# A NOVEL AND ENVIRONMENTALLY FRIENDLY PROCESS FOR THE TREATMENT OF BAYER PROCESS RESIDUE

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## Abstract

Sea water neutralisation of Bayer process residue has been used as a method for alkali and dissolved aluminium removal by direct disposal in the ocean for many years. The reaction mechanisms for such a process are quite complex. The neutralisation process does not eliminate hydroxide but converts the soluble, strongly caustic into less soluble, weakly alkaline solids with active participation of the magnesium content in seawater.

In order to achieve a status of '*Zero Harm*' towards the environment, Queensland Alumina has sought to improve residue disposal by commissioning a novel neutralisation process. This process permits the controlled reaction between 800 $m^3$/h of Bayer residue, containing 10 to 15 g/l liquor phase soda, with seawater in an appropriately sized reactor. The neutralised solids and magnesium deficient seawater are then separated via conventional clarifier, fitted with Vane Feedwell technology which provides a uniform rise profile, resulting in overflow solids of approximately 30 mg/l. The neutralised and de-watered mud is then pumped and prepared for semi-dry stacking.

## 1. Introduction

### 1.1 Basic mud disposal techniques

Over 100 million tonnes of red mud is produced annually (Power, *et. al*., 2011) predominantly from the Bayer process. Prior to the 1970s there were two main methods of residue disposal, these being marine discharge and lagooning. Marine discharge was deemed a favourable practice as it required no land for storage, limited capital and operating expenditure, little risk of caustic leaching into ground water and an abundant magnesium supply. It results however, in large quantities of red mud solids being dispersed over the local seabed. Environmental awareness and destruction of local ecosystems has seen a decline in this disposal method even if this practice was still recently in use (Official Journal of the European Union, 2006).

Lagooning is a land based wet disposal method, of what effectively is last washer underflow with little or no additional processing, but implies that the long term co-existence of a highly alkaline lake with an ecosystem must be workable. Such impoundments require rigorous engineering and maintenance of the dam walls. They risk ground water contamination and a dam rupture would result in catastrophic outcomes to both people and the environment; the 2010 Aijka disaster in Hungary is a classic example of this type of dam rupturing.

More recently 'Dry Stacking' or 'Semi Dry Stacking' has been proposed as a safe alternative technique. A smaller footprint is required, liquor can be either returned to the plant or processed further for safe disposal, and many of the environmental and safety issues associated with lagooning are mitigated. In dry or semi dry stacking, the red mud is concentrated so that it exhibits the correct rheological properties and can be farmed on sloped beds with the liquid phase draining away and pumped off to reclaiming ponds.

### 1.2 QAL's long term residue disposal plan

Queensland Alumina (QAL) has been neutralising red mud with seawater for a number of years (Graham and Fawkes, 1992). Up until recently the neutralisation technique was 'in situ' in the actual dam itself (Figure 1: Satellite photograph of QAL's residue disposal complex.1, Red mud dam #2). A recent shift in disposal strategy by QAL (Richter *et al*., 2008) resulted in the complete refurbishment of the original disposal area which was constructed in parallel with the original plant (Red mud dam #1). The disposal method employed is semi-dry stacking and, unlike other traditionally dry stacked disposal areas, the red mud is neutralised prior to stacking, requiring a dedicated seawater neutralisation plant.

**Figure 1:** Satellite photograph of QAL's residue disposal complex.

### 1.3 Seawater neutralisation as an alternative technique

Lagooning traditionally offered plants the possibility to discharge both liquor and solids phases of their residue, which allowed for refineries processing bauxites high in organic content to 'purge 'impurities. Dry stacking is an attractive technique to deal with solid phase residue, and allows for much of the liquid phase, highly alkaline in aluminate and caustic, to be reclaimed. This approach can prove to be problematic for refineries processing bauxites with high levels of impurities and without the benefit of liquor purifying unit operations such as liquor burning or wet oxidation. Alternatively, the liquor content can be further treated prior to disposal. Neutralisation of red mud with seawater is one such treatment technique.

Sea water neutralisation of red mud is a complex suite of reactions which results in a number insoluble compounds forming such as brucite, portlandite (Taylor, *et al*., 2011) and hydrotalcite that all reduce overall alkalinity. Hydrotalcite is a stable and insoluble compound acting as a sink for dissolved aluminium and hydroxide ions resulting in a net reduction in pH of the red mud (Smith and Parkinson, 2005 and Palmer *et al*., 2009).

