

# SETTLER AND WASHER ALUMINA REVERSION

Kiriazis M\*

*Queensland Alumina Limited, Gladstone, Queensland, Australia*

## Abstract

Bayer refinery alumina recovery is a strong function of extraction in digestion and alumina losses throughout the plant. One of the most significant of these alumina losses is the auto-precipitation, or reversion, of alumina in the clarification section of the plant. Settler and washer alumina reversion has been the focus of an ongoing research and development project at QAL.

Work done at the QAL refinery to minimise alumina reversion in clarification includes:

- Studies into the reaction kinetics of reversion
- Development of a plant model incorporating the reaction kinetics, and the validation and tuning of this plant model against plant data
- Use of the plant model to evaluate options to reduce reversion
- Plant trials
- Implementation of improvements into plant operation

This work has led to significant improvements in plant performance, including a reduction in lead washer reversion by approximately 80%.

## 1 Introduction

Alumina is a commodity material, and as such the real value of alumina is continually declining with time. Thus, Bayer refineries must consistently produce greater volumes of alumina at decreased cost to remain competitive. One of the most important cost parameters in a Bayer refinery is the recovery of alumina, which is the net percentage of available alumina recovered from the bauxite. This recovery is a strong function of extraction in digestion and alumina losses throughout the plant (e.g. consumption of alumina through lime usage, dust losses etc.). One of the most significant alumina losses in a Bayer refinery is the auto-precipitation, or reversion, of alumina in the clarification section of the plant.

Dissolution of alumina in the digestion section increases the alumina concentration of the liquor to within a small margin of the equilibrium alumina solubility at the prevailing digester conditions. As this liquor is flash cooled to atmospheric boiling point, the equilibrium solubility of the alumina is decreased significantly, causing the liquor entering clarification to be highly supersaturated with respect to alumina. During the gravity separation of the mud residue in clarification settlers and washers the solid mud particles act as a seed for alumina precipitation. It is this seed in combination with the supersaturation of the liquor that causes the alumina reversion observed in clarification thickeners.

The focus of this research has been the reversion of alumina in settlers and washers at the QAL refinery, and the objectives were to:

- Model the alumina reversion kinetics over a wide range of liquor conditions and temperatures, similar to those encountered throughout clarification
- Incorporate these kinetics into a validated settler/washer train mass balance model, which can be used to identify and evaluate options to reduce the alumina reversion
- Conduct plant trials to verify the findings of the plant model with regard to the identified options
- Implement improvements into plant operation

## 2 Reversion kinetics

### 2.1 Experimental

Batch reactions were performed using a full factorial experimental design, varying initial caustic concentration (20, 50, 120 and 220 g/L), initial A/C (0.5, 0.6 and 0.7), and reaction temperature (55°C, 75°C, 95°C). Each condition was tested using two bottles at two different reaction times (between 10 minutes and 6 hours), thus making a total of 72 tests (4x3x3x2). All tests were performed using the same mud

with the same solids concentration of 300 g/L. Mud properties, such as specific surface area and Gibbsite/Boehmite content, were not studied in this work.

Pregnant liquor (PL) and spent liquor (SL) (post evaporation) were collected from the plant the day before each run was performed. Liquors were vacuum filtered through a Buchner funnel using a Whatman GFC filter paper, and left to stand in bottles overnight. The next day they were re-filtered using the same set up and analysed for alumina, caustic, and total soda (ACS). A sample of each was taken for both TOC and XRF analysis to establish the impurity levels. The ACS titration results were used to determine the amounts of PL, SL, and distilled water required for the desired liquor caustic concentrations and A/C ratios. The liquor blends were made up in a 1L-measuring cylinder and the weights added to the blend were recorded. An initial sample was kept for titration analysis to confirm the starting caustic concentration and A/C of the liquors.

Plant settler underflow mud was collected and ammonia washed three times to remove any residual caustic. The dried mud was then ring ground for a period of 1 minute. The resultant powder was then sieved to remove the coarse particles, which were then reground using a mortar and pestle and added back to the bulk of the sample. The mud powder was then stored in sealed bottles. Samples were analysed for total available alumina (TAA) (12.04%) and Gibbsite (7.11%).

Each batch reaction was performed in a 250mL Nalgene bottle with a reaction volume of 200 mL. The bottles with liquor were first placed in a pre-heated rotating water bath and allowed time to reach the reaction temperature. Once the liquor was up to temperature, mud solids (in pre-heated 60 g allotments) were added and allowed to undergo reaction for a predetermined time. After the desired reaction time each bottle was centrifuged, and the resultant supernatant sampled for ACS titration analysis.

