

CARBONATION OF BAUXITE RESIDUE

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Abstract

Alcoa World Alumina Australia (Alcoa) has been investigating residue carbonation as a potential major improvement opportunity for achieving residue storage with lower environmental risk and reduced potential for long-term management requirements. Comprehensive laboratory and pilot scale testing of residue carbonation was conducted during the period 1991 to 1996. Results from these pilot scale trials were promising with carbonated mud pH of 9 being achieved and leachate quality from the drying beds being maintained at around pH 10.

During the design for a drying area expansion at Kwinana in 1998/99, it was decided to include funds for the installation and operation of a full scale prototype carbonation facility, which would allow carbonation of all the residue deposited in this new drying area. This facility was commissioned during mid 2000 and has been the subject of a detailed monitoring and evaluation program. This paper details the findings from this evaluation.

1. Introduction

Alcoa World Alumina produces 16 million tonnes of alumina annually at its refineries located in Australia, the United States of America, South America and the Caribbean. This represents 22% of the world production of alumina. These refineries also produce over 20 million tonnes of an alkaline residue annually. Storage of this residue poses some major environmental challenges. The entrained solution in the residue contains caustic soda and other soluble compounds resulting from the reaction of the caustic soda with bauxite ore (such as a range of sodium-organic species and dissolved alumina) and also from reaction with air (such as sodium carbonate). From an environmental viewpoint it is mainly the alkalinity of the bauxite residue, which is of concern. Typically the solution entrained with the residue is alkaline with a pH of 13. If this material comes into direct contact with the natural environment it can result in undesirable increases in pH with adverse impacts. In addition to the alkalinity, the presence of small quantities of dissolved organic compounds and metals could be of environmental significance.

Alcoa has undertaken a number of development projects aimed at improving the methods of residue storage. This development work commenced in the early 1970s, with the primary focus coming from the discovery of ground water contamination below the Kwinana storage areas. The original containment areas had been constructed on the sandy coastal plain and relied upon a single 380mm thick clay layer to prevent contamination of the underlying aquifer. While the clay seal has been effective in preventing general seepage, there were a number of places where the clay was damaged during the operation life of the storage area. The damaged areas were possibly the result of cracking of the clay due to desiccation or erosion caused by rainfall.

As a result of the ground water contamination, improved methods of sealing the storage areas were adopted. New containment areas at Kwinana were constructed with a composite clay/synthetic membrane seal, and a drainage layer placed above this composite seal to reduce the hydrostatic head at the base of the residue, further reducing the potential for seepage. The drainage layer had the added advantage of increasing the consolidation of the residue, improving the storage efficiency of the area,

and recovering alkaline drainage water for return to the refinery.

Development work began in the early 1980s on alternative techniques and in 1985 "dry stacking" was adopted for Alcoa's Western Australian refineries. Dry stacking utilises a large diameter Superthickener to de-water the fine tailings, which is then spread in layers over the storage areas to de-water by a combination of drainage and evaporative drying. By utilising the coarse fraction of the tailings for construction of drainage layers and upstream perimeter embankments, the storage area can be constructed as a progressive stack, thus avoiding the need for full height perimeter embankments and allowing continued stockpiling on areas which were previously "wet" impoundments.

The initial cost of establishing dry stacking at Alcoa's three Western Australian refineries exceeded \$150 million. To justify the transition to dry stacking, a long term view of residue storage was adopted, and a number of considerations, other than simply costs, were brought into the cost benefit analysis:

- Solar drying of the residue produces higher density than can be achieved with wet disposal, reducing the overall volume of stored tailings.
- Progressive stacking allows the deposit to be taken to a height, which would not be economic with conventional wet impoundments.
- Higher density and increased deposit height means less land is used.
- Exposure of less land area to residue and the drained condition of the dry stack significantly reduce the risk of ground water contamination.
- Improved surface stability and drainage mean that completed areas can be reclaimed and re-vegetated quickly.
- Safety hazards to people and wildlife are reduced.