Based on QAL's long term residue disposal plan and sustainable refinery operation with zero harm to the environment, the two main objectives for a dedicated seawater neutralisation plant are to:

1. Provide sufficient contact and residence time for a net reduction in liquor phase alkalinity of the red mud.
2. Provide continuous separation of the neutralised liquid phase and solid red mud.

Both these objectives will be explained in the following two sections.

## 2. Sea Water Neutralisation Plant and Reduction of Liquor Phase Alkalinity

Queensland Alumina can produce up to 800 kL/h of red mud slurry, which is treated with up to approximately 5000 kL/h of seawater.

Figure 2: Basic flowsheet of the neutralisation facility at Queensland Alumina2 illustrates the basic flowsheet behind the sea water neutralisation facility. The mud/seawater mixture is held in a neutralisation reactor so that the caustic is chemically neutralised. The hydrotalcite rich mud and magnesium deficient seawater are then decanted using a conventional clarifier fitted with 'Vane Feedwell' technology, and transported to red mud dam 1.

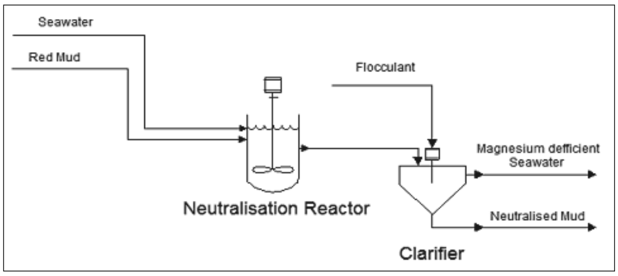

**Figure 2: Basic flowsheet of the neutralisation facility at Queensland Alumina**

The supernatant magnesium and aluminium deficient seawater is channelled to red mud dam 2, where it progresses through the main decant pond and is released to the environment. Figure 3: Aerial view of the neutralisation facility at Queensland Alumina3 is an aerial view of the whole neutralisation plant.

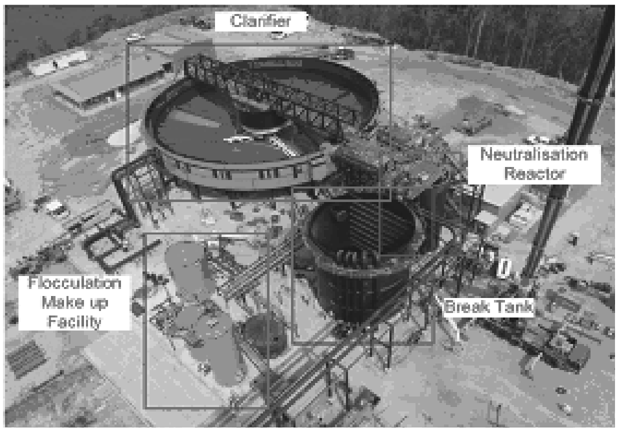

**Figure 3: Aerial view of the neutralisation facility at Queensland Alumina**

This small facility is able to treat the entire rate of production of red mud from Queensland Alumina to environmentally acceptable levels. As highlighted in section 1.3, magnesium actively reacts with the liquor phase constituents of red mud, namely aluminium and hydroxide ions. Figure 4: Aluminium and magnesium levels of clarifier overflow and magnesium levels of influent seawater.4 highlights magnesium content in the sea water pre-neutralisation, and the magnesium and aluminium content measured at the clarifier overflow. During the neutralisation process the magnesium levels drop from approximately 1200 mg/L to around 300 mg/L and the aluminium levels drop to less than 5 mg/L. These net reductions of magnesium and aluminium are a result of the formation of the insoluble salts of which hydrotalcite is a product.

The other important aspect of the neutralisation is the net reduction of alkalinity. The pH of the supernatant liquor post neutralisation consistently remains around 9 (Figure 5: Clarifier overflow pH, post seawater neutralisation.5) thus demonstrating the efficacy of the process.

