

**PHYSICAL CHEMISTRY CONSIDERATIONS
IN
ALUMINUM HYDROXIDE PRECIPITATION**

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A B S T R A C T

Importance of physical chemistry principles in the precipitation of aluminum hydroxide in a Bayer alumina plant is discussed. Specifically, the roles of solution chemistry and kinetics of precipitation reaction in developing the criteria for precipitation circuit operation are delineated. Application of these criteria to develop strategies to maximize precipitation yield in both batch and continuous precipitation circuits is also addressed.

INTRODUCTION

Crystallization of aluminum hydroxide, $\text{Al}(\text{OH})_3$, with required physical properties and chemical purity, from supersaturated alkaline aqueous solution is accomplished in the precipitation facility in a Bayer plant. In order to meet the particle size distribution requirement - a major physical property specification - the precipitation facility includes, in addition to the crystallization operation, a size classification operation, which yields a clear aluminate ion depleted solution - spent liquor - for recycle to the grinding and extraction facilities. Figure 1 is a schematic overview of the unit operations in the precipitation facility.

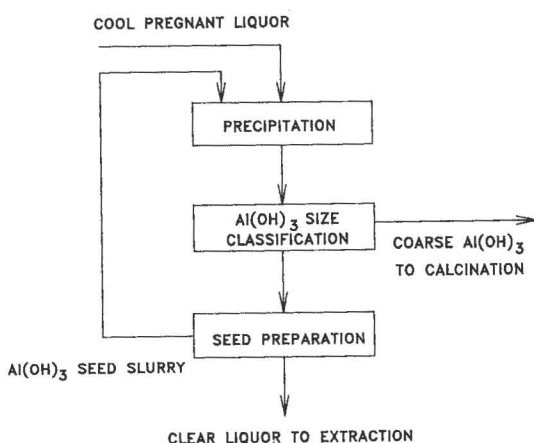


Figure 1: Precipitation Flow Diagram.

The operation of the precipitation facility is based on the understanding and application of the physical chemistry of the Bayer plant solution. The solution chemistry aspects of the chemical reactions under consideration as well as the kinetics of the precipitation chemistry are reviewed. The effect of precipitation temperature on precipitation rate presents a conflicting direction by its effect on equilibrium aluminum hydroxide solubility and specific reaction rate constant. The methods by which this dichotomy can be used to achieve high precipitation reaction efficiency are

examined. Also discussed is the application of these principles in developing strategies to maximize precipitation yield in both batch and continuous precipitation circuits.

SOLUTION CHEMISTRY

The alkaline aqueous solution used for precipitation of aluminum hydroxide, $\text{Al}(\text{OH})_3$, in an ideal case, can be presumed to contain only aluminum, hydroxyl and hydronium ions. Precipitation of $\text{Al}(\text{OH})_3$ from such a solution can occur by either of the following two acid-base reactions:



The amphoteric nature of $\text{Al}(\text{OH})_3$ is exhibited by the above reactions, where it can act as a proton donor or acceptor. The Bayer process solutions are alkaline, and therefore, reaction (1) is the reaction responsible for $\text{Al}(\text{OH})_3$ precipitation.

It should be noted that the ionic specie $\text{Al}(\text{OH})_4^-$ exists in alkaline solution. The existence of this specie has been confirmed by several investigators^(1,2,3). Other aluminum hydroxy complexes, as well as aluminum ion, are feasible in an aqueous solution and include $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})^{+2}$, and Al^{+3} . It is possible to construct an ionic specie equilibrium concentration distribution diagram with the help of available thermodynamic data. Figure 2, constructed by Baes and Mesmer⁽⁴⁾ for solutions saturated with gibbsite, indicates that $\text{Al}(\text{OH})_4^-$ is the predominant aluminum specie present in alkaline solution while the other hydroxy complexes are also present in very small concentrations.

