

Decomposition Kinetics of Argentian Lead Jarosite in NaOH Media

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Abstract. Argentian lead jarosite was obtained with the maximal dissolution technique, and it was thoroughly characterized. In this work we studied the decomposition kinetics and cyanidation of the argentian lead jarosite in NaOH media. The reaction order and activation energy for the alkaline decomposition are of $n = 0.7$ and $Ea = 101.85 \text{ KJmol}^{-1}$, and of $n = 0$ and $Ea = 109.54 \text{ KJmol}^{-1}$ for the cyanidation process. The global cyanidation process consists of two stages: decomposition reaction followed by the instant cyanidation of the decomposition products.

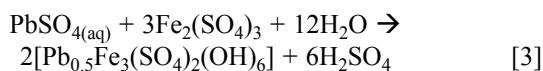
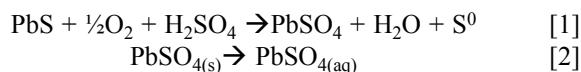
Key words: Kinetics, decomposition, argentian, lead, jarosite, cyanidation, alkaline.

Resumen. Se obtuvo jarosita de plomo argentífera con la técnica de disolución máxima, la cual se caracterizó exhaustivamente. Se estudia la cinética de descomposición y cianuración de la jarosita de plomo argentífera en medio NaOH. El orden de reacción y energía de activación para la descomposición alcalina fueron de $n = 0.7$ y $Ea = 101.85 \text{ KJmol}^{-1}$ respectivamente, mientras que para la cianuración fueron de $n = 0$ y $Ea = 109.54 \text{ KJmol}^{-1}$. El proceso global de cianuración consiste en dos etapas: reacción de descomposición, seguida de la cianuración instantánea de los productos de descomposición.

Palabras clave: Cinética, descomposición, argentífera, plomo, jarosita, cianuración, alcalino.

Introduction

The jarosite technology is mainly used in the zinc industry as a medium to eliminate unwanted impurities, such as iron, lead, copper, arsenic and cobalt [1, 2]. However, the silver values contained in the zinc-rich solutions of the hydrometallurgical circuits of this industry are incorporated in the structure of the precipitates of the jarosite-type compounds, which means loss from an economic point of view. It is common, for the zinc concentrates, to be attached to lead sulfide, which will give rise to the formation of argentian lead jarosite. This compound is placed in the waste mounds and it is attractive, not only for its silver contents, but also because it makes it possible to eliminate lead and arsenic, which are very toxic elements [3, 4]. In Mexico there are two mining metallurgical plants that use this kind of technology: Industrial Minera México in San Luis Potosí, and Grupo Peñoles in Torreón, Coahuila; in these plants, besides ammonium and sodium jarosite residuals, argentian lead jarosite residuals are also formed. This kind of compound is generated according to the following reactions [5]:



The argentian lead jarosite has been synthesized and characterized by different researchers [1, 5, 6]. Dutrizac and his collaborators have developed this subject in order to avoid the incorporation of silver into the structure of the jarosites during hydrometallurgical processes [2, 6], and Patiño and collaborators have developed this subject with the purpose of recovering the silver in the jarosite waste mounds [7, 8, 9, 10, 11].

Therefore, thorough studies have been carried out on the alkaline decomposition and cyanidation kinetics of the argentian jarosite, argentian natrojarosite, argentian potassium jarosite and argentian ammonium jarosite. The studies of Patiño and collaborators on lead jarosite have been carried out in CaO media, and there are few studies in NaOH media [12, 13]. In this work, the argentian lead jarosite was prepared by means of an innovative synthesis technique [14]. Decomposition and cyanidation in NaOH media were studied in a wide range of experimental conditions, such as $[\text{OH}^-]$ and $[\text{CN}^-]$ concentration and temperature, obtaining the reaction orders and activation energy.

