

Filtration Efficiency of Tricalcium Aluminate Filter Aid Synthesized with Batch and Continuous Stirred Reactors

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Abstract

The filtration rate specific cake resistance (α) of tricalcium aluminate (TCA) aided filtration of dilute bauxite residue slurry were measured and calculated. TCA was firstly crystallized from synthetic and industrial Bayer liquor in both batch and continuous reactors. From the particle size distribution, when synthesized in continuous operation, the majority of the particles were smaller than 5 μm while a decrease in the amount of fine particles and a relatively narrow particle size distribution was observed in batch synthesis. Shorter filtration times and lower solids content in the filtrate were observed with the TCA prepared in batch mode. Filter aid quality is an important factor in determining the performance the Bayer liquor filtration unit operation.

Keywords: Filter aid, Tricalcium aluminate, Cake resistance.

1. Introduction

In alumina refineries, fine particles in the post-digestion thickener overflow are removed from the pregnant leach liquor by filtration. These fine particles have a tendency to flow through or block the filter cloth pores compromising alumina product quality and resulting in undesirable process downtime and costs associated with cleaning and replacing the filters [1]. To aid the filtration process, the filter cloth is coated with tricalcium aluminate filter aid which provides a porous network permitting solution flow while trapping the fine particles and delaying the onset of cloth blinding [2, 3].

It has been shown that filter aid particle size distribution has a profound effect on filtration performance. In a study by Kinnarinen et al. [4], the effect of particle size of wet ground calcium carbonate slurries was investigated. It was found that, the finer particles slow down filtration due to blinding the filter cloth. In another system, the influence of crystal morphology and particle size distribution on porosity, cake resistance for l-glutamic acid and an aromatic amine derivative was studied. It was found that spherulites resulted in higher cake resistance values than needle shaped particles. Comparably high cake resistance for the spherulites particles are accounted for by lower mean particle size as compared to needle-like particles [5]. It has been stated that “*If the particle properties could be specified for filtration, the target properties would be for the particles to have a higher mean size, be as near to spherical as possible, and have a monosize distribution*” [3].

Many studies have been carried out to investigate the effect of reaction conditions used for the preparation of TCA on the composition, particle size and particle morphology [6, 7, 8, 9]. Other work linking TCA properties to filtration performance consider filtration pressure, TCA concentration, flocculants, slaking conditions, and TCA synthesis reaction conditions [6, 1, 10]. The effect of batch and continuous TCA particle formation was recently studied [11]. TCA particle characteristics were found to be relatively sensitive to operating parameters such as

agitation intensity and residence time. The fine particle concentration was considerably higher for the continuous reactor compared with the batch test which was ran for a time equivalent to the mean residence time. Also, the continuous reactor yielded dense agglomerates with minimal void space which are not desirable features for filter aid. In this study, a quantitative method was used to determine the effect of TCA produced by batch and continuous on filtration performance.

2. Methods and Materials

2.1. Bayer Liquor

Synthetic Bayer liquor was prepared from Gibbsite (C-31 grade, 99.4 % $\text{Al}(\text{OH})_3$ by weight), sodium hydroxide (2.2 % Na_2CO_3 by weight), anhydrous sodium carbonate (99.9 wt %) and deionized water. The mixture was heated to 95 °C to form an optically clear solution. An industrial Bayer liquor solution was also used to synthesize the “Plant” TCA. The composition of the Bayer liquors used to synthesize the TCA samples are shown in Table 1.

Table 1. Bayer liquor compositions.

Bayer Liquor	A g/L as Al_2O_3	C g/L as Na_2CO_3	A/C	Carbonate g/L as Na_2CO_3	S Total Soda g/L as Na_2CO_3	C/S
Plant	137	243	0.56	20.5	263.5	0.92
Synthetic	172	214	0.80	42	256	0.83

2.2. Lime Slaking

Hydrated lime slurry was prepared by mixing 10 g of pure CaO (> 96 % pure) with 100 mL deionized water. The density of slurry was 1.06 g/mL at 90 °C. It was confirmed by XRD that $\text{Ca}(\text{OH})_2$ was the only crystalline phase present in the slaked lime. Approximately 95% of the slaked lime particles were below 2 μm in diameter according to Accusizer particle counting. The size was confirmed by SEM analysis and the shape of the slaked lime particles appeared to be irregular.

