

# EFFECT ON ALUMINIUM SOLUBILITY WHEN ACID IS USED TO NEUTRALISE RESIDUE

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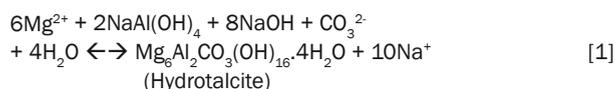
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## Abstract

The RTA Yarwun alumina refinery currently produces 1.3Mtpa of residue. Seawater is used to neutralise the residue prior to mud stacking and effluent discharge. Equipment limitations and altered process conditions have resulted in insufficient seawater being available for complete neutralisation. As a result, sulphuric acid is being used to supplement the neutralisation process. This has significantly altered the neutralisation chemistry, particularly the solubility of aluminium. It was also found that the pH required to precipitate dissolved aluminium from the supernatant liquor is significantly lower when acid is used compared to seawater.

## 1. Introduction

Waste liquor generated by the Bayer process contains high concentrations of sodium aluminate. In order to meet environmental requirements, the removal of aluminium and other metal impurities from solution is required prior to discharge. Sea water is commonly used to effectively neutralise red mud. The magnesium in sea-water reacts with aluminium in solution to form hydrotalcite, during which free hydroxide is also consumed, reducing pH and removing the aluminium from solution (equation 1). Excess sea water forces this equilibrium to the right:



Hydrotalcite belongs to a group of minerals known as double layered hydroxides and has the ability to incorporate anionic species from solution (Smith and Parkinson, 2005). The general formula for hydrotalcite is  $[(\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2)_n\text{X} \cdot n\text{H}_2\text{O}]_n$ , where X can be any anion present when precipitation occurs (Anderson, 2007). Carbonate ( $\text{CO}_3^{2-}$ ) is the most strongly bound anion due to its high charge density and strong affinity for  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ . Incorporation of other anions such as vanadates and molybdates, also found in waste liquor, is dependant on the pH. The more strongly bound carbonated hydrotalcite is preferentially formed at high pH. It is not until pH 8.5 is achieved that other anions can become included into the hydrotalcite matrix (Smith and Parkinson, 2005).

At Yarwun, last washer underflow, LWU, and oxalate settler underflow are sent to a neutralisation tank. Frequently, the quantity of seawater did not reduce the pH of the effluent sufficiently for discharge to the environment. In order to overcome this problem, Yarwun implemented a seawater-sulphuric acid neutralisation process.

The purpose of this investigation was to assess the changes in neutralisation chemistry, in particular aluminium solubility, as a result of the use of acid with seawater. Further, a model was developed to enable a prediction of aluminium concentration in the neutralised supernatant based on the refinery's current neutralisation strategy. Species such as vanadium, molybdenum and arsenic, which are also considered detrimental to the environment and removed through the neutralisation process, were not investigated.

## 2. Experimental method

**Samples:** Samples of last washer underflow and oxalate settler underflow were collected and mixed in a volumetric ratio similar to that observed in the refinery.

**Initial Titrations:** Incremental amounts of seawater were added to the last washer/oxalate underflow mixture and the pH recorded. The same titration was then performed with 10% sulphuric acid.

Titration were performed to enable calculation of the volume of seawater or acid required, to neutralise the mixture to a specific pH.

**Neutralisation simulations:** All neutralisation simulations were performed in a beaker with overhead stirrer, at room temperature for 5 minutes. A series of last washer/oxalate underflow samples were neutralised to various pH values with either seawater, acid or a combination of the two. In the case of a combination, seawater and acid were dosed simultaneously. Neutralised mud samples were centrifuged and the liquor collected for analysis. Soluble aluminum was measured using ICP.