### 2.2 Reversion kinetics modelling

The form of the kinetic model for alumina reversion was formulated by combining the experimental results and general knowledge of precipitation kinetics. Optimisation of the equation parameters by minimising the sum of the 'residuals squared' yielded the following kinetic model:

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

Eqn (1)

$$\text{here: } k = k_0 \times e^{-5470 \left( \frac{1}{T} - \frac{1}{T_0} \right)}, \text{ and } k_0 = 492.3, T_0 = 323.15 \text{ K}$$

Where  $A$  is the liquor alumina concentration (g/L),  $t$  is time (h),  $A^*$  is the equilibrium alumina concentration (g/L),  $I$  is the free caustic concentration (g/L  $\text{Na}_2\text{CO}_3$ ),  $I$  is the ionic strength (mol/L),  $k$  is the rate constant ( $\text{g}^{2.93} \cdot \text{L}^{2.07} \cdot \text{mol}^{-5} \cdot \text{h}^{-1}$ ),  $k_0$  is the rate constant at the reference temperature ( $T_0$ ), and  $T$  is the temperature (K). The ionic strength ( $I$ ) and alumina equilibrium ( $A^*$ ) were calculated with the initial liquor properties as input to the equations developed by Rosenberg and Healy (Rosenberg and Healy 1996).

The model predicted alumina concentrations were determined through numerical integration of Eqn (1) and then compared with the experimental final alumina concentration. As seen from Figure 1, which shows the measured alumina drop versus the model predicted alumina drop, the model matched the experimental data very well (Adjusted  $R^2 = 0.909$ ).

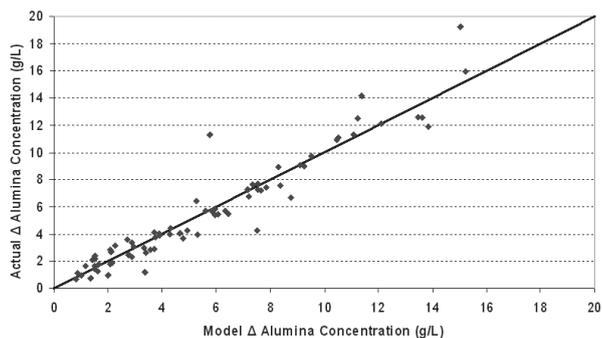


Figure 1: Model Prediction Vs Experimental Alumina Concentration

Figure 2 shows the residuals versus model alumina concentration. As seen, more than 75% of the residuals are within the automatic titrator 3-sigma range, and are randomly distributed around zero. The 25% outside of the automatic titrator 3-sigma range can be attributed to random errors introduced in the process of sample preparation and analysis. Again, this demonstrates that the model is an excellent fit to the experimental data.

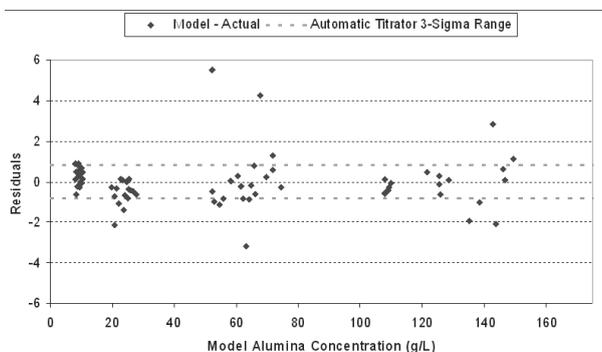


Figure 2: Plot of Model Error Versus Model Alumina Concentration

### 3 Plant modelling

Now that a kinetic model had been developed, based on the laboratory experiments, for alumina reversion on red mud, this model needed to be validated by comparison to plant operational data. To do this:

- A mass balance model of a settler and washer train incorporating the reversion kinetics was developed
- Plant sampling was required to collect sufficient data for model inputs and to compare the model results against
- The model parameters were tuned to match the plant data

#### 3.1 Simulation of a settler and washer train

A mass balance model was set-up over a single Settler and Washer train, a basic flow diagram of which is shown below in Figure 3. The solid lines represent the flow of mud down the washer train, while the

dashed lines indicate the water flow up the washer train, for simplicity none of the side stream flows are shown.

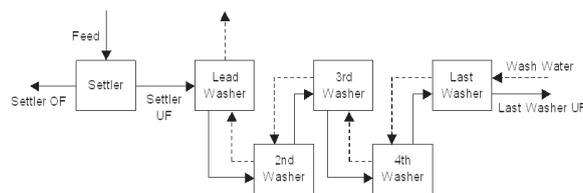


Figure 3: Basic Flow Diagram of a Settler and Washer Train

A generic schematic of the model used to simulate each of these vessels is shown in Figure 4.