Despite the high initial cost of implementing dry stacking, the process was successfully implemented at all three of Alcoa's Western Australian refineries over the period 1986 to 1991. A number of operational techniques have since been developed to optimise the slurry distribution and drying processes, and these have now become standard practices. The advantages of reduced environmental risks and lower overall storage costs are now being realised.

2. Alcoa's Strategic Residue Planning

Alcoa has been preparing Long Term Residue Management plans for each of its WA refineries. The planning has involved extensive consultation with a range of stakeholders. While most are aware of the improvements made to residue storage practices over the past two decades, neighbours and local community continue to express concerns over the ongoing storage of an alkaline residue. Feedback from local residents and the broader community has focussed on;

- The potential for environmental impacts from dust or from the alkalinity of drainage waters effecting either ground or surface waters.
- The potential for direct impacts, particularly health risks associated with dust and odour.
- Concern over the sheer magnitude of the ultimate deposit that will be created. Questions remain over the visibility of the storage areas, particularly as the height of the deposits can now be significantly increased.
- Limitations to the potential for future land uses on areas used for residue storage.

Of particular concern, was the effect these issues would have on the re-sale value of their properties.

In response to the feedback received, Alcoa has limited the horizon for its residue planning to 30 years. During this 30 years, Alcoa has committed to a focussed effort on a number of the issues raised by the community. These include;

- Demonstration of an ability to contour and re-vegetate the outer slopes of the deposit, softening the visual impact of the deposits.
- Review of the approach to buffer management, with a focus on re-vegetation and creation of natural screening of the deposits.
- An ability to manage dust, demonstrating continued improvement on current performance.
- Clearly demonstrate that alkaline water is not going to impact on local ground water or surface water.

Alcoa has also committed to progressing key strategic initiatives, which include;

- Modification of the residue properties to the point where the residue can be considered of low risk to the surrounding environment, thus providing an opportunity to address concerns related to potential environmental impacts.
- Reduction in the volume of residue, reducing the ultimate size of the footprint. Through either beneficiation of the bauxite or re-use of the residue, a reduction in the volume will extend the life of the nominal 30-year footprint.

Alcoa has investigated a wide range of neutralisation techniques including sea water neutralisation, treatment with a sea water concentrate, acid neutralisation, sintering and treatment with waste CO₂. Of these, CO₂ treatment appeared to offer the best overall fit with the refineries located in WA.

3. Residue Carbonation

3.1 What is Residue Carbonation?

Residue carbonation is the addition of gaseous CO₂ to the thickened residue slurry, prior to the deposition of this slurry onto the residue drying areas. The CO₂ reacts with the alkaline components within the liquor, and if held in contact with the slurry for long enough, the adsorbed and solid forms of alkalinity are also reacted. The table below lists the stoichiometric carbon dioxide demand requirement to attain a pH of approximately 8.3 for entrained liquid in a typical kwinana superthickener underflow (slurry density of 48% solids wt/wt).

3.2 Prototype Installation

Alcoa conducted comprehensive laboratory and pilot scale testing of residue carbonation during the period 1991–1996. Small-scale field trials were completed at Kwinana in 1996, which included testing of a range of mixing devices and studies on the behaviour of carbonated mud deposited in small drying cells. Results from these pilot scale trials were promising, with carbonated mud pH's of 9 being achieved and leachate quality from the drying beds being maintained at around pH 10. A number of alternative slurry/gas mixing techniques were tested during this trial work with varying results. The relatively small scale of the mud slurry flow through the test rig limited the applicability of the results, so further development work on full-scale equipment was considered necessary to optimise the process.

During the preparation and planning for a drying area expansion at Kwinana in 1998/99, it was decided to include funds for the installation and operation of a full scale prototype facility that would allow carbonation of all the residue deposited in this new drying area. These facilities were commissioned mid 2000, and performance monitoring of these facilities has been done over the past two years.

