

Mass Balance of Precipitation Process of the Bayer Process to study the Anti-scaling effect of the IPI Technology

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Abstract

Scale formation particularly around the walls of precipitators is an issue which has not only resulted in significant financial and environmental cost for many alumina refineries, but exposure to personal safety risk as well. Research in the field, however, has been very limited particularly regarding to scaling kinetics in precipitation tank; this is due to the difficulty of obtaining industrial materials and plant data for testing purposes. The goal of this study is to formulate a mass balance model to predict the effect of scaling on the yield of alumina specifically on the white side of alumina production process. It is also used to study the benefit of the IPI technology based on electrochemical technique, which prevents scale formation. King's form of rate equation was used as the growth equation in the mass balance model based on validation against typical industrial yield. The alumina yield is observed to reduce significantly once the scale volume exceeds 10% of the tank volume.

1. Introduction

Precipitation of alumina trihydrate ($\text{Al}(\text{OH})_3$) or gibbsite during the Bayer process often results in extensive gibbsite and oxalate scale formation on the internal surfaces of the precipitation tanks and the thickeners. The problems caused by scaling usually include direct production loss, reduction in available volume of the tanks for production, possible damage to the internal vessels when large sections of scale are detached from the wall, high cost and downtime involved with the de-scaling procedure and loss of heat transfer efficiency.

Savcor has developed an anti-scaling technology which minimizes the build up of scale in precipitation tanks through a patented electrochemical polarization technique. It controls the electrochemical potential at the vessel wall such that it acts to discourage scale from attaching to the vessel walls, without affecting normal precipitation processes. Consequently, the effective volume for production within the precipitation tanks will increase, which results in direct increases in potential yield.

There exist very few mass balances models which are based on a few different alumina precipitation kinetic equations. The most prominent growth kinetic equations include Pearson's rate equation (Pearson 1955), White and Bateman's model (White & Bateman, 1988) and King's model (King 1973). However, even fewer of them consider the effect of tank volume reduction on the yield of alumina in production. The main objective of this work seeks to fill this gap by developing a steady state mass balance model based in precipitation

tanks for a generic plant and analyse it under volume reduction conditions in particular to study the benefits of application of the anti-scaling technology on the alumina yield.

2. Background

2.1 Alumina precipitation kinetics models

The precipitation reaction can be illustrated by Equation 2.1.1 below:



It is widely assumed to be in the second order (Habashi, 1997) (Misra & White 1971) (Scott & Overbey 1978). Pearson (1955) developed a second order rate equation (Equation 2.1.2) that has been used by most researchers (Misra & White 1971) (White & Bateman, 1988):

$$-\frac{dx}{dt} = k * A_t * \frac{(x_t - x_\infty)^2}{(a)^2} \quad (2.1.2)$$

- dx/dt = rate of disappearance of alumina in solution or growth rate of gibbsite (kg/L/hr)

x_t = alumina concentration at time t (g/L)

x_∞ = solubility of alumina (g/L)

A_t = seed surface area at time t (m^2/L)

a = caustic concentration leaving the precipitator, expressed as Na_2CO_3 g/L

k = kinetic constant

Compared to Pearson's model, King (1973) suggested the use of free caustic (caustic in solution that is not bound to aluminium species), which gives the best fit of data when compared to the model which uses total caustic concentration within the liquor. King's equation can be expressed as follows:

$$-\frac{dx}{dt} = k * A * \frac{(x_t - x_\infty)^2}{FC^2} \quad (2.1.3)$$

where

A = Seed Surface area (m^2/g)

FC = free caustic concentration (g/L)

$$FC = \text{caustic concentration} - \text{alumina concentration} * \frac{\text{molecular weight of Al}_2\text{O}_3}{\text{molecular weight of Na}_2\text{CO}_3}$$

Molecular weight of Al_2O_3 = 102 g/mole

Molecular weight of Na_2CO_3 = 106 g/mole

White and Bateman (1988) observed that a decrease in growth rate is caused by an increase in caustic concentration, while supersaturation remains constant. The supersaturation in this case is defined as the difference between the initial A/C and equilibrium A/C ratio. The growth rate is a function of the supersaturation squared and has half order dependence on the caustic concentration. The White and Bateman (WB) model is illustrated by Equation 2.1.3 below:

$$-\frac{dx}{dt} = k * A_t * \frac{\left(\frac{X_t}{a} - \frac{X_\infty}{a}\right)^2}{a^{1/2}} \quad (2.1.4)$$