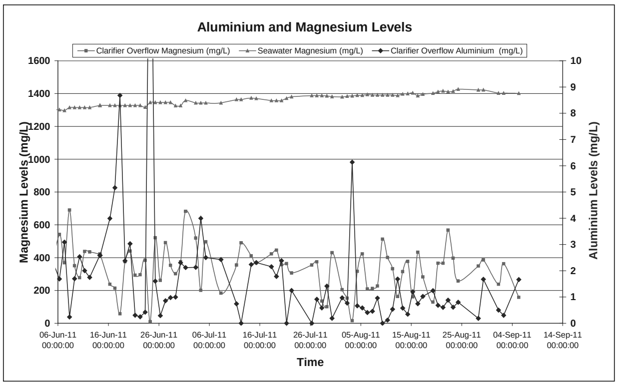

**Figure 4: Aluminium and magnesium levels of clarifier overflow and magnesium levels of influent seawater.**

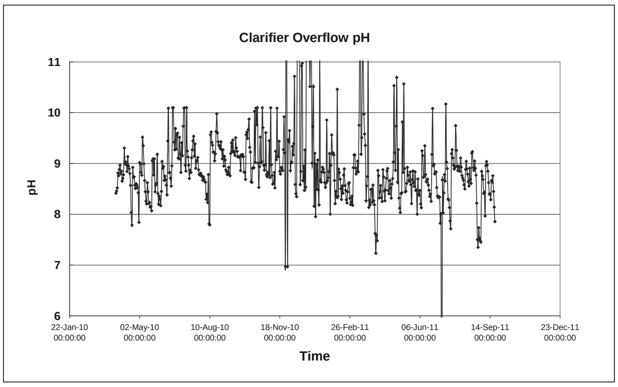

**Figure 5: Clarifier overflow pH, post seawater neutralisation.**

## 3. Feedwell Technology

Recent industry trends demand for smaller footprint clarifiers which can handle larger slurry flowrates.

The QAL sea water neutralisation clarifier separates 5800 kL/h of neutralised red mud whilst also achieving a consistent and desirable underflow density of 340 g/L.

These objectives become challenging when hydrotalcite is present, as it reduces the bulk density of the neutral thickened mud. Hydrotalcites have a specific gravity of 2, which can result in adverse solids compaction.

In order to achieve these objectives a new type of feedwell was used which effectively maximises flocculation efficiency whilst dictating bulk clarifier fluid dynamics.

Early feedwell designs unfortunately resulted in significant feed short-circuiting, inefficient feed and dilution liquor mixing, high aggregate shear forces on exit and hence overall inadequate feedwell and thickener performance. Consequently it was decided that additional efforts must be made to achieve density targets resulting in the installation of a new so called "Vane Feedwell" design at Queensland Alumina.

The Vane Feedwell is the result of many years of internal research and extensive in-house CFD by Outotec, followed by AMIRA and CSIRO CFD analysis and subsequent site testwork. A detailed description of feedwell types, history and development can be found in previous publications (Triglavcanin, 2008a and Triglavcanin, 2008b).

High energy in the incoming feed is required to maintain adequate mixing of the feed, dilution liquor and flocculant, however, a zone of low energy and low shear is required for aggregate growth. The concept of utilising axially sloped vanes, coupled with a radially sloped shelf within the feedwell, was incorporated into the Vane Feedwell design as a means to increase hold-up of the high density feed slurry, remove energy from the feed stream, effectively splitting the feedwell into an upper and lower zone.

The upper zone, into which feed, dilution water and flocculant are added, provides enhanced mixing and energy dissipation. This maximises flocculant adsorption, eliminates the possibility of coarse/fines segregation and ensures all particles are aggregated together by the flocculant. The lower zone promotes gentle mixing for continued aggregate growth, with the option for secondary flocculant dosing. This zone also enables aggregates to uniformly discharge under low shear conditions.

The resulting Vane Feedwell, is now the subject of seven international patents by Outotec and is diagrammatically depicted in Figure 6: Vane Feedwell design6.

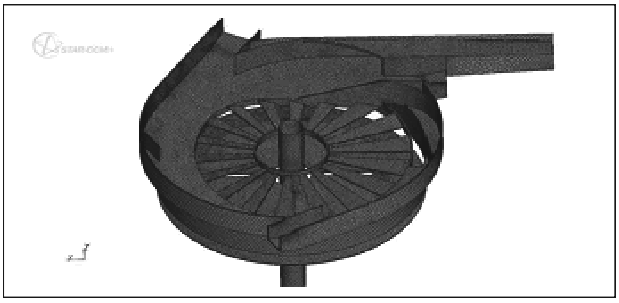

Figure 6: Vane Feedwell design

### 3.1 CFD modelling

The feedwell performance before and after the Vane Feedwell retrofit was modelled using computational fluid dynamics (CFD) by the CSIRO (Heath A R, 2008). Eulerian-Eulerian multiphase CFD was used with buoyancy included to correctly incorporate density effects. The k-e turbulence model was used with a mesh of ~1.6 million nodes, grouped predominantly in the feedwell region.

