Formation study and influence of tricalcium aluminate (TCA) on the polishing process of green liquor

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Abstract

Tricalcium aluminate hexahydrate (TCA) is a compound used in the Bayer process, in the step of green liquor polishing whose function is to act as a filter aid. It is obtained by reaction of the slaked lime which is added to the Bayer liquor. This liquor could be green, spent or refiltered. The paper aims at consolidating knowledge about the TCA, studying its formation mechanism, using different liquors (as described above) and comparing products to indicate which ones is the best to use in the polishing step. Additional studies such as characterization and morphology of formed products with the aid of electron microscopy (SEM) and X-ray diffraction (XRD) were important to reveal by the microstructure of formed calcium compounds, the influence of caustic concentration on the quality of TCA formed. The paper indicates that the green liquor is more appropriate to be used because it presents a higher concentration of alumina and temperature when compared to the spent liquor.

Keywords: Tricalcium aluminate hexahydrate; Bayer liquor; X-ray diffraction; electron microscopy.

1. Introduction

TCA, whose chemical composition is $Ca_3Al_3(OH)_{12}$, is used in the Bayer Process as a filter aid, in the step of green liquor polishing, before the crystallization process. Its function is to help retain the solid impurities present in this liquor, by increasing the filtration efficiency due to minimization of the filter cake resistance [1]. As this material is considered an aid, particle morphology and size distribution of those have great importance on the efficiency of that compound in the polishing process.

One of the main steps in the process of obtaining alumina is polishing or clarification of the green liquor (solution containing high concentration of dissolved aluminum hydroxide, resulting in alkaline lixiviation of bauxite in the Bayer process), it is at this stage that retains the unwanted solid particles contained liquor (red mud), before crystallisation of the aluminum hydroxide.

The clarification process of liquor is done using vertical filters under pressure with the help of tricalcium aluminate - TCA prepared in a previous step for polishing, a reaction between sodium aluminate contained in spent liquor (solution containing low concentration dissolved aluminum hydroxide) and slaked lime [$Ca(OH)_2$]. The resulting product of reaction is a suspension whose size distribution and shape of the particles should meet the requirements of filtration efficiency and quality of the filtrate [2].

Among the variables that influence the characteristics of tricalcium aluminate it is important to note the temperature, the addition of reagents (source of calcium, concentrations), the presence of impurities, the stirrer speed and reaction time, which are decisive for which quality of TCA formed in the Bayer process [1, 3, 4].

In some refineries, the tricalcium aluminate is prepared with spent liquor whose concentration of dissolved aluminum hydroxide and temperature are smaller than the green and refiltered liquors whose raw materials which are most indicated for obtaining TCA. Therefore, it is necessary to get a better knowledge of the material obtained by reaction of spent liquor with slaked lime. Moreover, it is important to know information about TCA prepared with the green and refiltered liquors and its influence on clarification process by comparing which the two liquors is most recommended in the preparation of tricalcium aluminate, in order to optimize this process.

2. Objectives

The objective of this paper is to study and compare the formation mechanism of the TCA obtained from the spent liquor, green and refiltered, in order to get specific knowledge of these products. Moreover, also aims to study the parameters of influence in the preparation of TCA and characterize the products.

2. Methodology

Tests were performed in order to simulate in the laboratory the preparation of TCA, using the same conditions used in the industry, using for this purpose, slaked lime and spent, green and refiltered liquors, from staging area tricalcium aluminate in order to compare the obtained product, characterized by the particle size distribution analysis, XRD, SEM and EDX.

The formation study of TCA, using different liquors as raw material, occurred in two different steps as below.

3.1. Preparation of TCA using spent, green and re-filtered liquors

The sample preparation was performed in the laboratory, similar to the process conditions, and the lime suspension (slaked lime) and liquors (spent, green and refiltered) were coming from the industrial area of preparation of TCA.

To simulate the process of preparing was used an oven with rotary device to simulate the shaking (single speed), with digital temperature control, according to Figure 1.

Figure 1. Equipment used in the process of preparation of TCA in the laboratory. Source: Hydro Alunorte, 2013.

Considering the useful volume of 125 mL of the bottles used in the tests and conditions for adjustment volumetric of process, the following volumes were established for the tested conditions: liquor (50 mL) and $Ca(OH)_2$ with concentration of 20 % (12 mL), using a temperature of 105 °C for 6 hours, under suave stirring effect.

