THE MANUFACTURE OF TRICALCIUM ALUMINATE

Lawrence Joseph Andermann, Jr.[1]; Geoffrey Joseph Pollet[1]
[1]Kaiser Aluminum and Chemical Corporation, Commodities Techl. Services, Gramercy, LA

Abstract

In the Bayer Process, production of alumina is limited by the rate of liquor passing through Kelly Presses. Kelly Presses are utilized for secondary clarification, and filter clothes in combination with Tricalcium Aluminate (TCA) are used to trap solids after the initial clarification in gravity settlers. Desirable qualities of TCA permit fast liquor flow rates and filtering solids to low concentrations. Inconsistent performance of Kelly Presses is not fully understood, so this paper offers some explanation on how physical and chemical conditions in TCA production govern desirable properties. Slaking temperature, lime to alumina ratio, and soda concentration affect TCA particle size distribution, crystal structure, and composition. TCA particle size distribution, crystal structure, and composition are thought to affect the flow of liquor through Kelly Presses. By controlling slaking conditions of TCA, Kaiser's Gramercy Works has reduced the number of daily press dumps by 33%.

Introduction

Within the Bayer Process, a majority of the red mud is separated from the sodium aluminate liquor by means of conventional settlers with the addition of synthetic polymers. Afterward, low concentrations of red mud still remains within the overflow liquor, and the liquor is clarified for a second time by filtration. Kelly Presses are the most common means of secondary clarification [3,5]. Tricalcium Aluminate (TCA) is one filter medium (sand and pisolites are another examples of filtration medium). The variable quality of the filter aid is one of many reasons for poor filter press performance (others include high phosphate concentrations within press feed liquor and residual polymer within the press feed liquor). This paper will look at only filter aid quality, and how the make-up affects filtration.

There have been many studies that looked at causticization, calcium solubility, liquor polishing, and calcium aluminate. However, causticization studies make up the majority of the studies that look at calcium usage within the Bayer Process. In addition, other studies have looked at the chemistry of calcium with regards to reaction mechanisms and thermodynamics. However, most studies only touch on the chemistry that goes into manufacturing a filter aid that has consistent filter press performance.

The composition of the filter aid is important in the flow of liquor through the Kelly Presses; that is, the chemical composition, shape, and size of the filter aid dictates the filtration rate. Therefore, the manufacture of the TCA is an important step in the Bayer Process because of the negative implications that poor quality TCA has on plant flow.

It is thought that process conditions can be set to affect the shape, size, and chemical composition of the filter aid. Kaiser utilizes a liquor slaked lime produced from slaking quicklime with spent liquor. It was found that the lime to alumina ratio, alkalinity, and slaking temperature affected the manufacture of TCA.

Low lime/alumina ratios for low A/C ratios were needed to produce a filter aid (TCA) with a good filtration index. Higher temperatures and higher total alkalinity seem to drive the TCA reaction further to completion. Also, it seems that higher caustics produce higher gpl TCA solids.

Typically, TCA is prepared by the reaction of quicklime or slaked lime with a sodium aluminate solution. Most companies within the alumina industry use either spent liquor (SPL) or Liquor to Precipitation (LTP, otherwise referred to as "Green Liquor") to make filter aid. The idealized reactions are as follows:

$$3CaO + 2NaAlO_2 + 7H_2O \rightarrow 3CaO \bullet Al_2O_3 \bullet 6H_2O + 2NaOH \quad (1)$$

$$3Ca(OH)_2 + 2NaAlO_2 + 4H_2O \rightarrow 3CaO \bullet Al_2O_3 \bullet 6H_2O + 2NaOH \quad (2)$$

These reactions are idealized, and the actual reactions are much more complicated. There are multitudes of hydrated calcium aluminates and other compounds that can be produced. Reaction conditions and impurities within the slaking liquor govern the make-up of the filter aid [5].

Certain experimental conditions were held constant. Most of the slaking was done at 96°C for 30 minutes, and alkalinity and lime to alumina ratio were varied.

Experimental

Preparation of Tricalcium Aluminate

Plant Lime (quicklime available CaO 94%) was slaked with either spent liquor (SPL), test-tank liquor (TTL), liquor to precipitation (LTP), or washer-overflow liquor (WOF). All slaking was conducted at 96°C for 30 minutes of slaking time. For all tests, Lime was added slowly for the first 15 minutes. The following is an explanation of terminology. The total caustic (TC) and total alkalinity (TA) are expressed in gpl Na_2CO_3. Sodium Aluminate (A) is expressed as gpl Al_2O_3. The liquor analysis is presented in Table I.

Table I. Composition of Various Liquor Used for Slaking.

Liquor Type	A	TC	TS
SPL	93.24	211.90	267.13
TTL	99.80	239.90	296.17
WOF	47.16	71.47	87.58
LTP	151.29	211.30	267.13

Slaking ratio of g $CaO/g\ Al_2O_3$ is the gpl CaO added in the slaking vessel to the gpl A. The slaking was conducted in a stainless steel vessel with a watch glass cover (to prevent loss of moisture). The slaking temperature was kept to within ±1°C, and the material after slaking was filtered with 0.22 µm Millipore® Durapore PVDF Membrane filters. The filter aid was then placed in a desiccator overnight to dry.