**Figure 7: Elevation view of flow pattern and solids concentration in unmodified feedwell.7** and Figure 8: Elevation view of flow pattern and solids concentration in Vane Feedwell. 8 show an elevation view of the flow pattern and solids concentration in the unmodified and retrofitted feedwell respectively. It is immediately obvious that the retrofitted Vane Feedwell has much better solids retention. In contrast, the unmodified feedwell has virtually no solids in the top half of the feedwell, with this zone being bypassed and not effectively utilised for flocculation.

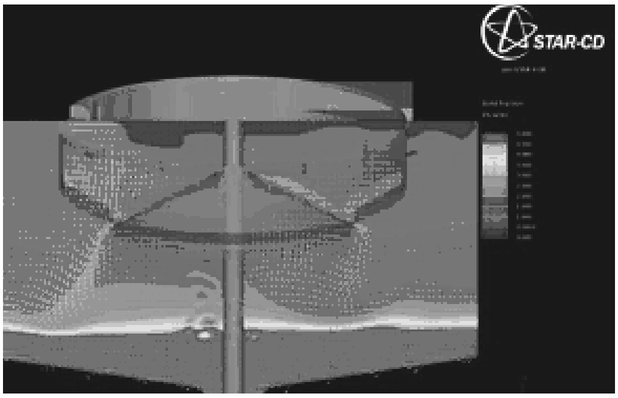

Figure 7: Elevation view of flow pattern and solids concentration in unmodified feedwell.

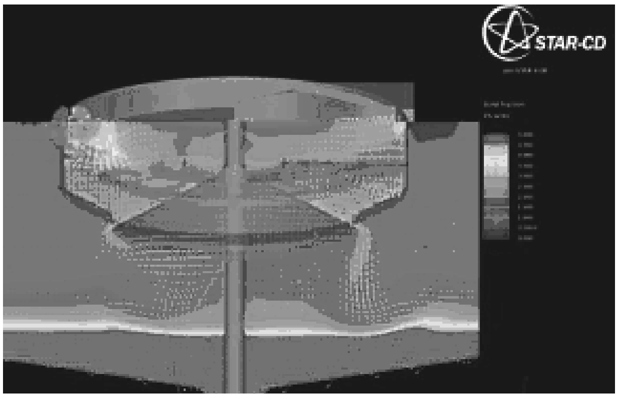

Figure 8: Elevation view of flow pattern and solids concentration in Vane Feedwell.

Figure 9: Flow pattern and solids concentration in the unmodified feedwell. Plane section is just below the surface level.9 to Figure 12: Flow pattern and solids concentration in Vane Feedwell. Plane section is just above the shelf/vanes at 0.75 m below surface. 12 show the reason for the improved solids distribution in the top of the feedwell. In the unmodified design the pre-diluted feed comes in the inlet area (Figure 9: Flow pattern and solids concentration in the unmodified feedwell. Plane section is just below the surface level.9) but plunges rapidly with little mixing (Figure 10: Flow pattern and solids concentration in the unmodified feedwell. Plane section at 1.0 m below surface.10). There is little swirl or solids in the top of the feedwell.

By comparison (Figure 11: Flow pattern and solids concentration in the Vane Feedwell. Plane section is just below the surface level.11 and Figure 12: Flow pattern and solids concentration in Vane Feedwell. Plane section is just above the shelf/vanes at 0.75 m below surface. 12) with the Vane Feedwell, the shelf and vanes have held the feed stream up in the top half of the feedwell and the swirl is maintained right the way around the surface, ensuring effective feed solids and flocculant distribution and mixing.

