activation energy

T = absolute temperature

The equation assumes that the overall reaction rate is controlled by
the actual dissolution reaction at the surface of the particle and not by
the diffusion process of the ions through the liquor phase and boundary
layers. Most investigators[3,4,6] have found that this assumption holds at
temperatures below about 200°C.

At temperatures below 50°C and average caustic concentration the
overall rate is slow and time for complete extraction is to be measured
in hours. The rate increases rapidly with temperature and at around 140°C
it takes only minutes to fully digest gibbsite.[14]

Figure IV

Zone Where Liquor with 150 gpl Caustic (as Na₂CO₃) is Unstable with Respect to Boehmite and Relative Conversion Rate versus Temperature

RATE OF BOEHMITE PRECIPITATION RELATIVE TO THE RATE AT 143°C. (LAB TEST)

The extended residence time practiced in most "low temperature" digestion plants is not needed for gibbsite extraction, but for desilication. The gibbsite extraction therefore has no bearing on the reactor design.

Conversion from Gibbsite to Boehmite. As is indicated in Figure I, the equilibrium solubility of boehmite for given temperature and caustic concentration is lower than for gibbsite. A liquor held at a point in the zone between the two equilibrium lines for boehmite and gibbsite is unstable. See Figure IV.

Given enough time liquors in this zone will yield boehmite and gibbsite added will eventually all convert to boehmite.

The rate at which this occurs is sometimes so low that at practical digestion times this is not a problem.

The rate of boehmite formation $\frac{dB}{dt}$, is a function of seed surface area (S_b), driving force ($A - A_\infty$), the activation energy (k), and temperature (T) or

$$\frac{dB}{dt} = f\ (S_b,\ (A - A_\infty),\ e^{\frac{-k}{T}}) \tag{5}$$

The driving force ($A - A_\infty$) depends on how far the liquor A/C ratios are above the equilibrium for boehmite. For a given A/C ratio, this driving force reduces with temperature.

The temperature dependent rate factor $e^{\frac{-k}{T}}$ increase exponential with temperature.

The product of driving force and rate factor has a maximum for a given liquor A/C ratio. The product will be low at low temperatures and very little transformation will be observed at temperatures below say 150°C. That is why the normal "low" temperature digestion is done around this temperature.

The product increases to reach a maximum of about 200°C and falls off rapidly to zero where the equilibrium A/C ratio of boehmite is reached.

Figure IV shows the rate of boehmite precipitation at various temperatures relative to rate of precipitation at 143°C.

The reaction rate will be different for each bauxite or bauxite combination, and for a given temperature, C concentration, and A/C ratio in the liquor will depend only on the effective boehmite seed surface.

Without any seed surface area (clean liquor) the process is extremely slow.

Mud present will have some surface activity high enough for boehmite formation and the presence of boehmite itself will represent real seed surface.

Sweetening. Sweetening is the name for a Bayer process variant developed originally by Kaiser ACC. It was developed because of the availability of good quality "trihydrate" bauxite to Kaiser and because the plant at which it was first practiced was designed for digestion temperatures too low to economically extract all boehmite.

By lowering the charge of boehmite bauxite to ratios below equilibrium, all boehmite is extracted. The trihydrate bauxite is then added in the next level at temperature (or after cooling) to bring the ratio up to higher levels, thus enhancing liquor productivity.

To approximate what will happen in a plant where sweetening is to be practiced, a break point analysis for various temperatures is to be done with the bauxites in question.

These breakpoints are not true equilibria determinations. These are merely determinations of the A/C ratio where conversion to boehmite becomes significant for the projected digestion time.

At temperatures around 140°C the breakpoint will invariably fall close to the gibbsite equilibrium. They will divert to lower values as higher temperatures are tried, to reach a maximum. At even higher temperatures, the breakpoint will be lower until it asymptotically reaches boehmite equilibrium.

Figure V gives a typical example.

In this two digestion step process the conditions of the first step are chosen to extract all of the boehmite by keeping the charge A/C ratio below the boehmite equilibrium. In the second step the "low monohydrate" bauxite is added usually at a lower temperature and preferable at the temperature where the highest A/C break point is achieved for the given retention time.

A schematic A/C "cycle" illustrating this principle has been presented in Figure VI.

Desilication. Clay minerals are quite soluble in Bayer liquor even at low temperatures, while quartz, depending on particle size, will dissolve at temperatures over 200°C; therefore, particle size, bauxite mineralogy, and digestion conditions dictate whether or not silica is reactive.
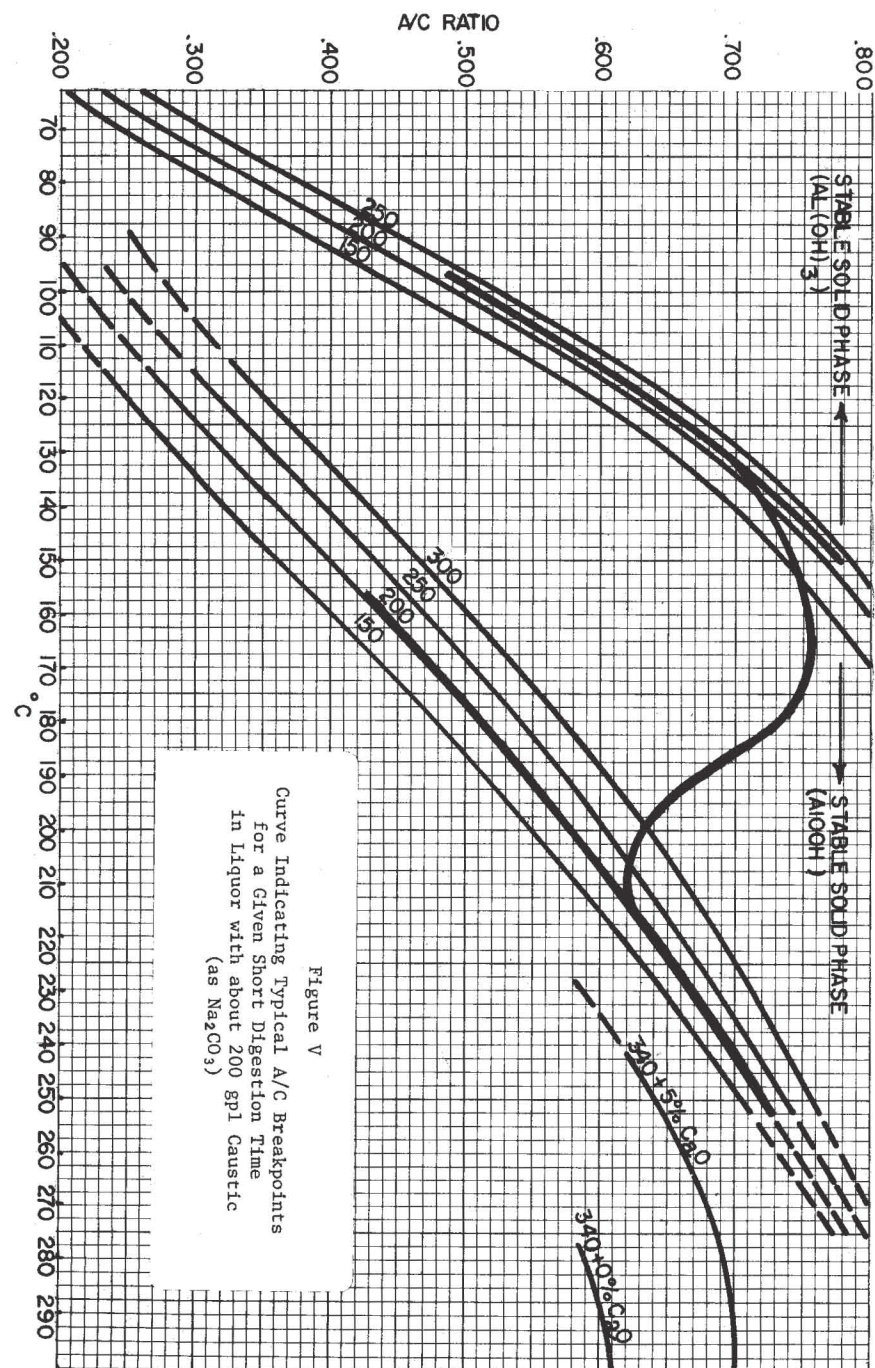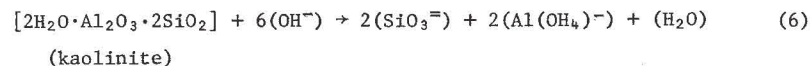
The reactive silica dissolves but is unstable in Bayer liquor. It forms insoluble orthosilicates called desilication product (DSP).
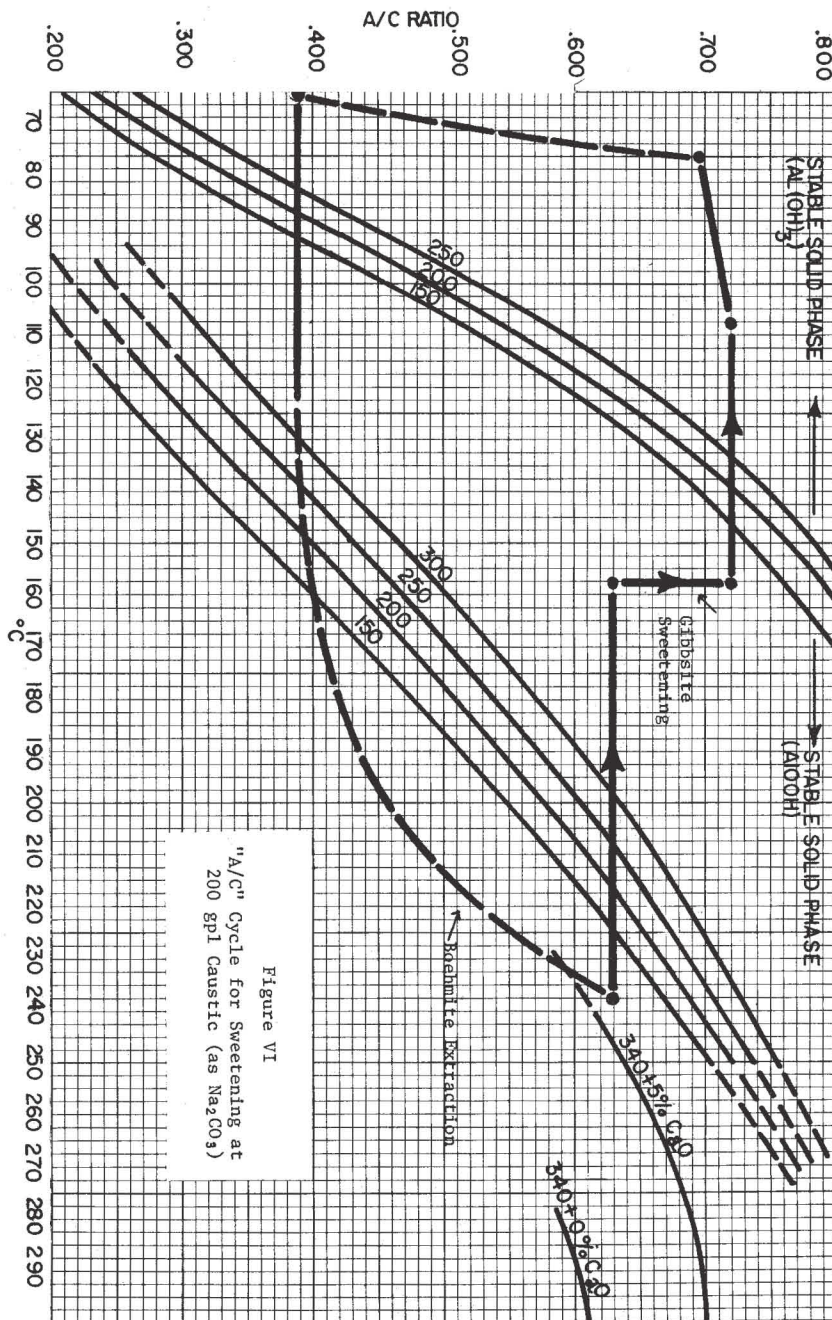
Therefore, desilication involves two main reactions:

1. The dissolution of reactive silica (usually kaolinite).

2. The precipitation of DSP.

Those chemical reactions can be described approximately by:

Dissolution:

$$[2H_2O \cdot Al_2O_3 \cdot 2SiO_2] + 6(OH^-) \rightarrow 2(SiO_3^=) + 2(Al(OH_4)^-) + (H_2O) \qquad (6)$$

(kaolinite)

Figure V

Curve Indicating Typical A/C Breakpoints for a Given Short Digestion Time in Liquor with about 200 gpl Caustic (as Na_2CO_3)

Figure VI
"A/C" Cycle for Sweetening at 200 gpl Caustic (as Na₂CO₃)

Precipitation:

$$2(SiO_3^=) + 2(Al(OH_4^-)) + 2(Na^+) \rightarrow [Na_2O \cdot Al_2O_3 \cdot 2SiO_2] + 4(OH^-) + 2(H_2O) \quad (7)$$
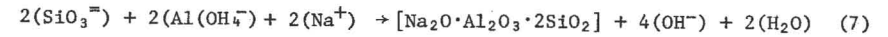
DSP (sodalite; haüyhite; noselite; natrodyvene; depending on attached salt molecule.)

The dissolution rate will depend on:

1. Temperature.

2. Kaolinite surface area.

3. Caustic concentration.

4. Silica concentration in the liquor.

5. Alumina concentration in the liquor.

The precipitation reaction will depend on:

1. Temperature.

2. Silica concentration in solution.

3. Alumina concentration in solution.

4. Caustic concentration in solution.

5. and (since nucleation of crystals takes too much energy), DSP surface area.

Note immediately that:

1. High caustic concentration promotes dissolution, but hinders precipitation.

2. High alumina concentration hinders dissolution, but promotes precipitation.

During digestion condition the alumina concentration reaches the desired level in a short time. During predesilication of dense gibbsitic bauxite slurries the A/C ratio in the liquor will go from spent liquor conditions up to high values over .700 and usually come back down to values of say about .550. In other words, gibbsite dissolution may affect the desilication reaction considerably.

Since the activities of the solid phases can be assumed to constant and close to 1, the equilibrium constants can be described as Kd for dissolution:

$$Kd = \frac{(SiO_3^=)^2 \, (AlO_2^-)^2 \, (H_2O)}{(OH^-)^6} \quad (8)$$

and for precipitation, Kp:

$$Kp = \frac{(OH^-)^4 \, (H_2O)^2}{(SiO_3^=)^2 \, (AlO_2^-)^2 \, (Na^+)^2} \tag{9}$$

Note that the overall equilibrium K = Kd x Kp is independent of the silica and alumina activities (concentrations) and only dependent on the caustic concentration and off-course temperature.

$$K = Kd \times Kp = \frac{(H_2O)^3}{(Na^+)^2 \times (OH^-)^2} \tag{10}$$

Over the years several aspects of the kinetics of these reactions have been determined either by laboratory work or in the field. Experiments and lab work have shown that kaolinite from most bauxites will go into solution quite rapidly (less than 15 minutes) providing the temperature during pre-desilication is kept close to atmospheric boiling. Lower temperatures will have a very detrimental effect in that not only the rate of dissolution reduces rapidly but also that not all kaolinite will dissolve.

So no matter what the design of the desilication system is, the temperature in the initial phase must be as close to the maximum as possible.

The maximum temperature for predesilication is dictated by the conversion from gibbsite to boehmite in low temperature digestion plants and by the recovery heat level or construction criteria at high temperature digestion plants.

Experiments have also shown that a seed surface area is necessary to form DSP. Plots of reaction rate invariably show the famous "S" curve if no seed is added no matter how high the silica in solution. (See Figure VII.)
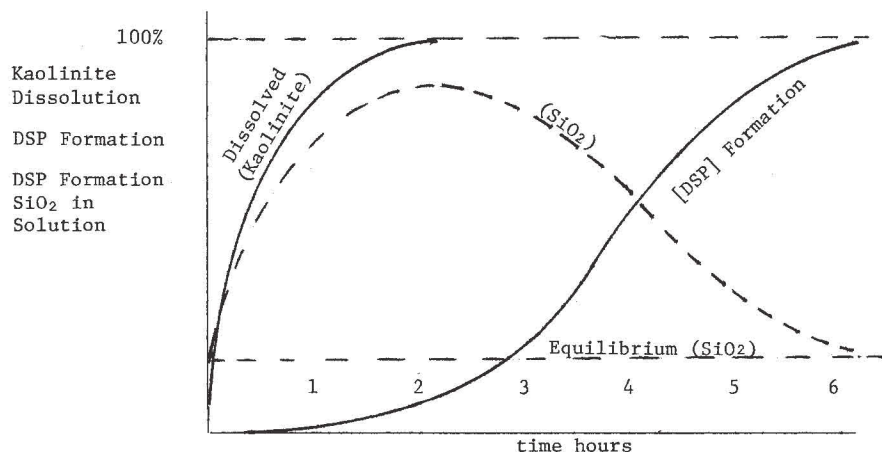

Figure VII
Typical Desilication Reaction Pattern

For this reason addition of DSP seed will improve the overall reaction rate.

