Study on Formation and Characterization of TCA (Tricalcium Aluminate Hexahydrate) Filter Aid in the Bayer Process

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ABSTRACT

Filter aids are used to permit fast liquor flow rates and for filtering solids to low concentrations. Tricalcium aluminate hexahydrate (TCA) - Ca₃Al₃(OH)₁₂, is used in the alumina industry (Bayer Process) as a filter aid, in the step of pregnant liquor polishing, before the crystallization process. In general, it is produced by reactions between pregnant liquor and quick lime and the particle formation can be affected by many factors, including the alumina liquor concentration; reaction time and temperature; mixing speed, source of calcium, lime quality and use of chemical additives, such as magnesium compounds. These variables are decisive in the quality of the produced TCA, mostly particle morphology and size, which will have direct influence on filtration efficiency in the liquor polishing step.

Therefore, in this paper we focused on a detailed investigation to provide the knowledge and consequently the control of the variables involved in the TCA formation. The TCA was prepared with both industrial and synthetic (doped industrial liquor) Bayer liquor. Preliminary results based on XRD and SEM techniques shown that the formation of TCA particles begins partially, in the first minutes of reaction, but their morphology and particle size distribution depends on lime particle size distribution and impurities, which play an important role in the lime reactivity and in the kinetic of the TCA formation.

The use of pregnant liquor in the TCA synthesis promoted the formation of particles with well-defined morphology and narrow particle size distribution, besides the reduction in the reaction time from 6 to 2 hours, which can promote process cost reduction.
INTRODUCTION

In the Bayer process, the overflows from gravity settling may still contain a small amount of fine suspended solid matter, which may not pass into precipitation step, due to the possibility of contamination in the final product, mainly with iron and titanium compounds. This solid matter might be removed from the pregnant liquor by polishing filters; this process is well known as security filtration and it is getting the most attention from alumina refinery operators and equipment suppliers.

The tricalcium aluminate hexahydrate (TCA) - Ca$_3$Al$_3$(OH)$_{12}$ - is used in the alumina industry (Bayer Process) as a filtering aid in the step of pregnant liquor polishing, before the crystallization process. TCA acts as a filter aid by forming a porous coating on the filter leaves, thereby significantly reducing the tendency for the RM, to blind the filter cloths and shorten the cloth life (HuiLing, 2002). Considering materials for filter aids, the particles morphology and size distribution have great importance in the efficiency of that filtration process.

TCA is obtained through the reaction of hydrated lime with sodium aluminate (present in Bayer liquor), shown in equations 1 and 2. The TCA formation, with an adequate granulometric distribution and particle morphology, is fundamental for a good filtration performance of liquor Bayer, otherwise there will be an increase in the pressure in the filters as well, a drop in the rate of filterability (França et al., 2010; Santos et al., 2011; Salimi et al., 2018).

\[3 \text{CaO} + 2 \text{NaAlO}_2 + 7 \text{H}_2\text{O} \leftrightarrow 3 \text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O} + 2 \text{NaOH}\]  

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Therefore, an adequate lime slaking to produce milk of lime (as lime is employed in the Bayer process) and control of TCA formation reaction (residence time, temperature, among others) are fundamental to ensure the correct formation of its particles.

França et al. (2010) reported the operational difficulties to produce a good TCA filter aid by using the spent liquor as reactant, based on operation conditions applied in an alumina refinery located in northern Brazil. A similar approach was presented by Santos et al. (2011), showing the better quality of a TCA produced with pregnant liquor, in another refinery, in southwest Brazil. So, the use of pregnant or spent Bayer liquor might have such influence on the TCA synthesis, reflecting in the particle morphology and crystallinity, as shown by the mentioned authors. Besides, impurities present in the lime and chemical additives can play an important role on the synthesis step.

The desired characteristics for the industrial TCA filter aid are well-defined particle morphology, close to spherical or orthorhombic dodecahedrons, and particle size mean diameter of 15-17 µm.

Therefore, in this R&D project reaction conditions for TCA formation were investigated, allowing the knowledge to control of the variables involved in the process. The results of this study will be used towards the evaluation of industrial applicability of these products.
METHODOLOGY

Samples and reagents

The samples of spent liquor and alumina hydrate from an alumina refinery (Brazil) were used in the experiments. Sodium hydroxide flakes - NaOH was purchased from Vetec Laboratory.

Sample characterization

Samples of raw material and products were evaluated in terms of chemical and mineralogical characterization. For chemical determinations, the Al₂O₃ concentration and Al₂O₃/NaOH concentration ratio were analyzed by titration methods, based on the Alcan® methodology. These concentrations were monitored before the reaction takes place and during all the reaction time. Comparison of results was used to indicate the reaction efficiency, in terms of reagent consumption.