Filter Index

Kaiser Aluminum utilizes a simple filtration test to evaluate filter aid and future sources of quick lime. Kaiser has found that Filtration Index (FI) is a good indicator of how filter aid quality relates to performance of the Kelly Filter Presses. This filtration test compares the flow time through a filter medium of green liquor (Liquor to Precipitation that has been filtered to remove any solids or residual polymer) to that of green liquor that possesses a known quantity of filter aid under specified conditions.

The Filtered LTP and LTP/Filter Aid slurry are heated and passed through a filter medium at a constant temperature of 96°C and constant vacuum of 10 inches Hg. The filtration medium consists of a Fisher® glass microanalysis filter apparatus (47mm filter size; 9.6 cm^2 filtration area) and a Whatman® 934-AH filter paper. This filtration medium is placed into a filtering flask with a vacuum gauge attached.

The filtration index is calculated by using Equation 3, and classified in the Table II.

$$FI = T_{FA} / T_{LTP} \quad (3)$$

Where

T_{FA} is the flow time of the LTP with a known quantity of filter aid.
T_{LTP} is the flow time of the LTP without any solids present.

Table II. Explanation of the Filtration Index Parameters.

Filtration Index	Filtration Quality
0.39 <FI	Poor Filtration
0.4 ≤ FI ≤ 0.59	Fair Filtration
0.6 ≤ FI ≤ 0.79	Good Filtration
0.8 ≤ FI ≤ 1.0	Excellent Filtration

Particle Size, Particle Shape and Filtration Index

The size and shape of the particles of the filter aid affect the flow of green liquor through the Kelly Presses. When filter aid is produced, a range of mixtures of compounds is produced according to the slaking conditions (calcium oxide or calcium hydroxide, calcium carbonate, TCA6 and dehydrated versions of calcium aluminate as well as intermediate compounds such as carbonated aluminates (hemicarbonate or monocarbonate).

Particle size of the TCA has a correlation to filtration index. (TCA) has is an octahedral crystal (Figure 1).

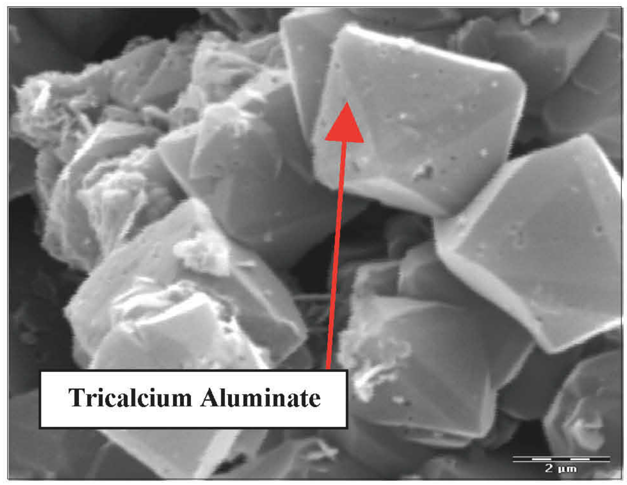

Figure 1. SEM (7500X) of Tricalcium Aluminate Crystal: Quicklime (calcium oxide, CaO) slaked with Test Tank Caustic at 96°C for 30 minutes.

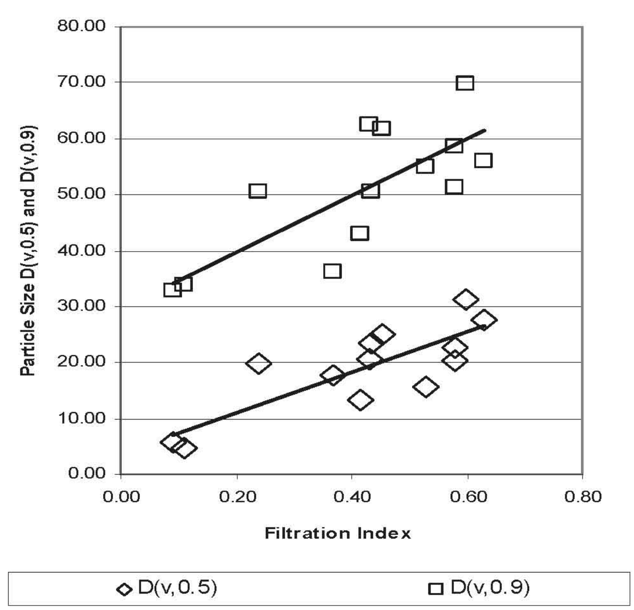

Figure 2. Particle Size (Microns) versus Filtration Index. 50 Percentile D(v,0.5) and 90 Percentile D(v,0.9). Analyzed on Malvern Mastersizer-S ®.

