Alkaline Decomposition of Solid Solution of Ammonium-Sodium Jarosite with Arsenic

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Abstract: In this study, a solid solution of arsenical ammonium-sodium jarosite, with the approximate formula [(NH4)0.72 Na0.06(H2O)0.21]Fe3(2.52SO4)1.85 (AsO4)0.15 [(OH)4.41 (H2O)1.59], was synthesized. The precipitate particle main size was 38 μm, with spherical morphology. A decomposition reaction in alkaline media was carried out; this decomposition comprised three stages: an induction period, a progressive conversion and a stabilization period. The process was controlled by the chemical reaction, and the progressive conversion period was consistent with the shrinking core model. The dissolution reactions of the compound in NaOH media were characterized by an ash layer formed by solid residues made of Fe(OH)3 and adhered around an unreacted core through an adsorbed arsenate surrounding an unreacted core through an adsorbed arsenate surrounding an unreacted core. At the same time, OH− ions diffused from the solution into the reaction front until the core disappeared, indicating the end of the reaction.

Keywords: synthesis; characterization; alkaline decomposition; NH4-Na jarosite with arsenic

1. Introduction

Arsenic is classified as a metalloid, as it presents metallic and non-metallic properties, as well as a wide range of chemical reactivity [1]. The toxicity of this element depends mainly on the kind of bond—organic arsenic compounds are less toxic than inorganic arsenic compounds, while species with As (III) are essentially less toxic than As (V) compounds [2,3]. Arsenic is an impurity in metallurgical minerals and concentrates, and usually enters solution as AsO43− during feeding of hydrometallurgical processes [4].

Arsenic contamination of water is a problem in different countries [5]. The strictest regulations in Australia, the U.S. and Europe have set 10 μg/L as the highest acceptable level of contamination by arsenic in drinking water. Contaminated streams are often treated with both physicochemical and biological processes which are effective. However, the sediment formed as a byproduct of these technologies can create a waste problem [6].

Arsenic is not easy to remove, but it can be transformed into an insoluble and stable compound in the environment by combining with other elements, such as Fe [7]. Heavy elements, particularly arsenic, can be removed by applying jarosite technology. This type of compound, which may come from hydrometallurgical circuits and acid mine drainage, can be incorporated into jarosite-type compounds, reducing the contamination
of hydrologic streams by arsenic and other elements. Jarosites are minerals that belong in the alunite supergroup. Precipitation of these compounds, whose general formula is (MFe$_3$(SO$_4$)$_2$(OH)$_6$, where M = K$^+$, Na$^+$, NH$_4^+$, Ag$^+$, $\frac{1}{2}$Hg$^{2+}$, H$_3$O$^+$ or $\frac{1}{2}$Pb$^{2+}$, is used in the metallurgical industry for control of Fe, SO$_4^{2-}$, alkaline elements, and other impurities in solutions of processes [8].

Dutrizac and Jambor [9,10] conducted a study of the incorporation of arsenic in jarosites, in chloride and sulfate media. More recent studies [11,12] have confirmed that there is a relationship between iron and arsenate during the nucleation of solid materials, such as potassium jarosite with arsenic; this causes retention of arsenic during weathering of minerals with this metalloid. Reyes et al. [13] synthesized natrojarosite with arsenic and managed to incorporate 1% AsO$_4^{3-}$ inside its structure. They conducted a study on the alkaline reactivity in Ca(OH)$_2$ and NaOH media where the induction period and particle size were independent, finding it increased exponentially as temperature decreased. The decomposition of arsenical sodium jarosite is characterized by the formation of an iron hydroxide gel with adsorbed arsenate, the removal of sulfate and sodium ions from the lattice, and their diffusion into solution.

Research on the alkaline reactivity of argentian jarosite in Ca(OH)$_2$ and NaOH media has been conducted by studying the effects of temperature (293–333 K), particle size and OH$^-$ and CN$^-$ concentration. The stoichiometry of the reaction, dependence of the induction periods, activation energy and orders of reaction were determined, and the stability of these compounds was studied under different conditions [14–16].