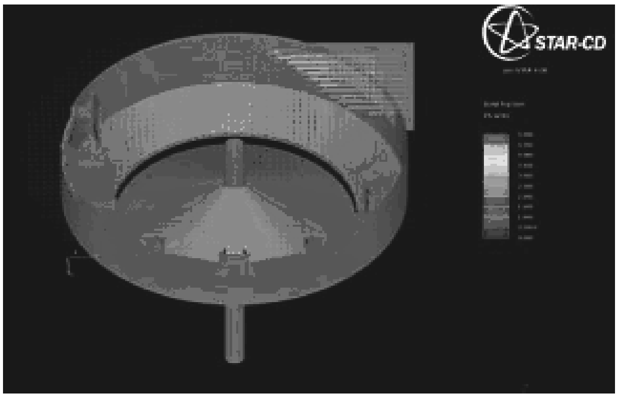

Figure 9: Flow pattern and solids concentration in the unmodified feedwell. Plane section is just below the surface level.

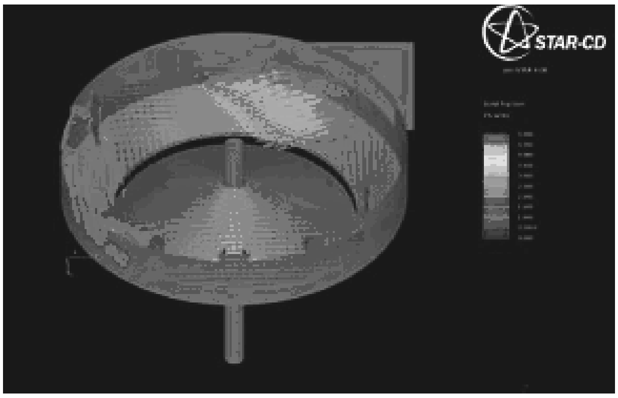

**Figure 10: Flow pattern and solids concentration in the unmodified feedwell. Plane section at 1.0 m below surface.**

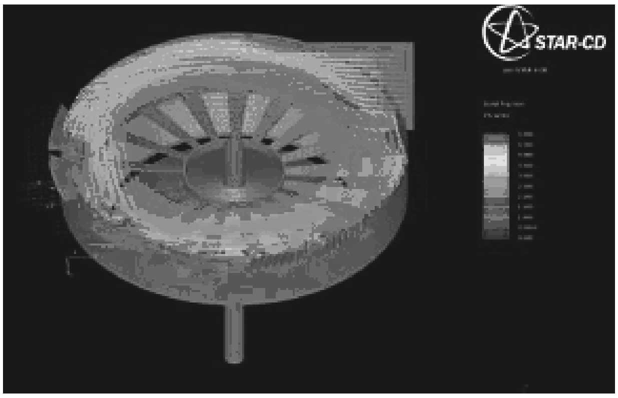

**Figure 11: Flow pattern and solids concentration in the Vane Feedwell. Plane section is just below the surface level.**

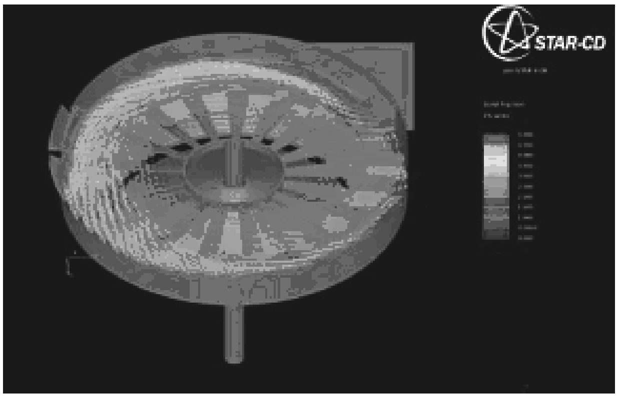

**Figure 12: Flow pattern and solids concentration in Vane Feedwell. Plane section is just above the shelf/vanes at 0.75 m below surface.**

Figures 13 and 14 show the elevation views of the flow patterns and shear rate distributions. Shear is a natural by-product of the turbulence dissipating the feed momentum/kinetic energy, however it is also a critical factor in flocculation. Turbulence provides mixing, both of feed and dilution liquor, but also flocculant and feed slurry. Moderate shear rates are then also required to create the particle collision required for flocculation. However, excessive shear rates will cause irreversible aggregate break-up, especially if they are applied late in the flocculation process. Ideally, shear rates should be moderate in the top of the feedwell where the flocculant is added, and then be lower in the lower zone to ensure the aggregates safe passage through to the settling and clarification zones out in the thickener tank.