Mineralogical characteristics were determined by X-ray diffractometry (XRD), with a Bruker-AXS D5005, using Co Kα (λ=1,78897 Å) radiation (35 kV and 40 mA); and scanning electron microscopy (SEM), with a Leica F440 (high vacuum mode). The samples were adhered to SEM studs using carbon tape and coated with gold using a sputter-coater (BAL-TEC, SCD 005). The PSD analysis was run in a Malvern Particle Size Analyzer, Mastersizer 2000, using sonication to promote particles disaggregation. Stereo microscope Leica EZ4D was also used to identify contaminants in the row material.

TCA synthesis

TCA was produced with both spent and pregnant liquors. The spent liquor was sampled in a refinery and the pregnant one was produced at the laboratory, by adding dissolved alumina hydrate (produced in the same refinery) to the spent liquor. Table 1 shows the liquors characteristics.

Table 1 Chemical characteristics of liquors used in the TCA Synthesis

<table>
<thead>
<tr>
<th></th>
<th>NaOH (g/L)</th>
<th>Al₂O₃ (g/L)</th>
<th>Al₂O₃/NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spent liquor (from refinery) –SL(ref.)</td>
<td>300.1</td>
<td>123.3</td>
<td>0.41</td>
</tr>
<tr>
<td>Pregnant liquor [SL (ref) + alumina hydrate]</td>
<td>283.0</td>
<td>200.0</td>
<td>0.70</td>
</tr>
</tbody>
</table>

The original source of calcium was a quick lime sample, with particle size -1.0 mm, and chemical composition as follow: 3.9 % lost on ignition and 5.4 % insoluble in HCl.

Slaked lime (20 % CaO w/w) was used as reactant to TCA formation. The volumetric ratios 2:1 and 3:1 (liquor/slaked lime) were used, based in operational conditions adopted in the alumina refinery. The reaction temperature was controlled in the range 90-95 °C and the reaction time was 2-6 hours.
The pregnant liquor concentration was set in the range of 170-200 g/L Al₂O₃, which corresponds to an Al₂O₃/Na₂CO₃ ratio in the range of 0.70-0.73.

For the TCA synthesis the experimental apparatus (Figure 1a) is composed by a 316 stainless steel reactor (1), 0.3 m diameter and 5.0 L capacity, adapted with heating and insulation system (2) (max. 120 °C) which provides effective and efficient temperature control and measurement (3, 4). The controlled stirring (5) and sampling valve systems (6) are also adapted in the reactor to ensure homogeneous mixing during the reactions and reliable sampling. Figure 1b shows the experimental apparatus for the pregnant liquor preparation, with the addition of alumina hydrate solution.

![Figure 1](image)

Figure 1 Laboratory apparatus (CETEM) for the TCA production (a); alumina hydrate dissolution for pregnant liquor preparation (b)

The TCA samples grabbed during the tests were washed, dried and analysed in terms of particle size and morphology as a function of the reaction time. Comparison with samples of TCA produced in the refinery was made aiming to a better understand of the influence of variables in the filter aid formation.

RESULTS AND DISCUSSION

The TCA synthesis with spent liquor (Al₂O₃/NaOH=0.41) seemed do not provide enough aluminum to yield the formation of particles with defined morphology. In a previous investigation França et al. (2010) showed the particle morphology is improving with reaction time but to the investigated reaction time (2 h), no appropriate morphology and particle size distribution were reached (Figure 2a, 2b and 2c). These results are very similar to those obtained in the refinery, for 6 h residence time (Figure 2d, 2e and 2f).
Figure 2 Scanning electron microscopy images and particle size distribution of TCA particles produced with spent liquor [volumetric ratio 2:1 liquor/slaked lime]: laboratory scale, 2 h (a, b, c) and refinery, 6 h (d, e, f)

Once in the refinery the lime grinding prior to the slaking process is made by the addition of a portion of spent liquor, the presence of additional salts can affect the CaO hydration process, reducing the amount of Ca(OH)$_2$ available to the next reaction steps, as the lime slaking and TCA formation, allowing the formation of intermediate products (Whittington et al., 1997; Mugnier et al., 2001; Salimi and Vaughan, 2016; Smith, 2017). Possibly after lime slaking quick lime particles still remains in the reactant and they can lead to the formation of heterogeneous solid, which presents cemented blocks (Mugnier et al., 2001), as shown in the Figure 2e. Even so, some evolution in TCA formation can be noted by the discrete increase in the mean particle diameter (Figures 2c and 2f).