3.2. Characterization of TCA produced from spent, green and refiltered liquors

TCA samples produced were characterized to determine the particle size distribution and mineralogical characterization. The liquors used were analyzed before the reaction to determine the ratio Al_2O_3/NaOH.

The techniques used in these determinations are detailed below.

3.2.1. Chemical analyses

Chemical analyzes were performed in order to know the ratio between concentration of Al_2O_3/NaOH (A/C) of liquors samples used in the preparation of tricalcium aluminate. They were performed on an automatic titrator (METHRON) using standard reagents.

3.2.2. Particle size distribution

The particle size distribution analyzes were performed in order to know the particles sizes present in the TCA samples and thus evaluate the percentage of particles with fraction less than 5µm and average size.

They were made in light scattering equipment (Mastersizer 2000 da Malvern). The sample compartment was filled with distilled water and the suspension was gradually added until the obscuration required for performing the measure. The particles have been kept dispersed by stirring at 1450 rpm for 30 minutes. The considerations used in the calculations of the average particle sizes were normal sensitivity and spherical particle.

The particle size distribution curves were obtained by using Mie theory, and refraction index 1.627 (solids) and 1.33 (water). Operational data used were: agitation 2600 rpm and 3 minutes of ultrasound to dissociate the particles.

3.2.3. Particle Morphology

The scanning electron microscopy is a technique used for microstructural analysis, both morphological as superficial of solid materials.

The EDX or EDS analysis is an analytical technique used for the measurement of chemical elements present or chemical characteristics of a sample, it is possible not only to identify these elements, but also to determine its concentration with high accuracy.

The morphological images of the materials under study were obtained from a scanning electron microscope, the brand HITACHI, TM 3000 model, with a range of 30000 x EDS detector.

3.2.4. Mineralogical analysis by X-ray diffraction

The diffraction of X-rays is one of the methods used in determining crystalline phases in various types of materials, whether natural or synthetic origin.

The analyses were performed on an X-ray diffractometer model X'PERT PRO MPD (PW 3040/60) of PANalytical with Goniometer PW3050 / 60 (theta / theta), ceramic X-ray tube anode and copper ($K\alpha 1$ = 1.540598 Å), model PW3373 / 00 with long fine focus (2200W-

60kV) and nickel Kβ filter. The detector used is X'Celerator, type RTMS (Real Time Multiple Scanning), operating in scanning mode and an active length of 2,122º.

The software used for analysis of the data processing was the X'Pert Data Collector, Version 2.1a, and the software used in the identification of crystalline phases was the X 'Pert High Score version 2.1b, both from PANalytical.

4. Results and Discussions

4.1. Chemical Analyses

Table 1 shows the chemical characterization of the liquors used to develop this work. Tests were conducted to determine the total alumina, caustic concentration and ratio alumina/caustic. Note that the values of ratio the alumina caustic range between 0.412, featuring spent liquor (SL); of 0.734, featuring green liquor (GL); and 0.731, featuring refiltered liquor (RL), and this is the rich liquor passing through another filtration step.

Table 1. Chemical analyzes of Bayer liquors used in preparation of TCA.

Liquors	$Al2O3$ (g/L)	Na_2CO_3 (g/L)	Ratio A/C
SL	123,5	300,1	0,412
GL	203,0	276,5	0,734
RL	200,5	274,2	0,731

4.2. Particle size distribution

According to the results of the particle size distribution analyzes shown in Figures 2, 3 and 4, done for the TCA samples prepared with spent, green and re-filtered liquor respectively, it is observed that the average diameter of the particles lies TCA-in the range between 13 and 14 micrometres in the median expected in the industrial process, which is in the range between 12 and 15 micrometres second industrial information.

It is also noted that the smaller fraction than 5 µm (fine) is around 4 %, as shown in Table 2. If the percentage of TCA fines is greater than 5 %, it will hinder the clarification process, as solid residues from green liquor feature a significant amount of particles with this diameter.

Table 2. Median and fraction < 5 µm of TCA samples.

TCA	SOLIDS TCA (g/L)	>5um (%)	Mediana (um)
SL	129,0	4,27	13,37
GL	129,3	4,07	13,42
RL	116,6	4,43	14,07

The specification of median value is directly related to the values of the project operating variables of Kelly filters, which the TCA will act as a filter aid. Particle with size distribution lower than the specified promote the formation of cakes with less permeability and thus more pressure drop (higher operating pressures) in the process. If the particle size distribution of TCA formed is in a higher range (coarser particles) than foreseen in the project (12 – 15 µm), the efficiency of polishing the green liquor will be impaired due to the formation of a pre-filter cover with greater permeability, resulting in lower retention of solid particles (unwanted material) suspended in the green liquor. Thus, the cake formed by the filter aid will have lower retention capacity of the suspended particles of unwanted material in the green liquor, which should not be present in the later stages of crystallization / decanting aluminum hydroxide [2].