Figure 13 and Figure 14 show the improvements from the Vane Feedwell retrofit. Without it, the shear rates are essentially too low throughout the feedwell. Moderate shear rates are seen on the middle LHS of Figure 13 due to the feed stream plunging through this region, but the solid residence time is too short in this region for good mixing or flocculation. Shear rates are higher at the exit gap. Normally this is to be avoided, however in this case the shear rates are so low that the bulk of the flocculation may well have been taking place in this exit region.

Fitting the Vane Feedwell components (Figure 14: Elevation view of flow pattern and shear rate in modified Vane Feedwell.14) clearly remedies this situation considerably. There are higher shear rates in the top of the feedwell which, when associated with the better solids retention in this area, will result in improved flocculation. Higher shear rates in this region also indicate better feed momentum dissipation. Finally, the shear rates are decreased in the exit region, indicating a reduction in flocculated aggregate breakage when discharging into the thickener body.

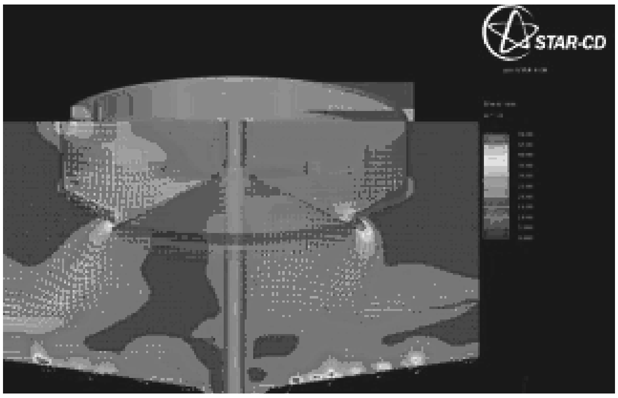

**Figure 13: Elevation view of flow pattern and shear rate in unmodified feedwell.**

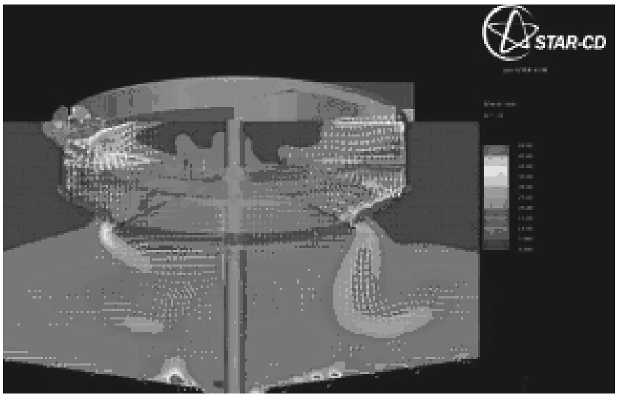

**Figure 14: Elevation view of flow pattern and shear rate in modified Vane Feedwell.**

The following two figures (Figure 15: View from below, horizontal plane through the feedwell discharge region for the unmodified feedwell.15 and Figure 16: View from below, horizontal plane through the feedwell discharge region for the retrofit Vane Feedwell. 16) show the exit symmetry. The views are from below, looking up at the bottom of the feedwell, with the vectors in the plane going through the discharge gap of the feedwell. Discharge symmetry is required to effectively use the entire thickener settling area, this ensures a near uniform rise rate from the liquid phase, thus resulting in improved overflow clarity.

**Figure 15: View from below, horizontal plane through the feedwell discharge region for the unmodified feedwell.**

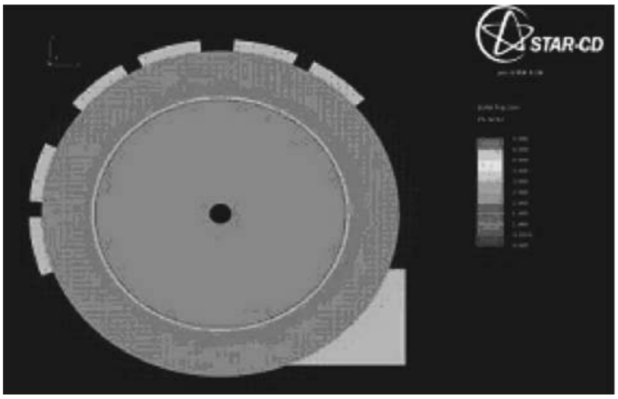

Figure 16: View from below, horizontal plane through the feedwell discharge region for the retrofit Vane Feedwell.