Results and discussion

Decomposition of argentian lead jarosite in NaOH media

Stoichiometry

For the study of the reaction stoichiometry several samples of argentian lead jarosite were treated with NaOH at different times. Then, the sulfates in solution were analyzed and the remainders were characterized by XRD and EDS. The typical results of the evolution of sulfates in solution are shown in figure 4. Figure 5 shows the diffractograms of the remainders corresponding to figure 4. In this figure it can be observed that the alkaline decomposition of the argentian lead jarosite presents an induction period and a progressive conversion period. During the induction period no morphological or chemical changes are observed on the surface of the solid observed by SEM and EDS; the diffractograms for this period were identical to those of the original jarosite, and only traces of sulfate were found in the solution. The progressive conversion period is characterized by the increase of sulfate ion concentration in the solution and

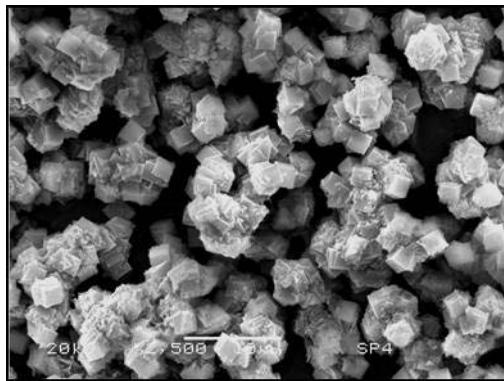


Figure 1. General image of the particle sizes of the argentian lead jarosite synthesized with the maximal dissolution technique at 94.5 °C-24h. SEM.

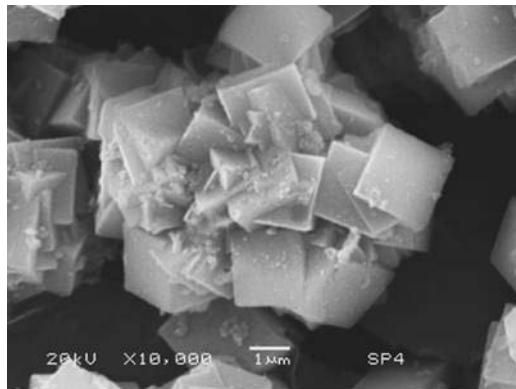
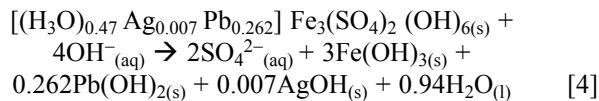


Figure 2. Detail of the crystal aggregates of argentian lead jarosite formed by rhombohedral microcrystals. SEM.

by the decrease of reflection intensities of the lattice planes of the argentian lead jarosite until disappearing; they do not evolve into crystal phases for long periods of residence once the total decomposition has occurred (Fig. 5).

The completely decomposed solids are amorphous, as observed in the decomposition of the sodium, potassium and ammonium jarosite-type compounds [8, 9, 11]. They are also similar to the completely decomposed solids of the argentian lead jarosite in $\text{Ca}(\text{OH})_2$ media [12]. However, the amorphous products of the argentojarosite decomposition do evolve into crystal phases of the silver ferrite type [7], which is an exception in the nature of the alkaline decomposition of this kind of compound.

According to the previously discussed points, the stoichiometry of the process, under the studied conditions, is expressed by a reaction of the following kind:



For the previously discussed reasons, the kinetics have been described with the data of the progressive conversion period. Due to the small size of the crystals, and since they are

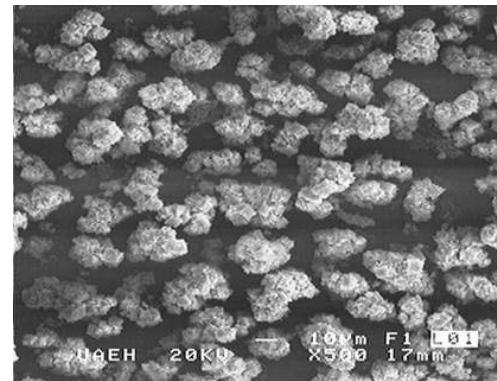


Figure 3. General image of the particle sizes of the argentian lead jarosite obtained from a second seeding at 94.5 °C-24h. SEM.