Figure 3 shows XRD patterns for slaked lime and TCA synthetized along the 3 reaction tanks-in-series and SEM images of the products: TCA and portlandite [Ca(OH)$_2$], which is an undesirable due to its hexagonal plate morphology, detrimental to the filtration operation.
According to Whittington et al. (1997), the morphology of the TCA particles is related to the molar ratio CaO/Al₂O₃. In the specific step of TCA production in the refinery the molar ratio is about 0.98 (equivalent to a volumetric ratio of 2:1 spent liquor/slaked lime), based in data presented in Table 1. CaO/Al₂O₃ molar ratios between 1.8 and 3 will likely promote the formation of particles with well-defined morphology, similar to rhombic dodecahedrons; on the other hand, CaO/Al₂O₃ molar ratios above 1.8, the TCA particles will probably have poorly defined morphology.

Based in the characterization of TCA produced in the refinery it is possible to conclude that the poor formation of TCA particles in the preparation tanks, might be closely related to the low CaO/Al₂O₃ molar ratio (between 0.9 and 1.4), while literature and other refineries worldwide practice CaO/Al₂O₃ molar ratio in the range of 1.8 to 3. This issue may be related to the preparation of TCA with poor liquor; in addition, the reactants are added in the first stage, whose tank hosts the liquor flushing process, so the addition of spent liquor is about 7 m³/h, that possibly explains the Al₂O₃ low concentration, which may respond for the production of intermediate compounds - possibly 3CaO·Al₂O₃·(8-12)·H₂O - an amorphous phase with very fine particles or low crystallinity (Whittington et al., 1997). This fact reinforces the need to perform TCA formation experiments with pregnant liquor.

Aiming to reach molar ratios above 1.8, the TCA synthesis was then carried out by using pregnant liquor (Al₂O₃/NaOH = 0.71) as reactant. To the preparation of the pregnant liquor with 200 g/L Al₂O₃ and 283 g/L of NaOH (ratio Al₂O₃/NaOH = 0.71), by doping aluminum hydrate in the spent liquor it was necessary to solubilize part of the aluminum hydrate in sodium hydroxide solution, held by temperature control of 90 °C, aiming to improve the solubility of aluminum hydrate.

Figures 4 and 5 show, respectively, results to the TCA produced with 2:1 and 3:1 pregnant liquor/slaked lime volumetric ratios. In both experimental situations was possible to produce particles with a better defined morphology than those produced with spent liquor, suggesting bipyramidal or octahedral isometric crystallography.
Comparing the SEM images of TCA samples obtained in the laboratory (Figures 4 and 5) with pregnant liquor was possible to notice a significant difference in the particle morphology, with well-defined particles being produced under those experimental conditions. This fact might certainly be due to the better stoichiometric balance of the reaction, with a higher amount of available aluminum to the TCA synthesis. Furthermore, the results obtained for the pregnant liquor/slaked lime volumetric ratios 2:1 were even better than those obtained to 3:1 volumetric ratio, probably due to the higher concentration of available calcium in the reaction. The presence of portlandite particles was noticed in both cases (Figures 4a and 5a), but the peaks showed higher intensity in the 3:1 reaction system.

The bi-pyramidal particles obtained in the present study, by the reaction of pregnant liquor and slaked lime can be characterized as CAIS (calcium aluminate iron silicate) crystals, as suggested and observed by Mugnier et al. (2001). It is known that the reaction for TCA synthesis are not simple, with several by-products being formed in this process, most of them influenced by the mechanisms of dissolution of CaO or Ca(OH)₂ in aqueous solution and impurities present in the lime source (Whittington et al., 1997; Suss et al., 2008; França et al., 2010).

In both TCA synthesis experiments, using spent and pregnant liquor as reactant, it was possible to reach $d_{50}$ around 12 µm in 2 h reaction time, against $d_{50}$ of 17 µm after 6 h of reaction (residence) time.
in the refinery. These results corroborated with Mugnier et al. (2001), which reported the influence of the continuous process in the particle size distribution, producing smaller particle diameter.

CONCLUSION

The results of characterization of the TCA produced in this study were confronted with results from the literature, as well as results of characterization of TCA samples produced at the Brazilian refineries (Avelar et al., 2008; Santos et al., 2011). The particle morphology for TCA produced with pregnant liquor is still close to the one desired to filter aid applications, but even better than those produced with spent liquor; particle size distribution can reach the specification for filter aid, and with the advantage of a smaller reaction time (2 h). Filtration tests might be conducted to better evaluate the quality of the TCA’s produced under different operational conditions.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the contribution of Brazilian refineries – Alunorte (belonging to Vale during project) and CBA, for providing samples of spent liquor and alumina hydrate to the development of this research project. We also appreciate the collaboration of Brazilian Council for Research and Development (CNPq) for supporting scholarships to members of this technical group.

REFERENCES