## 3. Results and discussion

### Aluminium levels in neutralised supernatant

The concentration of dissolved aluminium in washed mud is reduced when neutralised with seawater. The dissolved aluminium concentration of neutralised LWU as a function of pH can be found in Figure 1. The neutralisation reaction was performed with either seawater or 10% sulfuric acid over a range of pH values, ~10.00 – 8.45 (Tables 1a and 1b).

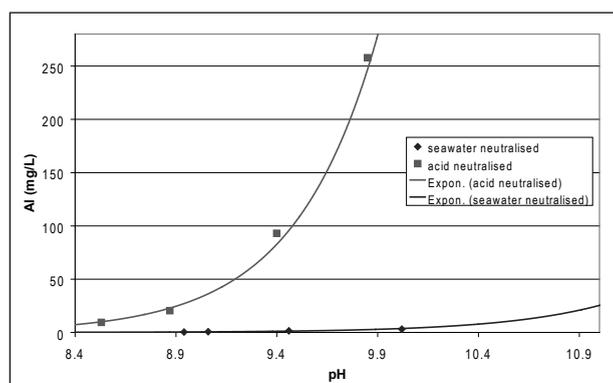


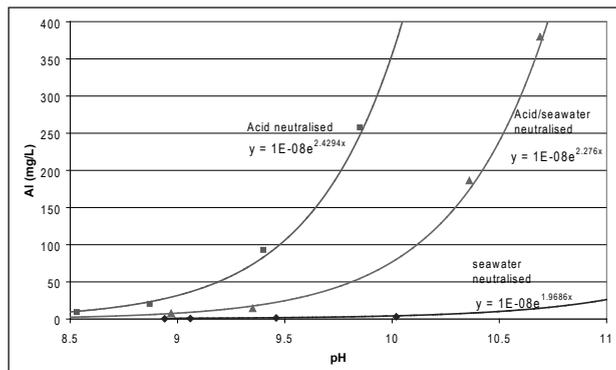
Figure 1. Soluble Aluminium present in neutralised mud

**Table 1. Dissolved aluminium levels in mud neutralised with acid (a) or seawater (b)**

a)		b)	
pH	Acid neutralised mud Dissolved Al (mg/L)	pH	Seawater neutralised mud Dissolved Al (mg/L)
9.85	258	10.02	3.07
9.4	93	9.46	1.46
8.87	20.4	9.06	0.66
8.53	9.4	8.94	0.38

The soluble aluminium content of mud neutralised with acid is significantly greater than mud neutralised by seawater for equivalent pH values. For example, at a pH of ~9.0, the dissolved aluminium concentration of acid neutralised mud is 30 times greater than the aluminium concentration of sea water neutralised mud. At a pH of ~10.0, a 90 fold increase in the aluminium concentration is evident.

Figure 2 displays a curve representing the aluminium concentration versus pH of LWU after it was neutralised in the laboratory with a seawater-sulfuric acid mixture. The volumetric ratio of seawater to acid was kept constant for each reaction, and this uncovered an exponential relationship between dissolved aluminium concentration and pH in the neutralised effluent



**Figure 2. Soluble Aluminium in mud neutralised with seawater-sulphuric acid mixture**

#### Development of model to predict soluble aluminium in neutralised mud

Using data from Figure 2 a model was proposed to predict aluminium concentration in neutralised mud as a function of pH, seawater and acid. The model (equation 2) states:

$$Al \text{ (mg/L)} = 1 \times 10^{-8} \exp(\beta \times \text{pH}) \quad [2]$$

where  $\beta$  is dependant on the amounts of seawater and acid used in the neutralisation. The formula for  $\beta$  (equation 3) states:

$$\beta = C_1[A] + C_2[SW] \quad [3]$$

- [SW] is the seawater fraction. [SW] is equal to the moles of equivalent caustic-neutralising ions from seawater divided by the total moles of caustic-neutralising ions added to the system;

$$[SW] = \frac{2 \times n(\text{Mg}^{2+})}{2 \times n(\text{Mg}^{2+}) + n(\text{H}^+)} \quad [4]$$

- [A] is called the acid fraction and is equal to the moles of  $\text{H}^+$  ions from the acid divided by the total moles of caustic-neutralising ions added to the system;

$$[A] = \frac{2 \times n(\text{H}^+)}{2 \times n(\text{Mg}^{2+}) + n(\text{H}^+)} \quad [5]$$

- $C_1$  and  $C_2$  are constants equal to 2.429 and 1.969 respectively.