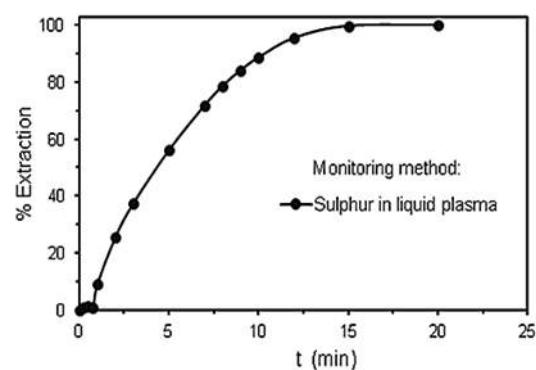


Figure 4. Decomposition curve of the argentian lead jarosite in NaOH media: pH 12 and 35 °C.

weakly soldered in the crystal aggregates, it is very difficult to observe, by SEM, devastated and polished sections of the solids formed in the progressive conversion period; thus, unlike similar compounds, the reaction front cannot be observed [8, 9, 11]. However, it was possible to obtain the microanalyses of the reacting and unreacting areas, indicating that the progressive conversion period takes place through a reaction front (Fig. 6). The experimental results of the progressive conversion period are consistent with the decreasing core and chemical control model, as observed in figure 7. The expression of the model is the following [16, 17, 18]:

$$1 - (1 - x)^{1/3} = k_{\text{exp}} \quad [5]$$

$$K_{\text{exp}} = v k q C_A^n / r_0 \quad [6]$$

Where x = reacted fraction; kq = chemical constant; C_A = reactant concentration; v = molar volume of the solid; r_0 = initial radius; n = reaction order.

Progressive conversion

In the decomposition process in NaOH media, the reaction order, in relation to the OH^- concentration, was 0.7 (fig. 8),

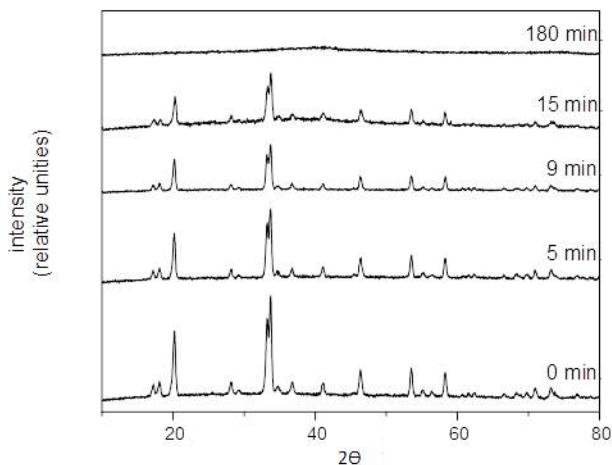


Figure 5. Diffractograms at different decomposition times of the argentian lead jarosite in NaOH media: pH 12 and 35 °C.

which is slightly higher than the decomposition in NaOH media of other jarosite-type compounds [7, 8, 9, 11]. This order shows the dependence of the reaction on OH^- concentration, and it is indicative of the chemical control, which is incompatible with the control by layer diffusion.

The temperature effect was studied at a constant concentration of 0.11M NaOH. Since the ionization constant of water varies considerably with temperature, the Arrhenius plot (Fig. 9) was obtained by using the $\ln k_{\text{exp}}/[\text{OH}^-]^{0.7}$ in order to eliminate the $[\text{OH}^-]$ effect on the temperature dependence. An activation energy of 101.85 KJmol⁻¹ was found, confirming the chemical control of the reaction. This activation energy is higher than that of other jarosite-type compounds [7, 8, 9, 11] decomposed in NaOH media, which indicates that the argentian lead jarosite is the one with the highest stability.

Cyanidation of argentian lead jarosite

The global cyanidation process of the argentian lead jarosite was studied in the range of 5-50 mN NaCN; this is the concentration range used in the cyanidation circuits. The cyanidation curve presents an induction period followed by a progressive conversion period, as observed with the decomposition in NaOH media (Fig. 10). In this period, the cyanidation rate was independent under the studied range of CN^- concentration, thus, the cyanidation reaction order was 0 (Fig. 11).

This effect is inconsistent with the control by complexation in the global cyanidation process, and it indicates that the cyanide ion diffusion through the decomposition gel is instant. Therefore, the global cyanidation process can be described as a process consisting of two serial stages: the initial stage of alkaline decomposition that controls the global process (equation 4), followed by a stage of instant complexation of the decomposition products.