3.3 Performance Monitoring of the Full Scale Prototype

The Kwinana dry stacking of residue relies upon thickened slurry being deposited across a drying bed. A large diameter thickener, called a Superthickener produces this slurry. The average underflow rate for the superthickener is 250kl/hr at a solids content of 48% (wt/wt), however the underflow rate can vary between 170 and 350 kL/hr at solids content ranging from 45.6 to 49.0 % (wt/wt). The carbonation plant has been operated at a range of dose rates varying between 16 and 25.5 kilogram of CO₂ per kiloliter of slurry (kg/kL). The lowest pH measured was 8.5 at a carbon dioxide dose rate of 25.3 kg/kL. The typical pH of liquor from the slurry is shown in Figure 1 as a function of the carbon dioxide dose rate.

The pH of liquor from samples of carbonated residue stored in sealed containers was found to increase with time up to a maximum within approximately 300 hours. A similar increase in pH was also found to be occurring within

Table 1 — Stoichiometric carbon dioxide demand required to treat a thickened residue slurry

Feed	kg CO ₂ /kL	Reaction
Al ₂ O ₃ (liquor)	5.1	NaAl(OH) ₄ + CO ₂ ⇒ NaAlCO ₃ (OH) ₂ + H ₂ O
TC (liquor)	6.4	NaOH + CO ₂ ⇒ NaHCO ₃
TA (liquor)	0.8	Na ₂ CO ₃ + CO ₂ + H ₂ O ⇒ 2NaHCO ₃
TC (adsorbed)	3.4	NaOH + CO ₂ ⇒ NaHCO ₃
TA (adsorbed)	0.2	Na ₂ CO ₃ + CO ₂ + H ₂ O ⇒ 2NaHCO ₃
TCA-6	15.8	3Ca(OH) ₂ .2Al(OH) ₃ + 3CO ₂ ⇒ 3CaCO ₃ + Al ₂ O ₃ .3H ₂ O + 3H ₂ O
DSP Na ₂ O	1.8	Na ₆ [AlSiO ₄] ₆ 2NaOH + 2CO ₂ ⇒ Na ₆ [AlSiO ₄] ₆ + 2NaHCO ₃
Total	33.7	

