

PRELIMINARY ASSESSMENT OF TRICALCIUM ALUMINATE HEXAHYDRATE FLUE GAS DESULPHURISATION

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Abstract

As aluminium is the world's second most used metal and a large proportion of the energy used for its production is derived from coal-fired power stations, it follows that the alumina industry is a significant contributor to global SO_x emissions. Early attempts to address this issue quickly recognised that the combined Bayer Process residue can be used for flue gas desulphurisation (FGD). However, this waste stream can contain as little as 5.0 wt% reactive components, therefore limiting overall process efficiency and promoting the identification of alternative residue streams better suited to the purpose. One such waste stream is tricalcium aluminate hexahydrate (TCA6). This paper provides data of a preliminary examination of TCA6 as a wet FGD medium with comparisons made with calcium carbonate in both sulphuric acid and simulated flue gas trials. This work supports TCA6 as an efficient and economically viable FGD medium for the alumina industry.

1. Introduction

The high-intensity steam demands required to sustain the Bayer Process frequently results in alumina refineries possessing their own steam and power generation facilities. As coal is still the dominant fuel source for steam and power generation, it follows that the alumina industry is a significant contributor to global SO_x emissions.

SO_x emissions can be mitigated via several commonly applied flue gas desulphurisation (FGD) processes;^[1] the choice of which is generally dictated by alkaline medium availability and overall process economics. Fortunately for the alumina industry, the major and many minor residue streams have potential for application to this purpose. Although the combined residue stream has been applied in past works,^[2] this indicates a significant process inefficiency, due to high volumes of non-reactive components circulating within the system. Therefore, a more ideal medium would be one of the alkaline Ca mineral species synthesised within the Bayer Process, such as calcite (CaCO₃), desilication product (DSP) or tricalcium aluminate hexahydrate (TCA6). Due to the economics of separation of CaCO₃ and DSP as dictated by their particle size and synthesis location within the Bayer Process, the most viable option for most alumina refineries is TCA6.

Extensive use of lime within the Bayer Process leads to an extent of TCA6 synthesis within causticisation (in the absence of an inhibitor), but more so in a side-circuit whereby particle size and purity can be strictly controlled in order to optimise characteristics for subsequent application as a process liquor filter aid.^[3] The latter pathway and use also provides an existing recovery point for further reuse of TCA6, thus placing economic advantage over calcite and DSP for use in FGD.

The purpose of this work is to examine the comparative performance of TCA6 and AR-grade CaCO₃ as FGD mediums in laboratory trials to allow for preliminary assessment of economic viability and performance of TCA6 to serve as an alternative FGD option for the alumina industry.

2. Methods

2.1 Sample Characterisation

Washed, filtered and dried TCA6 provided by BHP Billiton Worsley Alumina (BWAPL) was subjected to a three-step characterisation process (AR grade CaCO₃ was only analysed for steps 1 and 2).

1. Particle size analysis via a Malvern Mastersizer 2000. One to three grams of dried sample were added to the water-filled analysis chamber with results graphed as logarithmically increasing particle size versus volume percentage; the curve peak thus indicating the mode of the dominant particle size of the sample.
2. Surface area determination via a Quantachrome Quadrasorb. 0.05-0.1 g of as-received TCA6 and 2g of CaCO₃ were placed within a 9 mm sample bulb and degassed for 16 hr at 200°C, followed by N₂ adsorption analysis. Surface area determination via N₂ adsorption was graphed by relative pressure versus volume in cm³ (cc). This was plotted as pressure increased from vacuum to atmospheric and back again to yield a characteristic curve type. Surface area is reported in m²/g.
3. Bulk and trace elemental composition via X-ray fluorescence - 0.6 g of dried sample added to 6 g of flux (57% lithium tetraborate and 43% lithium metaborate) and fused at 1000°C on a Phoenix 60.0 Autofusion bead preparation machine with analysis conducted on a Phillips MagiX Pro with reference standards and analysed through Super Q software. Due to the CaCO₃ possessing a certified composition, it was not subjected to XRF.