2.3. TCA Synthesis

“Batch” TCA was synthesized in a batch stirred baffled reactor and “Continuous” TCA was synthesized in a continuous stirred tank reactor as described in a previous paper [12]. The batch synthesis time and continuous reactor mean residence times were both 120 minutes. For the continuous reactor, feed solutions were supplied from two separate heated stirred tanks to the reactor using Masterflex peristaltic pump. The flowrate of the 10 % (w/w) $\text{Ca}(\text{OH})_2$ slurry was 2 mL/min and the flowrate of the Bayer liquors was at 4 mL/min. The TCA was freshly synthesized ahead of each filtration test. The resultant TCA slurry densities were similar at 1220 and 1244 g/L for batch and continuous TCA respectively. Filtration tests were also conducted on a TCA sample from an alumina refinery termed “Industrial” TCA.

2.4. Tricalcium Aluminate Characterization

The particle size distribution of tricalcium aluminate was determined by an Accusizer; (The Accusizer instrument consists of five parts: autodiluter, optical sensor, pulse-height analyzer, computer processor and software controller). To ensure that the particles were not dissolving upon dilution, the dilution solution consisted of a saturated solution of tricalcium aluminate. A separate beaker of this saturated solution (100 mL), with baffles and a stirrer to ensure homogenous slurry distribution. Then, a small amount of slurry from the experiment (1 mL)

was diluted 100x by mixing it into the beaker. Then 1 mL of the diluted slurry was introduced into the Accusizer where it was further diluted 80x. Note that all the reported particle size data has been corrected back to the counts that would have been in the stainless-steel beaker, i.e. 8000x more concentrated. The density of the TCA suspension was determined weighing a measured volume in a graduated cylinder.

2.5. Bauxite Residue Preparation

In order to compare relative filtration performance, a bauxite residue slurry was prepared by mixing industrial bauxite residue with deionized water. The density of the bauxite residue slurry was 1080 kg/m^3 . The mean particle size of the bauxite residue was $3 \text{ }\mu\text{m}$.

2.6. Filtration Apparatus

The filtration device employed in this study (shown in Figure 1) is made of stainless steel with a maximum design pressure of 490 kPa. The height of the filter cylinder is 218.5 mm and filter diameter is 36 mm. The device was secured with a retort stand and two clamps. It was pressurized using regulated compressed air.

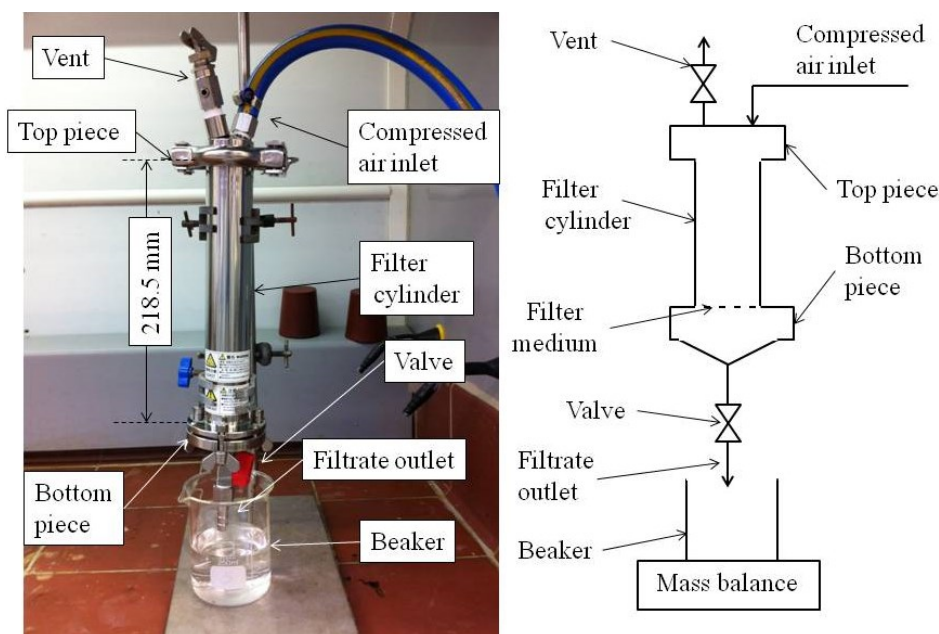


Figure 1. Pressure filtration experimental set-up.

The filter medium used for filtering bauxite residue, TCA suspension mixture and bauxite residue slurry is a filter cloth supplied by Clear Edge Filtration which is shown in Figure 2. The cloth was cut to a diameter of 47 mm in order to fit into the bottom piece of the filtration device. The filter cloth was positioned above the porous plate and beneath the rubber O-ring as shown in Figure 2. The technical specifications for the cloth are shown in Table 2.