3. Mass balance modelling process

3.1 Assumptions behind the mass balance model

Firstly, gibbsite precipitation is assumed to be the primary reaction occurring in precipitation tanks, there will not be any nucleation, agglomeration and breakage, just gibbsite growth mechanisms. Secondly, Bayer liquor within the precipitation tanks is reasonably well mixed throughout. Thirdly, temperature of the Bayer liquor within each precipitation tank is assumed to be isothermal. Lastly, volumetric flow rate of the Bayer liquor will be constant throughout the precipitation circuit, each precipitation tank can be considered as a constantly stirred tank reactor (CSTRs).

The generic alumina plant will have an annual production of 1 million tonnes per year which, at an initial estimate of 75 g/L yield in precipitation, results in a refinery flow rate of 1550 m³/hr. The precipitation circuit will consist of 10 tanks in series, which includes 2 agglomerators, 4 intermediates and 4 final precipitators (intermediate and final precipitators are also known as growth tanks). All of the tanks will have the same size, and the different types of tank are only differentiated by the different cooling stages. The values of parameters used in the mass balance model are listed in Table 2.2 below:

Parameters	Values
C(AO) = initial alumina concentration (as Al ₂ CO ₃ g/L)	174
Caustic concentration, expressed as Na ₂ CO ₃ at 25°C (g/L)	240
A/C	0.725
Soda concentration (g/L)	267
C/S	0.9
Total Organic Content (g/L)	15
Na ₂ SO ₄ (g/L)	5
NaCl (g/L)	5
Temperature (2 stages cooling) (C)	84, 72, 60
V = precipitation tank volume (m ³ or kL)	4500

Table 2.1 Assumed values for the parameters used in the mass balance model

3.2 Modelling method

The statement of conservation of mass can take the following forms:

$$\text{Rate of accumulation of reactant} = \text{Flow in} - \text{Flow out} - \text{Rate of reactant loss} \quad (3.1)$$

In the CSTR, the rate of accumulation is equal to the differential of the total number of moles Vx_t , and keeping the volume (V) constant. Thus for the initial feed component A (Al(OH)₄⁻):

$$\text{Rate of accumulation} = V * \frac{dx_t}{dt} \quad (3.2)$$

Where

V = volume of the liquor in the precipitation tank (L)

dx_t/dt = rate of reaction (kg/L/hr)

The flow in and out can be represented by:

$$\text{Flow in} - \text{Flow out} = Q * (x_o - x_t) \quad (3.3)$$

Where

- Q = volumetric flow rate (m³/hr) $Q_{in} = Q_{out}$,
- x_0 = initial feed concentration (kg/m³)
- x_t = final concentration at time t (kg/m³)

Finally, the rate of reactant loss is the disappearance of the reactant $Al(OH)_4^-$ by reaction. It can be determined by using the Arrhenius equation, as the rate of reaction is both temperature and concentration dependent:

$$\text{Rate of loss of reactant} = V * (-r_A) \tag{3.4}$$

Where

- $-r_A$ = rate of reaction/gibbsite growth rate equation,
- $-r_A = -dx_t/dt$

Combining all these equations, we get:

$$V \frac{dx_t}{dt} = Q * (x_0 - x_t) - V(-r_A) \tag{3.5}$$

Rearranging and noting that dx_t/dt (accumulation) is equal to zero at steady state:

$$Q * (x_0 - x_t) = V(-r_A) \tag{3.6}$$

Equation 3.6 can be easily solved given all the values except for x_t . The result based on the model is shown by using Microsoft Excel.