2.2 Experimental

After preliminary performance characterisation at pH 4.75 - 7.15, all sulphuric acid experiments were conducted at pH 5.15 - 5.30, (within the nominal operational pH range of commercial FGD systems) and at standard laboratory conditions with a slurry of 5 g/L solids. Initial experiments were undertaken in a 0.5 L CSTR through addition of 1 M H₂SO₄ controlled via a Metrohm Titrando™ system with four experiments at varied temperature (25 ± 1, 34 ± 1, 50 ± 1 and 58 ± 1.5°C) with both TCA6 and CaCO₃ to determine performance and activation energy. Experiments were run for 90 min, or less if the slurry was spent (as indicated by flat-lined acid dosing).

Subsequent gas phase experiments were undertaken in a flow-through mini-CSTR with a 20 mL standing liquid volume (Figure 1). The gas feed contained 920-935 ppmv SO₂, (with 12-15 % CO₂ and the balance provided by air) maintained at 815-830 mL/min. The solids content of the slurry was 0.1% (1 g/L) and flow was controlled via a twin-feed peristaltic pump at 3.2-5.5 mL/min resulting in a gas:liquid ratio range of 150 - 255 and a contact

time ranging from approximately 1.46 sec. The experiments were conducted with TCA6 in RO water at 25 ±1, 34±1, 43±1 and 48±1.5°C (equipment maximum), with SO₂ (g) outflow concentrations, temperature and pH monitored.

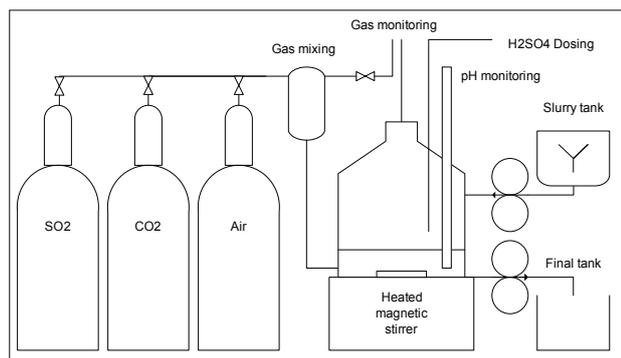


Figure 1. Mini-CSTR setup used for steady-state simulated FGD and controlled H₂SO₄ dosing experiments.

3. Results

3.1 Particle size analyses

The un-sonicated sample of TCA6 displayed a particle size distribution mode of around 16 μm (Figure 2) consistent with refinery objectives^[3,4] and therefore representative of ideal TCA6 synthesis conditions for BWAPL. Figure 2 also indicates that the PSD mode of the AR CaCO₃ lies around 50 μm and is more narrow than TCA6.

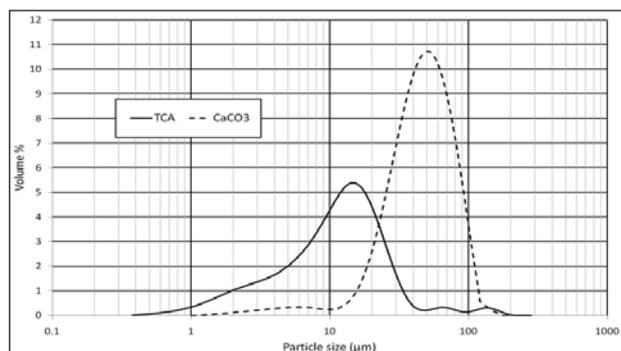


Figure 2. Particle size distribution of as-received TCA6 and AR grade CaCO₃.