Thus far, the discussion has been treated as if the Bayer plant solutions contained only aluminum hydroxy ions; but the solution contains numerous other ionic species. The other significant ionic species are sodium, carbonate, hydroxide, chloride, sulfate, phosphate, and fluoride. Furthermore, ions of calcium, iron, and silicon and ionized

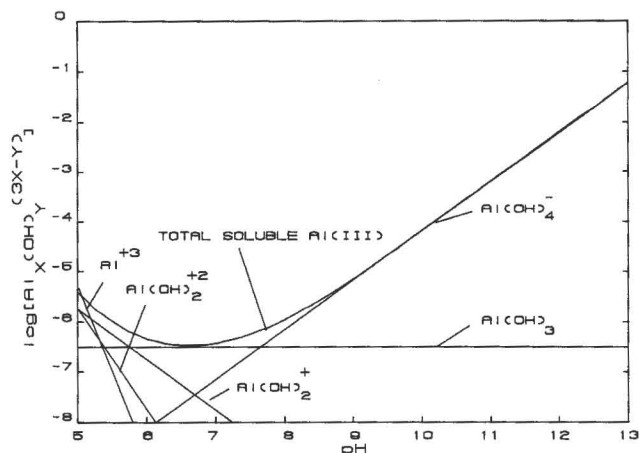


Figure 2: Distribution of Hydrolysis Products at 25 °C in Solution Saturated with Al(OH)₃, Gibbsite⁽⁴⁾

sodium salts of organic compounds are also present in solution along with traces of other compounds. The concentrations of these ionic species and other compounds in Bayer liquor differ significantly among Bayer plants. Most significantly, the range of organic compounds and their concentrations is different depending on the bauxite source. The presence of these constituents in the Bayer plant solutions affects the solution properties, and a strict thermodynamic treatment becomes difficult. In light of this fact, certain liberties have been taken in the published literature with regard to the nature of the aluminate ion in solution and also the ionic species of the sulfate and carbonate. However, these assumptions-approximations have been used to arrive at values of solution properties that are sufficiently accurate for engineering studies.

The solution property that is of importance in understanding the aluminum hydroxide precipitation phenomenon in the laboratory as well as in the plant environment is equilibrium aluminum hydroxide solubility. Dewey and McCoy^(5,6) have reported their successful efforts in determining correlation to be able to calculate accurately equilibrium aluminum hydroxide solubility. Their approach was based on concepts which delineated a

technique to determine ionic strength of an electrolyte and, hence, certain physical properties of the electrolyte. The extension of this concept to the properties of Bayer solutions has allowed an improved understanding of the precipitation process as well as facilitated the use of numerical modelling of the kinetics of the aluminum hydroxide precipitation process.

The method Dewey and McCoy used for the calculation of equilibrium solubility of aluminum hydroxide requires the knowledge of molality of solution and temperature of solution. Mathematical manipulation of the equation yields the familiar equilibrium A/C ratio - the alumina to caustic (expressed as Na₂CO₃) ratio.

The ability to determine the equilibrium concentration of aluminate ion is tremendously useful and necessary to be able to describe the kinetics of solution decomposition, or more familiarly, the kinetics of aluminum hydroxide precipitation. A number of investigators^(7,8,9,10,11) have addressed the subject of decomposition kinetics from supersaturated Bayer solutions and basically similar relationships have been derived.

The rate of the heterogeneous reaction or the rate of decrease in aluminate ion concentration due to precipitation of gibbsite, as described by equation (1), is related to: the concentration of involved species, the surface area available for reaction, and a specific reaction rate constant.

A generalized expression can be written as:

$$\frac{-d(\text{Al}(\text{OH})_4^-)}{dt} = A e^{-E_a/RT} f(a, C_{\text{Al}(\text{OH})_4^-}, C_{(\text{OH})^-}, C_{\text{Na}^+}, \dots) \quad (3)$$

where

- A = frequency factor
- R = Universal gas constant, cal/gm mole °K
- T = Temperature in °K
- E_a = Activation energy, cal/gm mole
- a = Surface area available for reaction, m²/liter
- C_x = Concentration of ionic species, moles/liter

Pearson (7) expressed this expression simply as:

$$\frac{-dx}{dt} = k A_t \frac{[x_t - x_\infty]^2}{[a_\infty + x_\infty]^2} \tag{4}$$

where

k = Overall temperature dependent rate constant

A_t = Area of seed surface at time 't', m²

x_t = Molar concentration of NaAlO₂ at time 't'

x_∞ = Equilibrium molar concentration of NaAlO₂

a_∞ = Equilibrium molar concentration of NaOH

Kanehara⁽⁸⁾, King⁽⁹⁾, Brown⁽¹⁰⁾, and Overby and Scott⁽¹¹⁾ have given similar expressions with the second order dependence on reacting layer ionic species. Through their experimental work using either synthetic or Bayer plant solutions, these investigators determined the activation energy for the precipitation reaction to be in the range of 12.7 Kcal/mole to 19.7 Kcal/mole. This magnitude of activation energy is normally associated with a surface reaction being the overall rate controlling step in the reaction sequence⁽¹²⁾. The precipitation of gibbsite from alkaline solutions, a heterogeneous reaction, can be visualized as a five step process as delineated in Figure 3.

