

USE OF FLUE GAS FOR CARBONATION OF BAUXITE RESIDUE

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Abstract

Alcoa World Alumina Australia has been investigating residue carbonation as a potential major improvement opportunity for achieving residue storage with lower environmental risk and reduced long term liability. Results from comprehensive laboratory studies, pilot scale trials and operation of a full scale prototype carbonation facility have demonstrated the full scale viability of this technology. However, the current process requires a stream of concentrated CO₂ which is mixed with a thickened residue slurry prior to deposition of this slurry into drying beds as a part of Alcoa's current residue dry stacking.

Alcoa is currently investigating an alternative approach to residue carbonation which avoids the need to separate and concentrate CO₂ from a dilute flue gas stream. This paper details this novel approach to residue carbonation, outlining the findings from preliminary testing and describing how this process of residue carbonation may be integrated into the refining and residue storage operations.

1 Introduction

Alumina refineries produce large quantities of alkaline residue and in many cases large quantities of acidic carbon dioxide (CO₂) gas. This paper examines the use of carbon dioxide to neutralise residue and investigates the possibility of flue gas scrubbing as a source of CO₂.

Concern over climate change has made CO₂ capture from flue gases a major priority in energy research (Pearce 2005). Carbon dioxide is already captured in ammonia production and natural gas purification (Thambimuthu 2004). The capture technologies under investigation are solvent adsorption (Chinn 2004), CO₂ selective membranes (Kazama 2004) and Oxyfuel boilers (replacing air with oxygen in boiler combustion systems) (Anderson 2004, Simmonds 2004).

Adding CO₂ to residue is an effective way to reduce residue slurry pH. This has been demonstrated in plant trials at Alcoa's Kwinana alumina refinery, and has been previously reported (Cooling 2002). Figure 1 shows the reduction in residue under drainage pH recorded from a full scale prototype of residue carbonation tested at Alcoa's Kwinana refinery. Residue carbonation produces a number of operational benefits:

- Bayer residue can be rendered non-hazardous by reducing the pH with CO₂. Sodium hydroxide and sodium carbonate are converted to sodium bicarbonate and sodium aluminate is precipitated.
- Faster drying rates of the residue placed into drying beds. This means reduced area is required to sustain dry stacking and hence the capital required for drying bed construction can be deferred.
- Reduced potential for dusting from the drying beds.
- Biological activity in the residue drying area underdrain system reducing total organic carbon and sulfate in the carbonated residue leachate. This has a positive impact on the Bayer process.

There are also a number of longer-term benefits that have been demonstrated during residue carbonation trials:

- The overall refinery CO₂ emissions can be reduced by up to 4%.
- The residue underdrain water quality is improved.
- The risks of clay and synthetic liner degradation are reduced.
- The opportunities for residue reuse are enhanced.

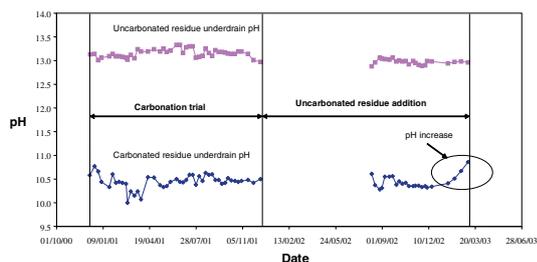


Figure 1: Residue area underdrain pH

The potential drawbacks of the residue carbonation process include:

- Negative process impacts associated with an increase in overall soda loss and the alumina precipitated. This has been shown to be small and of little impact on the overall economics.
- Negative process impacts from increased carbonate return to the liquor circuit. This can be countered by adding slaked lime to the underdrain liquor. This apparent increase in lime use is offset by the higher causticising efficiencies (95%). This causticisation also results in a higher TC/TA ratio in return liquor to the refinery with positive impacts on the Bayer process.

Several alternative flow sheets for adding CO₂ to bauxite residue slurry have been investigated by Alcoa:

- Inject concentrated CO₂ into thickened slurry under pressure, as depicted in Figure 2;
- Mix flue gas with a dilute slurry, as depicted in Figure 3; or
- Use flue gas in a contactor with a recirculated carbonated/bicarbonate solution and two thickeners, as depicted in Figure 4.

