Autoprecipitation Modelling in a Thickener

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Abstract

One of the principal alumina losses within the Bayer process is autoprecipitation or gibbsite reversion in the clarification circuit, yet rigorous modelling of this process remains poorly understood. This paper proposes a conceptual model for the autoprecipitation process within a clarification circuit decanter, considering the kinetics of the reaction within the complex solid-liquid separation environment. The model discretizes a Bayer process decanter into N stages with each stage comprising mixing, reaction, and splitting, while adhering to, a typical depth versus solids concentration profile. A degrees of freedom analysis to ensure that the models results are possible is presented. A batch of simulations are shown to demonstrate the impact of process variables such as feed volumetric flow, underflow solids concentration, and feed A/C ratio on the ratio drop of both underflow and overflow of the thickener.

Keywords: Gibbsite reversion, autoprecipitation, mud thickener, modelling.

1. Introduction

Typically, the objective of a refinery's red side is to deliver filtered green liquor with as high alumina concentration as acceptable to the white side, considering product quality, operability, type of equipment, etc. The higher the alumina concentration attained, the greater the propensity to lose it during the thickening of the blow-off slurry. While the optimal A/C ratio can be discovered through operation experience, a more structured way to do this would be using a model that accurately represents the complex behavior of the thickeners, including solids profile, liquor composition, temperature, and residence time.

The gibbsite reversion (or autoprecipitation) phenomenon has been studied by multiple authors in the past [1] [2] [3] [4] [5], arriving at a good level of agreement concerning the contributing factors.. The solids concentration affects the process but so too does the mineral composition of the solids. In that regard, the literature agrees that goethite is the second most influential mineral on the enhancement of the autoprecipitation rate, after gibbsite. These results regarding the mineral impact are consistent with results reported by researchers from the Kirkvine refinery [3], in which aluminous goethite was found to play an important role in gibbsite reversion. A correlation between the specific alumina loss through autoprecipitation has been estimated based on the goethite to alumina ratio [2] has also been encountered and used for estimate of the bauxite composition impact on the losses. Additionally, insights regarding mechanisms of gibbsite precipitation on foreign surfaces have been studied through in-situ X-ray diffraction shown by Webster et Al. [4] [5] demonstrating both diffusion controlled bidimensional crystal growth and unidimensional diffusion in different conditions, more representative of a scale growth condition.

Quantitative modelling of this process has been less explored. In [6] the kinetics of this reaction was estimated experimentally in the laboratory in conditions similar to batch reactors. Their kinetic data was applied to a model that simulated the reaction in a Plug-Flow Reactor inside the thickener geometry. The base kinetic equation used is Equation 1.

$$\frac{dA}{dt} = k \cdot (A - A^*)^{2.28} \cdot FC^{-4.21} \cdot (0.195 + I)^5 \cdot e^{-0.957 \cdot I} \tag{1}$$

$$k = k_0 \cdot e^{\left(-5470\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \tag{2}$$

Where:

A is the concentration of alumina in g Al_2O_3/L;
A^* is the Alumina solubility in g Al_2O_3/L;
FC is the free caustic concentration in g Na_2CO_3/L;
I is the Ionic strength in mol/L;
k is the rate constant ($g^{2.93} \cdot L^{2.07} \cdot mol^{-5} \cdot h^{-1}$);
k_0 is the rate constant at the reference temperature;
T_0 is the reference temperature in K;
T is the temperature in K;