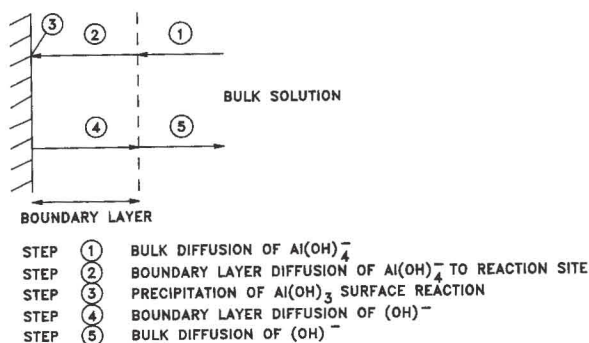


Figure 3: Precipitation Reaction Mechanism .

Equation (4) is modified to use initial surface area rather than instantaneous surface area since the gibbsite particle growth phenomena is yet to be accurately defined. Then the equation becomes:

$$\frac{-dx}{dt} = kA_0 \frac{[x_t - x_\infty]^2}{[a_\infty + x_\infty]^2} \tag{5}$$

Equation (5) can be modified to reflect the terminology used in a Bayer plant to yield:

$$\frac{-d[A/C]}{dt} = \text{Constant } (A_0)(e^{-E_a/RT})[(A/C)_t - (A/C)_{\text{eqm}}]^2 \tag{6}$$

where

A = Aluminum concentration in solution

expressed as Al₂O₃, grams/liter

C = Sodium hydroxide concentration in solution

expressed as Na₂CO₃, grams/liter

An analytical solution to this differential equation is not feasible; therefore, numerical integration can be used to arrive at the extent of decomposition of a Bayer solution during precipitation as a function of time.

A number of investigations^(13,14,15,16,17) have been reported that link the kinetics of the precipitation reaction and the kinetics of particle growth of aluminum hydroxide in essentially pure alkaline solutions. However, the effect of differing quantities of impurities present in Bayer plant solutions, though quantified for reaction kinetics, has not been quantified for particle growth kinetics. As a result, in that which follows, emphasis is placed on examining the reaction chemistry aspects to illustrate possibilities for improved precipitation process efficiency.

DICHOTOMY IN SOLUTION DECOMPOSITION

Equation (6), which defines the Bayer solution decomposition kinetics, contains two terms that are temperature dependent, namely, the exponential term containing activation energy and the equilibrium A/C ratio. Figure 4 illustrates the effect of temperature on the exponential term and Figure 5 illustrates the effect on

the equilibrium A/C ratio. Both increase in value as temperature is increased in the normal Bayer plant precipitation temperature range of 50°C to 90°C.

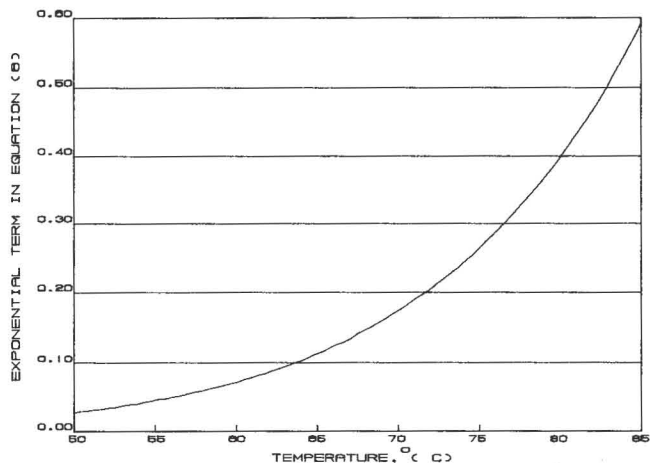


Figure 4: Effect of Temperature on the Exponential Term in Equation (6).