Table 1. Major oxide analysis (wt%) and LOI from XRF analysis of TCA6.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	V ₂ O ₅	P ₂ O ₅	TiO ₂	Na ₂ O	K ₂ O
3.23	22.94	0.14	40.45	2.53	0.30	0.17	0.14	0.80	0.14
LOI up to 550°C			20.90		LOI 550-1000°C			6.74	

Table 1 also indicates trace elements of V, P, Ti and K, which are expected within BWAPL TCA6 because synthesis conditions are maintained to promote intercalation and removal of these elements (in addition to F) to benefit the process.^[3, 8] LOI data indicates a total loss of 27.64%, attributed to dehydroxylation and consistent with expected values for pure TCA6 (28.79%). The above results approximate the stoichiometry of the sample as:



Taking the reactive hydroxides as Ca, Mg and Na, the combined stoichiometric value represents 58 wt% of the sample and support WAPL TCA6 being a suitable FGD medium.

3.2 Surface area determination

Results of the surface area determination are displayed in Figure 3. Comparison of this data with standard isotherms^[5] indicates the TCA6 sample is characteristic of nonporous or macroporous adsorbents with unrestricted monolayer-multilayer adsorption. Also, the shape of the area between the two isotherms is indicative of slit-shaped pores, further supported by the failure of the two isotherms to meet prior to the origin, which demonstrates residual adsorption of nitrogen within the sample. Overall, the TCA6 sample displayed a surface area of 72 m²/g and CaCO₃ 1.2 m²/g, indicating that the AR CaCO₃ is essentially non-porous.

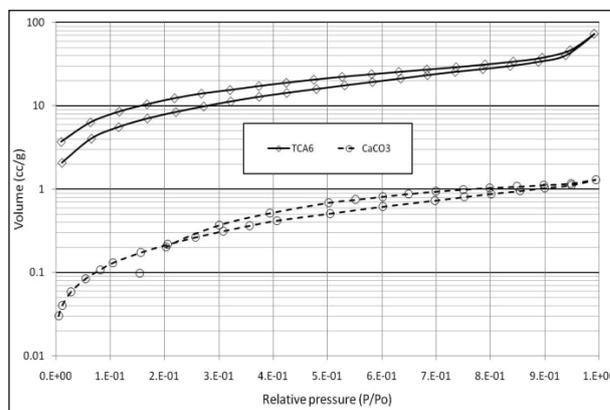


Figure 3. N₂ absorption isotherms for the determination of TCA6 and AR CaCO₃ surface areas.

Although CaCO₃ formed within the Bayer Process usually displays a PSD mode of around 12 μm, which therefore indicates a greater surface area, its lack of porosity will prevent its surface area surpassing TCA6.

3.3 Composition and LOI

The bulk oxide composition (via XRF) and LOI data of the as-received TCA6 sample are given in Tables 1 and 2. From Table 1 it can be seen that the sample is predominantly calcium and aluminium oxides. The presence of Si, Mg, Na and Fe indicate an indicative katoite / hydrogrossular composition.^[6, 7]

3.4 H₂SO₄ trial results

Constant pH (5.15-5.30), variable temperature experiment results from 0.5 L CSTR trials presented in Figures 4 and 5 indicate TCA6 displays less sensitivity to the four temperatures compared to CaCO₃. Assuming all Ca is present as Ca(OH)₂, the overall available Ca consumed from TCA6 ranged from 88 - 100 % whereas the consumption from CaCO₃ ranged from as little as 74 % at 25°C to 100 % at 58°C. The reaction rate of TCA6 is therefore greater than CaCO₃ in this system.