### 3.2 Vane Feedwell results

The red mud from Queensland Alumina is produced via three separate counter current washers, whereas the Vane Feedwell fitted clarifier at the neutralisation facility is a single unit with a relatively small footprint. Figure 17: Top and side view of the Vane Feedwell fitted at QAL's seawater neutralisation facility.17 is the top and side view of the Vane Feedwell installed at the seawater neutralisation plant, clearly indicating the sloped shelf, vanes, inlet channel and conical bottom.

Installation of this feedwell at Queensland Alumina has resulted in low solids overflow. Figure 18: Clarifier overflow solids.18 highlights the low level of solids carryover from the clarifier at the neutralisation facility, demonstrating how the solids in the overflow consistently varies between 25 and 35 mg/L. The low solids overflow concentration supports the CFD results in Figures 8 and 16, demonstrating how the uniform flow distribution leaving the feedwell and rising up through the clarifier has a positive impact on solids carryover. Likewise this clarifier has demonstrated it can deliver a consistently thick underflow solids (Figure 19: Clarifier underflow solids.19), the target underflow was 340 g/L, results show that concentrations between 360 and 420 g/L are consistently achieved.

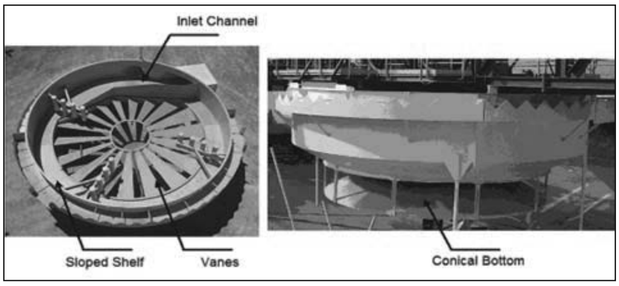

Figure 17: Top and side view of the Vane Feedwell fitted at QAL's seawater neutralisation facility.

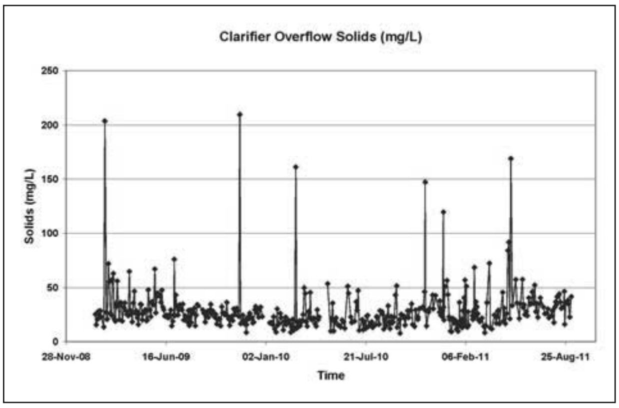

Figure 18: Clarifier overflow solids.

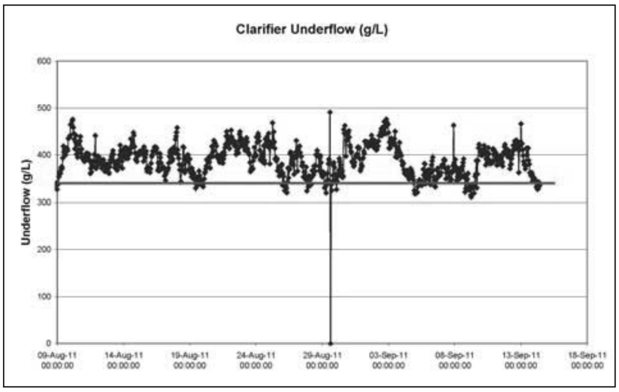

Figure 19: Clarifier underflow solids.

## 4. Conclusion

This process demonstrates that large scale seawater neutralisation of red mud, with an environmentally acceptable discharge, is achievable. The general objectives of this seawater neutralisation plant were to neutralise alkalinity present in the red mud and thicken neutral red for semi dry stacking. Results suggest that when sufficient seawater is added, the abundance of magnesium produces insoluble salts that reduce liquor phase alkalinity and soluble aluminium. One of the main precipitation products is hydrotalcite, a low density compound that proves difficult to thicken. The challenge of effectively thickening such a mixture and produce a clear overflow using a small footprint clarifier requires a feedwell which maximises its entire volume to effectively mix flocculant and mud, aggregate particles and minimise their breakage.

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