The aim of this investigation was to study the kinetics of the alkaline decomposition in NaOH media of a solid solution of ammonium-sodium jarosite with arsenic to provide information on the stability, in extreme conditions of alkalinity and temperature, of this compound. The most used method to mitigate acid effluents is increase in pH by the addition of a source of alkalinity, such as caustic soda (NaOH). Understanding the dissolution reactions of phases commonly present in acid mine drainages (AMD), such as jarosite-type compounds, is very important for environmental assessment, since elements such as As(V) could return to the environment after the mitigation process with a chemical-neutralizing agent.

2. Materials and Methods

2.1. Synthesis and Characterization of NH$_4$-Na Jarosite with Arsenic

Based on studies reported by Dutrizac and Jambor [9] and Patiño and Reyes [17], the synthesis of a solid solution of ammonium-sodium jarosite with arsenic was undertaken. Synthesis conditions are shown in Table 1.

| Reagents and Parameters | Conditions         |
|--------------------------|--------------------|
| Na$_2$HAsO$_4$·7H$_2$O   | 0.03 mol/L         |
| (NH$_4$)$_2$SO$_4$       | 0.3 mol/L          |
| Fe$_2$ (SO$_4$)$_3$      | 0.25 mol/L         |
| pH                       | 1.2–1.8            |
| T                        | 367 K (94 °C)      |
| stirring                 | 500 min$^{-1}$     |
| T                        | 24 h               |

The substances used were of reagent-grade. On the heating plate with automatic temperature control, a liter of the synthesis solution was placed in a glass reactor with a coupled spiral condenser (Super-Nuova/Thermo Fisher Scientific, Waltham, MA, USA) and mechanical stirring with a 3-blade propeller (IKA-RW16 basic, IKA Werke GmbH & Co. KG, Staufen, Germany). The duration of the synthesis reaction was 24 h at 367 K (94 °C) and 500 min$^{-1}$ mechanical stirring. The obtained precipitate was vacuum-filtered with Whatman # 40 filter paper and washed with deionized hot water (338 K), removing
the excess iron and $\text{SO}_4^{2-}$. The precipitate was dried at 333 K (60 °C) for 5 h in a Felisa F-291 stove.

The precipitate was characterized by X-ray diffraction-XRD (Bruker D-800, Bruker, Billerica, MA, USA) using Cu Kα radiation (1.54056 Å), and scanning electron microscopy, SEM (JEOL JSM-670 equipped with an energy-dispersive X-ray detector, EDS, INCA, JEOL Ltd., Tokyo, Japan). The infrared spectrum was obtained with a PerkinElmer FT-IR System 2000 Fourier transform infrared spectrophotometer (FT-IR, PerkinElmer, Waltham, MA, USA) with a spectral resolution of 4 cm$^{-1}$ using the potassium bromide pellet technique (KBr). Atomic absorption spectroscopy, AAS (PerkinElmer Analyst 200), inductively coupled plasma optical emission spectrometry, ICP (PerkinElmer Optima-300XL), dichromatometry to determine Fe, and gravimetry to determine $\text{SO}_4^{2-}$ as BaSO$_4$ were conducted for elemental analysis. The N content was determined in a PerkinElmer 2400 Series II elemental analyzer (combustion 1233 K reduction 913 K) [18]. The thermogravimetric analysis of the precipitate was conducted by a TGA 851e Mettler-Toledo, with a heating of 10 K/min using pure argon with a flow of $667 \times 10^{-3}$ m$^3$/s. Particle size was measured using a series of Tyler sieves (USA standard testing sieve, ASTM-11 specifications) with mesh diameters: 150, 90, 75, 53, 44, 38 and 25 μm.