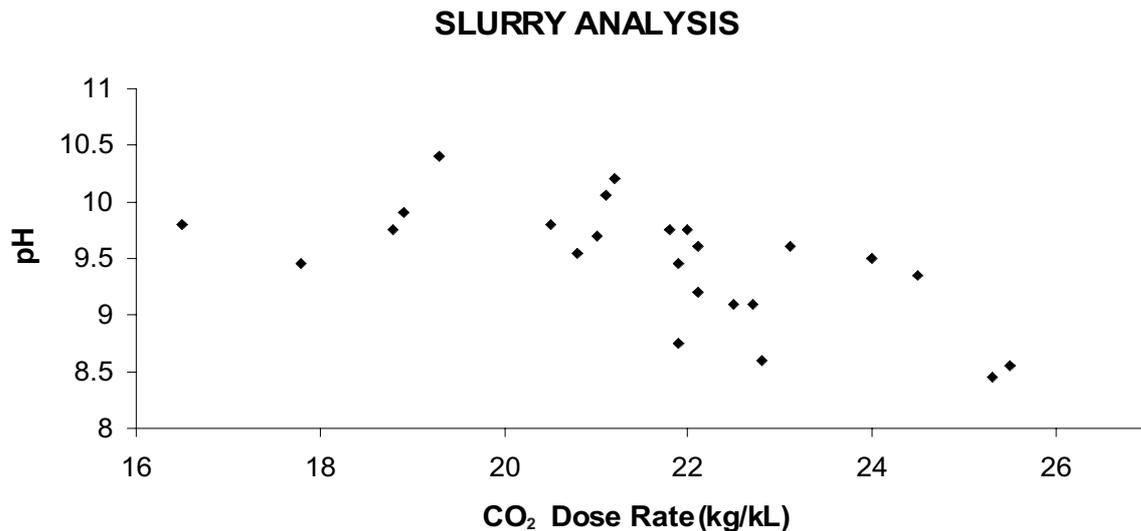


Figure 1 — The initial pH of the treated slurry as a function of CO₂ dose rate

the drying beds. The average increase in the pH was 2.5 units. This increase in pH is believed to be the results of incomplete carbonation of the solid phase alkalinity, in particular the tricalcium aluminate (TCA-6). The TCA-6 is one of the secondary minerals formed when lime is added to plant liquor in the Bayer process.

The drying bed, into which the carbonated residue is deposited, has been extensively monitored. Parallel monitoring has been undertaken in a non-carbonated drying bed. Some of the results from this monitoring are shown in Figures 2, and 3.

Measurements of the drying rates of both carbonated and non-carbonated slurries have been made. This has been done through regular sampling and analysis of the drying residue, as well as recording the overall storage efficiency of the drying beds. As shown in Figure 4, the strength of the carbonated residue is significantly greater than the strength of the non-carbonated residue at a given solids concentration.

This is thought to be the result of precipitates, which form when the CO₂ is mixed with the slurry. The target

minimum strength to ensure long term deposit stability is 25kPa, hence carbonation may allow this target to be reached a lot earlier in the drying cycle, allowing cycle times to be reduced. Monitoring of the overall drying performance of the treated and untreated residues has also shown significant improvement in the rate of moisture loss to evaporation, further reducing the drying cycle time. This increase in the rate of moisture loss is thought to be a result of eliminating an alumina based crust, which normally forms on non-carbonated residue and early cracking which is a flow on effect of the early strength development.

4. Benefits anticipated from Residue Carbonation

Residue carbonation offers a major improvement opportunity for achieving residue storage with lower environmental risk and reduced implications for long term management of the storage areas. While the carbonated residue is not chemically benign, if the pH, or strong alkalinity, can be reduced significantly, future deposits would be less likely to be regarded as hazardous waste landfills.