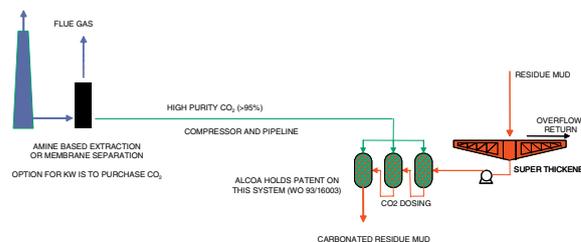


Figure 2: Direct injection of concentrated CO₂ into thickened slurry



Figure 3: Mix flue gas into a dilute slurry

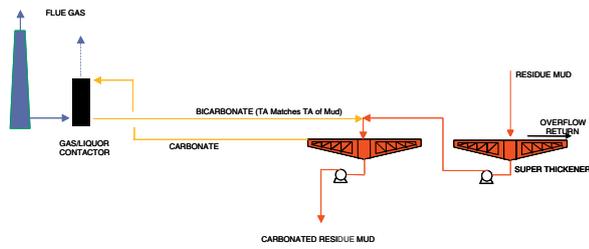


Figure 4: Gas contactor, dual thickener and recirculated bicarbonate solution

This paper reports on the preliminary work using a flue gas contactor to absorb CO₂ and utilise this absorbed CO₂ via the process described in Figure 4.

The rate of solute transfer from gas to liquid (n_a) is given by the equation (Perry 1999)

$$n_a = K^0_{Ga} \times m^3 \times \Delta pp$$

The rate of transfer is a function of the difference in partial pressure of CO₂ in gas and liquid phase multiplied by the mass transfer coefficient and the volume of the column. The partial pressure difference through the column between the liquor and gas over the desired pH range is given in Figure 5.

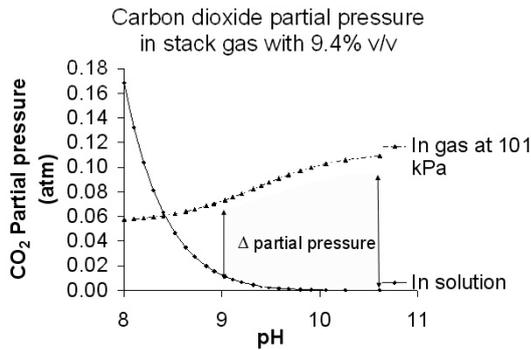


Figure 5: Carbon dioxide partial pressure through column

The mass transfer rate is a function of the interfacial area per unit volume of the packing as well as the gas-liquid contact efficiency (Kohl 1979a). The mass transfer rate decreases as carbonate is converted to bicarbonate (Perry 1999). The mass transfer rate in the carbonate system has been found to approximately double as gas temperature increases from 25°C to 54°C (Kohl 1979b).

2 Results

Two types of scrubbers have been tested. The first used a fixed bed random packing with synthetic stack gas that consisted of an air and CO₂ mixture. The second used a Turboscrubber™ with Kwinana gas fired boiler stack gas.

2.1 Fix bed random packing

The column was 300 mm in diameter with a 1m packed height as shown in Figure 6. The superficial linear liquor rate was 0.013 m/sec. The superficial linear gas rate was 1.3 m/sec. The pressure drop across the column was 0.25kPa.

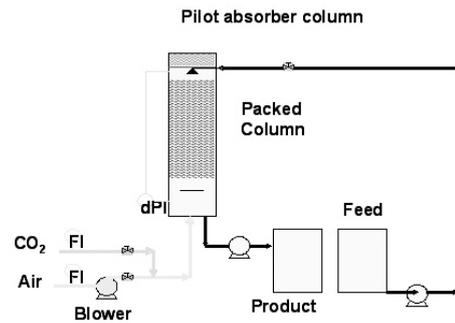


Figure 6: Packed column with synthetic stack gas

Three types of packing were investigated under equivalent conditions with 9%v/v CO₂ and 1m³ of recirculated carbonated lakewater at 25°C. The 25 mm Dynarings gave the best results as shown in Figure 7.