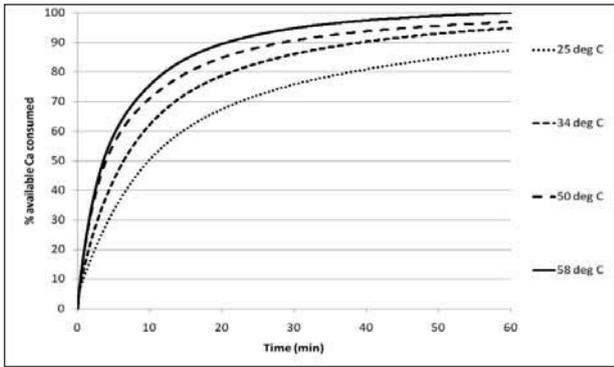


Figure 4. Effect of temperature on Ca consumption rate from TCA6 at pH 5.15-5.30

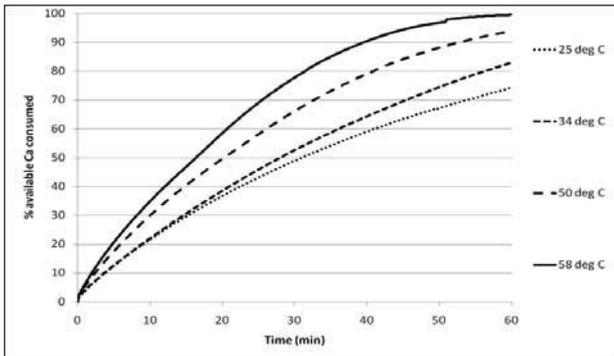


Figure 5. Effect of temperature on Ca consumption rate from CaCO₃ at pH 5.15-5.30

The data provided in Figures 4 and 5 also indicate that the Ca consumption rate of TCA6 is maintained across a broader range of temperatures, whereas, although the Ca consumption rate from CaCO₃ is only optimal in a narrow range of temperature, it is still adequate for commercial FGD due to the low cost of industrial limestone. However, particle size of industrial grade CaCO₃ may lower performance.

In order to fully understand the comparison of the two FGD mediums, the 58°C trials at pH 5.15-5.30 for both TCA6 and CaCO₃ is provided in Figure 6 and equal weight equivalent SO₂ absorption in Figure 7.

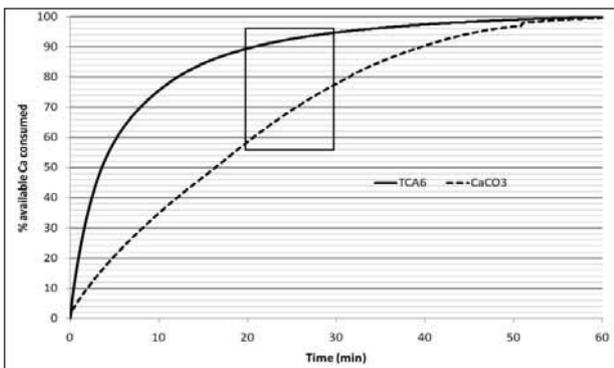


Figure 6. Extent of available Ca consumed between TCA6 and CaCO₃ at pH 5.15-5.30 and 58°C. The box between 20 and 30 min indicates the nominal slurry recycling time in commercial application to promote CaSO₄·2H₂O crystallisation and precipitation.

Figure 6 indicates that within the expected maximum recycling time of a commercial FGD system, TCA6 expends 90-94% of its available Ca whereas CaCO₃ expends 58-77%.

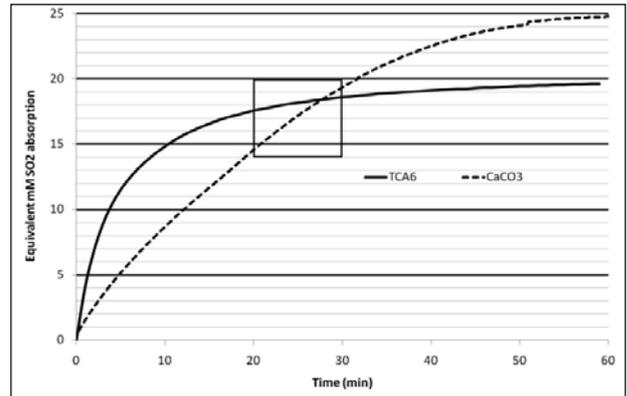


Figure 7. Comparison of actual SO₂ equivalent absorption on an equal weight basis between TCA6 and CaCO₃.

Figures 6 and 7 indicate that TCA6 demonstrates a more rapid expenditure of available Ca, on an equal weight basis although the actual potential SO₂ absorption capacity for both mediums are near equivalent at 28 min with each able to absorb approximately 0.46 T SO₂/T of medium. However, for CaCO₃, this indicates that only around 77% of the available Ca will be consumed. Subsequently, although TCA6 has a much lower available Ca content, it reacts faster and more completely within 30min.