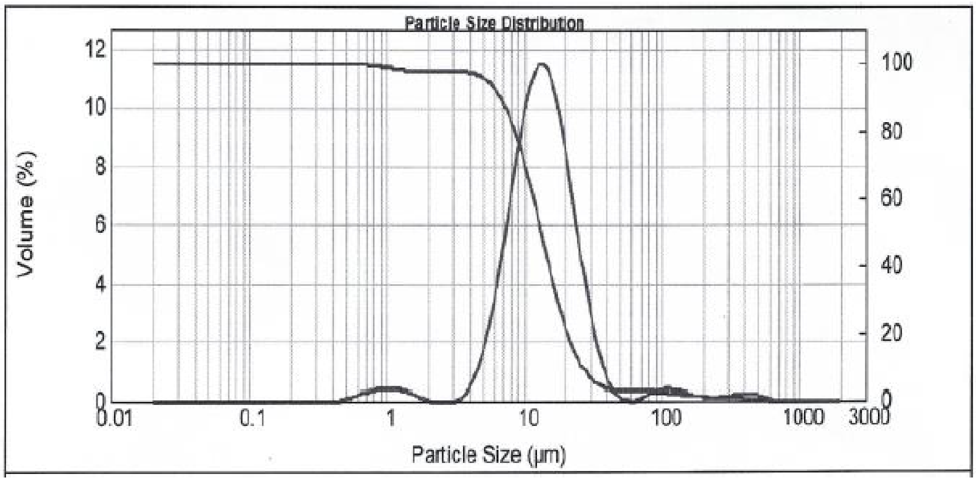

Figure 2. Particle size distribution to TCA sample – SL.

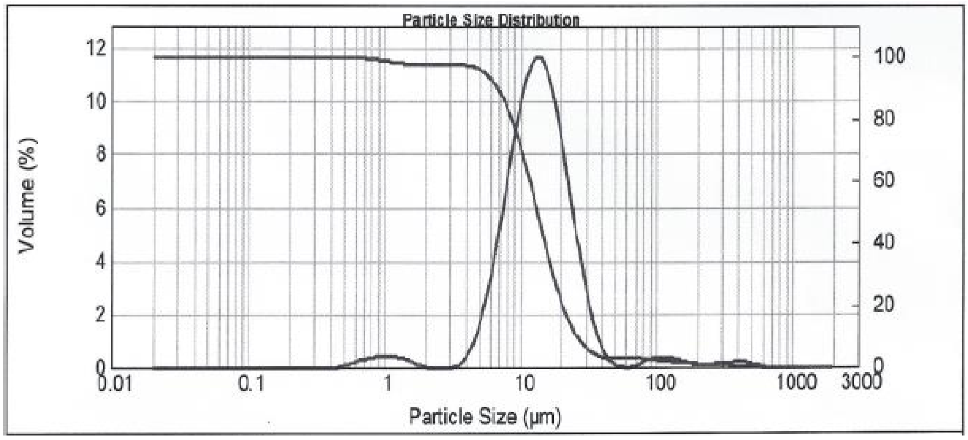

Figure 3. Particle size distribution to TCA sample – GL.

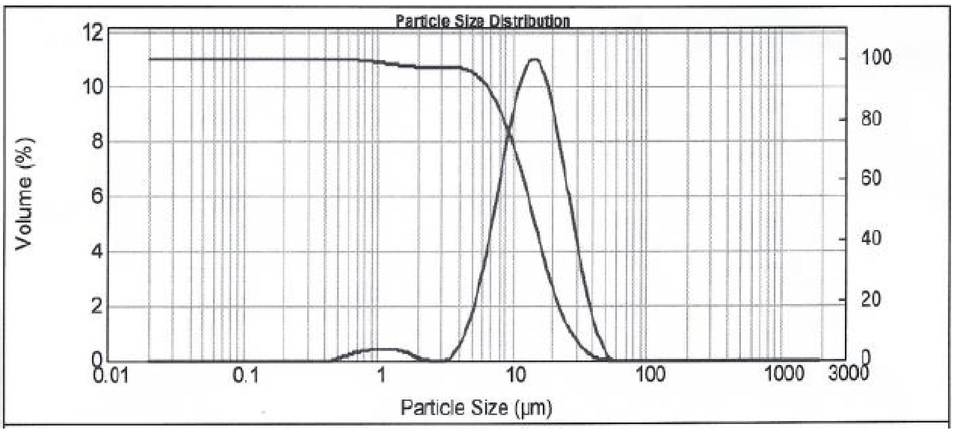

Figure 4. Particle size distribution to TCA sample – RL.