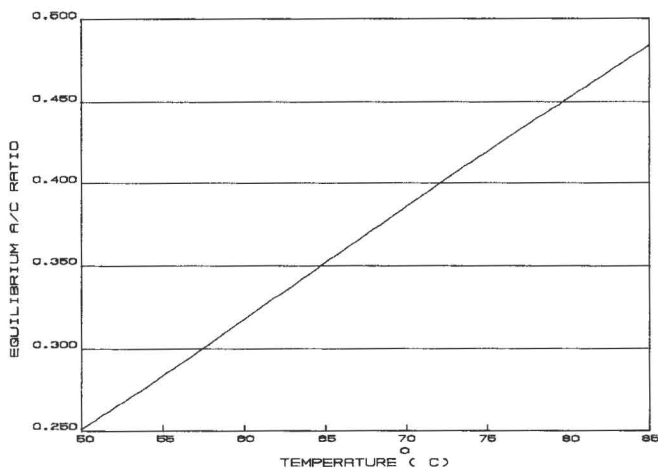


Figure 5: Effect of Temperature on Equilibrium A/C Ratio.

A closer examination of equation (6) leads to the consideration of the term $[(A/C)_t - (A/C)_{eqm}]^2$, the supersaturation term. The effect of temperature on this term is shown in Figure 6 at several values of $(A/C)_t$. It is noted that as temperature increases, the value of this term decreases.

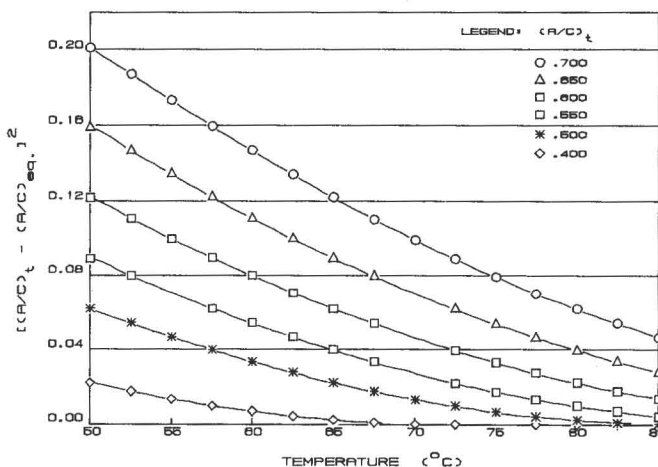


Figure 6: Effect of Temperature on Supersaturation Term in Equation (6) at Various A/C Ratios.

Thus, it becomes apparent that the precipitation rate is affected by decreasing and increasing terms as the temperature increases; the supersaturation term contributes a decrease and the activation energy term contributes an increase, which expresses the dichotomy in the solution decomposition process. This is clearly illustrated in Figure 7 where the pseudo-precipitation rate (the product of the activation energy term and the supersaturation term) is plotted as a function of temperature. The data show that the pseudo-precipitation rate exhibits a maximum which is dependent on the solution A/C ratio under consideration. The data also show that, as the solution decomposition proceeds, the precipitation rate decreases significantly by one or two orders of magnitude. A typical Bayer liquor decomposition curve shown in Figure 9 illustrates this fact, where the rate of decomposition is high initially then decreases rapidly as decomposition proceeds.

The data and concepts presented so far show that a maximum precipitation rate at a particular A/C ratio can be achieved at a unique temperature. This is true if and only if the surface area for reaction is not variable. This is not strictly correct, since the surface area available for reaction does change as precipitation proceeds. This change in

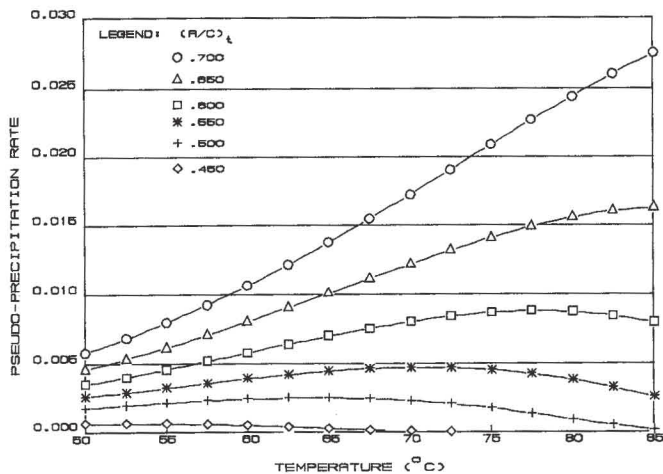


Figure 7: Effect of Temperature on Pseudo-Precipitation Rate at Various A/C Ratios.