Figure 2 indicates that Filtration Index seems to be related to the particle size. That is, filter aid with finer particles results in lower Filtration Indexes. In addition, the percent of sub-micron particles also seems to negatively affect Filtration Index (Figure 3). It indicates a correlation between the particle size of TCA and filtration. The smaller particle size may be attributed to the insufficient growth of the particles due to slaking conditions or composition of the slaking materials. Intermediate compounds may be present (such as the monocarbonate $[Ca_2Al(OH)_6]_2.CO_3.nH_2O$ and the hemicarbonate $[Ca_2Al(OH)_6]_2.1/2\ CO_3.nH_2O$) that may also contribute to poor filtration [2,4,7]. These carbonated aluminates are flat particles that affect the filtration index if present in great quantities (Figure 4). The diffraction scan of this carbonated aluminate indicates that it is a mixture between monocarbonate and the hemicarbonate. The d-spacing for the material was found to be approximately 7.6 Å, reported in literature as the d-spacing for the hemicarbonate [8,9]. Either physical or chemical conditions may affect the conversion of the carbonated aluminate to that of a highly crystallized Tricalcium Aluminate, $[Ca_2Al(OH)_6]_2.(OH)_2.6H_2O$ that is of sufficient particle size to promote good filtration. In addition, other compounds are may be present in the filter aid; such as, calcium carbonate, calcium hydroxide, or other hydrate forms of calcium aluminates. All of which may have varying degrees of effect on Filtration Index because of particle size or shape.

Lime to Alumina Ratio

Kaiser Aluminum, at the Gramercy Works Facility in Gramercy, Louisiana currently uses SPL to slake its lime to be used as a filter aid at the Kelly Presses. It has been reported in past studies that the rate and direction of the reaction of quick lime with Bayer Liquor is partially dependent on alumina and hydroxide concentrations [1]. Therefore, this investigation utilized several liquors with differing amounts of alumina concentrations to slake quicklime (CaO). That is, SPL, TTL, LTP, and WOF were used to slake Gramercy's lime to determine the effect that alumina had on producing filter aids with high filtration indexes. The lime to alumina tests kept the slaking temperature, slaking time, and the TA concentration constant. It was found that all of the liquors produced filter aid with good filtration indexes as long as specific lime to alumina (g CaO /g Al_2O_3) ratios were observed. High lime charges for low A/C liquors depleted the available alumina; as a result, TCA with poor Filtration Indexes were produced (Figure 5).

Although there is not conclusive evidence that the carbonated aluminates affect the filtration index by either producing small TCA particle sizes or the carbonate may itself plug the filtration medium, observations of this study will be stated.

When liquors with high A/C ratios were used to slaked the lime, poor filtration indexes were observed when low lime to alumina ratios were used. Conversely, liquors with low A/C ratios required high lime to alumina ratios to achieve filtration indexes that were classified as good. In the first case where the lime is being slaked with high A/C ratio liquor, there may not have been sufficient time for the intermediate compounds to convert completely to TCA. Furthermore, longer reaction time needed to convert the intermediate compounds may not allow sufficient time for growth of TCA crystals after they are initially formed.

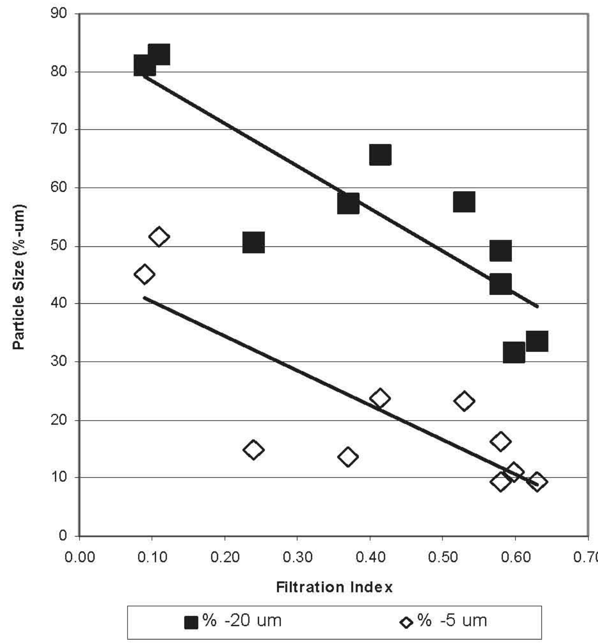

Figure 3. Percent Sub-micron Particles versus Filtration index. Analyzed on Malvern Mastersizer-S®.

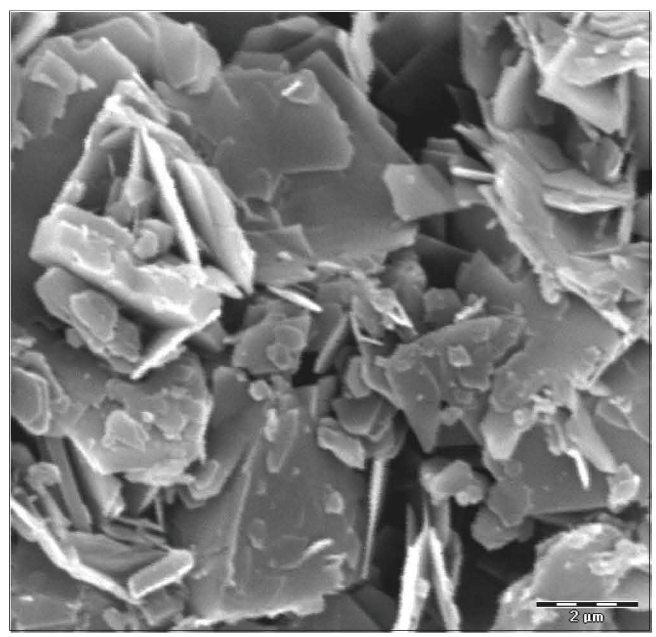

Figure 4. SEM (7500X) of Carbonated Aluminate Crystal (Possibly hemicarbonate) Quicklime (calcium oxide, CaO) slaked with diluted spent liquor (~73 gpl caustic) at 96°C for 30 minutes.

