

## Impact of beneficiated seawater on red mud neutralization

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### Abstract



The neutralisation of Bayer liquor with seawater triggers precipitation of stable alkaline products. This precipitation causes a reduction in solution pH and dissolved metal concentrations in the effluent, which is suitable for discharge into marine environments. Magnesium and calcium are the key reagents in the neutralisation process. Enhancing the concentration of these reagents in seawater could potentially improve the volume efficiency of the neutralisation process as well as the kinetics associated with precipitation of the neutralisation products. This investigation compared alternative sources of seawater where the magnesium and calcium were both beneficiated using water filtration technology: nanofiltration and reverse osmosis. The investigations indicated that solutions with beneficiated magnesium and calcium increase the productivity potential of the neutralisation process with minimal implications on the composition and stability of precipitates formed. The application of the beneficiated sources also enhances the associated environmental benefits. The study also compared potential capital and energy savings associated with the use of beneficiated calcium and magnesium on downstream neutralisation processes by looking at a range of possible flow sheet options.

**Keywords:** Seawater neutralisation; nanofiltration; reverse osmosis; hydrotalcite; calcite.

### 1. Introduction

Bauxite residue produced by the Bayer process is a complex alkaline tailings containing many different metal oxides, oxyhydroxides and trace metals. The alkalinity of the residue exists in both solid and solution as [1]:

- Entrained liquor (sodium hydroxide, sodium aluminate and sodium carbonate)
- Calcium compounds, such as hydrocalumite, tri-calcium aluminate and lime
- Sodalite.

McChonchie *et al*, [2] described a red mud neutralisation procedure that uses magnesium and calcium from seawater, or enriched sources of magnesium and calcium such as seawater brines, as the most cost-effective neutralisation procedure for red mud at the time. The neutralisation involves the precipitation of predominantly hydrotalcite ( $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ ) and calcium carbonate ( $CaCO_3$ ) [3, 4] as a result of mixing magnesium and calcium salts with alkaline Bayer liquor entrained within red mud. Large volumes of seawater are required (15 to 20 times the volume of red mud) to achieve the required neutralisation and the environmental standards necessary for discharge back to marine environments [5].

The cost of alumina production is generally increasing and one aspect of this is the mining of lower grade bauxite ore for processing. It is therefore necessary to find opportunities to reduce capital and operating costs to offset this trend. Taylor *et al* [6] explored the option of beneficiating the calcium and magnesium using nanofiltration. The goal was to reduce the volume of seawater required for the neutralisation reaction and to improve the reagent

efficiency of the precipitation reactions. These reductions in reagent flows could translate into increased productivity with reduced infrastructure and energy costs. Some high level cost analyses were also performed.

The solutions used in this assessment were unaltered seawater and two beneficiated seawater brines produced using reverse osmosis (SWRO) and nanofiltration (NF) membranes. In basic terms, RO rejects 99.5 to 99.8 % of all salts at relatively neutral pH. The degree of concentration of salts in seawater is primarily controlled by the osmotic pressure of the solution and as a result the volume recovery of the filtered permeate ranges between 40 and 50 %. For a plant that achieves a 50 % volume recovery, the net concentration factor for all salts is approximately double. NF has a slightly different rejection mechanism, which largely relies on the charge density of the membrane polymer and dissolved species. In general, at near neutral pH, multivalent ions, such as Mg and Ca, achieve a 98.5 – 99.5 % rejection whereas monovalent ions, such as Na and Cl, achieve minimal to no rejection. The deportment of these monovalent ions is largely dependant on the overall solution charge balance between the permeate and concentrate streams. A significant advantage of using NF over RO, in addition to the higher concentration factors for  $Mg^{2+}$  and  $Ca^{2+}$ , is the considerably lower  $Na^+$  and  $Cl^-$  concentrations relative to the enhanced  $Mg^{2+}$  and  $Ca^{2+}$  concentrations. This could have significant benefits when considering re-use options for red mud (Taylor *et al*, 2011, Couperthwaite *et al*, 2014).

This study has expanded on the work completed by McConchie *et al* [2] and Taylor *et al* [6] by comparing the neutralisation efficiency of different membrane filtered seawaters and completing cost estimate comparisons for different flow sheet options. The cost analyses were conducted to assess whether the capital associated with a purpose built membrane plant could be offset by reductions in downstream pumping, piping, tailings storage and other neutralisation capital. The laboratory tests for this study were completed using unaltered seawater, seawater beneficiated by a NF membrane (70 % volume recovery) and SWRO (50 % volume recovery). The concentration factor for both  $Mg^{2+}$  and  $Ca^{2+}$  in these beneficiated seawaters is approximately triple and double respectively. The cost analyses for the NF plant option were based on a volume recovery of 75 % and a  $Mg^{2+}$  and  $Ca^{2+}$  concentration factor of 4, a recovery achieved by the investigators in additional tests. The cost analyses for the RO plant option were based on a volume recovery of 40%, which is a standard recovery for SWRO plants. This provides a concentration factor of 1.7.

## 2. Experimental

### 2.1 Materials

Bayer liquor used in this study was created from a saturated evaporated liquid (SEL) with a  $Al_2O_3$  concentration of 96 g/L. Solutions similar to those used in previous studies were prepared by the dilution of SEL with known amounts of ultrapure water, sodium hydroxide (NaOH) and sodium carbonate ( $Na_2CO_3$ ) as required to simulate the decant liquor from red mud discharge (Couperthwaite *et al*. 2013).

Seawater (SW) was collected from Perth (Western Australia) at a depth of 4 m. The SW was pre-filtered using 5  $\mu m$  cartridge filters before membrane filtration. A portion of this seawater was then processed by NF and SWRO filtration to provide the beneficiated test solutions. Another portion was spiked with known amounts of AR grade magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ ) and calcium chloride dehydrate ( $CaCl_2 \cdot 2H_2O$ ).

NF seawater was prepared using a 101.6 mm (4") diameter spiral wound DK membrane from GE Power and Water at a constant pressure of 2500 kPa and flux of 30 L/m<sup>2</sup>h

- There may be a business case for a refinery to increase its red mud neutralisation capacity during an upgrade by installing a membrane plant to beneficiate seawater rather than upgrade much of the existing plant neutralisation infrastructure.

## 5 References

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