area is minimal, and normally the assumption of constant area is sufficiently valid for prediction purposes. One can, therefore, construct an optimum temperature profile that can ensure a maximum precipitation rate at each point during the precipitation process and yield the maximum process efficiency as delineated by precipitation yield. Figure 8 displays such a temperature profile for a hypothetical Bayer plant liquor to precipitation solution. Each Bayer plant would exhibit a different optimum temperature profile based on its solution chemistry and operating constraints. In any case, for the hypothetical solution decomposition following this optimum temperature profile, the liquor decomposition would follow the optimum precipitation decomposition profile shown in Figure 9. Note that a normal decomposition curve is also shown in Figure 9. These relationships show that an increase in Δ A/C of 0.100 is feasible and translates directly to a 30% increase in precipitation yield. Such a feasible increase translates directly into increase in the precipitation process efficiency and, therefore, an increase in the total Bayer process efficiency.

Admittedly, a major and necessary criterion for successful precipitation process, the particle size distribution, is not addressed in this discussion due to lack

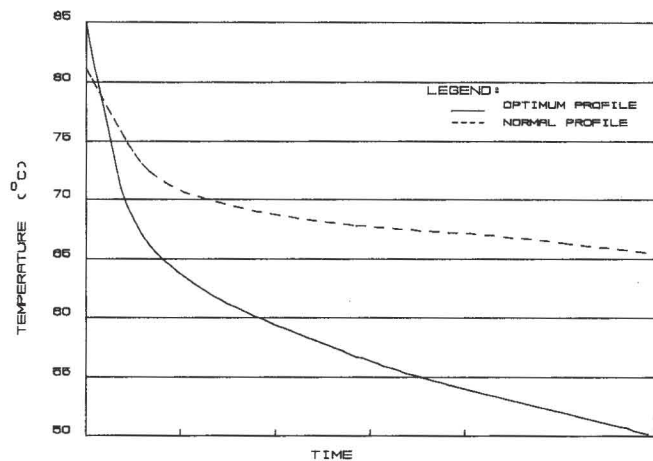


Figure 8: Normal and Optimum Precipitation Temperature Profile.

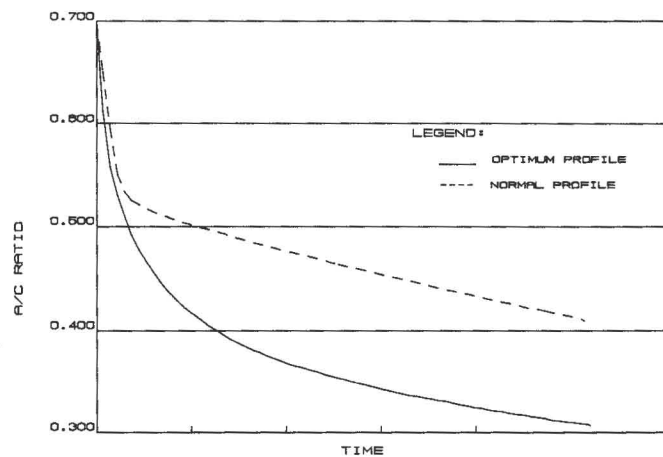


Figure 9: Comparison of Normal and Optimum Precipitation Decomposition Profile.

of a quantitative description of the fundamentals of the particle growth process. However, although the particle growth is not considered in the above discussion of the solution decomposition dichotomy, the concept can still be applied to maximize precipitation yield. To apply this concept, a Bayer technologist needs a thorough understanding of the aspects of the dichotomy and the ability to manipulate Bayer plant operating conditions. Under these conditions, one can improve the precipitation process efficiency while satisfying the particle size distribution criteria.

APPLICATION TO PRECIPITATION CIRCUIT

The practice of aluminum hydroxide precipitation started as a batch process, which is still being practiced in older plants. In recent years, as a result of a more complete understanding of the precipitation reaction, continuous precipitation systems have become the alumina industry standard. Since both batch and continuous processes are in operation, in that which follows application of concepts delineated earlier is considered for both types of precipitation systems.

Batch Precipitation Considerations

The batch precipitation process offers limited operating flexibility needed to take advantage of the delineated concepts; however, a few hypothetical possibilities can be considered.