High Temperature, Medium to High Caustic Concentration

This range is chosen to extract boehmite and gibbsite and some or all of the alumina bound in the goethite lattice. Gibbsite dissolves so fast in this range, relative to boehmite, that its dissolution rate becomes irrelevant to reactor design. Desilication takes place at a much more rapid rate than under low temperature conditions. Therefore, only boehmite dissolution and the iron transformation will be discussed.

Boehmite Extraction. Boehmite dissolution is described[1,3] as follows:

$$[AlOOH] + 2H_2O + (OH^-) \rightleftarrows (Al(OH)_4^-) \tag{11}$$
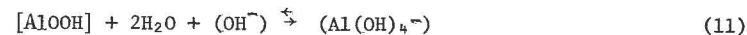
For gibbsite only activity of the caustic and alumina in solution determine the equilibrium. For boehmite also the activity of water must be considered.

Experimental equilibria[1,3,5,10,11] in synthetic liquors have been presented in Figure I.

These are considerably lower for a given temperature and caustic concentration than the ones for gibbsite.

In the process of dissolving a boehmite particle, two steps can be recognized.

a. Dislodging the molecule into the boundary layer.

b. Transporting the molecule through the boundary layer to the surrounding liquor.
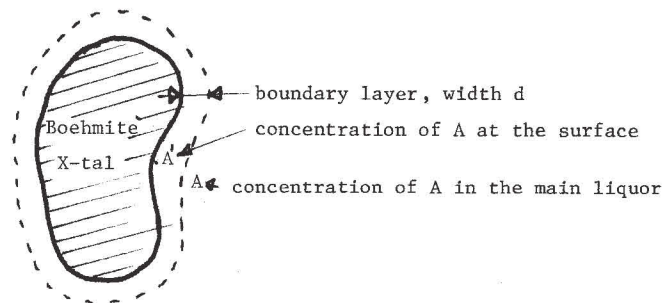
Figure VIII illustrates this.

boundary layer, width d
concentration of A at the surface
concentration of A in the main liquor

Figure VIII
Boehmite Particle in Liquor

The rate in which alumina molecules are entered into the boundary layer

$$\frac{dA}{dt} = f\left(S, (A_\infty - A^1), e^{-\frac{k_r}{T}}\right) \qquad (12)$$

, where k_r = activation energy measure for the reaction and
S = the specific surface area.

and the rate of transport of these molecules through the boundary layer by diffusion

$$\frac{dA}{dt} = f\left(S, \frac{1}{d}, (A^1 - A), e^{-\frac{k_d}{T}}\right) \qquad (13)$$

, where k_d = the activation energy measure for diffusion and
d = thickness of the boundary layer.

will be the same and the slowest of the two will control the overall dissolution rate. At relative low temperatures, Step 'a' is the slowest, and as many researchers[3,4,6] have found, the overall dissolution rate increases exponentially with temperature.

However, at a certain temperature, the rate of Step 'a' catches up with that of the diffusion rate of Step 'b'. Although the diffusion process is also an exponential function of temperature, its "activation" energy is much lower and the temperature effect on its rate is small.

Packter[7] determined the dissolution rates of synthetic boehmite very accurately at temperatures up to 65°C and found an exponential increase with temperatures, i.e., a 5 fold increase for every 15°C.

Korcsmaros[23,25] proposed a rate equation based upon a diffusion theory only, but that is mathematically identical to the chemical reaction rate, by keeping the specific surface area and the diffusion layer thickness (d) constant. This makes his model theoretically little acceptable.

Druzhina[3] found that rate increased relatively slowly above 230°C indicating that the diffusion process in the liquor phase had become the limiting reaction. This phenomena has been schematically presented earlier in Figure II.

This suggests that careful testing should be done to predict the effect of higher temperatures instead of exponentially extrapolating from known lower temperature rates.

The rate will differ strongly with the degree of crystallization or OH bond strength of the boehmite[18,20,23,25]. Average rates at, say 210°C over a 30 minute period, may vary by 50%; at 240°C by 10%; and over 250°C, the rates vary only slightly, indicating that the diffusion transfer rates limit the reaction independent of the type of boehmite.

In conclusion it can be said that unless vigorous agitation, such as by turbulence in a high velocity tube digester[9] is applied to reduce the boundary layer (d) and increase the diffusion rate, temperatures over say 230°C will not increase the dissolution rate of boehmite significantly.

Goethite to Hematite Conversion. The overall conversion can be described as follows:

$$2[FeOOH] \rightleftharpoons [Fe_2O_3] + (H_2O) \qquad (14)$$
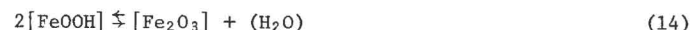
Both goethite and hematite are separate solid phases which means that no equilibrium is reached, but that, depending on the temperature and pressure, only one phase is stable and the reaction will be complete in one direction. Under normal high temperature conditions, hematite is the stable phase.

The reaction mechanism is not exactly known, although various investigators[9,12,13,17] have studied the transformation reaction. Laboratory test work by Reynolds has shown that the conversion does not take place "inside" the goethite crystal and that conversion must take place via the liquid phase. This confirms Brown's[12] conclusions and the reaction can be described therefore as:

$$2[FeOOH] \rightarrow (liquid\ phase) \rightarrow [Fe_2O_3] \qquad (15)$$
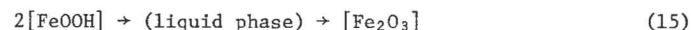
The liquid phase is believed[13] to be sodiumferrite.

The reaction, therefore, should be viewed as two reactions, i.e. the dissolution of goethite and the precipitation of hematite.

The analogy with the behavior of silica should be noted.

The reaction(s) are influenced by the presence of some lime compounds[9,12,13] other compounds[9] and temperature. In the absence of lime compounds, the goethite is not completely[13] destroyed even at 300°C with some bauxites in 30 minutes. This indicates that the lime compounds aid the dissolution of goethite and not the precipitation of hematite.
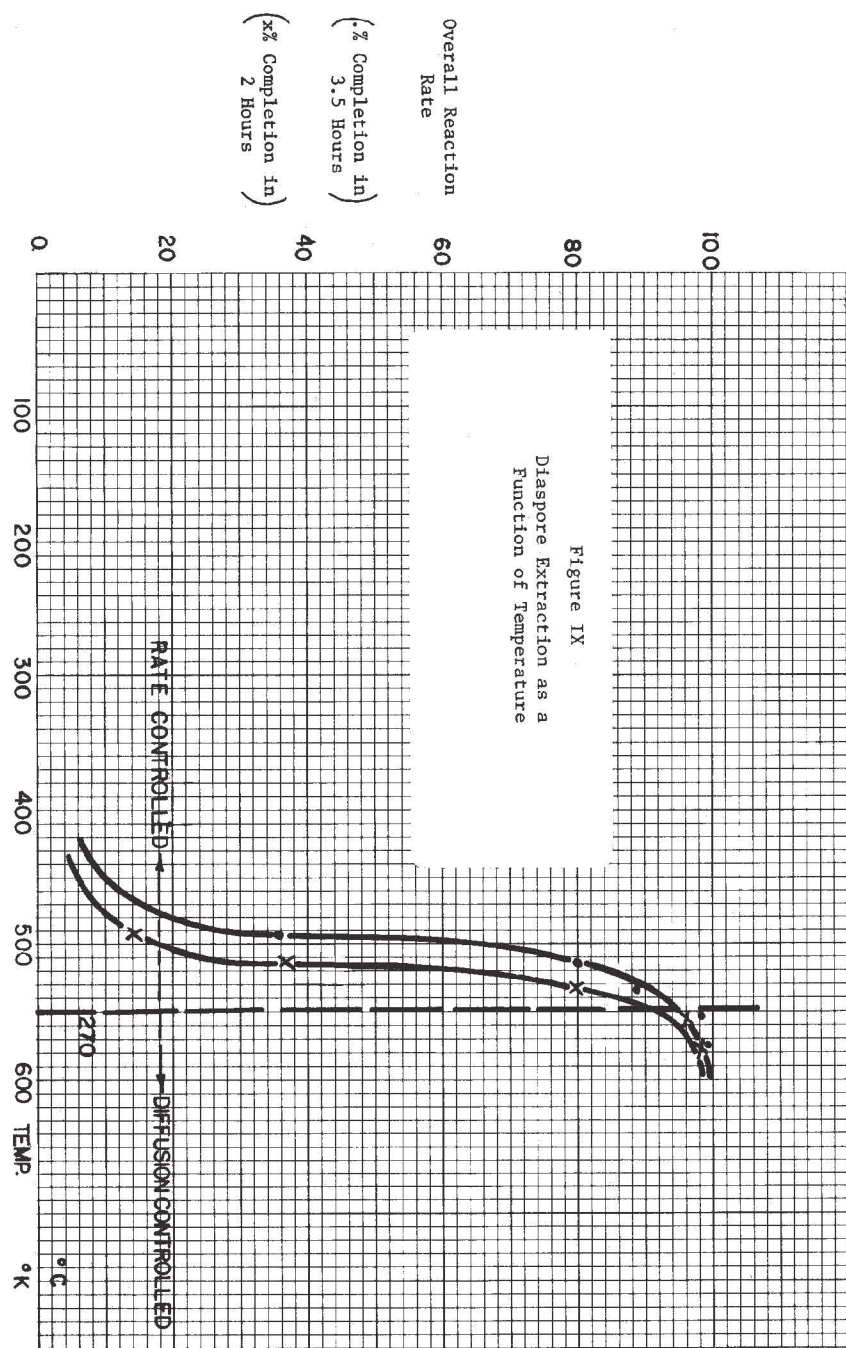
Furthermore, the goethite dissolution would be proportional to the specific surface area available and the precipitation reaction proportional to the hematite specific surface area available.