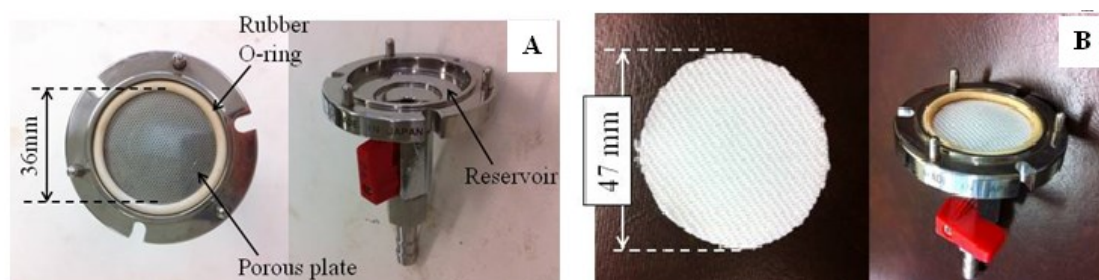


Figure 2. A: Close up of the bottom piece showing the reservoir and the diameter of the filter area. B: A cut filter cloth and its position in the bottom piece.

Table 2. Technical data for the filter cloth (Clear Edge Filtration Australia).

Quality	ALUTEX® HP34		
Polymer	Polypropylene Staple		
Weight (g/m ²)	400		
Air Permeability (m ³ /m ² /min @ 125 Pa)	4		
Air Permeability (Lt/dm ² /min @ 200 Pa)	64		
Water Permeability (l/m ² /min @ 400 mm Static head)	1500		
Breaking Load (N/5 cm)	2000		
Finish	Heat Set		
Particle retention:			
> 45 µm	45 – 25 µm	25 – 15 µm	14 – 10 µm
100 %	70 %	55 %	51 %

For determining the solids content in the filtrate, the filtrate from the pressure filter experiments was then pressure filtered using a 0.2 µm Nylon filter membrane. The dimension of the filter membrane was the same as the filter cloth but was pre-cut.

2.8. Experimental

Pressure filtration was performed at a temperature of 22±2 °C. For the filtration experiments, 9 mL of the bauxite residue slurry mixed with 150 mL of deionized water and 10 mL of TCA slurry. This mixture was stirred at 300 rpm to ensure a well-mixed suspension was introduced into the pressure filter. For some experiments, only the bauxite residue or only the TCA were included.

Each experiment used a new filter cloth which was pre-wetted. The suspension was mixed and then transferred into the filtration device. The pressure filter was quickly closed, and the gauge pressure was regulated to 100 kPa. Once pressurized, the discharge valve was opened to start the filtration process. The time and mass of the filtrate was recorded every 10 s until filtration was completed. Once the filtration was complete, filter and filter cake were recovered, dried to constant mass at 60 °C and weighed. An image of the dried filter cake from an experiment with both bauxite residue and TCA is shown in Figure 3.



Figure 3. Formed dried filter cake showing a layer of TCA particles (white) and a layer of bauxite residue particles (red) above it.

For filtration of samples containing both bauxite residue and TCA suspension mixture, or samples of only bauxite residue slurry, the same method was applied and the filtrate was filtered again using a 0.2 μm filter membrane at 100 kPa. The filtered solids were dried in an oven at 60 $^{\circ}\text{C}$ and weighed after 2 hours to determine the amount of solids in the filtrate. The turbidity of the filtrate was quantified by calculating the concentration of solids in the filtrate as a percentage by weight (% w/w).

The general filtration equation is derived from Darcy's Law and by performing a mass balance over the system. This equation is valid for all incompressible cake filtration. It is given as in Equation 1 [2]:

$$\frac{dt}{dV} = \frac{\mu\alpha c}{A^2\Delta P}V + \frac{\mu R_m}{A\Delta P} \quad (1)$$

Where t = filtration time,
 V = volume of filtrate,
 μ = liquid viscosity,
 α = specific cake resistance,
 c = dry cake mass per filtrate volume,
 A = filter area,
 ΔP = total pressure difference,
 R_m = medium resistance

A t/V versus V plot is constructed in order to calculate the specific cake resistance. From Equation 1, the slope of the linear t/V versus V plot is:

$$\text{slope} = \frac{\mu\alpha c}{2A^2\Delta P} \quad (2)$$

It was assumed that the mixture was dilute and the density of the mixture was close to the density of water, 1000 kg/m^3 . A plot of time divided by volume (t/V) versus volume was constructed to calculate the specific cake resistance, α using Equation 3.