The most obvious modification of a batch precipitation system is the alteration of the natural temperature profile in a way to match the optimum temperature profile shown in Figure 8. This would result in an increase in the precipitation yield of about 30 % for the hypothetical case presented in Figure 9. Such a cooling of the batch reaction vessel contents can be achieved, for example, by a heat exchange surface inside the vessel through which cold water is circulated. Another method of cooling is the continuous flow of controlled cooling water down the outside wall of the precipitator.

These cooling methods can result in a spent liquor temperature decrease of the order of 15°C from the normal expected temperature. This additional heat loss is unrecoverable and will result in an increase in energy input for liquor heating. Thus, the benefits of a significant increase in yield will have to be judged against the operating difficulties and costs associated with the cooling requirements as well as the increase in total energy consumption.

Another alternative that may be considered is the addition of cool green liquor to a batch precipitation process that has been in progress for a few hours. Addition of cool green liquor at 50°C can lead to an increase in precipitation yield of 10% as shown by data in Figure 10, provided positive size control can be maintained.

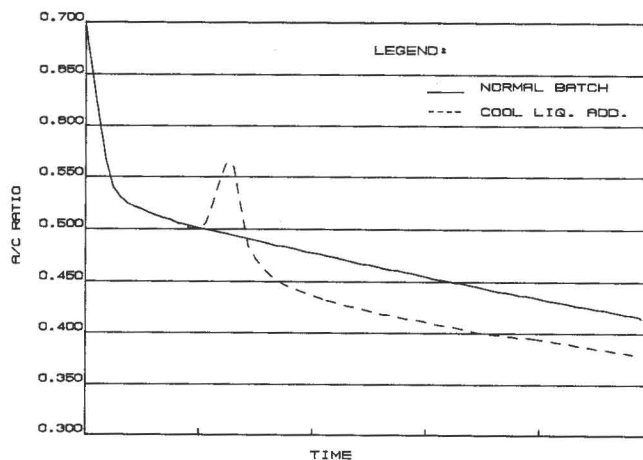


Figure 10: Effect of Cool Green Liquor Addition on Liquor Decomposition in Batch Precipitation.

Yet another hypothetical alternative method to improve batch precipitation yield involves cooling of the entire contents of a batch reaction vessel after the reaction has proceeded for a few hours, and then continuing the precipitation process. If cooling of 7°C takes place, such an operation can improve precipitation yield by 15% as shown by data presented in Figure 11.

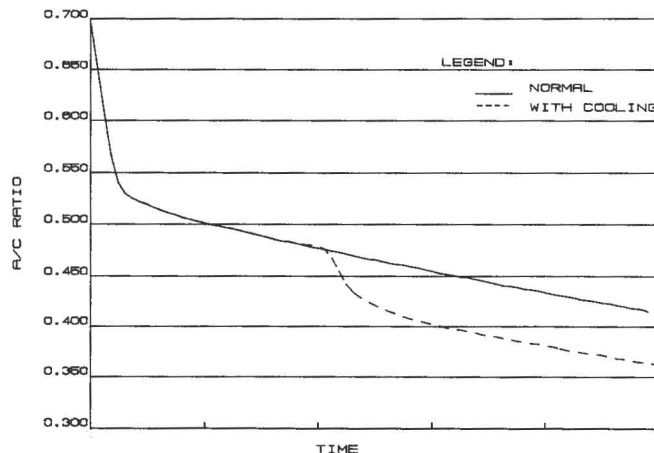


Figure 11: Effect of Precipitator Cooling on Liquor Decomposition Profile.

These scenarios involve significant expenditures for modifying existing batch precipitation circuits and most likely are uneconomical. Nevertheless, these techniques offer intriguing alternatives for improving batch precipitation process yields.

Continuous Precipitation Considerations

A continuous precipitation system with a limited number of stages cannot achieve the same precipitation yield as a batch system with an equivalent liquor retention time. The continuous system can approach the batch precipitation reaction yield if the number of stages is increased dramatically⁽¹⁸⁾. This seemingly major disadvantage can be eliminated by modifying the operating parameters, such as temperature and solids content of precipitators. An understanding of the mechanism of precipitation of aluminum hydroxide makes it feasible to change the precipitation temperature profile and therefore achieve higher precipitation yield, and thus higher precipitation process efficiency.