4.3. Particle morphology

The scanning electron micrograph shown in Figure 5, 6 and 7 refer to samples of TCA prepared with spent, green and refiltered liquors, respectively.

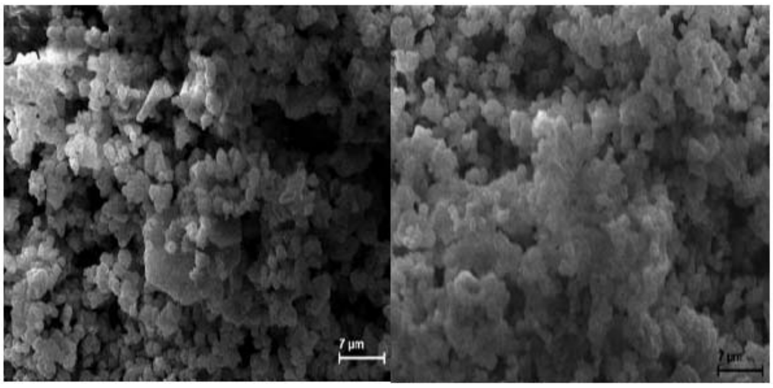

Figure 5. Scanning electron micrograph of TCA prepared with spent liquor.

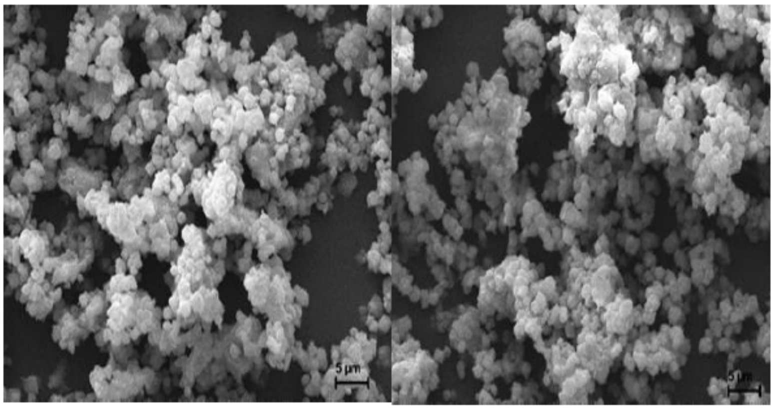

Figure 6. Scanning electron micrograph of TCA prepared with green liquor.

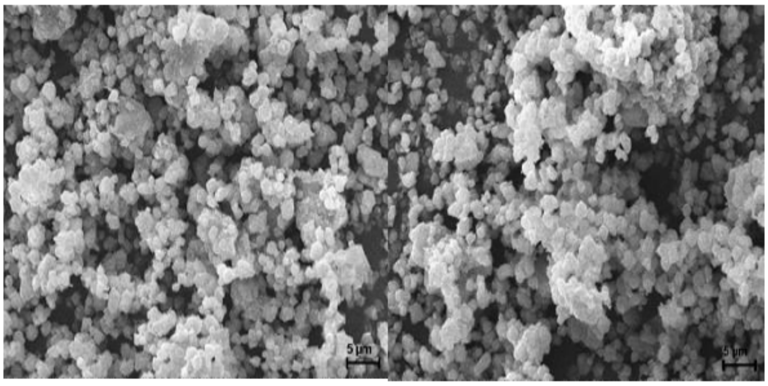

Figure 7. Scanning electron micrograph of TCA prepared with refiltered liquor.

Note the discrete formation of TCA grain for the product synthesized with spent liquor (Figure 5), with not well defined morphology. One can also notice the presence of spherical particles, which is probably unreacted aluminate, and particles with euhedral hexagonal morphology, characterized portlandite. Similar results were also reported by [5].

The products synthesized with green and refiltered liquor (Figure 6 and 7) have a much more defined morphology, suggesting an isometric bipyramidal or octahedral crystallography. Similar results were also reported by [2]. One can also observe the presence of particles with euhedral hexagonal morphology, featuring portlandite.