2.2. Decomposition Experiments in NaOH Media

These experiments were conducted in a 0.5 L Pyrex reactor set on a heating plate with magnetic stirring (500 min$^{-1}$) and automatic temperature control to keep the particles in suspension. The pH was constantly measured with a pH Orion 3 Star pH meter with a Thermo Ross Ultra Sure Flow pH electrode (Thermo Fisher Scientific, Waltham, MA, USA). In all the experiments, the pH was kept constant by adding controlled amounts of NaOH 1.0 mol/L. Initial volumes of 0.5 L, 0.2 g of jarosite were used in all the decomposition experiments. The effects of T, [OH$^-$], and $d_0$ were assessed by keeping two parameters constant and changing the other parameter for each experiment, as shown in Table 2. The decomposition experiments in NaOH media were performed under similar conditions to those reported by Reyes et al., Flores et al. and Patiño et al. [13,17,19].

| Parameter | [OH$^-$] Effect | T Effect | $d_0$ Effect |
|-----------|----------------|----------|--------------|
| T/K       | 303 K (30 °C)  | 293–363 K (20–70 °C) | 303 K (30 °C) |
| [OH$^{-1}$]/mol/L | 0.1–0.003 | 0.05 | 0.05 |
| $d_0$/μm | 38 | 38 | 150–25 |
| t/min    | 0–230 | 0–35 | 0–30 |

In other studies on the decomposition of jarosite compounds with and without arsenic, it was found that the reaction was characterized by the release of Na$^+$ and $\text{SO}_4^{2-}$ ions from the jarosite structure to the solution [13–17,19]. Therefore, samples of the solution were taken at different times ($\approx$5 mL) to monitor the progress of the reaction according to the conditions of each experiment. Sulfur was determined by ICP. In addition, it was possible to monitor the progress of the reaction by gravimetrically determining $\text{SO}_4^{2-}$ as barium sulfate [18]. Through mass balance, alterations in the reaction volume, due to sample taking and reagent addition, were corrected.

3. Results

Synthesis of Jarosite and Characterization

An elemental analysis of the obtained precipitates during synthesis was performed. Table 3 presents the chemical composition of the obtained ammonium-sodium jarosite with arsenic. By difference the H$_3$O$^+$ + OH$^-$ + H$_2$O content was inferred.
Table 3. Chemical composition of the obtained jarosite.

| Element/Specie | W (%) | Analysis Method |
|----------------|-------|-----------------|
| Fe             | 29.4  | Volumetry       |
| SO₄            | 38.9  | Gravimetry      |
| As/AsO₄        | 1.72/3.19 | ICP          |
| Na             | 0.240 | ICP             |
| N/NH₄          | 2.11/2.71 | Elemental Analysis |
| OH⁻ + H₂O⁺ + H₂O | 25.6  | Difference      |

Based on the formula MFe₃(SO₄)₂(OH)₆, with the elemental analysis results and considering the molar relationships of Na⁺ + NH₄⁺ + H₂O = 1, SO₄²⁻ + AsO₄³⁻ = 2, OH⁻ + H₂O = 6, and by considering that the charge difference between SO₄²⁻ and AsO₄³⁻ was compensated by the conversion of OH⁻ into H₂O [20,21], it was possible to establish an approximate formula for the obtained product:

\[
[(NH₄)_{0.72}Na_{0.06}(H₂O)_{0.21}]Fe_{2.52}[(SO₄)_{1.85}(AsO₄)_{0.15}][(OH)_{4.41}(H₂O)_{1.59}].
\]

The ammonium-sodium jarosite with arsenic, based on the conditions shown in Table 1, yielded a brownish yellow precipitate. SEM characterization (secondary electrons, SE) showed that the precipitate was made up of spheroidal aggregates of size ranging between 10 and 40 µm (Figure 1a). In the semi-detailed image of a particle of the synthesized ammonium-sodium jarosite with arsenic, a spherical tendency could be discerned (Figure 1b); the particle was made up of rhombohedral microcrystals with sizes ranging between 2 and 6 µm (Figure 1c).

Figure 1. (a) Image of the aggregates of synthetic ammonium-sodium jarosite with arsenic. (b) Detailed image of an aggregate with spherical tendency. (c) Semi-detailed image of rhombohedral microcrystals of ammonium-sodium jarosite with arsenic (Images obtained by SEM-SE).