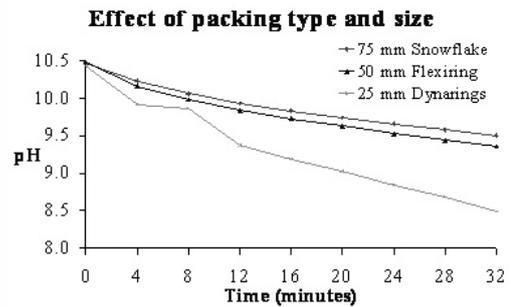


Figure 7: The effect of packing type and size

The CO₂ transfer rate through 25 mm Dynarings as a function of pH is shown in Figure 8. This test was carried out with runs consisting of 1m³ liquor being passed through a 1m column with the CO₂ concentration being adjusted as if the liquor was passing through multiple stages of a single column.

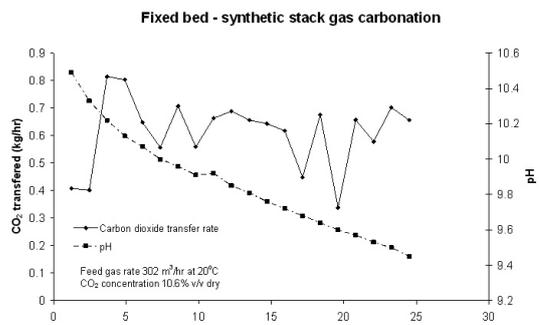


Figure 8: Fixed bed CO₂ mass transfer with synthetic stack gas

This testing suggested a full scale plant with a packed height greater than 30m would be required to reduce the pH from 10.5 to 9. The fixed bed contactor also had problems with flooding, foaming and scaling.

2.2 Turboscrubber

The turboscrubber is a fluidised scrubber patented by Davis and Ruff (Davis 1994). The turboscrubber allows for a higher gas and liquor flow rates and also has higher mass transfer rates. The same 300 mm diameter column was used with 1000 turboids giving an expanded bed depth of 1m as shown in Figure 9. The superficial linear liquor rate was 0.02m/sec. The superficial linear gas rate was 2.2m/sec. The pressure drop across the column was 1.6 kPa.

This test was carried out with runs consisting of 1m³ liquor being passed through a 1m column with stack gas from a refinery boiler fire with natural gas.

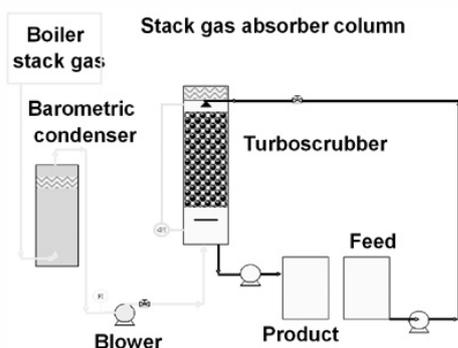


Figure 9: Turboscrubber with boiler stack gas

The turboscrubber achieved approximately double the mass CO₂ transfer rate of the fixed bed random packing with equivalent CO₂ concentration and column size as shown in Figure 10.

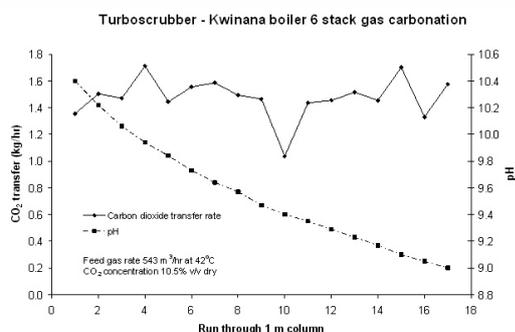


Figure 10: Turboscrubber mass transfer with boiler stack gas

Using this data a full scale turboscrubber plant would require 18 m of packing to reduce the pH from 10.5 to 9 in the recirculated carbonated lakewater. The turboscrubber did not have any problems with scaling, foaming or flooding under the test condition.

3 Discussion

A preliminary costing has been undertaken for a full scale flue gas turboscrubber with an additional thickener and the required pipework. The capital and operating costs compare favourably with an MEA scrubber at an equivalent CO₂ production rate. The turboscrubber has the advantage that it does not produce odours or the waste streams associated with MEA blowdown. A larger scale pilot plant with an 18m packed section is being built at Wagerup to confirm the mass transfer rates.

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