As the amount of acid is maximised and SW minimised,  $\beta$  increases. This was evident when exponential curves were fitted to experimental data in Figure 3.

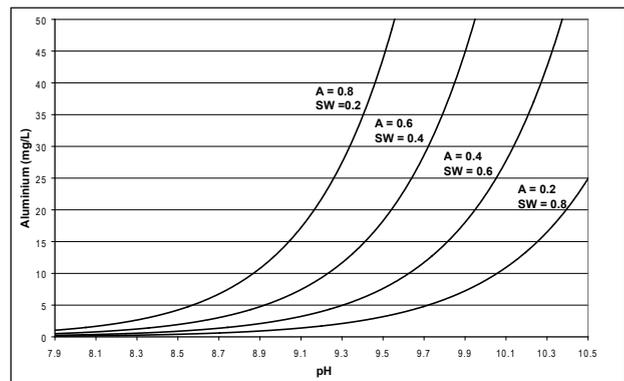
$$\text{When } [SW] = 1 \quad [A] = 0 \quad \beta = 1.969$$

$$\text{When } [SW] = 0.35 \quad [A] = 0.65 \quad \beta = 2.276$$

$$\text{When } [SW] = 0 \quad [A] = 1 \quad \beta = 2.429$$

The model is accurate for mud neutralised to pH values within the range 8.0 to 10.5. Within this range the model compared well with plant data. Importantly, this is the range over which refinery neutralisation will occur. Lab data indicated that above a pH of 10.7, the aluminium relationship with pH in the case of a seawater-acid mixture, is no longer exponential but forms an S-curve relationship.

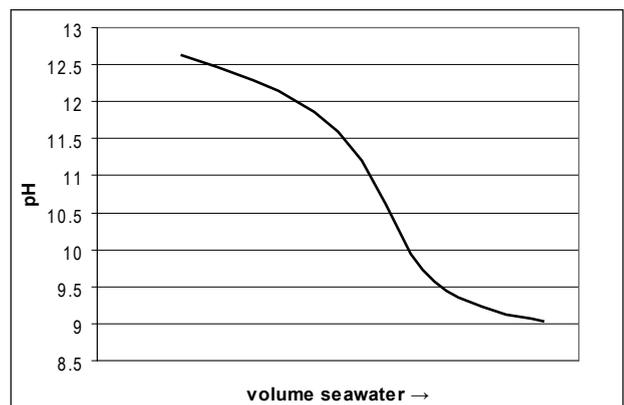
The model can be used to show that as the acid fraction increases, the pH required to reduce aluminium concentration to a specific level decreases significantly. This is best displayed in Figure 3, which plots aluminium concentration as a function of pH for various acid fractions.



**Figure 3. Soluble Aluminium as function of pH for different sea water and acid fractions**

#### Chemistry during neutralisation of mud with seawater-sulphuric acid mixture

The increase in soluble aluminium in neutralised mud as seawater is replaced with acid is best explained by the different products that precipitate and ultimately remove aluminium from solution. Hydrotalcite, formed when liquor reacts with  $\text{Mg}^{2+}$  in seawater, has a pH of about 10.6. This was equivalent to the endpoint of a titration curve when incremental amounts of seawater were added to LWU liquor, shown in Figure 4.

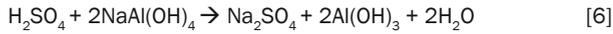


**Figure 4. Titration of LWU liquor with seawater**

In order to reduce the pH below 10.6, excess magnesium is required. Excess magnesium forces equation [1] to the right.