Poor agreement of the experimental data with the plant was encountered, but even so, the model was capable of guiding a reported reduction on alumina loss of 80 % in lead washers. The model did not take the solids concentration and composition into account, and the experimental procedure included sieving and ring milling of dried mud collected from settle underflow which can affect the surface area available for autoprecipitation. In an earlier approach from 1986, J.G. Lepetit [2] suggested that the kinetics have two different terms based on the autoprecipitation of both gibbsite and boehmite. The kinetic equation utilized was:

$$\frac{dRP}{dt} = -k_3 \cdot (RP - RPe_3)^2 - k_1 \cdot (RP - RPe_1)^2 \tag{3}$$

$$k_1 = a_1 \cdot m \cdot e^{\left(-\alpha \cdot I - \frac{E_1}{R \cdot T} + \beta_1\right)} \tag{4}$$

$$k_3 = a_3 \cdot m \cdot e^{\left(-\alpha \cdot I - \frac{E_3}{R \cdot T} + \beta_3\right)} \tag{5}$$

Where:

RP is the ponderal ratio expressed by g Al_2O_3/g Na_2O;
RPe_3 and RPe_1 are ponderal ratios at solubility for gibbsite and boehmite respectively;
k_3 and k_1 are the kinetic constants;
β_3, β_1, and α are terms independent of the processed red muds;
a_3 and a_1 are terms that represent the processed red mud;
m is the solids concentration in g/L;
E_3 and E_1 are the activation energies;
I is the Ionic strength;
R is the ideal gas constant;

The results from this study were in better agreement with plant data, but with less capacity as we move down the washer train, as it is observable in **Table *1***.

Table 1. Comparison between model and plant data, as studied by J.G. Lepetit [2].

Unit	Plant RP	Calculated Rp
Thickener	1.100	1.100
Washer 1	1.043	1.035
Washer 2	0.907	0.921
Washer 3	0.814	0.835
Washer 4	0.724	0.718

how much autoprecipitation affects the leaving streams. The underflow is much more impacted and that agrees with the fact that most of the solids are in fact in the bottom part of the tank and the amount of liquor present on that region is smaller, which attest to the fact that the impact should be higher. These results are a consequence of the larger supersaturation degree. The impact of increasing volumetric feed flow is also intuitive as a straight consequence is the reduction of residence time, giving the material less time to auto precipitate. Again, the effect of the variable is more relevant on the underflow and the cause is the larger solids concentration in the bottom of the tank, similar to the effect of the feed A/C ratio. The UF solids concentration change affects the slope of the region under the feed stage, which means that the total solids content of the tank is changed. If the UF solids increase, then the total amount of solids inside the tank should increase. Note here that the mud and interface level are not considered as these definitions are simply a reference of a specific point of the solids profile. Being so the model takes into account the mud and interface levels just by receiving the input of the solids profile and the increase of the UF solids concentration as done in this work has the consequence of raising both the interface and mud levels. The oversimplified solids profile is again part of the effort of proving concept with the simplest conditions. There are numerous studies which define the typical solids profiles (see for example [11] [12] [13] [14] [15] [16] [17]) and these represent the next logical improvement for the model. Further, with better evaluated kinetics considering different precipitation mechanisms and solids composition, the effects of the solids profile and residue composition can be estimated prior to operation if needed.

5. Conclusions

The proposed model adequately represents with stable results the expected tendencies of the process when certain parameters are manipulated. This refers to the fact that the ratio drop on both OF and UF increases when feed A/C ratio increases and decreases when feed volumetric flow increase. It naturally differentiates the liquor compositions of the overflow and underflow leaving the thickener. The number of stages influences the result and for this proof of concept 20 stages was enough, but depending on the process conditions (and kinetic equations utilized) the number of stages may not be the same. The model here developed is not only useful for autoprecipitation modelling but for any reaction that happens inside a thickener and for any number of components as the degrees of freedom analysis is 0 independently of number of components so long as the kinetics of each modelled reaction are known. The impact of different solid compositions can be considered in the model by using different kinetic expressions implemented on the reactor step for each solid component interference, if the information is available. The suggested following work is to validate kinetic expressions extracted through bench experiments and confirmation of applicability using plant data, observing the impact of different solid compositions and solid mass fraction profiles. After careful modelling of plant data, the obvious next step will be process optimization and control using these methods.

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