Good filtration for low A/C ratio liquors can be achieved when low lime to alumina ratios are used in the lime slaking. Again, liquors with low alumina concentrations, such as SPL and TTL, may produce TCA that has poor filtration qualities because of the composition of the slaked lime. That is, diffractograms, indicate that there are other compounds besides TCA present in the filter aid that was produced with SPL and TTL with high lime to alumina ratios. These compounds with crystal structures, such as carbonated aluminates or unreacted lime, may lead to pores being plugged by the very nature of the shape of the crystal. The filter aid that came from the SPL with high lime to alumina ratio charges left some calcium aluminate carbonate compounds that shown up on x-ray diffractograms at 10-12° 2Θ and 22-24° 2Θ.

Barham, et al., conducted testing that indicated that the residual molar ratio of CaO/Al_2O_3 of the filter aid increased the cake resistance [5]. The CaO/Al_2O_3 ratio was determined by XRF analyses, and this ratio is different from that of the g CaO/g Al_2O_3 in as much as the g CaO/g Al_2O_3 is the grams of CaO charged for every gram of Al_2O_3. It makes sense that if the reaction is not stoichiometeric that some of the alumina in solution will remain in solution. The analyses of the filter aid residue would show higher CaO to Al_2O_3, and this fact is evident because it is seen that with an increase in CaO/Al_2O_3 ratios cake resistances are higher. Thereby, the cake resistance may be due to compounds present other than TCA. Barham, et al, reported that CaO was present within the filter aid. The presence of CaO (present as $Ca(OH)_2$) may indicate that other compounds do play a role in decreased flow of liquor through the filter aid. The fact that the lowest cake resistance is at the lowest mole CaO/Al_2O_3 ratio supports the theory that charging high lime charges to low A/C liquors may result in the incomplete reaction of CaO to form TCA (Figures 5 and 6).

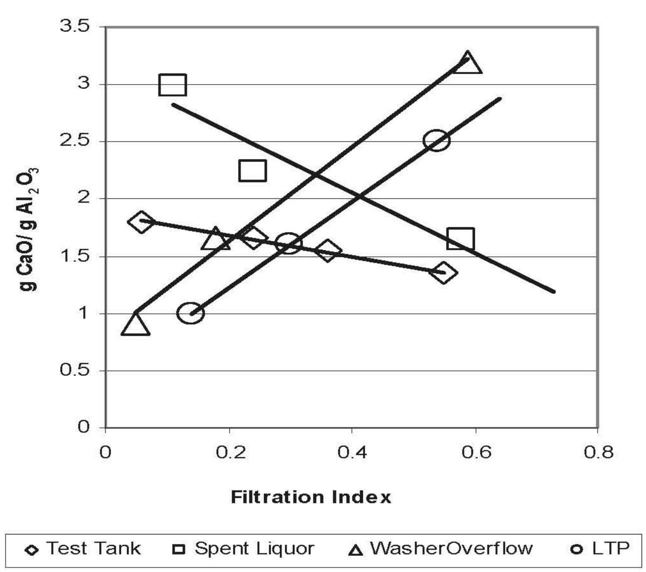

Figure 5. The Manufacture of Tricalcium Aluminate: Slaked at 96°C for 30 minutes; g CaO/g Al2O3 versus Filtration Index.

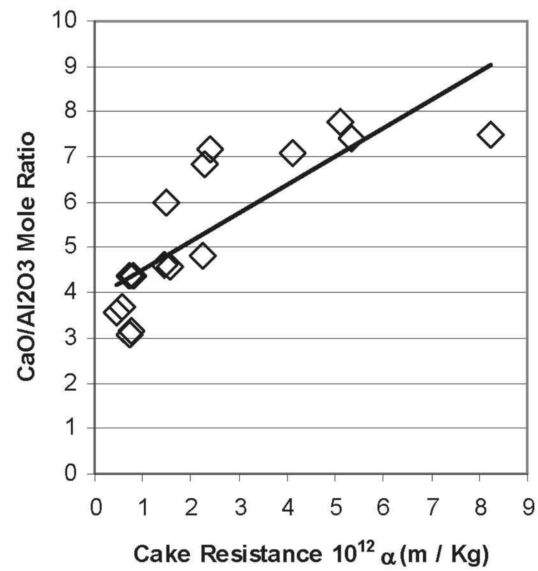

Figure 6. CaO/Al_2O_3 Mole Ratio versus Cake Resistance (α, m/Kg) chart constructed from data produced by Barham, et al, in their paper on "Optimization of Tricalcium Aluminate for Enhanced Bayer Liquor Filtration" [5].