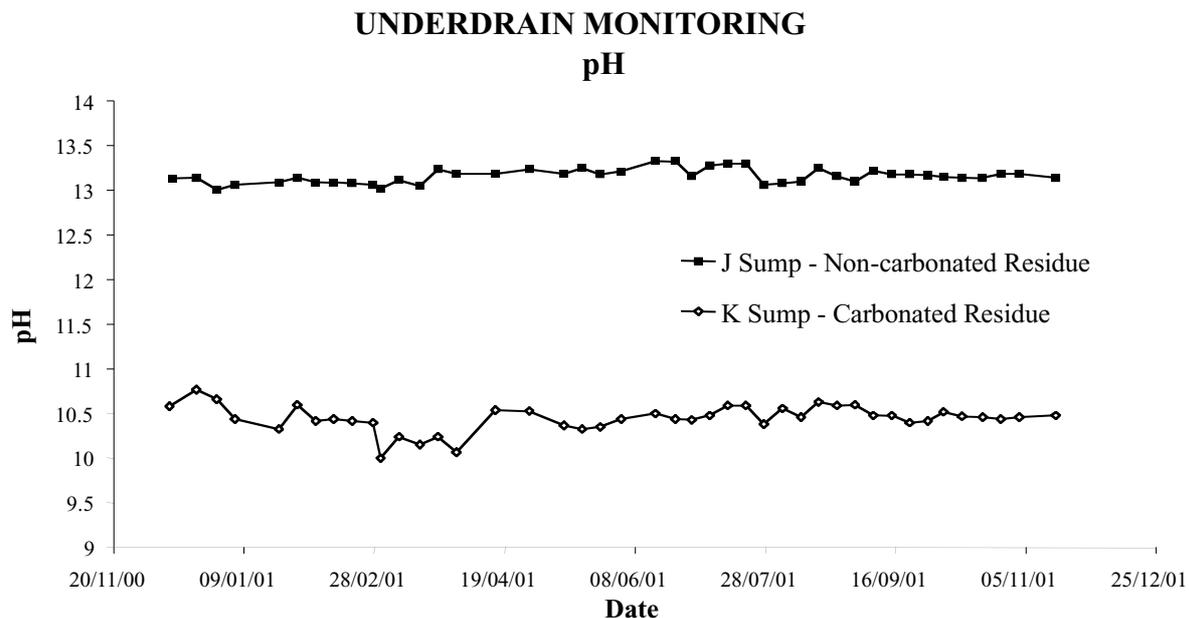


Figure 2 — Measurements of pH in the underdrains of carbonated and non-carbonated drying beds

UNDERDRAIN MONITORING

Alumina in solution

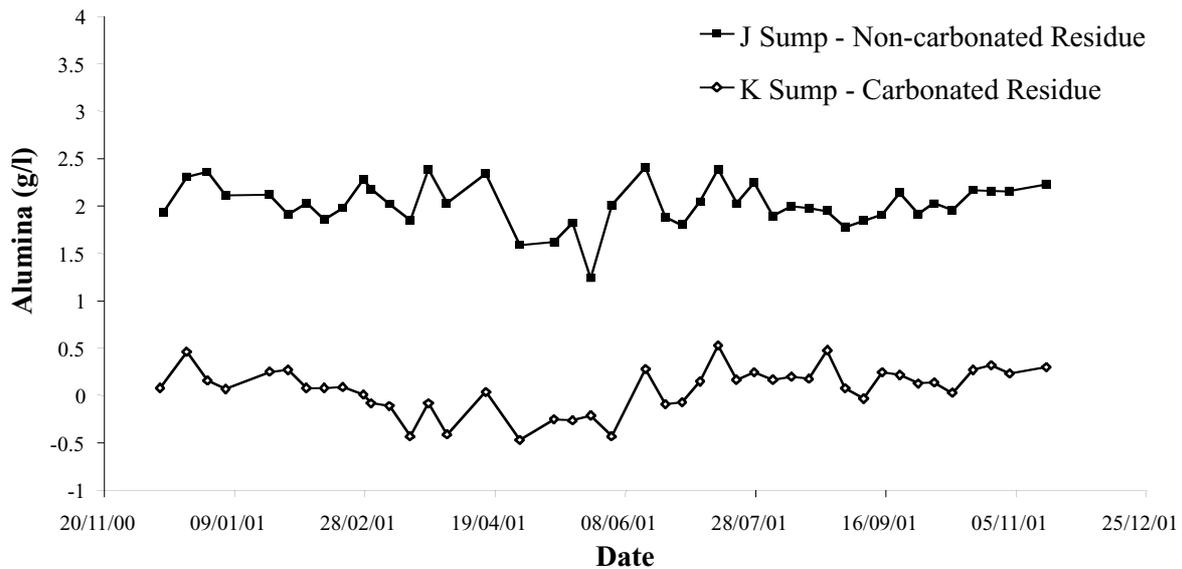


Figure 3 — Measurements of Alumina in the underdrains of carbonated and non-carbonated drying beds