3. Results and Discussion

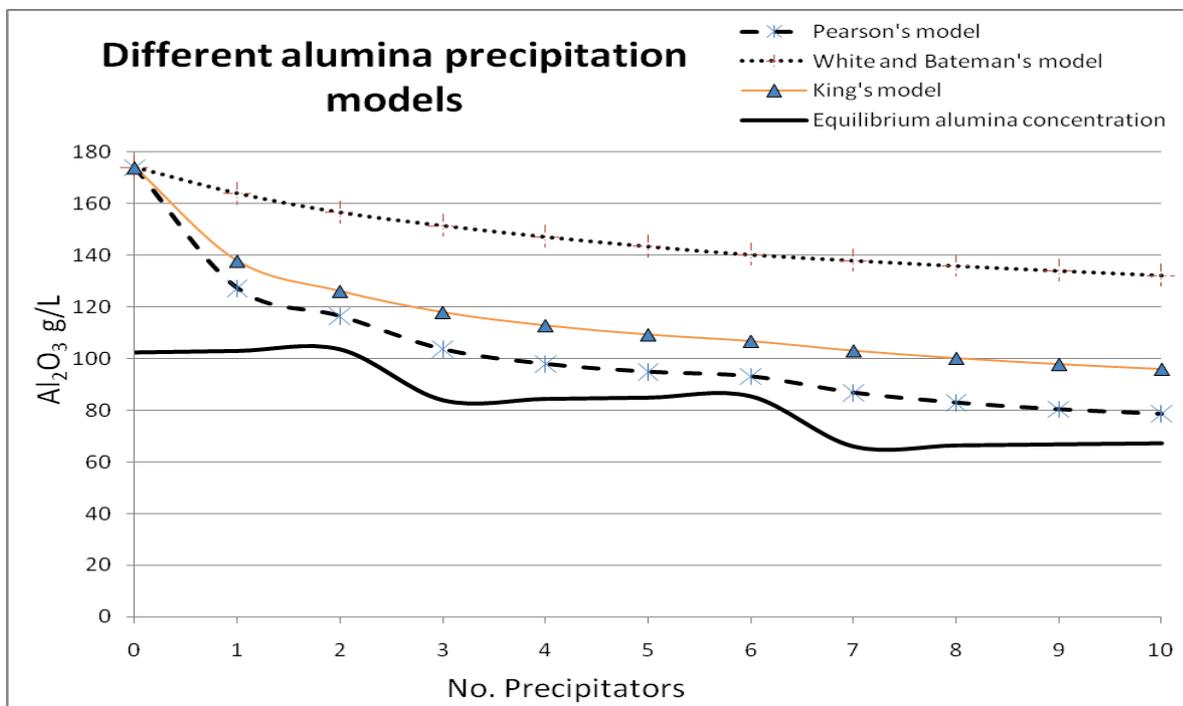


Figure 3.1 Comparison of the mass balance models based on different precipitation kinetic equations

Figure 3.1 shows the comparison between the mass balance models using different precipitation kinetic equations based on the given conditions. It shows the final alumina concentration (expressed as Al_2O_3 in g/L) within each of the tanks as the liquor flows through

the precipitation circuit. Whilst all three models take caustic concentration into account and are based on second order rate equations, the predicted final alumina concentration is very different. To validate the models, one can observe the supersaturation levels between the agglomerators and the growth tank, the ratios of x_t/x^∞ along the growth tanks and the final alumina yield.

Supersaturation is defined as the difference between final alumina concentration and equilibrium alumina concentration (Figure 3.1). To normalize for different caustic concentration, difference in A/C and $A(eq)/C$ is a better way to view results. Under industrial conditions, the supersaturation level of alumina should increase steadily as the temperature decreases, this is observed in all three models (Figure 3.1). Furthermore it is suggested that the supersaturation exit the agglomeration tanks (the first two tanks) will range between 0.16 – 0.24 (Lewi 2009) Whilst both WB and King’s model agrees well with this range, WB provides a much better fit with its normalized supersaturation value being 0.22.

The ratio of x_t/x^∞ is another conventional measure used to monitor the alumina concentration within growth tanks. Typical values for the ratio range between 1.3 – 1.6 (Thomas & Armstrong 2002). Only King’s model agrees with this range; it ranges between 1.25 – 1.55.

Lastly, typical precipitation yields ranges between 70 – 90 g/L (Tschamper 1985), and again only King’s model fits within this range with 85 g/L. Compared to all other models which are based on observations on seeded caustic aluminate solutions in which a large number of gibbsite crystals were present, King avoided the difficulty in controlling nucleation and agglomeration in such systems by measuring the linear growth rate of single crystals in a concentration environment; this allows his derived rate equation to resemble the industrial environment more closely than the others. Based on all of these factors, King’s model has been selected as the most suitable rate equation for the mass balance model.