Aluminium is precipitated as hydrotalcite, so there is very little sodium aluminate remaining in solution below pH 10.6. This was evident in lab simulations when, at a pH of 10.0, soluble aluminium in sea-water neutralised mud was measured to be as low as 3.1mg/L.

Gibbsite,  $\text{Al}(\text{OH})_3$ , thought to form when sulphuric acid reacts with LWU liquor (Smith 2005), is a neutral compound. In aqueous solutions close to neutral pH (~7), the solubility of gibbsite is very low (Wefers, 1987, p.3). The simplified reaction of sodium aluminate with sulphuric acid is shown below:



Gibbsite is also amphoteric, so the endpoint of the LWU titration using sulphuric acid is approximately 7 (Figure 5).

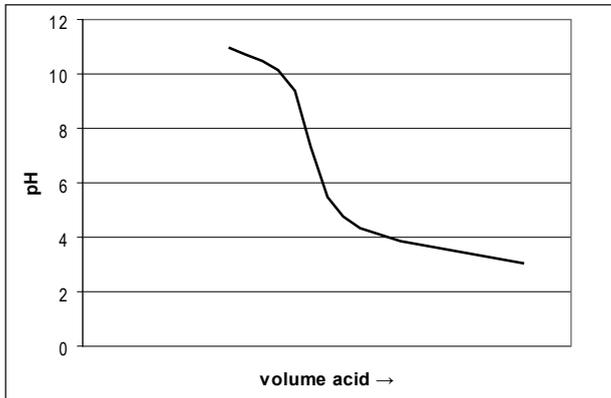


Figure 5. Titration of LWU liquor with 1% sulphuric acid

Therefore, a titration of LWU with sulphuric acid requires a much lower pH value (~8.0) to precipitate aluminium to below 3mg/L when compared to seawater (~10.6).

Neutralising LWU with a seawater-sulphuric acid mixture results in equations [1] and [6] occurring simultaneously. As the portion of acid in the mixture increases, the pH required to reduce aluminium concentration to an acceptable level is reduced. This is because there is more of equation [6] occurring and less of equation [1].

The formation of gibbsite in place of hydrotalcite not only causes a shift in soluble aluminium levels in the neutralised mud but is likely to have an affect on other elements such as vanadium. Although not investigated, the formation of gibbsite in place of hydrotalcite has the potential to reduce the incorporation of species such as vanadate into the hydrotalcite matrix.

#### 4. Conclusions

Neutralisation of last washer underflow reduces dissolved aluminium levels regardless of whether neutralisation is conducted with seawater, acid or a combination of the two. Seawater neutralisation, however, is more effective at removing aluminium from solution.

In the case of seawater neutralisation, soluble aluminium is removed from solution via the precipitation of hydrotalcite. At pH values below 10, there is very little aluminium in the liquor, <3mg/L. However, when acid is used for neutralisation,

aluminium is removed via precipitation of the neutral solid gibbsite ( $\text{Al}(\text{OH})_3$ ). As a result, a much lower pH value is required to achieve acceptable aluminium levels if all the neutralisation demand is met with sulphuric acid.

When a seawater-sulphuric acid mixture is used to neutralise red mud, the pH needed to achieve the required aluminium level is lower as the portion of acid is increased.

#### References

1. Smith H. D., Parkinson G. M., "Seawater Neutralisation: Factors affecting adsorption of anionic chemical species", 7th International Alumina Quality Workshop, 2005, pp 221-224.
2. Anderson J., Smith M., "Gove Seawater Neutralisation Testwork: Phase 1: Establishing Primary Neutralisation Parameters, Phase 2: Ecotoxicology Testing", QRDC Internal report, Q07/004 Sept 2007.
3. Wefers K., Misra C., Oxides and Hydroxides of Aluminium, Alcoa Laboratories, 1987.