RATE OF STRENGTH INCREASE

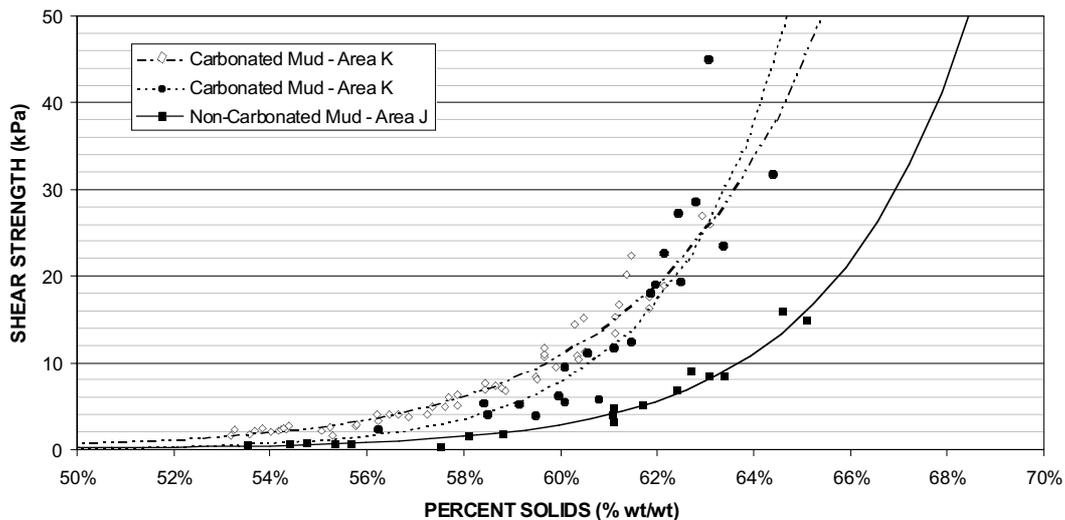


Figure 4 — Strength increase as a function of density for carbonated and non-carbonated slurries

4.1 Reduced risk to clay and synthetic seals and groundwater

Studies have been carried out by Alcoa World Alumina to investigate the potential impact of residue leachates on clay seal material. This test work indicated that, as the pH (and hence alkalinity) of the leachate in contact with the clay seal increases, the clay itself is increasingly susceptible to dissolution reactions which alter the chemical and mineralogical composition of the clay seal and probably its sealing properties.

By reducing the pH of residue leachate, carbonation will significantly reduce the potential risk of long term degradation to clay or synthetic liners. Also, any leachate which does escape from the impoundment will have a reduced impact on the receiving waters, hence the overall risk of groundwater contamination is reduced significantly.

4.2 Quality of runoff and drainage water

The trial work on carbonation has indicated that the quality of drainage water from a carbonated residue deposit will be lower in pH, total dissolved salts and soluble aluminium. There is also likely to be a significant change in the concentrations of some minor elements. While still not suitable for direct discharge, the cost and complexity of treatment of this water for discharge will be greatly reduced. Carbonation can improve the feasibility of implementing a cost effective solution for discharge of the drainage water from carbonated deposits and therefore reduce the costs associated with long term management of the storage deposits.

4.3 Reduced Drying Area

There are indications that carbonated residue dries more rapidly and develop higher shear strength than non-

carbonated residue. This may allow future drying area expansions to be deferred with significant financial savings.

4.4 Reduced Dust Risk

Observations of the carbonated mud suggested that the surface is less prone to dusting than the non-carbonated residue. Also, if the area that is required for drying the residue could be reduced, there will be a smaller active area exposed to dust generation at any one time.

4.5 Greenhouse Benefit

The carbon dioxide that will be consumed by full-scale carbonation across the three WA refineries represents around 2% of the total refinery carbon dioxide output. While this may be seen as a relatively minor offset, other opportunities for reducing aggregate emissions are limited. Also, future carbon credits that this consumption could represent may substantially offset the cost of the carbonation process.

4.6 Future Classification as Hazardous Waste

There is a trend towards including pH in the criteria for defining hazardous waste. The recent review of the Basel Convention, which controls the movement of waste materials internationally, resulted in pH 11.5 being adopted as a hazardous waste criterion. In Australia a National Environmental Protection Measure (NEPM) has been drafted which aims to regulate the movement of wastes across State borders. The Basel criteria have been adopted for defining 'controlled' wastes. The EEC has also considered classification and taxing systems for wastes and landfills and pH 11 has been proposed as a criterion for characterising hazardous waste. In the US bauxite residue is one of a number of high volume — low toxicity industrial wastes that were specifically exempted from the provisions of hazardous waste legislation (RCRA) by a legislative amendment known as the Beville amendment.