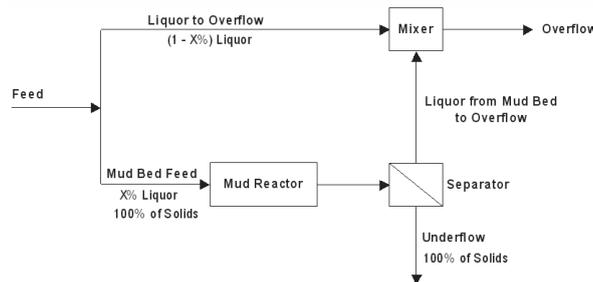


Figure 4: Model Schematic for Each Unit

The mechanism of Figure 4 is explained in the following:

- $X\%$  of the feed liquor goes to the mud bed and  $(1-X\%)$  of the feed liquor goes directly to the overflow during the settling process.
- During the compaction process in the mud reactor, alumina depleted liquor is 'squeezed' out and reports back to the overflow. An artificial separator splits off a required portion of  $X\%$  liquor to match the underflow solids g/L from the vessel. The total flow rate of overflow liquor is then the sum of  $(1-X\%)$  and the portion of  $X\%$  'squeezed out' from the mud.
- The parameter  $X$  allows one to vary the amount of feed liquor undergoing reaction and thus simulate reversion observed in the overflow.

Alumina losses (A/C drop) due to short contact time in the feed well and interfacial region are coupled together with the loss due to the mud bed as a single loss in the mud reactor.

The assumptions used in the simulation are:

- Steady state mass balance.
- Negligible solids in the overflow (model assumes zero)
- Feed, overflow and underflow have equal caustic strength.
- The ratio of impurity to caustic in side streams is equal to that in settler feed.
- Mud bed is modelled as a plug flow reactor with an average solids concentration of 300 g/L below the interface.
- The residence time is calculated from the volume below the interface and the flow rate leaving the mud reactor. The interface level is determined by converting the settler interface process data (a relative term referred to a 'zero' level) as recorded on the process information database (PI) to a real interface level (an absolute term from the bottom of the tank).

The A/C leaving the mud reactor is calculated by numerical integration from the kinetic model described above (Eqn (1)) using the feed conditions for each of the parameters with a step change in time of 0.001 hours.

#### 3.2 Model validation

A plant sampling campaign was carried out over the period from 29/07/02 to 09/08/02, in order to accumulate a set of plant data for

the model input and validation of outputs. Care was taken to minimise alumina reversion during sampling and analysis, by minimising the time elapsed between sampling and separating liquor and solids.

In order to match the model results to the plant data the following three parameters were tuned:

- To match the last washer underflow (LWUF) caustic concentration it was necessary to reduce the model wash water flow.
- The liquor split fraction (X) and the kinetic rate constant ( $k_0$ ) were tuned to match the overflow and underflow A/C profile respectively.

The tuned values for the liquor split fraction (X) used in the model are shown in Table 1, generally with higher X for higher feed solids concentrations. This is expected as the higher the feed solids the more surface area of mud for alumina precipitation in the feed well, and the lower the A/C in the overflow liquor.

TABLE 1: Model Values for Liquor Split Fraction and rate constant

Unit	Liquor Split Fraction (X)	Rate $k_0$ ( $\text{g}^{-2.93} \cdot \text{L}^{2.07} \cdot \text{mol}^{-5} \cdot \text{h}^{-1}$ )	Feed Solids (g/L)
Settler	0.13	36	40.55
Washer 1	0.35	30	181.75
Washer 2	0.2	40	98.38
Washer 3	0.22	40	92.79
Washer 4	0.25	35	103.47
Washer 5	0.25	40	107.58

The rate constant tuned to match plant operational data is approximately one tenth of that determined in the laboratory experiments (30 to 40 versus  $\sim 490 \text{ g}^{-2.93} \cdot \text{L}^{2.07} \cdot \text{mol}^{-5} \cdot \text{h}^{-1}$ ). Such a significant difference could be due to the combined effect of the following factors:

- The mud washing vessels do not have an ideal plug flow. Increasing the degree of mud by-pass to the underflow reduces the mean residence time of the mud.
- The kinetics may be slower in the plant, possibly due to:
  - Mud used in the lab tests was ground and ammonia washed, which may have generated a more reactive solid surface.
  - Flocculant may occupy the active precipitation sites on the plant mud.
  - The solids profile used in the model may not be indicative of that existing in the plant.