3.5 Kinetics

An Arrhenius Plot of the above data provided in Figure 8 indicates that even though TCA6 possesses a higher activation energy than CaCO₃ (17.6 kJ/Mol vs 14.5 kJ/Mol) it still maintains a higher reaction rate. The upper TCA6 value circled in Figure 8 is an expected outlier attributed to the dosing limitation of the equipment.

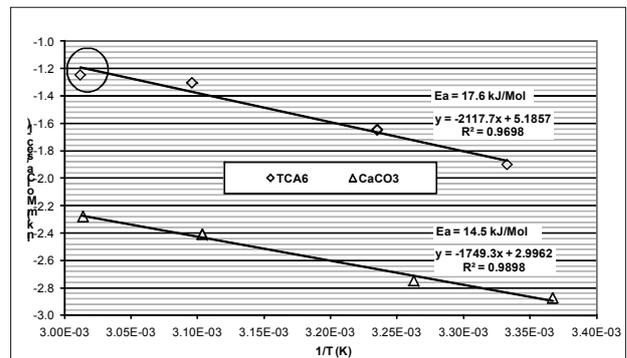


Figure 8. Arrhenius Plot of TCA6 and CaCO₃ experiments with H₂SO₄. The circled upper left value for TCA6 is an expected outlier derived from equipment dosing limitations.

3.6 Simulated Flue Gas Experiments

Results of the steady-state simulated flue gas trials with TCA6 in the mini CSTR provided in Figure 9 indicate a range of SO₂ removal efficiencies of 88-98% with a general trend of increasing efficiency with increased pH.

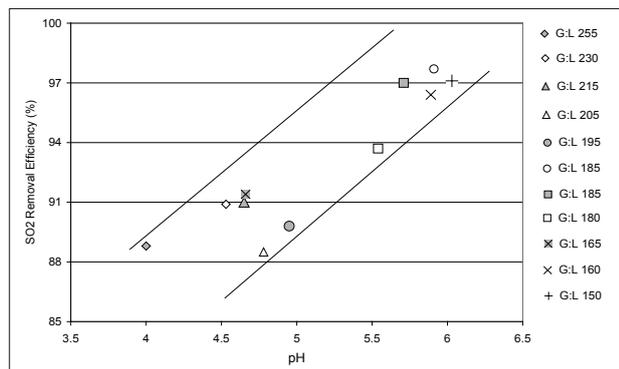


Figure 9. SO₂ absorption efficiency of 0.1wt% TCA6 slurry in mini-CSTR experiments. (G:L = gas:liquid flow ratio).

4. Discussion and recommendations

Although the PSD mode of the AR CaCO₃ used in this work is coarser than that synthesised within the Bayer Process, an economically viable separation process needs to be developed for residual CaCO₃ from causticisation for it to be a viable FGD medium for alumina refineries.^[9]

Results presented indicate that TCA6 possesses adequate SO₂ removal performance under conditions generally experienced within commercial FGD systems. The combination of fine particle size, high surface area and high proportion of available hydroxides overcome the higher activation energy to provide a reaction rate in excess of AR CaCO₃. Furthermore, the reaction is expected to be facilitated via the hydroxides of Ca and Mg (and not Al) due to maintenance of pH >5.0, whereby Al dissolution is not expected.^[10] This may hold potential for alumina recovery post-use, although this may need to be examined in a dry system due to the solubility of gypsum.

The absorption capacity of TCA6 and CaCO₃ in H₂SO₄ trials on an equal weight basis are also comparative and overall TCA6-SO₂ absorption in a mini-CSTR is similar to commercial FGD system performance.^[11]

The combination of the above results and data support the application of TCA6 for FGD, although the potential for liquid phase impurity cycling from FGD back to process may limit commercial viability of a wet process within the alumina industry. It is therefore recommended that further investigation of a dry process be undertaken to assess the potential for application within Bayer refineries.

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