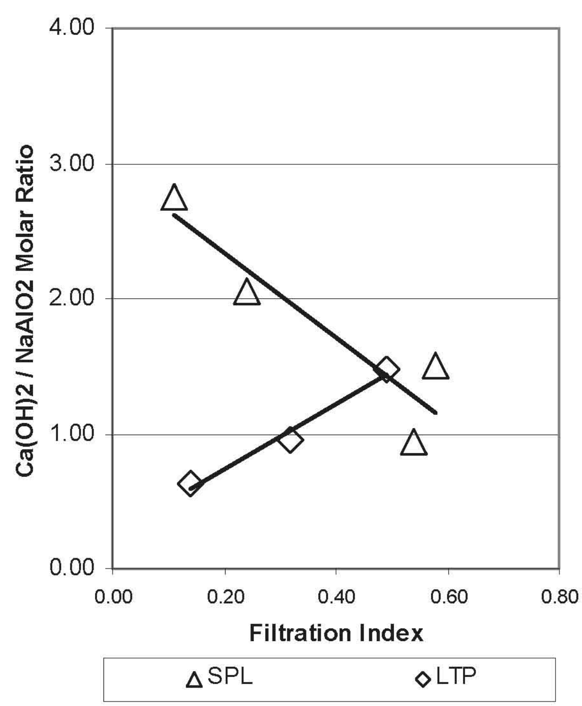

Figure 7. The Manufacture of Tricalcium Aluminate: Slaked at 96°C for 30 minutes; $Ca(OH)_2/NaAlO_2$ versus Filtration Index.

Figure 7 depicts the dependency of lime charge to the concentration of alumina. In these sets of tests, SPL and LTP were chosen because of the difference in the alumina concentration while the caustic concentrations are similar. In Figure 7, the quicklime charged was calculated as $Ca(OH)_2$, and this concentration of lime was divided by the alumina (as sodium aluminate) to give a molar ratio. Both the SPL and LTP seem to have the best filtration at about 1.0 to 1.5 molar ratio. A $Ca(OH)_2$ / $NaAlO_2$ ratio of 1.5 relates back to the stoichiometeric equation (3 mole $Ca(OH)_2$ / 2 mole $NaAlO_2$ =1.5).

The concentration of filter aid solids also seems to be affected by the g CaO/g Al_2O_3. Tests conducted with WOF seems to indicate that as the g CaO/g Al_2O_3 is increased the gpl solids also increases (Figure 8). Residues of the filter aid slaked at different lime to alumina ratios were analyzed by XRD. The diffractograms indicated that as the lime to alumina was increased for the WOF there were fewer compounds present. That is, the XRD analyses indicated that TCA was the predominant compound present at molar ratios 1.0 to 1.5.

The lime to alumina ratio seems to affect the particle size distribution (Figure 9). The median particle size for SPL goes down with higher the lime charge. This reduction in particle size is consistent with the reduction in filtration index. In addition, both the SPL and the LTP particle sizes increase as the lime charge approaches the stoichiometeric relationships of Equation 1.

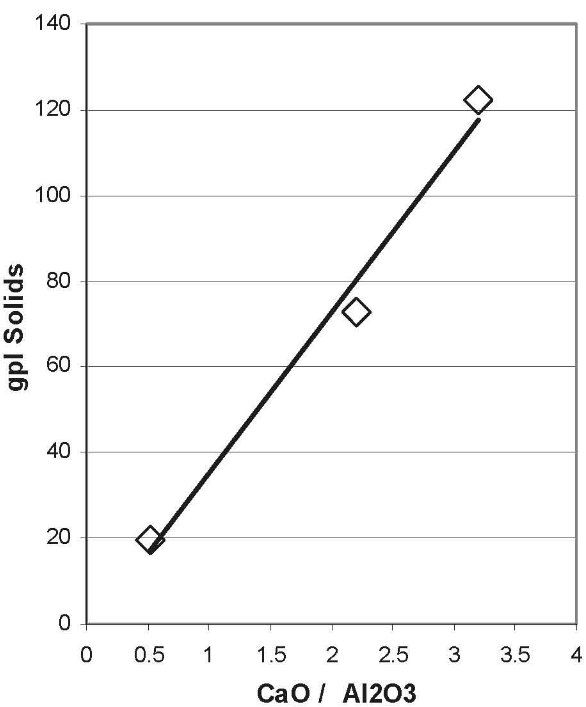

Figure 8. The Manufacture of Tricalcium Aluminate: Slaked at 96°C for 30 minutes; gpl Solids versus g CaO/g Al_2O_3.

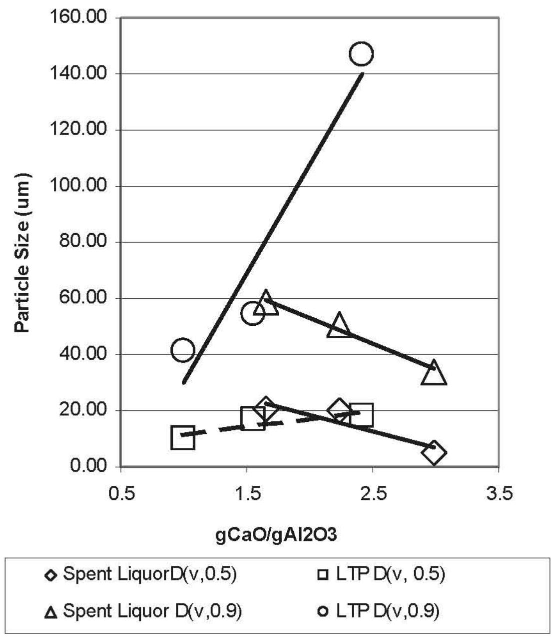

Figure 9. Particle Size (Microns) versus Filtration Index. 50 Percentile D(v,0.5) and 90 Percentile D(v,0.9). Analyzed on Malvern Mastersizer-S®.