The need for a hematite seed surface has been clearly demonstrated in several tests done at a Reynolds laboratory[15]. Bauxites with only goethite as the iron phase take much longer to convert.

The initial slow rate of reaction for goethite conversion is caused by the lack of hematite seed. Excessive addition of lime compounds and increased temperatures do not seem to influence this initial rate much.

Goethite is isomorphorus with diaspore and Fe in goethite may be substituted by Al up to a considerable amount[13,24]. The mixed crystals is called alumino-goethite or goethite-diaspore. [Fe(Al)OOH].

The destruction of goethite becomes more difficult[18] with increased Al substitution. Furthermore, the Al to Fe ratio in the alumino-goethite is not uniform for any given bauxite, but may vary from crystal to crystal, or the ratio changes during breakdown. This was demonstrated by several researchers[18] by analysing the Al to Fe ratio in the unconverted portions of alumino-goethite bauxite after several time intervals. The last

Figure IX

Diaspore Extraction as a Function of Temperature

Overall Reaction Rate

(x% Completion in 2 Hours)

(.% Completion in 3.5 Hours)

RATE CONTROLLED →

270

DIFFUSION CONTROLLED

°C

°K

TEMP.

fraction of goethite to be converted contained a higher Al to Fe ratio than the first fraction.

This indicates that in order to take the full advantage of the alumina extraction from the conversion, it is important to complete the conversion.

However, Al can also be substituted for Fe in hematite. The maximum possible substitution[24](12.5 mole %) is lower than in goethite (33 mole %). Reynolds has not found significant substitution of Fe in hematite[28].

High Temperature, High Caustic Concentration

Although the European plants use these conditions to digest boehmite bauxites as well, the reason for mentioning this type of digestion condition is that these are required to digest diaspore.

Diaspore being chemically identical to boehmite should exibit the same A/C equilibrium in liquor. The activation energy (k_r) however is so high that significant rates of dissolution can only be achieved at high temperature, 250°C and higher, high caustic concentration and only in the presence of considerable quantities of lime.

Reynolds studied the extraction of some Chinese diasporic bauxite and determined that extraction can be completed in 2 hours. Also that temperatures over 270°C have little effect on the rate indicating that diffusion processes take over rate control at that temperature.

Figure IX shows results of two series of tests determining overall extraction versus temperature for two different retention times.

It should be mentioned that diaspore digestion could be followed by sweetening by boehmitic bauxite to increase liquor productivity.

Reactor Design

General

The reactor needed to digest the bauxite should theoretically be of a different design for the dissolution reactions only, as compared to the conversion type reactions.

After initial mixing of all ingredients, the dissolution reactions would be completed most readily under plug flow conditions, and agitation would make little difference as long as all solid particles are freely suspended in the liquor, and temperatures do not exceed say 230°C.

For the conversion reactions, a feed-back flow reactor would be desirable to provide seed, and agitation in the reactor may be of benefit.

The residence time distribution of a reactor with a large feed-back flow is similar to that of an ideally mixed reactor.

For the same average residence time $\bar{t}$ the Residence Time Distribution (RTD) can be compared graphically as in Figure X.
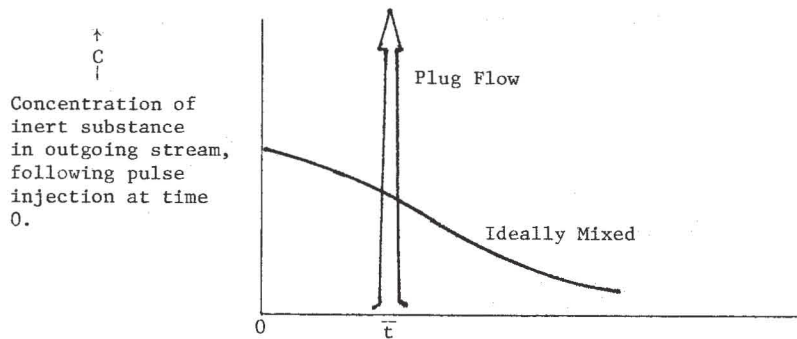
Figure X

Schematic Representation of RTD

C↑ — Concentration of inert substance in outgoing stream, following pulse injection at time 0.

Plug Flow

Ideally Mixed

0 $\bar{t}$

To accomplish both dissolution and conversion reactions, a reactor with an intermediate RTD should be desirable, combining sufficiently long average residence time $\bar{t}$ with reasonable precipitous RTD but allowing for some back mixing for seeding.

Known digestion reactor designs are as follows:

1. Small number of large vertical vessels in series with L/D >6 without agitation.
2. Small number of large vertical vessels in series with L/D >6 with large number of agitated compartments.
3. Large number of small vertical vessels in series with L/D >6 without agitation.
4. Large number of small vessels in series with low L/D with agitation.
5. Large number of small vessels in series with low L/D without agitation (including horizontal vessels with a slow moving rake).
6. Tube digester.

These can be summarized into three basic types:

a. Plug flow reactor.
b. The series of unstirred partially back mixing reactors.
c. The series of fully mixed reactors.

There were other criteria for reactor design such as scaling and sands accumulation. The development of digester vessels in the USA started with small horizontal vessels with slow paddle type rakes that aided sands transport and reduced scale formation. After the technology of predesilication was developed it was found that scaling in digestion reduced considerably. With the later developed vertical unstirred vessels the problem of sands was eliminated without the need of a rake. Thus scaling rate and sands accumulation are no longer criteria for digester vessel design.

The Plug Flow Reactor (Tube Digester)

This reactor will behave exactly as the bomb digest results will predict. Both alumina extraction and conversion reactions will require the same time in the plug flow reactor as in the laboratory bomb for the

same percent of completion, providing the temperature is kept below the value where the reaction is rate-controlled.

At higher temperatures the high velocity tube digester will show shorter required time [2,8] for complete extraction than a gently stirred or rotating laboratory bomb. Without added residence time at final temperature, it may give relatively low extraction of coarse crystalline boehmite and diaspore. High goethitic bauxites (Jamaican) digested in a tube digester would result in poor settling mud because goethite will almost not convert to hematite. Very little quartz dissolves in a tube digester due to its short residence time. [2]

The Unstirred Partially Back Mixing Reactor

The RTD in unmixed vertical vessels is very difficult to determine theoretically. A frequently used model for the RTD in such a vessel is the diffusion model [19] The model uses a parameter D called axial dispersion coefficient (m^2/sec) indicating the degree of back mixing in the vessel, similar to the diffusion coefficient in Fick's diffusion rate law.

This diffusion coefficient is used in a dimensionless group $\left(\frac{D}{uL}\right)$ where u = the average axial velocity in the vessel (m/sec) and L the length (m). $\left(\frac{D}{uL}\right)$ is called the dispersion number and for the same flow and volume $\left(\frac{D}{uL}\right)$ is inversely proportional to the square of L.

The RTD is best described by the variance σ^2 since this property is additive for vessels in series, thus:

$$\sigma^2 = \sum_{i}^{n} \sigma^2_i \quad \text{and} \quad \bar{t} = \sum_{i}^{n} \bar{t}_i \tag{16}$$

, where σ^2_i = variance for the individual vessels and $\bar{t}_i$ = the average residence time in the individual vessels.