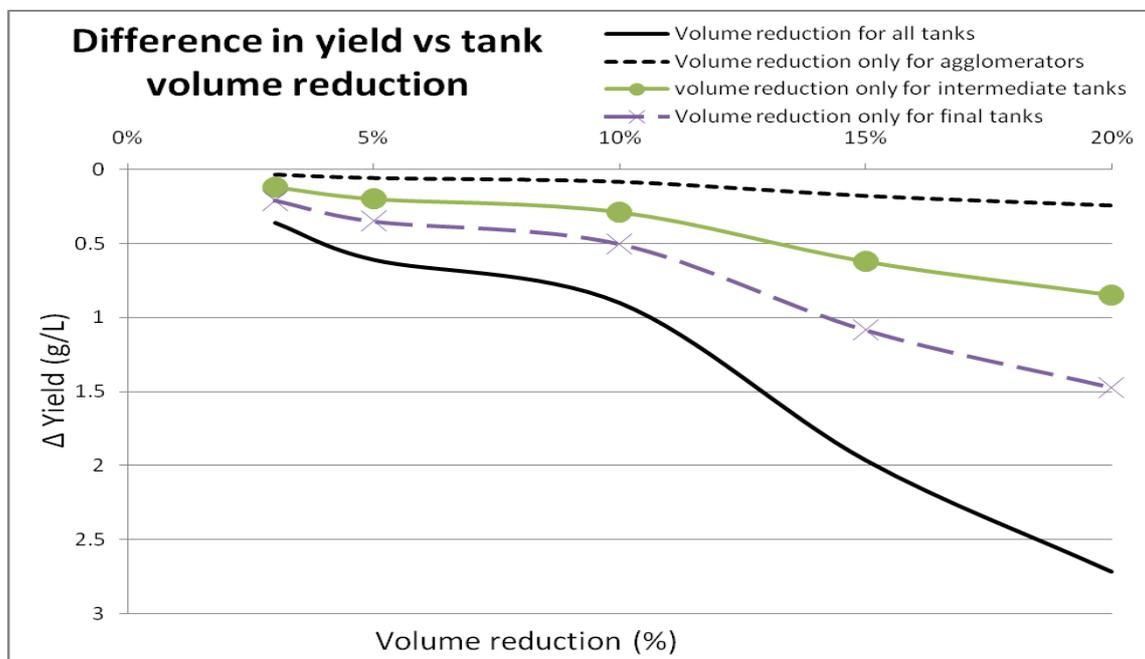


Figure 3.2 Comparison of the difference in yield between the precipitation circuits with different production volume. Δ Yield = Yield (100% tank volume) – Yield (% reduction in tank volume)

Figure 3.2 shows the comparison of differences in precipitation yields at different volume reduction conditions. Whilst the impact on the alumina yield becomes much more pronounced as the volume reduction exceeds 10%, even at volume reduction of 5%, the potential yield impact is still significant. With the annual production of 1 million tonnes of alumina, installation of IPI technology will result in an increase of 7000 tonnes per year of alumina for the refinery, worth about nearly \$1 million. Furthermore, the model shows that majority of the benefit can be derived from only installing the anti-scaling technology in agglomerators (on a per tank basis), where change in volume has the most impact on production.

The mass balance model can be easily modified to suit most of the given industrial conditions such as change in temperature and layout the tanks (e.g. parallel). Whilst the mass balance model takes into account scaling through tank volume reduction, it cannot be used to predict the amount of product lost due to scaling. To do this, one would need to establish a well defined nucleation rate equation together with the growth rate equation in the mass balance model.

4. Conclusions and Future Work

The mass balance model based on King's rate equation will give the most accurate estimation of cumulative alumina yield in each of the precipitation tanks. If the IPI technology can inhibit scale formation and hence prevent loss in production volume, this will result in significant increase in yield.

To achieve the objective of the project, a sensitivity analysis which is not included in this paper, will also be developed to study the effect of the change in alumina concentration and yield to different sources of variation in the input of the model, such as the number and size of the tanks, the temperature and the number of cooling stages.

Future work will need to include an energy balance model, which can be built upon the mass balance model to study the energy loss between the various stages of precipitation circuit due to scaling.

5. Acknowledgements

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6. References

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