Total Alkalinity

It has been reported in literature that causticization reaction is optimized at lower TA [1,4,5]. The alkalinity tests held the slaking temperature, slaking time, and the lime to alumina ratio constant. Figure 10 shows that the filtration index increases as the TA concentration increases. The tests that look at alkalinity also show a relationship to particle size and filtration index. At higher TA concentrations, the median particle size increases. In the reaction of lime and sodium aluminate, TCA is favored at higher TA concentrations. The particle size was greater at the higher TA. XRD analyses indicated that TCA was the predominant compound present at higher TA concentrations.

Filter aid solids seem to increase with increasing TA concentrations (Figure 11). This may be due to the additional conversion of the quicklime to TCA thereby resulting in increased solids content.

It is also interesting to note that an almost pure form of carbonate aluminate is formed at low alkalinity. The carbonated particles are flat and flake like (Figure 4). As previously stated, XRD analysis indicates that this compound to could be hemicarbonate with a d-spacing of ~7.6 Å.

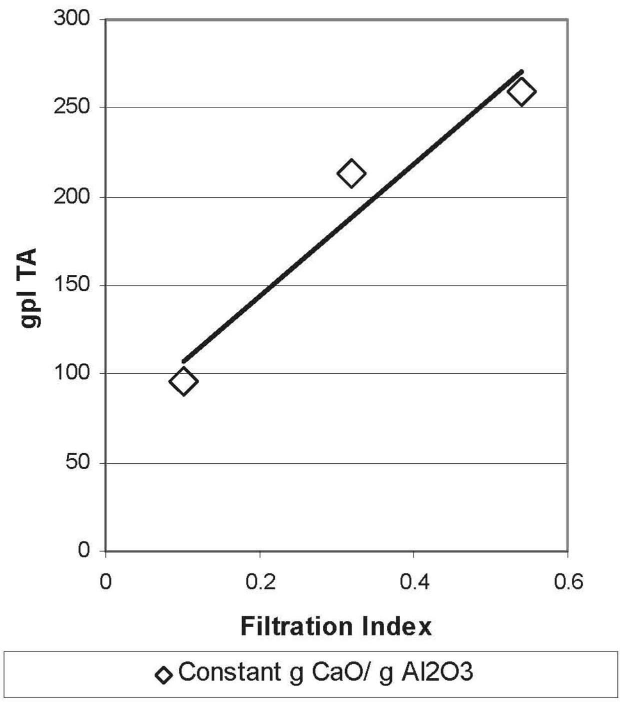

Figure 10. The Manufacture of Tricalcium Aluminate: Slaked at 96°C for 30 minutes; Spent Liquor, gpl TA versus Filtration Index

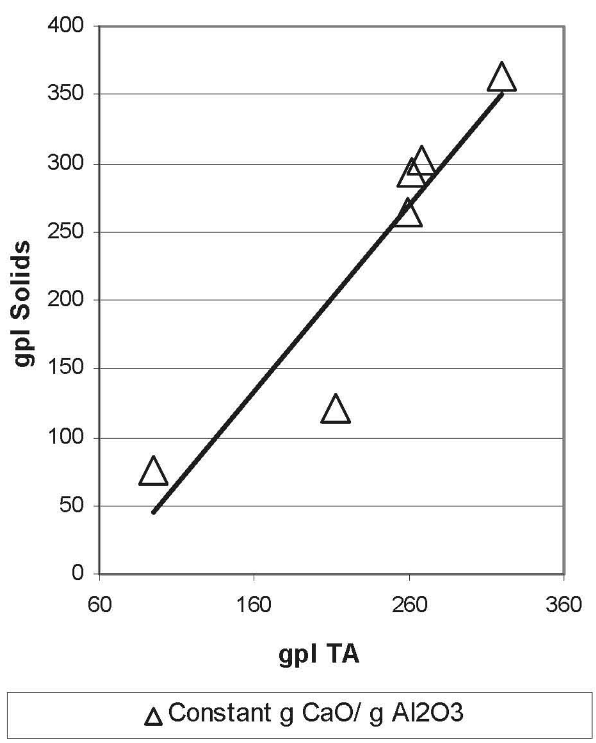

Figure 11. The Manufacture of Tricalcium Aluminate: Slaked at 96°C for 30 minutes; Spent Liquor, gpl solids versus gpl TA.

Temperature

Literature suggests that slaking temperature is important to produce a filter aid with low filter resistance. It has been reported that a minimum of 95° C is necessary to produce highly crystalline substances [1,2,4,5,6]. Figure 12 depicts a plot of slaking temperature versus filtration index. At higher slaking temperatures, there seems to be more conversion of the carbonated aluminates. XRD analyses of the filter aid produced at various temperatures indicates a reduction in the peak height at 10-12° 2Θ and 22-24° 2Θ (Table III).