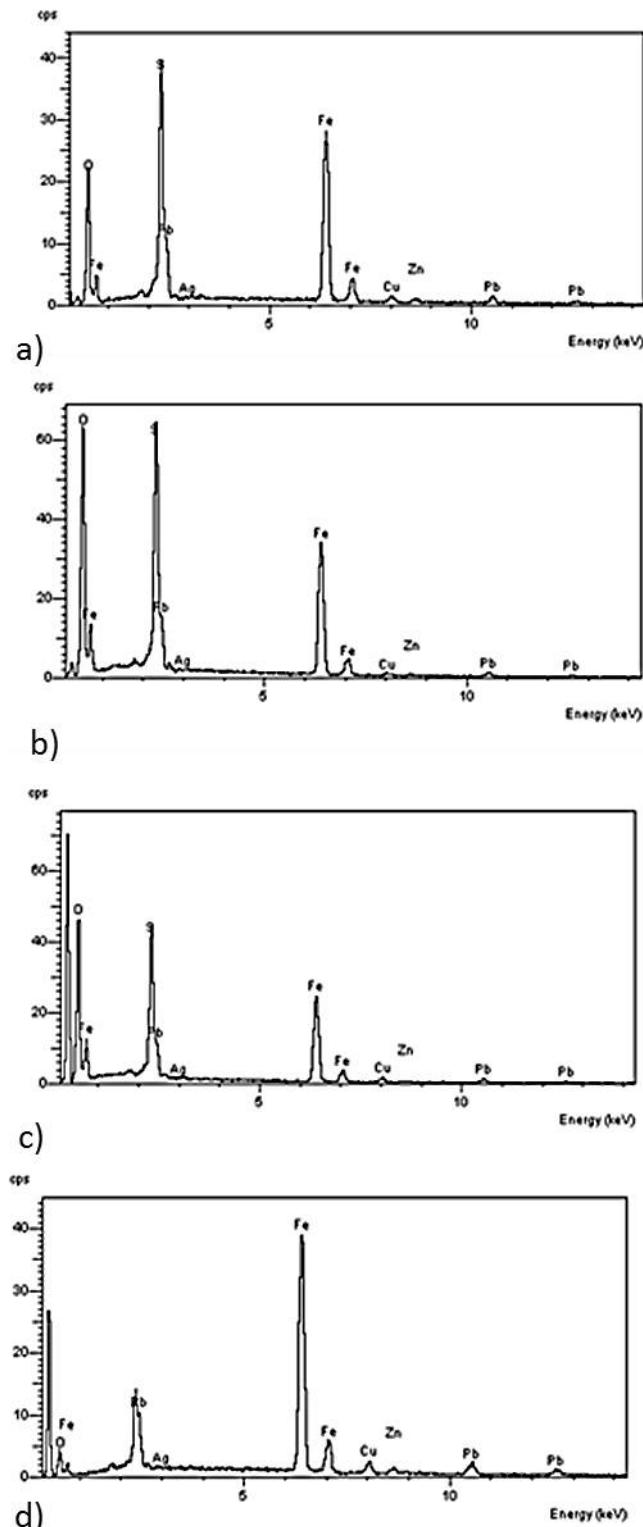
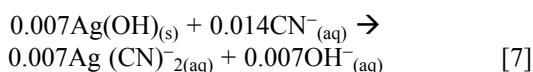


Figure 6. X-ray spectrum at different decomposition times of the argentian lead jarosite in NaOH media: pH 12 and 35 °C. a) Unreacting at 0 min. b) Partial reaction at 5 min. c) Partial reaction at 9 min. and d) Total reaction.

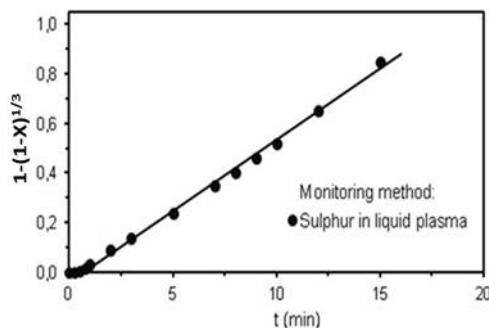


Figure 7. Representation of the decreasing core and chemical control model for the data in figure 4.