By rearranging Equation 2, the specific cake resistance can be calculated with known liquid viscosity, dry cake mass per filtrate volume, filter area and total pressure difference, Equation 3.

$$\alpha = \frac{2(\text{slope})A^2\Delta P}{\mu c} \quad (3)$$

The dry cake mass per filtrate volume is determined using the following equation, assuming that all the solids are retained in the filter cake:

$$c = \frac{\text{dry cake mass}}{\text{filtrate volume}} \quad (4)$$

The slope of only the linear section was estimated by ignoring the data points in the first minute and the last two data point of the plot due to non-linearity. In the initial stages of filtration non-linearity is caused by sedimentation [12]. The non-linearity at the end of the filtration test is due to desaturation of the filter cake where air displaces the liquid present in the voids of the formed filter cake.

3. Results and Discussion

The results from the pressure filtration experiments are summarized in Table 1 including the filtration time, solids in filtrate and the calculated specific cake resistance. For bauxite residue filtrations, inclusion of TCA significantly improved filtration for all three parameters i.e. decreased filtration time, decreased solids in the filtrate and decreased cake resistance.

Comparing the TCA produced by synthetic liquor and plant liquor reveals faster average filtration time (about 60 %), higher specific cake resistance (about half) and lower solids concentration in the filtrate (160 ppm instead of 260 ppm) for filtration using TCA produced from synthetic liquor. This suggests that the presence of impurities in the plant liquor may be detrimental to TCA filter aid performance although it is not possible to draw any strong conclusions as the main components of the liquor also differed.

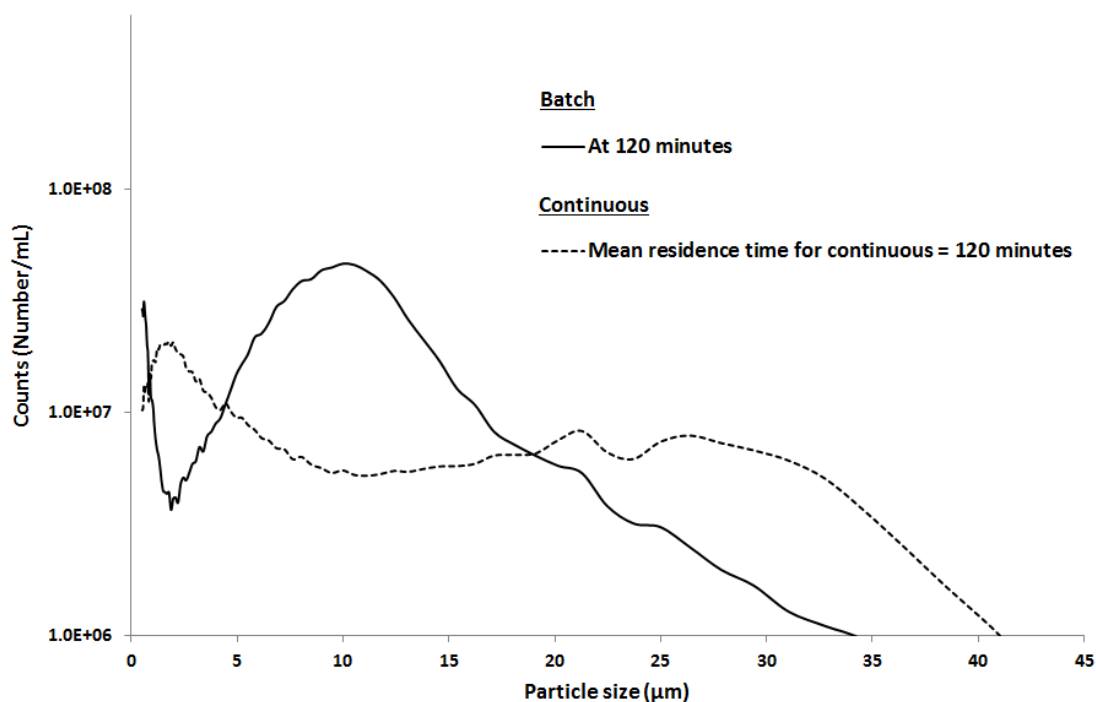
The filtration results for the bauxite residue slurry and TCA suspension mixture from batch synthesized TCA using synthetic liquor and continuous synthesized TCA using synthetic liquor were compared. The comparison indicates that the average filtration time for the mixture is shorter in the batch synthesis method than the continuous method or the industrial TCA.