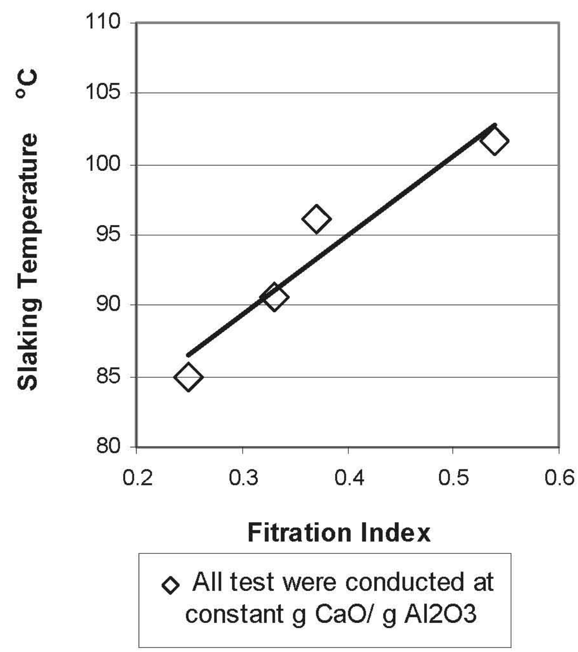

Figure 12. Slaking Temperature versus Filtration Index. The Manufacture of Tricalcium Aluminate: Slaked for 30 minutes; tests were conducted at constant 1.66 g CaO/Al_2O_3.

Table III. Temperature and Diffractograms Peak Heights.

Filtration Index	Peak Height, cps	Temperature, °C
0.25	2.86	85
0.33	18.5	91
0.37	27.6	96
0.54	30.4	102

Figures 13 and 14 show a relationship between slaking temperature, carbonate aluminate XRD peak height, and filtration index. It seems that complete conversion of the carbonated aluminate promotes better filtration. Also, the particle size of the filter aid increased with an increase in slaking temperature. Again particle size of the filter aid seems to play a role in the flow of liquor through the filter medium.

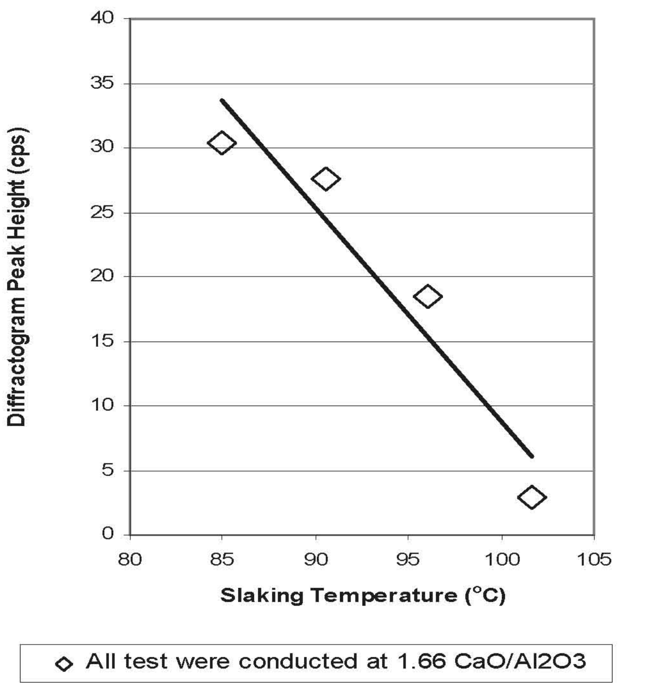

Figure 13. Peak Height versus Slaking Temperature. The Manufacture of Tricalcium Aluminate: Slaked for 30 minutes; . tests were conducted at constant 1.66 g CaO/Al_2O_3.

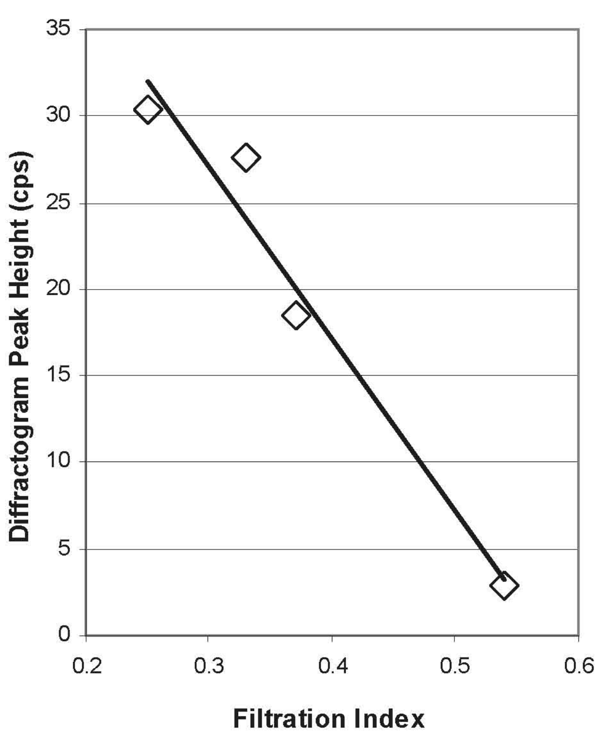

Figure 14. Peak Height versus Filtration Index The Manufacture of Tricalcium Aluminate: Slaked at various temperatures for 30 minutes; tests were conducted at constant 1.66 g CaO/Al_2O_3