It can be shown [19] that for the diffusion model:

$$\sigma^2_\theta = \frac{\sigma^2}{\bar{t}^2} = 2\left(\frac{D}{uL}\right) - 2\left(\frac{D}{uL}\right)^2 (1 - e^{-uL/D}) \tag{17}$$

σ^2 can be determined by experiment only. Using the measurement of the concentration of an inert substance (pulse injected in incoming stream) in the outgoing stream on a regular time interval (say 5 minutes) σ^2 can be approximated as:

$$\sigma^2 = \frac{\sum\limits_{o}^{n} t_i^2 \, C_i \, \Delta t_i}{\sum\limits_{o}^{n} C_i \, \Delta t_i} - \bar{t}^2 \tag{18}$$

Once σ^2 is determined this way, $\left(\frac{D}{uL}\right)$ can be calculated by trial and error method from equation (17).

For the simple low order dissolution reactions[22] with a reaction rate K_τ, it can further be shown[19] that the volume (V) of a vessel with diffusion number $\left(\frac{D}{uL}\right)$ compares approximately with the volume (V_p) of a plug flow vessel, for the same average of completion of the reaction as follows:

$$\frac{V}{V_p} = \frac{\bar{t}}{\bar{t}_p} = 1 + K_\tau \left(\frac{D}{uL}\right) \tag{19}$$

As expected, V becomes equal to V_p when $\left(\frac{D}{uL}\right)$ becomes very small (tube digester).

The Series of Fully Mixed Reactors

The RTD of an ideally mixed vessel or a series of ideally mixed vessels can be determined quite accurately from mathematical equations[19,4,21].

The variance of a series of (N) ideally mixed vessels is:

$$\sigma^2 = N \ \bar{t}_i^2 \text{ or for equal size vessels and since, } \bar{t} = N \times \bar{t}_i$$

$$\sigma^2 = \frac{\bar{t}^2}{N} \tag{20}$$

It can also be shown[19] that for a low order reaction, such as boehmite dissolution, with reaction rate (K_τ), we can relate the necessary average volume (V_N) or residence time ($\bar{t}_N$) to the plug flow volume (V_p) or residence time ($\bar{t}_p$) for an identical degree of completion is:

$$\frac{V_N}{V_p} = \frac{\bar{t}_N}{\bar{t}_p} = 1 + \frac{K_\tau}{N} \tag{21}$$

The simple mathematical relation will predict actual digester behavior from bomb analyses fairly accurately without the need for measurement of actual RTD's.

Comparison of Reactors for Dissolution Reactions

Comparing formulas (19) and (21) gives the relation between one unstirred reactor and mixed flow reactors in series.

V_N equals V when:

$$\frac{K_\tau}{N} = K_\tau \left(\frac{D}{uL}\right)$$

$$\text{or } N = \left(\frac{uL}{D}\right) \tag{22}$$

So far, it has been concluded that, for say boehmite extraction, both the unstirred partial back mixing reactor and the series of ideal mixed reactors need more average residence time than the plug flow reactor (bomb) for the same degree of completion, and that a series of N mixed vessels will give the same results as a similar total, but unstirred, volume for certain values of N depending on the geometry of the unstirred reactor.

Example Digester Comparison. Consider one vessel with $\bar{t}$ = 15 minutes continually fed, while a tracer or other pulse is added at time 0.

Results taken at 5 minute time intervals are as follows:

Time t_i	C_i (concentration of tracer)
0	0
5	3
10	5
15	5
20	4
25	2
30	1
35	0

$\Sigma C_i = 20$

$\Sigma t_i C_i = 5 \times 3 + 10 \times 5 + \ldots \ 30 \times 1 = 300$ min.

$\Sigma t_i^2 C_i = 25 \times 3 + 100 \times 5 \ \ . \ . \ 900 \times 1 = 5440$ min.^{2}

$$\sigma^2 = \frac{5450}{20} - \frac{(300)^2}{(20)^2} = 47.5 \text{ minutes}^2$$

$$\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} = \frac{47.5}{(15)^2} = 0.211$$

$$\sigma_\theta^2 = 0.211 = 2\left(\frac{D}{uL}\right) - 2\left(\frac{D}{uL}\right)^2 (1 - e^{-uL/D})$$

Approximate $\left(\frac{D}{uL}\right)$ by ignoring the second term $\rightarrow \left(\frac{D}{uL}\right) \cong 0.106$

Trial and error using second term $\rightarrow \left(\frac{D}{uL}\right) = .120$

How does this vessel compare with a series of mixed reactors with a total average $\bar{t}$ = 15.

From (22) $N = \left(\frac{uL}{D}\right) = \frac{1}{.120} \cong 8$

In words, if the unstirred reactor were divided into 8 ideal mixed compartments, the RTD and boehmite extraction would be about the same.

Comparison of Reactors for Conversions Reactions

The conversion reactions (desilication, goethite to hematite, gibbsite to boehmite, etc.) are all affected by initial seed surface area of the solid product as mentioned before.

Under plug flow conditions (laboratory bomb), the initial precipitation reaction rate is proportional to the seed surface, or:

$$\frac{dP_p}{dt} = \alpha \cdot P_p^{\frac{2}{3}} \qquad (23)$$

,where P_p is the amount of product (plug flow condition), α is a constant (called "surface independent rate"), t is the unit of time.

Integration gives:

$$P_p^{\frac{1}{3}} = \frac{1}{3}\alpha t + P_o^{\frac{1}{3}} \qquad (24)$$

Where P_o is the initial effective quantity of product (seed).

Equation (24) describes the initial hematite formation at high temperature digestion, boehmite precipitation, or DSP formation, all taking place in the laboratory bomb or plug flow reactor.

Under partially mixed flow conditions (one partially mixed, constantly fed, and discharging vessel) a small quantity of reacting mass can imaginably be isolated, in which we can assume laboratory bomb conditions.
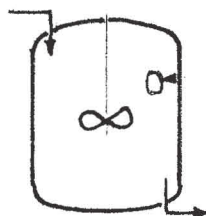

Imaginary Small Laboratory
Bomb Quantity

Figure XI

Within this quantity, equation (24) will describe the initial formation of product.

However, when an ideal mixed vessel is sampled at any particular point, the concentration of product (P) in the sample equals the concentration in the outgoing stream (P_1).

Therefore, the feed to the vessel is immediately exposed to the seed surface equivalent to that of P_1 in the outgoing stream and the rate of formation of P is linear with time.

or, $\frac{dP}{dt} = \alpha \cdot P_1^{\frac{2}{3}}$ and integrating gives

$$P = P_1^{\frac{2}{3}} \alpha t + P_o \qquad (25)$$

,where P_o is the effective seed quantity in the feed to the vessel.

The average residence time of the first vessel is t_1, so for $t = t_1$, $P = P_1$, it follows that:

$$P_1 = P_o + P_1^{\frac{2}{3}} \alpha t_1 \qquad (26)$$

This equation (26) is solved by trial and error by entering an arbitrary value of P_1 in equation (25) resulting in a fictitious value for t_1, etc.

To compare the overall rates obtained in the laboratory bomb with that of one ideally mixed vessel using the same average residence time, or comparing formulas (24) and (26) it can be said that: if αt becomes very large compared to P_o or $\alpha t >> P_o$ the formulas can be approximated by:

$$P_p^{\frac{1}{3}} \cong \frac{1}{3}\alpha t \text{ and}$$

$$P_1 \cong P_1^{\frac{2}{3}} \alpha t \text{ or } P_1^{\frac{1}{3}} \cong \alpha t$$

Or dividing these approximations gives:

$$\left(\frac{P_1}{P_p}\right)^{\frac{1}{3}} \cong 3 \quad \text{or} \quad \frac{P_1}{P_p} \cong 27$$

This means that the maximum amount of product from a mixed flow reactor can be as high as 27 times that from the plug flow reactor or lab bomb for the same average time when seed surface is the only controlling factor.

When the opposite is true or $P_o >> \alpha t$ it can be seen from equations (24) and (25) that:

$$P_p^{\frac{1}{3}} \cong P_o^{\frac{1}{3}} \text{ and } P_1 \cong P_o$$

$$\text{or } \frac{P_1}{P_p} \cong 1$$

In other words, there will not be much difference between the amount of product from the mixed reactor as compared with that from the laboratory bomb.