The morphology of the TCA particles is related to the molar ratio CaO/Al_2O_3. This molar ratio refers to the number of moles CaO/n° moles of Al_2O_3. In the TCA obtained with spent liquor, this molar ratio is about 0.99; for the TCA obtained with green liquor is about 1.68; and the TCA obtained refiltered liquor is about 1.65. These molar ratios were calculated from the ratio between the process flows in the formation of TCA and the data contained in Table 1. According to [4], molar ratio CaO/Al_2O_3 between 1.8 and 3 promotes the formation of particles with better defined morphology, similar to rhombic dodecahedron; to molar ratios lower than 1.8, the TCA particles will be probably morphology with lower definition.

Figures 8, 9 and 10 show scanning electron micrograph and their corresponding spectra of semiquantitative analysis (SEM/EDS), referring to samples of TCA prepared with spent, green and refiltered liquors, respectively.

In the EDS analyzes it was observed that the basic composition of the analyzed material is represented by Ca, Al, O, Si. These elements characterizing the formation of tricalcium aluminate, and other elements such as $Ca(OH)_2$ (portlandite) and possibly aluminate traits that do not reacted.

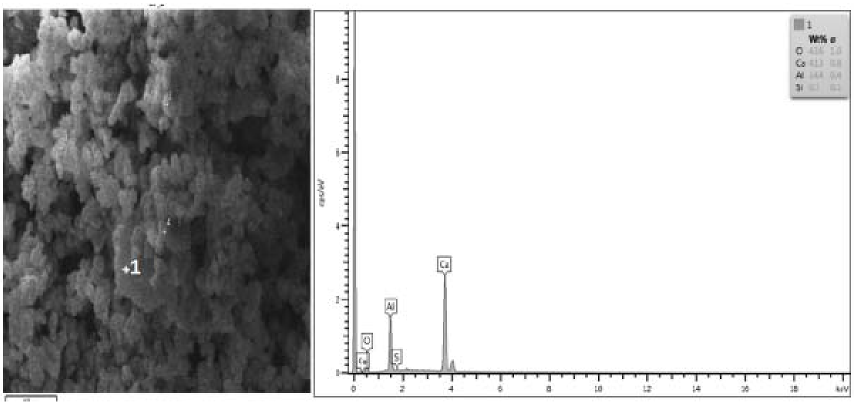

Figure 8. SEM /EDS of TCA prepared with spent liquor.

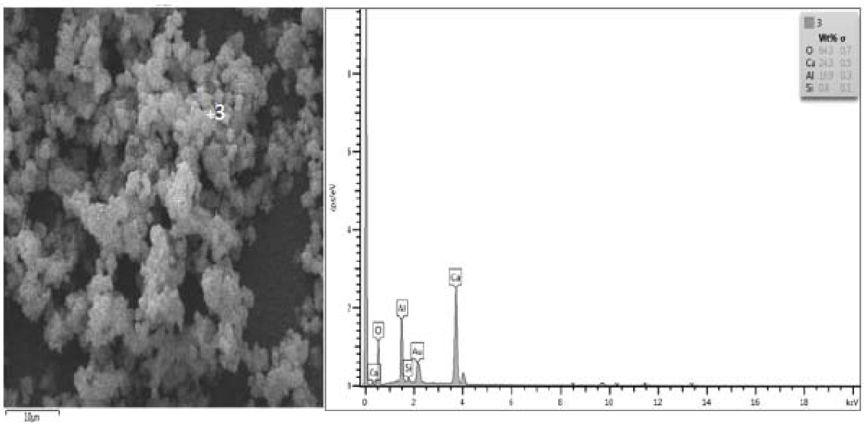

Figure 9. SEM /EDS of TCA prepared with green liquor.

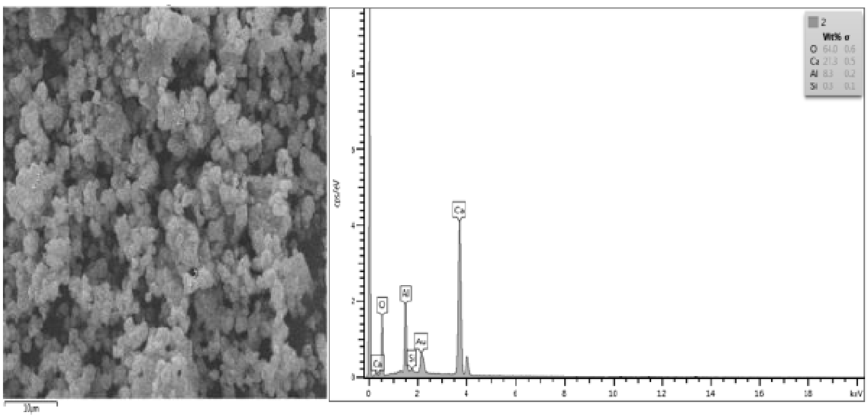

Figure 10. SEM /EDS of TCA prepared with refiltered liquor.