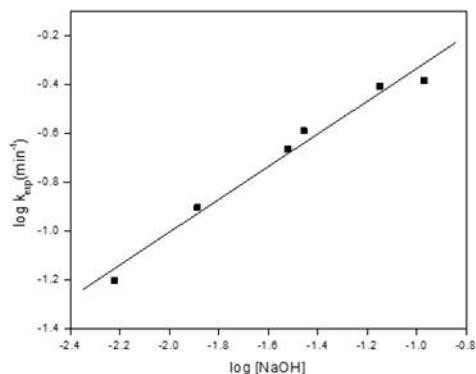


Figure 8. Dependence of k_{exp} vs. $[\text{OH}^-]$. Reaction order $n = 0.7$.

The temperature effect was studied at a constant concentration of 0.1M NaOH and 0.02M NaCN. Since $[\text{CN}^-]^0$ equals the unity, the Arrhenius plot (Fig. 12) was obtained by using the $\ln k_{\text{exp}}$. An activation energy of 109.54 KJmol $^{-1}$ was found, which is very close to the one obtained for the decomposition in NaOH media; therefore, the chemical control of the global cyanidation process is confirmed.

Conclusions

The alkaline decomposition curves of the argentian lead jarosite in NaOH media present an induction period followed by a progressive conversion period. The cyanidation in NaOH media presents only the progressive conversion period. The experimental data for this period are consistent with the decreasing core and chemical control model. We observed a dependence of $n = 0.7$ in relation to $[\text{OH}^-]$, and a dependence of $n = 0$ in relation to $[\text{CN}^-]$. The activation energy of the decomposition process in NaOH and NaCN media is of 101.85 and 109.54 KJmol $^{-1}$ respectively. These values are consistent with the chemical control of the process. The global cyanidation process can be described as a process consisting of two serial stages: the initial stage of alkaline decomposition followed by a stage of instant complexation of the decomposition products.

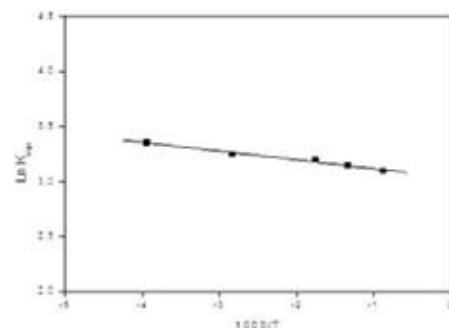


Figure 9. Dependence of k_{exp} vs. temperature. $E_a = 101.85 \text{ KJmol}^{-1}$.

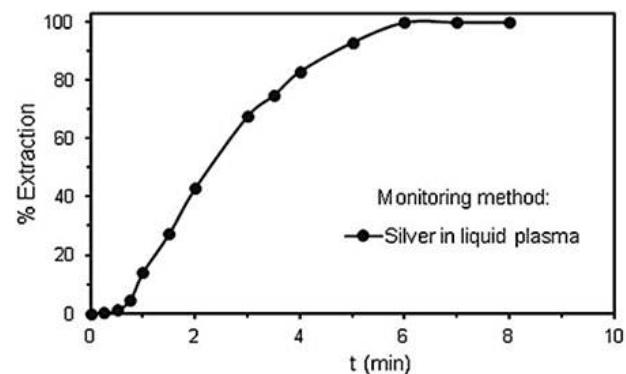


Figure 10. Cyanidation curve of the argentian lead jarosite in NaOH media, pH 12 and 35 °C.

Materials and experimental procedure

Materials

The kinetic study was carried out with the synthetic argentian lead jarosite. We used the method of maximal dilution synthesis, which was developed by Canales [14]. It is an innovative method which consists of dissolving 18 g of PbSO_4 in 1L of deionized water at 50 °C, with a mechanical stirring of 500 rpm for 10 hours. It was later filtered, obtaining a solution with the maximal dissolution of lead sulfate; 33.8 mg Ag_2SO_4 , 0.3 M $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and 0.01 M H_2SO_4 were hot-added. The process of this solution was carried out at 94.5°C for 24 hours. Two new syntheses were subsequently performed with the recycled product of the first and second syntheses in order to improve the morphology and size of the argentian lead jarosite particles. The results of characterization by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray microanalysis (EDS) prove that it is a simple phase product. The resulting chemical composition (0.13% Ag, 9.62% Pb, 34.39% Fe, 33.27% SO_4 and 22.59% $\text{H}_3\text{O} + \text{OH}$) corresponds to that of a solid solution of lead jarosite-hydronium jarosite-argentian jarosite, with the following formula:



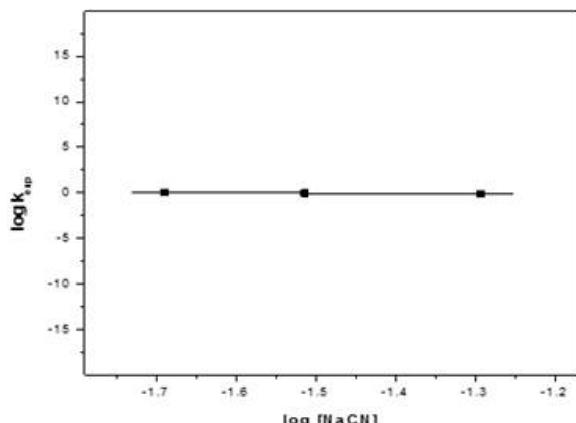


Figure 11. Dependence of k_{exp} vs. NaCN concentration. Reaction order $n = 0$.

This is very similar to the products obtained by Dutrizac [2], and Patiño [5], but without the superficial absorption of the sulfate ions, which has been observed in the products obtained by these cited works. Density measurement yields out a value of 3140 kg/m^3 .

A point rarely discussed in literature, but which is important in the kinetic study, is the matter of the morphology and particle size.

The synthesis of the argentian lead jarosite under the described conditions gives rise to the formation of aggregates in the shape of grape clusters, with particle sizes ranging from 8 to $12\mu\text{m}$ (Fig. 1). They are made of rhombohedral crystals with sizes ranging from 1 to $5\mu\text{m}$ (Fig. 2) in a relatively compact texture. The seed recycling procedure in two consecutive syntheses resulted in $20\text{-}30\mu\text{m}$ particle sizes tending to sphericity (Fig. 3). The particle family of the second seeding was used for the kinetic study (Fig. 3).

Experimental procedure

The decomposition of argentian lead jarosite in NaOH and NaCN media was carried out in a thermostated kettle with magnetic stirring. The solution pH was permanently measured and the experiments were designed so that the reagent concentration could be kept constant.

For the study of the decomposition in NaOH media, 0.15 g of argentian lead jarosite were used in an initial volume of 0.5 L. pH was kept constant by adding small amounts of NaOH solution until the experiment was over. The OH^- concentration was calculated by considering the constant of the ionic product of the water [15] and the pH of the alkaline solution according to the working temperatures we used. All of the experiments were carried out under high stirring conditions (500 r.p.m.) in order to avoid the liquid film diffusion effect. A series of alkaline reactivity tests of the argentian lead jarosite were previously carried out, and it was observed that the sulfate ions of this compound's lattice diffuse towards the solution. For this

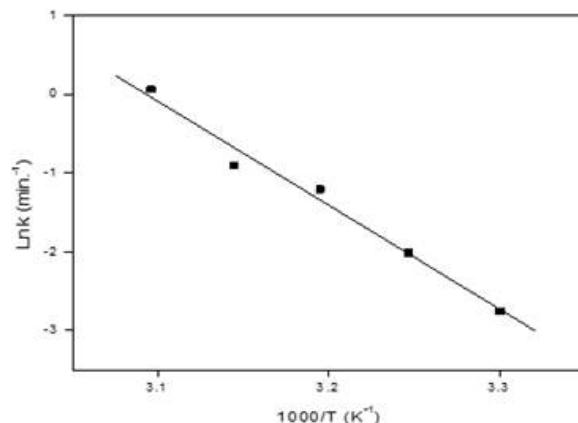


Figure 12. Dependence of k_{exp} vs. temperature. $E_a = 109.54 \text{ KJmol}^{-1}$.

reason, the follow-up of the alkaline decomposition kinetics was carried out by analysis of the sulfate ion in the liquid; 5ml samples were taken and analyzed by Inductively Coupled Plasma Spectrometry (ICP). A similar technique was applied for the study of the cyanidation in NaOH media; the reaction progress was determined by taking samples of the solution and analyzing them for silver by Atomic Absorption Spectrometry (AAS). The alterations caused by sampling and addition of reagents were corrected by mass balance. During experimentation, samples of solids were taken at different conversion levels. These solids were characterized by chemical analysis, XRD, SEM and EDS.

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