The rate constant for each vessel varies between 30 and  $40 \text{ g}^{-2.93} \cdot \text{L}^{2.07} \cdot \text{mol}^{-5} \cdot \text{h}^{-1}$  over a wide range of caustic concentrations. Such relatively small variation indicates that the kinetic equation (Eqn (1)) is very robust in terms of caustic concentration range.

The tuned model predicts the plant values very well, as shown in Table 2 for the A/C profile in overflow and underflow, and in Table 3 for the caustic profile, respectively. Table 3 also shows the breakdown of reversion loss along the settler and washer train.

TABLE 2: UF and OF Model A/C Error

Unit	Underflow A/C Error (Model – Plant)	Overflow A/C Error (Model – Plant)
Settler	0.001	0.000
Washer 1	-0.002	-0.005
Washer 2	0.003	-0.012
Washer 3	0.003	-0.005
Washer 4	0.000	-0.004
Washer 5	0.002	-0.003

TABLE 3: Model Caustic Concentration Error and Model Reversion

Unit	Caustic Error (Model – Plant) (g/L)	Model Reversion (% of Total)
Settler	2.94	59.71%
Washer 1	4.21	28.13%
Washer 2	5.72	7.07%
Washer 3	4.19	3.17%
Washer 4	-0.64	1.15%
Washer 5	-0.56	0.72%

The model predicted a reversion of approximately 80% of the total reversion measured over clarification during the same period. This is due to the fact that the model is based on a washer train (C-Train) in which the 1st and 2nd washers are smaller than the corresponding tanks in other clarification washer trains (A-Train and B-Train). As such, the mud residence time is lower in these washers and there is less reversion than in the higher volume 1st and 2nd washers of A and B trains.

As can be seen in Table 3, the bulk of the reversion occurs in the settlers and first washing stage, and these are the areas that were focussed upon in further improvement work.

### 3.3 Evaluation of potential improvements

Following validation and tuning of the plant model, a number of potential improvements were investigated using the model to quantify the impacts on alumina reversion. The simulation results identified an option with the potential for a significant impact on reversion in the washer trains, particularly in the lead washers. When the operating strategy was implemented in the plant, an on/off trial showed that an 80% reduction in lead washer reversion was realised (Figure 5), much greater than predicted using the model. The model underestimation was attributed to the fact that it was based on C-Train washers (as mentioned above).

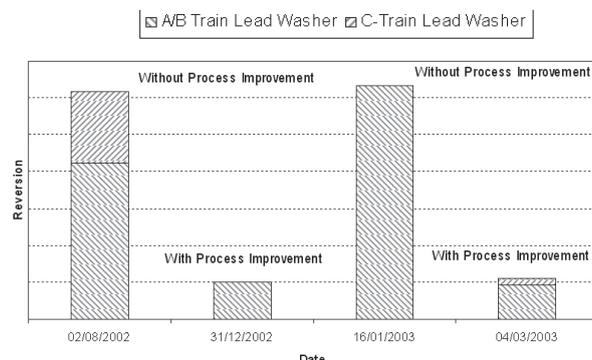


Figure 5: Impact of Process Improvement on Lead Washer Reversion (No C-Train Samples for 31/12/2002 and 16/01/2003)

## 4 Conclusions

A kinetic model for the reversion of alumina under conditions experienced in clarification has been developed. The rate of alumina loss due to reversion is a function of alumina supersaturation, free caustic, ionic strength, and temperature. It agrees with the experimental data extremely well over a wide range of caustic concentrations (20–220 g/L), A/C's (0.5–0.7), and temperatures (55°C–95°C).

This kinetic model has been incorporated into a mass balance model of a settler and washer train, allowing the prediction of clarification reversion losses. Once tuned this model showed very good agreement with plant operational data. Model parameters requiring tuning to achieve this agreement were the process water flow (for caustic profile), reversion rate constant (for UF A/C), and liquor split fraction (X) (for OF A/C).

The rate constant tuned to match plant operational data is approximately one tenth of that determined in the laboratory experiments, which may be due to the following factors:

- Reduced mud residence time due to mud bypass
- Faster kinetics in the lab due to the preparation of the mud seed
- The effect of flocculant on kinetics
- The solids profile in the model not truly indicative of plant operation

However, the fact that the tuned rate constant in the plant model is consistent over the entire settler and washer train indicates that the kinetic equation (Eqn (1)) is very robust in terms of caustic concentration range.

This predictive plant model has been used to evaluate the impact on reversion of potential process improvements. Implementation of these process improvements has led to the reduction of lead washer reversion by approximately 80%.

### References

- Rosenberg S and Healy S** (1996) 'A Thermodynamic Model for Gibbsite Equilibrium Solubility in Bayer Liquors', Proceedings of Fourth International Alumina Quality Workshop, pp. 301–310.