Analyzing the individual effects of P_o, α and t it can be said that:

a. If the initial product P_o (and therefore the initial seed surface area) is small, the mixed reactor will produce relatively much more than the plug flow reactor. While for large values of P_o the production will be about the same.

b. If the reaction rate (independent of seed surface), which is represented in α, is very small, there will be little difference between laboratory bomb production and the mixed vessel. And also if α is very high then the mixed vessel will produce relatively more.

c. If the time t is long, the mixed vessel will produce relatively more. This means that one vessel with an average residence time long enough, but not exceeding the period that the reaction is seed surface area controlled, will produce more product than two or more mixed vessels in series with the same total residence time. This is demonstrated in the later example. Commensurate with this, it follows that for very short times t, there is very little difference between mixed vessel and the plug flow or laboratory bomb. But this can also be deduced from the fact that a plug flow reactor can be simulated by an infinite series of mixed vessels.

Apparently $1 < \dfrac{P_1}{P_p} < 27$ and what $\dfrac{P_1}{P_p}$ will be depends on α t and P_o. To get a feel for what will happen in a mixed vessel α must be determined from the laboratory bomb test and P_o analyzed or also calculated from the bomb test.

To determine quickly an order of magnitude of effect, $\dfrac{P_1}{P_p}$ has been calculated for a discrete series of ratios of $\dfrac{P_o^{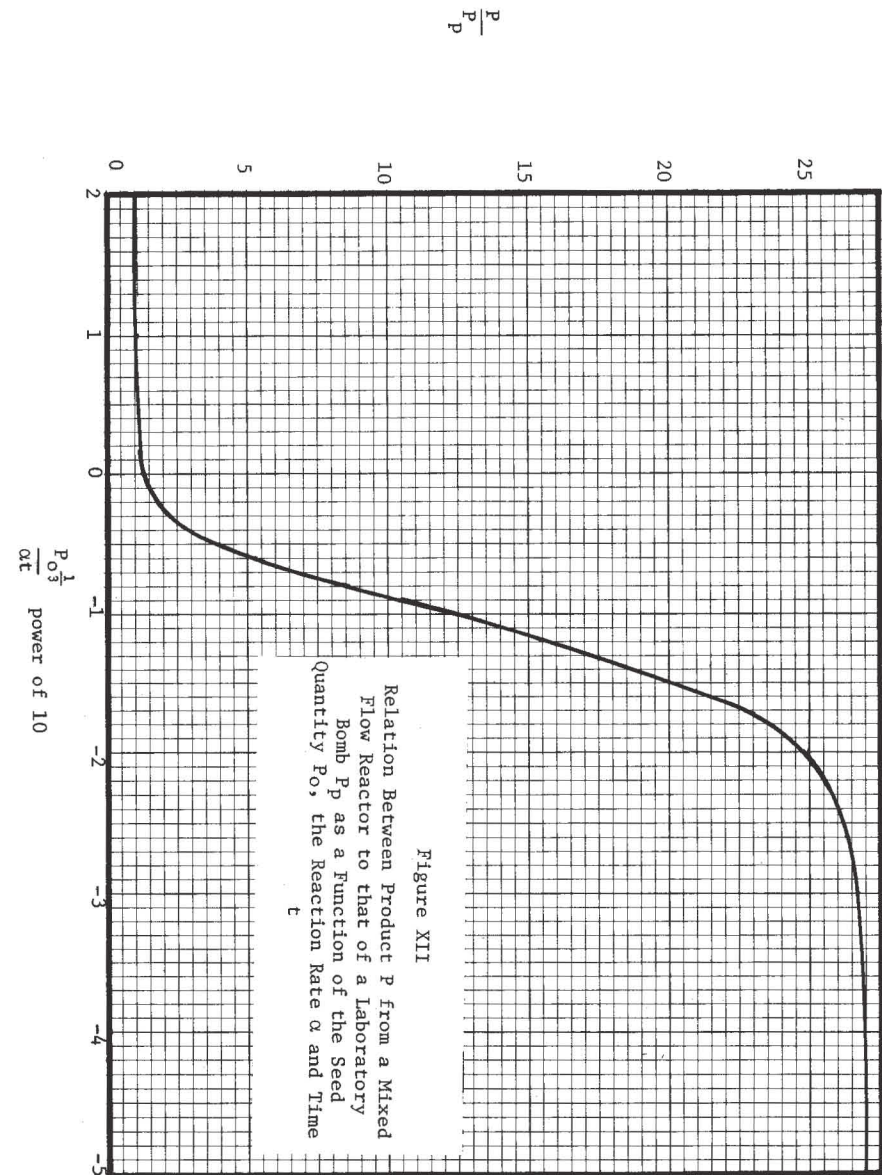\frac{1}{3}}}{\alpha t}$ and plotted in Figure XII. This plot shows that a significant difference between P_1 and P_p occurs only if $\dfrac{P_o^{\frac{1}{3}}}{\alpha t} < 1$.
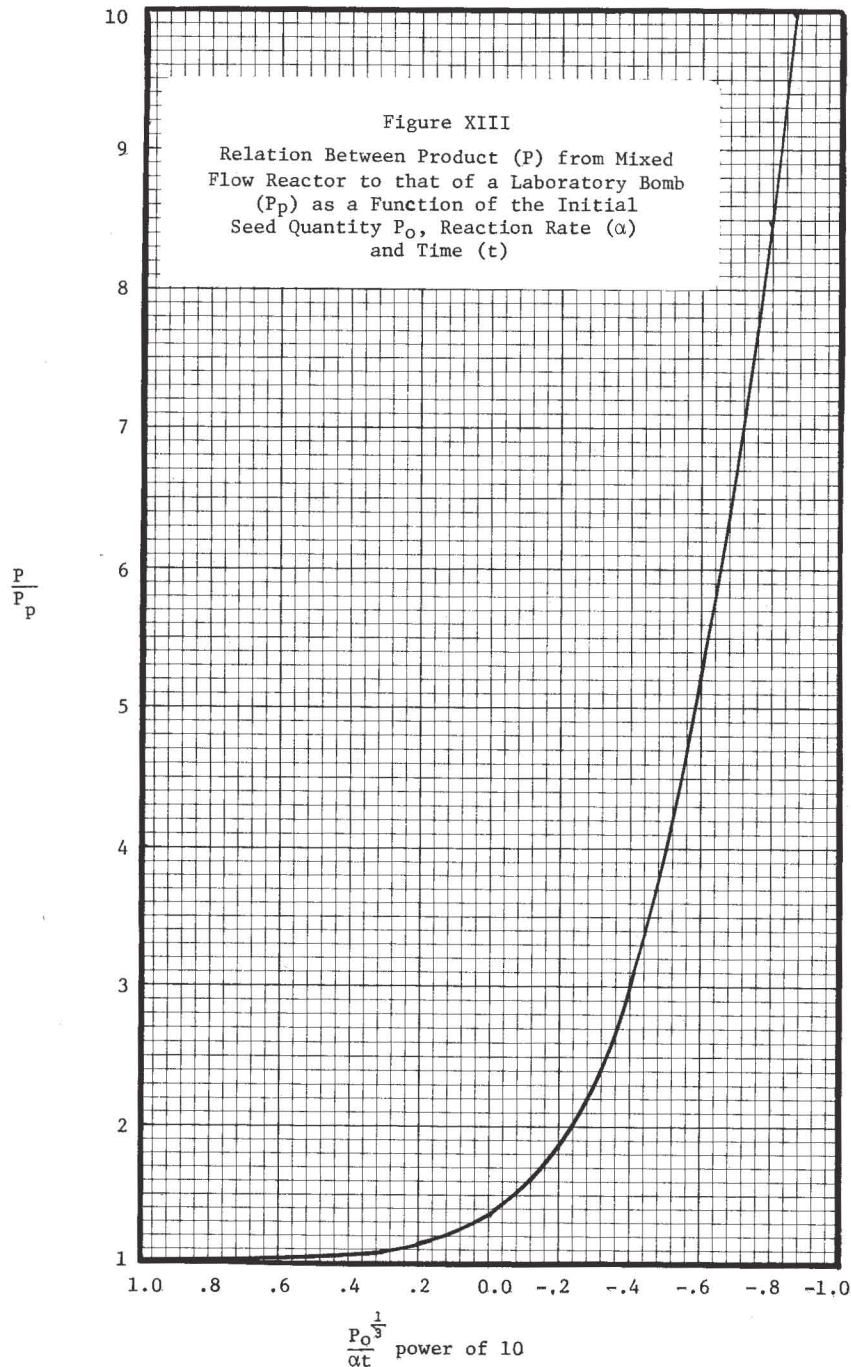
Note: $\dfrac{P_o^{\frac{1}{3}}}{\alpha t}$ was chosen because it is dimensionless.