A continuous precipitation system liquor decomposition profile is shown in Figure 12. If this circuit is modified to include the provision for cooling after the first precipitation stage to the optimum temperature, then the data presented in Figure 12 show a possible increase in precipitation yield of 4.8%. If the precipitation circuit is modified further to include another three stages of cooling, for a total of four interstage coolers, then a yield increase on the order of 7.5%, as compared to continuous precipitation, is feasible as indicated by the data in Figure 12. The practical limit to the number of interstage coolers is dictated by particle size considerations and economics.

An understanding of the relationships that determine the maximum precipitation rate can identify the optimum placement of interstage cooling. In Figure 13, the data from two hypothetical liquor decompositions are shown. The first case involves interstage cooling after the third and sixth

stages, while the second case involves interstage cooling after the second and fifth stages in a continuous precipitation circuit. The interstage cooling duties were identical in both cases. Yet, the placement of the devices in the second case is apparently more beneficial as it results in an increase in precipitation yield of 2%. This example shows the importance of understanding the mechanism of the precipitation reaction and its application to practical systems.

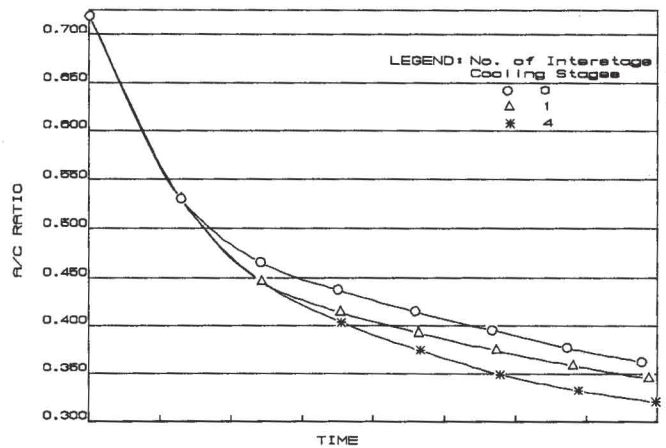


Figure 12: Effect of Interstage cooling on Continuous Precipitation Liquor Decomposition Profile.

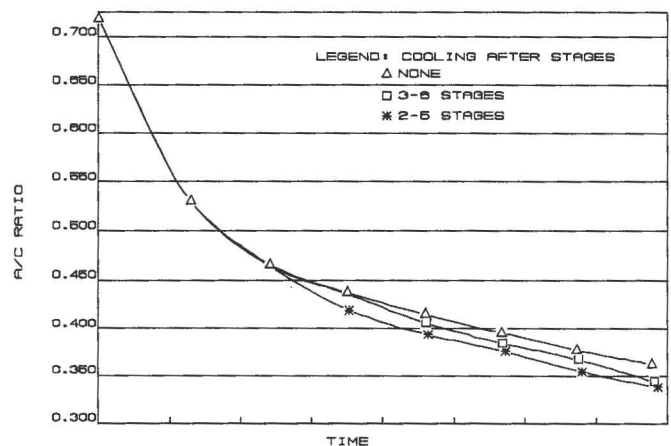


Figure 13: Effect of Placement of Interstage Cooling Stages in Continuous Precipitation.

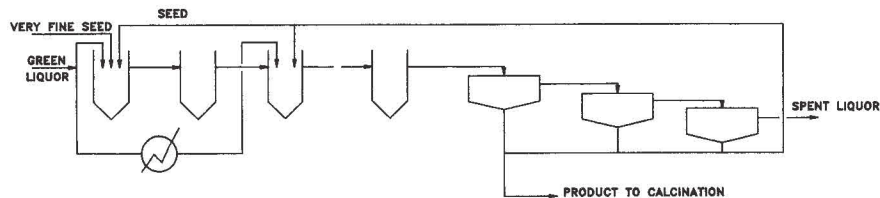


Figure 14: Sumitomo Continuous Precipitation Scheme⁽¹⁹⁾.

Sumitomo⁽¹⁹⁾ presented the precipitation scheme shown in Figure 14. This scheme, if practiced with the green liquor feed to the second stage cooled to 50°C, shows an increase in yield of the order of 5.6%. Again, this indicates that as the temperature of reaction decreases, the supersaturation term plays an ever increasing role in maximizing precipitation reaction efficiency.

CONCLUSIONS

The data and concepts presented have shown that a maximum precipitation rate at a particular A/C ratio can be achieved at a unique temperature. Application of this principle to achieve high precipitation yield, in both batch and continuous precipitation circuits, has been delineated.

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