4.3. Mineralogical analysis by X-ray diffraction

The analysis of X-ray diffraction of the TCA samples synthesized with spent, green and refiltered liquors, respectively. show the presence of different calcium compounds present in the liquor, mainly on the stable form of tricalcium aluminate, as shown in Figure 11. However, it is clear the formation of other phases such as portlandite.

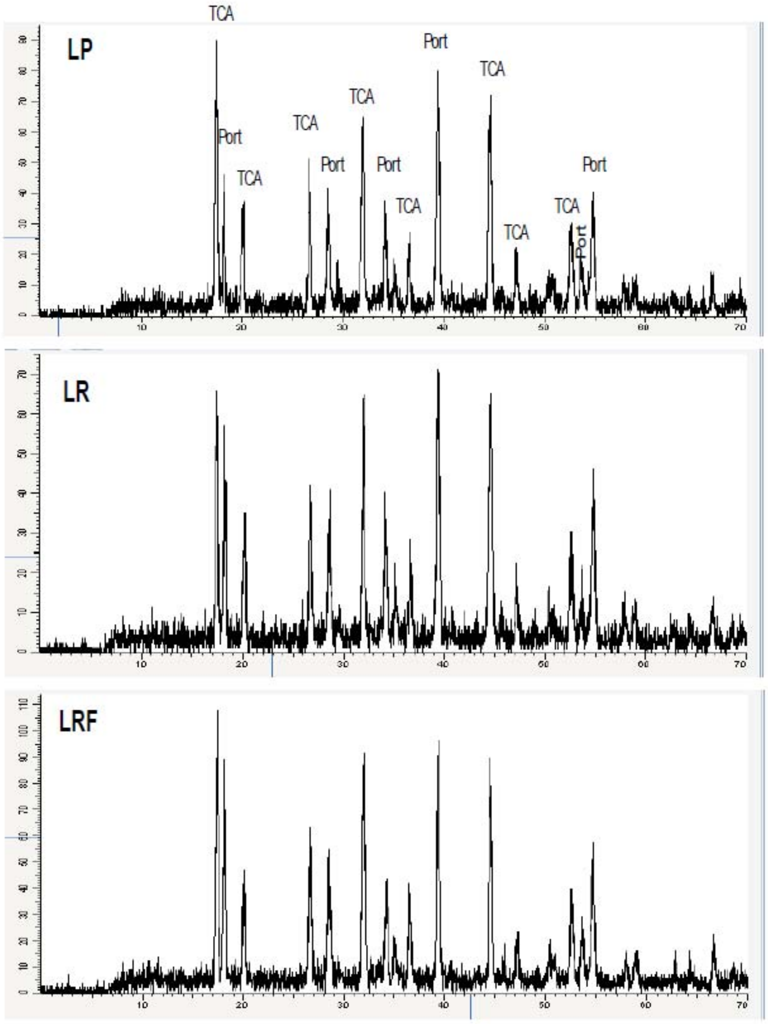

Figure 11. X-ray diffractograms of the TCA samples (SP, GR and RL).

5. Conclusions

The study showed that the use of spent liquor to the formation of tricalcium aluminate, is connected the formation of multiple parallel compounds, which interfere directly in the TCA properties. Moreover, it was noted throughout the study that the use of green liquor to the preparation of TCA is most appropriate, because it presents a higher concentration of dissolved aluminate, which favors the formation of tricalcium aluminate disadvantaging calcium reaction with other possible existing elements in Bayer liquor (impurities).

It was also observed that the difference of the structure of TCA formed from the spent, green and refiltered liquor may be related to the precipitation of aluminum hydroxide from sodium aluminate, who suffers direct influence of temperature.

It is evident the influence of impurities such as Na_2CO_3 (carbonates), in the reactions with CaO (calcium oxide) to form structures with different particle size and morphology expected to tricalcium aluminate. The temperature of the liquor at the moment of formation of TCA could directly affect the appearance of unwanted structures, because there is a strong precipitation of compounds that should be dissolved, especially in spent liquor.

6. References

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