The curve (Figure XII) does not have enough resolution to determine $\dfrac{P_1}{P_p}$ to more than one significant figure, in the area close to $\dfrac{P_o^{\frac{1}{3}}}{\alpha t} = 1$. For this reason, Figure XIII has been added for better resolution when $10 < \dfrac{P_o^{\frac{1}{3}}}{\alpha t} < 10^{-1}$.

For a group of N mixed vessels, in series, the calculations need to be repeated for every stage. Assuming the product concentration in the discharge of each stage as P_1, P_2, P_3......P_n and, realizing that the product concentration in the discharge of one stage is also the starting concentration for the following stage, it can be seen that:

$$P_n = P_o + P_1^{\frac{2}{3}}\ \alpha t_1 + P_2^{\frac{2}{3}}\ \alpha t_2 + \ .... P_n^{\frac{2}{3}} \alpha t_n \qquad (27)$$

Figure XII

Relation Between Product P from a Mixed Flow Reactor to that of a Laboratory Bomb P_p as a Function of the Seed Quantity P_o, the Reaction Rate α and Time t

Figure XIII

Relation Between Product (P) from Mixed Flow Reactor to that of a Laboratory Bomb (P_p) as a Function of the Initial Seed Quantity P_o, Reaction Rate (α) and Time (t)

(y-axis: $\frac{P}{P_p}$)

(x-axis: $\frac{P_o^{\frac{1}{3}}}{\alpha t}$ power of 10)

To compare P_n with P_p for the same overall time as given in $P_p^{\frac{1}{3}} = \frac{1}{3} \times \alpha \times \Sigma t + P_o^{\frac{1}{3}}$ the curves on Figure XII or XIII can be used instead of a lengthy step-by-step calculation.

For the unstirred reactor still another step is necessary to compare laboratory (plug flow) with actual product formation.

The RTD of the unstirred reactor is to be first determined in terms of the variance σ^2. Using equation (17) the dispersion number $\left(\frac{D}{uL}\right)$ is calculated from σ^2. The number of equal steps N of ideal mixing that will give the same RTD, using the same overall volume and residence time, is then determined using equation (22).

The product concentration out of this unstirred vessel is then calculated using equation (27) and, since $t_1 = t_2 = t_3 .... = t_n$, the procedure for the series of mixed vessels is repeated easily for each step using the curves on Figures XII or XIII.

For more than one unstirred vessel in series this process of calculation is to be followed for each vessel.

Example Comparison and Methodology. Consider a laboratory bomb (plug flow) in which a seed surface controlled reaction takes place. The initial product P_o = .10 (arbitrary units). After 5 minutes of holding at temperature the product is analysed as P_p = .20.

Equation (24) gives $(.2)^{\frac{1}{3}} = \frac{1}{3} \times \alpha \times 5 + (.1)^{\frac{1}{3}}$ or $\alpha = 0.073$ and $\frac{P_o^{\frac{1}{3}}}{\alpha t} = 1.25 = 10^{.1}$

A fully mixed reactor with an average residence time of 5 minutes fed continuously with the same material as was put in the laboratory bomb would produce P_5.

According to Figure XIII, for $\frac{P_o^{\frac{1}{3}}}{\alpha t} = 10^{.1}$

$\frac{P_5}{P_p} = 1.25$ or $P_5 = 1.25 \times .2 = .25$

Were the reaction in the bomb to continue to 10 minutes, using the same α = .073 the product would analyze as P_p = .36.

A larger mixed reactor with 10 minutes average residence time would produce P_{10}.

From Figure XIII, for $\frac{P_o^{\frac{1}{3}}}{\alpha t} = .63 = 10^{-.2}$

$\frac{P_{10}}{P_p} = 1.83$ or $P_{10} = 1.83 \times .36 = .66$

Similarly it can be shown that two mixed vessels in series each with 5 minutes residence time would produce $P_{5 + 5}$ = .48 (use P_5 for P_0 in the second vessel calculation).

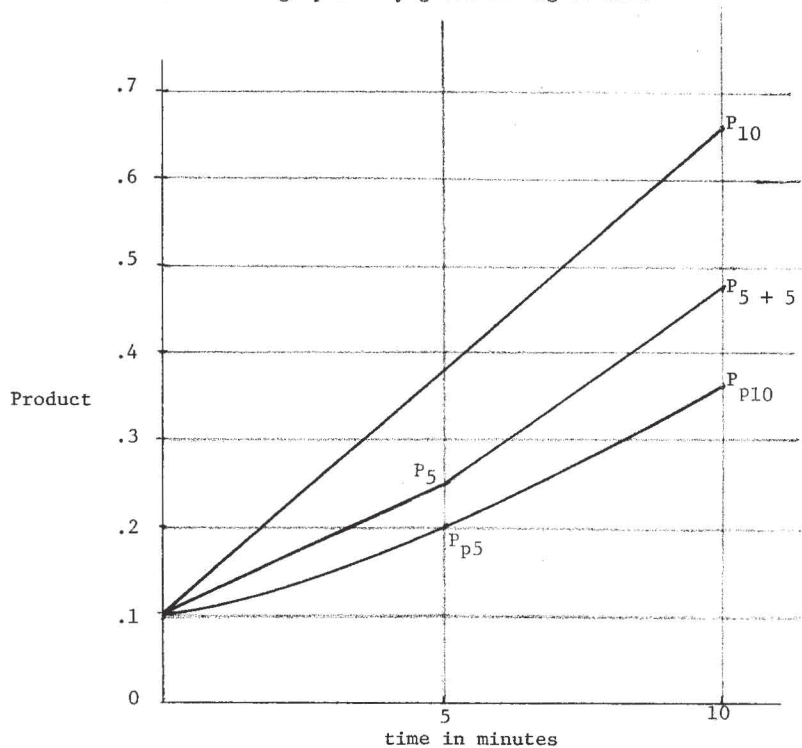These results are graphically given in Figure XIV.

Figure XIV

Graphical Comparison of Laboratory Bomb

and Mixed Flow Reactor Results

Case Studies

Determination of the Size of a Predesilication Reactor Vessel

Assume that the bauxite for this particular case needs to be predesilicated prior to digestion.

The bauxite silica is 2.21%.

The laboratory has determined the desilication rate in a laboratory bomb held at 99°C for 12 hours and sampled at irregular intervals. Desilication product is analysed by determining the Na_2CO_3 to SiO_2 ratio in the washed residue. Results are:

time, hours	Na_2CO_3/SiO_2
.5	.02
1	.03
3	.22
4	.29
12	.41

The plotted data in Figure XV indicate that the reaction stopped to be seed surface controlled after about 3 hours.

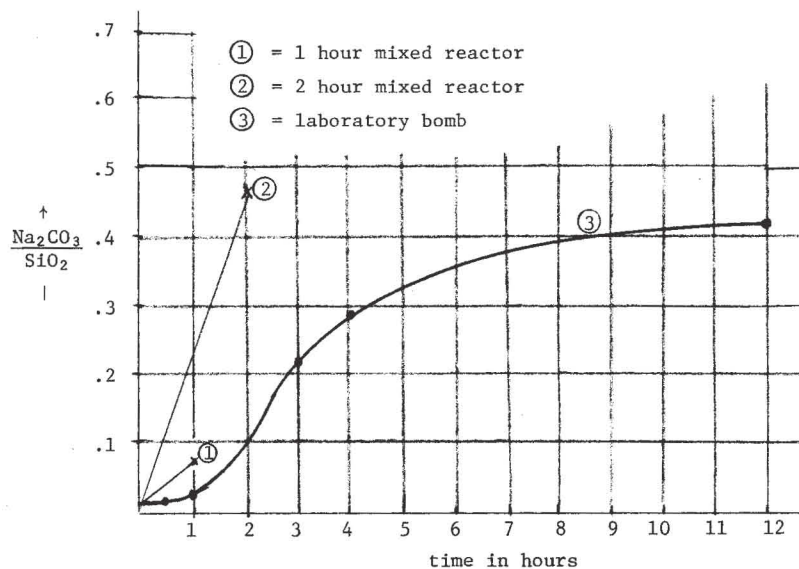Equation (24) applied to the data for .5, 1, and 3 hours gives:

Figure XV

Desilication in the Laboratory and What it Would Be in a Mixed Reactor

$$(.02)^{\frac{1}{3}} = \frac{.5 \times \alpha}{3} + \left(P_0\right)^{\frac{1}{3}}$$

$$(.03)^{\frac{1}{3}} = \frac{1 \times \alpha}{3} + \left(P_0\right)^{\frac{1}{3}}$$

$$(.22)^{\frac{1}{3}} = \frac{3 \times \alpha}{3} + \left(P_0\right)^{\frac{1}{3}}$$

From these three equations, an average $\left(P_0^{\frac{1}{3}}\right)$ of .20 is found indicating that the equivalent initial DSP was P_0 = .01 (as Na_2CO_3/SiO_2). The average

for $\alpha = .38$.