Conclusions

Filter aid particle size and chemical composition are affected by the lime to alumina ratio, slaking temperature and total alkalinity. Particle size does plays a role in the filter aids performance. Moreover, there is a relationship between the filter aid's particle shape and good filtration. Higher temperature and higher alkalinity promotes formation of a larger, highly crystalline TCA that has good filtration qualities. In addition, as long as the reaction of lime and alumina is stoichiometric, high quality, pure filter aid is produced. Since the lime and alumina reaction is stoichiometeric, any Bayer Liquor can be used to produce high quality TCA. While it is true that other slaking conditions such as slaking time, impurities in the lime and slaking liquor may affect the final filter aid filtration quality, the evidence of this study indicates that the variables listed do affect the performance of the filter aid.

Acknowledgements

Much thanks is given to W. Liimatta and B. Simoneaux for their valuable contributions to this study.

References

1. N. T. Chaplin, " Reaction of Lime in Sodium Aluminate Liquors," Light Metals 1971, 47-61.
2. R. C. Young, "Chemistry of Bayer Liquor Causticization," Light Metals 1982, 97-117.
3. R. P. Mahoney and L. Connelly, "Bayer Liquor Polishing," Light Metals 1993, 85-88.
4. G. I. D Roach, "The Equilibrium Approach to Causticisation For Optimising Causitisity," Light Metals 2000, 97-103.
5. S. L. Barham, S. U. Khan, J. T. Malito, and W. J. Rennick, "Optimization of Tricalcium Aluminate For Enhanced Bayer Liquor Filtration," Light Metals 2000, 111-116.
6. P. M. Figueiredo, P. Hackett, and S. Ostap, "Control of Calcium Contamination in Alumina; The Ouro Preto Experience," Light Metals 2000, 117-119.
7. N. Mugnier, P. Clérin, and J. Sinquin, "Industrial Experience of Polishing Filtration Performance Improvement and Interpretation," Light Metals 2001, 33-39.
8. S. P. Rosenberg, D. J. Wilson, and C. A. Heath, " Some Aspects of Calcium Chemistry in The Bayer Process," Light Metals 2001, 19-25.
9. J. H. N. Buttery, V. A. Patrick, S. P. Rosenberg, C. A. Heath, and D. J. Wilson, "Thermodynamics of Hydrogalumite Formation In Causticisation," Light Metals 2002.

Recommended Reading

Azevedo, E., and W.H. Brancalhoni. Monitoring of filter press performance by the cake and cloth resistance factor (1995, pp. 103–112).

Bagatto, P.F., and D.L. Puxley. Retrofitting conventional multideck thickener-clarifiers into high rate thickeners (1986, pp. 161–166).

Borges, A., and J. Aldi. Using a statistical model in the red mud filtration to predict the caustic concentration in the red mud (2009, pp. 117–119).

Bounds, W.M. A method for evaluating operating parameters of alumina refinery seed classifiers using a mathematical model for solids settling (2002, pp. 153–156).

Connelly, L.J., D.O. Owen, and P.F. Richardson. Synthetic flocculant technology in the Bayer process (1986, pp. 61–68).

De Roccaro, V.G., et al. Red mud filtration (1998, pp. 103–106).

Dias Gomes, A.M., et al. Applied mineralogy studies: An important tool to understand the red mud sedimentation process (2005, pp. 43–46).

Eckart, D., et al. Improved performance of red mud settlers at Worsley Alumina (2010, pp. 107–112).

Emmett, R.C., and R.P. Klepper. High density red mud thickeners (1991, pp. 229–233).

Franca, S., et al. Some aspects of tricalcium aluminate hexahydrate formation on the Bayer process (2010, pp. 63–66).

Gagnon, M.L., et al. A fractal model for the aggregate size distributions generated during red mud flocculation (2003, pp. 105–111).

Geppert, G.A. Specific surface area analysis of red mud as a tool in Bayer clarification operations (1981, pp. 155–162).

Hudson, L.K. Alcoa's process filter (1974, pp. 737–744).

Imre, M., and G.P. Kelton. Enhancing operation of a desanding circuit with hydrocyclones (1998, pp. 115–119).

Malito, J.T. Improving the operation of red mud pressure filters (1996, pp. 81–86).

Porter, J.L., and H.F. Scandrett. Interpretation of settling test data for estimation of area requirements for settling and consolidation of muds (1963, pp. 95–111).

Speedy, B., and M. Tsockallos. Automatic control techniques for stabilising washer trains (1991, pp. 51–59).

Spitzer, D., and Q. Dai. Effect of flocculant molecular weight on rheology (2006, pp. 11–15).

Weer, P. Redundancy of security filtration (2010, pp. 113–118).

Yanly, X., et al. The effect of organics on the settling of red mud slurry (2001, pp. 79–82).