It can therefore be argued that wastes going into storages or landfills that are below pH 11 are much less likely to attract future hazardous waste classification and associated higher containment requirements and/or taxes.

4.7 Alternative Use Opportunities

A great deal of research has been carried out on beneficial uses of residue by Alcoa, as well as other companies. Uses that have been identified to date include:

- Soil amendment to help retain nutrients and adjust soil pH (currently being implemented in the Peel Harvey region in WA).
- Neutralisation of acid mine drainage and amendment of acid producing soils, currently being trialed in a number of countries by Virotec.
- As a filtration medium to remove phosphorous and nitrogen from sewage effluent in domestic and industrial septic systems, through a partnership with Ecomax in WA.
- Fertiliser additive to improve phosphorous retention in soils currently being trialed by CSBP in WA.
- As an additive to compost to aid the retention of trace metals.
- Brick and tile manufacture, both fired and non-fired;
- Filler for plastics, to impart strength, resistance to UV, heat and chemicals, and colour;
- Road base, either using the sand fraction directly, or the mud as a component of a composite with gypsum or fly ash, for example.

- Raw material for the production of cement alternatives, such as mineral polymers and ceramics;
- As a pigment for a range of applications in coatings and materials manufacture.

However, despite this considerable wealth of research, only small quantities of residue are diverted to beneficial uses. Of the 14.7 million tonnes of residue produced in WA Operations in 2000, less than 5,000 tonnes were diverted to beneficial uses. There is a public perception of residue as a hazardous material, with negative connotations being attached to any re-use of an industrial waste. Carbonation of the residue offers a means of breaking down this barrier, by demonstrating that the residue is not a hazardous material.

4.8 Alumina Customer Concerns

The volume of residue produced and the potential for environmental effects from residue storage operations can have a negative impact when considering the total life cycle costs of aluminum products. Some alumina customers have recently requested data to allow comparative life cycle assessments of alternative suppliers. Major improvements in bauxite residue management which reduce environmental impacts, via means such as carbonation, and reduce volume through alternative uses will likely have a positive impact on these assessments and therefore may strengthen competitive positions in some markets.

5. Conclusions

A full-scale prototype residue carbonation plant has been successfully commissioned at Alcoa's Kwinana refinery, allowing a detailed evaluation of the overall carbonation process and impacts on residue storage operations. Work completed to date has shown that a dose rate of around 25kgCO₂/kl slurry is required to achieve optimum carbonation under the current operating conditions at the Kwinana refinery. Full carbonation of the solid alkalinity has not been achieved through the dosing plant. The presence of tricalcium aluminate (TCA-6) causes the pH in the residue to rise after the slurry has been deposited in the drying area. However, the liquor draining from the carbonated residue has been maintained at a pH of 10.5.

Performance of the carbonated residue in the drying bed has been enhanced through early strength development and increased rate of moisture loss, most likely the result of reduced crusting on the surface of the drying residue and early cracking that is a flow on result of the early strength development. This has the potential to reduce the area required to sustain the ongoing dry stacking operation, allowing capital for future drying bed expansions to be deferred.

The prototype of residue carbonation has highlighted a number of technical issues, primarily related to the presence of TCA-6. However, alternative approaches to carbonation continue to be further investigated which may allow a residue pH below 9.5 to be sustained, further enhancing benefits such as:

- Reduced risk to clay and synthetic seals and hence reduced risk of groundwater contamination
- Improved quality of runoff and drainage water
- Reduced potential for dust
- Providing a sink for greenhouse gasses
- Avoiding possible future classification as of the residue as a hazardous waste
- Opening opportunities for alternative uses for the residue
- Allaying Alumina Customer concerns when attributing life cycle costs to residues

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