While the specific cake resistance was estimated, it is difficult to draw strong conclusions from these numbers as the cake actually consists of two distinct materials (bauxite residue and TCA). Furthermore, the cake was actually being formed during the filtration experiment, therefore the value specified for the cake mass does not represent the cake mass at the beginning of the test. For these reasons, the specific cake resistances should not be considered meaningful and further work is required to determine accurate cake resistances for the TCA.

Table 1. Experimental conditions and pressure filtration results (error based on triplicate experiments).

Bayer Liquor	-	Synthetic	Plant	Synthetic	Plant	Industrial Sample
TCA Synthesis		Batch	Batch	Cont.	Cont.	
Filtration time (s)	308 ± 8	113 ± 6	195	187 ± 13	257 ± 8	256 ± 8
Solids in filtrate (%w/w)	0.042 ± 0.002	0.016 ± 0.004	0.026	0.021 ± 0.002	0.017 ± 0.003	0.031 ± 0.003
Sp. cake resistance ($\times 10^{10}$ m/kg)	27	16	7.0	3.7	8.3	25

The improved performance of the batch TCA can be explained by the particle size distribution (Figure 5). The particle size distribution of batch TCA crystallized using synthetic liquor exhibited a significant peak between 3 – 20 μm whereas the continuous TCA particle peak was around 2 μm . The elevated concentration of fine particles in the continuous TCA is corroborated by the SEM images of a 30 minute sample of the TCA during synthesis in Figure 6. It shows particles with irregular shape and rough surface of agglomerates in continuous reaction. This is associated with the attachment of some small particles to the surface of coarse particles. At the same time in batch operation, the particles have regular rounded shape without fines. In a continuous reactor a certain amount of the feed particles will spend much less than the mean residence time and therefore may not have had time to dissolve or grow into a well-formed TCA particle. In a particle size distribution, the smallest particles have the greatest effect on filtration, affecting the specific cake resistance, filtration rates, bleeding, and permeability of the filter cake [3]. The filter cloth data shown in Table 1 indicates that more than 50 % of the particles larger than 10 μm can be retained. Therefore, some degree of pore blocking is expected for both synthetic methods as they contain fines that are smaller than 10 μm .

**Figure 5. The particle size distribution of TCA produced using synthetic liquor.**

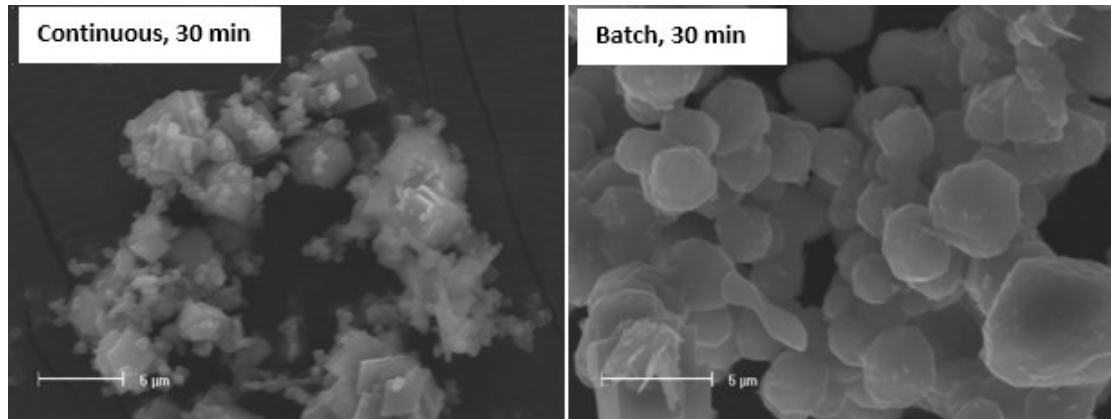


Figure 6. Morphology of TCA sampled with a mean residence time of 30 minutes for the continuous reactor and at 30 minutes for the batch reactor.

4. Conclusions

The filtration performance was measured considering filtration rate, carry-over solids concentration in the filtrate and the specific cake resistance. The filtration performance was found to be influenced by the amount and particle size distribution of the TCA. The filtration time was shorter and the filtrate clarity was improved when using TCA synthesized in a batch reactor compared to a continuous reactor.

It was shown that the batch synthesized TCA contained less fines than the continuous synthesized TCA. Fine TCA particles can pass through the filter cloth and also get stuck inside the cloth decreasing performance. The reason for the fines from the continuous reactor can be explained by short circuiting of some lime resulting in insufficient time to develop well-formed TCA.

The cake resistances were estimated, however, a different experimental approach is required to deconvolute the effects of the bauxite residue and the TCA.

5. References

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