Assume a fully mixed reactor was used in the first hour:

$$\frac{P_o^{\frac{1}{3}}}{1 \times \alpha} = \frac{.20}{.38} = .53 = 10^{-.28}$$

Figure XIII shows that $\frac{P_1}{P_p} = 2.2$ or $P_1 = 2.2 \times .03 = .07$.

A fully mixed vessel with two hour residence time would have resulted in P_2.

The laboratory bomb would have shown .09 (calculated using equation (24)), with $P_o^{\frac{1}{3}} = .2$ and $\alpha = .38$.

$$\frac{P_o^{\frac{1}{3}}}{\alpha t} = \frac{.2}{.38 \times 2} = .26 = 10^{-.6}$$

from Figure XIII follows $\frac{P_2}{P_p} = 5.2$ or $P_2 = 5.2 \times .09 = .47$.

A three hour vessel calculates $P_3 = 1.40$, but obviously this is impossible (maximum Na_2CO_3/SiO_2 around 1.1). Furthermore, the reaction stopped being seed surface controlled at about .3.

Therefore the first desilicator should have a residence time of say two hours and be fully mixed.

Determine if Boehmite Formation will be Significant at Low or Intermediate Temperature Digestion of Gibbsitic Bauxites

A particular Australian bauxite was tested in the laboratory bomb. Charged with liquor to achieve a .730 A/C ratio it was held for an extensive time at design temperature. Boehmite analyses by TGA were done at irregular intervals as follows:

time,hours	Boehmite % of Total Alumina
1	.3
2	.6
4	1.1
16	9.9
24	16.2

Applying equation (24) for the first two data pairs the effective starting boehmite P_o and the rate constant α were determined as:

$P_o = .13$ and $\alpha = .51$

For a digester vessel of one hour average time with a large degree of backmixing, Figure XIII indicates that for:

$$\frac{P_o^{\frac{1}{3}}}{\alpha t} = \frac{.50}{.51 \times 1} = .98 = 10^{-0.01}$$

that $\frac{P_1}{P_p} = 1.33$ or $P_1 = 1.33 \times .3 = .4\%$ boehmite

This is not very significant.

The test was repeated for one hour and a charge A/C ratio of .745.

The bomb mud analyzed at 5.9% boehmite (of total alumina).

Equation (24), $(5.9)^{\frac{1}{3}} = \frac{\alpha}{3} + .50$ gives $\alpha = 3.92$

A one hour digester vessel as before, for $\frac{P_o^{\frac{1}{3}}}{\alpha t} = \frac{.5}{3.92} = .13 = 10^{-.9}$ would, according to Figure XIII give $\frac{P_1}{P_p} \cong 11$ or $P_1 = 5.9 \times 11 = 65\%$ boehmite.

Thus, the charge of only .015 A/C over .730 could lead to disastrous results.

Conversion of Goethite to Hematite In a Series of Three Partially Backmixing Reactors as Compared to in a Laboratory Bomb[15]

The bauxite tested in the laboratory and in the plant contained iron of which 33% was hematite(H) and 67% goethite(G). Temperature, lime charge, liquor, and bauxite charge were kept identical.

The laboratory bomb experiment showed the following G-H conversion, also plotted in Figure XVI.

time,minutes	% Converted to Hematite
30	14
45	32
90	83
120	89

From these values the effective starting H seed quantity and plug flow reaction rate α were determined. The 30 and 45 values were used only assuming that this reaction up to 45 minutes was still seed surface controlled. Applying the data pair to equation (24): $P_p^{\frac{1}{3}} = \frac{\alpha t}{3} + P_o^{\frac{1}{3}}$ results in an effective starting seed quantity P_o of only .7% and $\alpha = .15$.

The real digesters have a retention time of 15 minutes. Assuming fully mixed condition, it can be calculated that for:

$$\frac{P_o^{\frac{1}{3}}\text{effective}}{\alpha t} = \frac{.89}{.15 \times 15} = .40 = 10^{-0.4}$$

,according to Figure XIII the ratio of the products converted H concentration out of the digestor (P_{15}) over the bomb's converted H concentration for the same 15 minutes P_{p15}:

$$\frac{P_{15}}{P_{p15}} = 3.0$$

P_{p15} using the effective seed quantity P_o is 4.4%.

The predicted value out of the first digester therefore becomes:

$$3.0 \times 4.4 = 13.2\%$$

Using this as the start for the second vessel it can be calculated that for:

$$\frac{P_o^{\frac{1}{3}}}{\alpha t} = \frac{1.64}{.15 \times 15} = .73 = 10^{-.14}$$

,the ratio of product H concentration out of the second vessel $\left(P_{30}\right)$ over a 15 minutes bomb H concentration $\left(P_{p30}\right)$

$$\frac{P_{30}}{P_{p30}} = 1.6$$

P_{p30} from equation (24) using $P_o = 13.2$ calculates to be 30.1 or $P_{30} = 1.6 \times 30.1 = 48.2$.

Using this as the start for the third vessel it can be calculated that the concentration out of the third vessel would be $P_{45} = 95.6\%$.

During the plant tests all three vessels were sampled and the mud analysed for converted hematite.

The results are plotted in Figure XVI.

As can be seen the calculated predicted values are higher than the actual plant results. However, the real vessels are only partially backmixing reactors. A more rigorous calculation using the RTD of the actual vessels may give closer predictions.

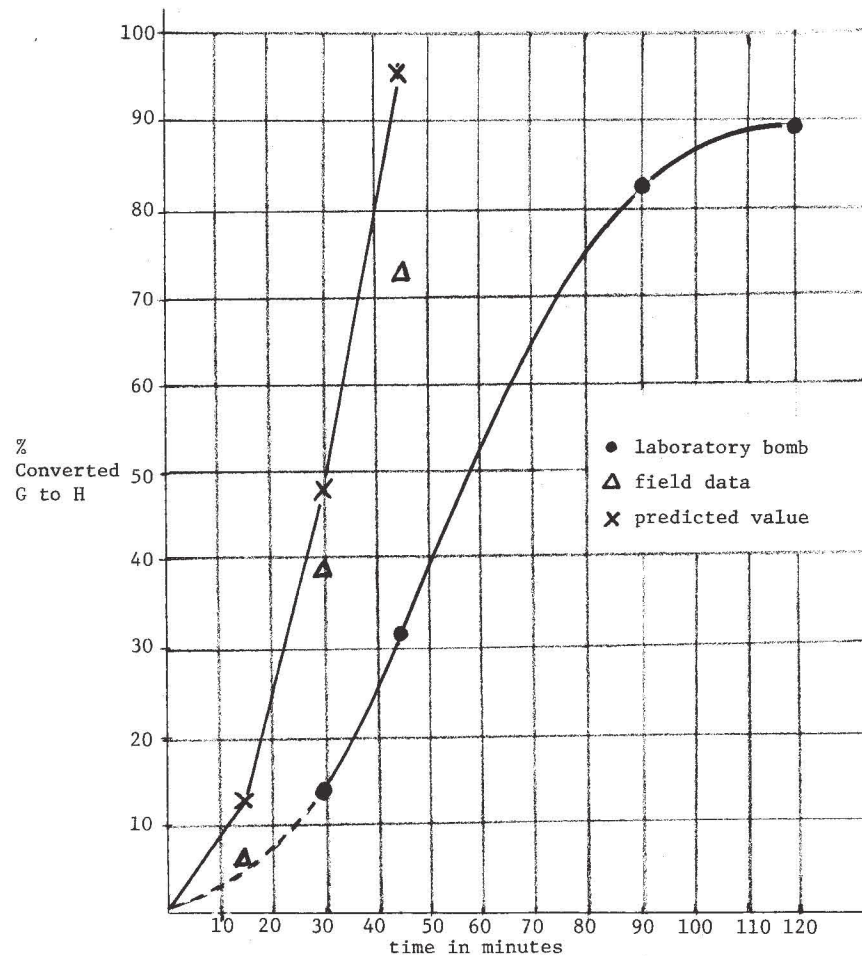Note that the importance of backmixing is most pronounced in the first vessel.

Figure XVI

Conversion of Goethite to Hematite in A
Laboratory Bomb as Compared to Predicted
and Actual Field Results

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