The obtained ammonium-sodium jarosite with arsenic presented a similar morphology and microstructure to those reported for arsenical potassium jarosite and sodium jarosite with arsenic [13,19]. Assessment of the obtained X-ray diffraction spectrum was conducted using Match Version 3. (Crystal Impact, Dr. H. Putz and Dr. K. Brandenburg GbR, Kreuzherrenstr, Bonn, Germany), which contains the International Center for Diffraction Data-Power Diffraction Files (ICDD-PDF). The intensity of the peaks shown in Figure 2 suggested the presence of crystallographic planes typical of ammonium jarosite, albeit slightly shifted to the left due to the unit cell’s expansion caused by the incorporation of the arsenate ion (AsO₄³⁻) [22]. No other compounds were identified, as there were no additional intense peaks.
Figure 2. X-ray diffractogram of ammonium-sodium jarosite with arsenic.

For infrared spectroscopy analyses, the spectrum (400–4000 cm\(^{-1}\)) was obtained in transmission mode after the preparation of the KBr pellet (Figure 3). The intense absorption in the region between 2600 and 3800 cm\(^{-1}\) was attributed to the lengthening of the bond O–H (\(\nu_{\text{OH}}\)). Due to increase in the bond energy of hydrogen with the mineral structure, this band changes to lower frequencies for Pb-jarosite (3352 cm\(^{-1}\)), Pb-As-jarosite (3343 cm\(^{-1}\)), Na-jarosite (3365 cm\(^{-1}\)), and increases for K-jarosite (3385 cm\(^{-1}\)) [18]. The band observed at 625 cm\(^{-1}\) was attributed to the deformation of the bond H–O–H. The band shown at 1640 cm\(^{-1}\) was attributed to the \(\nu_4\) bond mode of SO\(_4^{2-}\). Next, three intense absorption bands were observed near 1195, 1075 and 987 cm\(^{-1}\), which were attributed (respectively) to the \(\nu_3\) (double) and \(\nu_1\) vibrations of the sulfates. The spectral band at 1640 cm\(^{-1}\) corresponded to the flexion movement of water molecules. The band at 1420 cm\(^{-1}\) belonged to the bond N–H. The band at 828 cm\(^{-1}\) established the presence of the functional group As–O. The signal at 503 cm\(^{-1}\) was attributed to the vibration of the octahedral coordination of FeO\(_6\).

Figure 3. Infrared spectrum of the obtained ammonium-sodium jarosite with arsenic.
The thermogravimetric analysis is shown in Figure 4; it indicated that the thermal decomposition of ammonium-sodium jarosite with arsenic occurred in six stages, with mass losses from room temperature up to 1073K (800 °C). The first stage started at 518 K (245 °C) with a 2.4% mass loss corresponding to the evaporation of excess moisture absorbed in the sample. Dehydroxylation occurred between 521K (248 °C) and 693K (420 °C). Ammonium evaporated between 633 K (360 °C) and 713 K (440 °C), with a mass loss of 5.3%. The loss of SO₄ and O occurred between 808 K (535 °C) and 963 (690 °C), with a total weight loss of 48.7%. In a temperature range between 853 K (580 °C) and 893 K (620 °C), there was a slight mass loss, which corresponded to AsO₄.

Dehydration 373–518 K (100–245 °C)

\[
[(\text{NH}_4)_{0.72}\text{Na}_{0.06}(\text{H}_3\text{O})_{0.21}\text{Fe}_{2.52}(\text{SO}_4)_{1.85}(\text{AsO}_4)_{0.15}]([\text{OH}]_{4.41}(\text{H}_2\text{O})_{1.59}) \rightarrow ([(\text{NH}_4)_{0.72}\text{Na}_{0.06}]\text{Fe}_{2.52}(\text{SO}_4)_{1.85}(\text{AsO}_4)_{0.15}\text{OH})_{4.20} + 2.01\text{H}_2\text{O} \tag{1}
\]

Dehydroxylation 518–633 K (245–360 °C) and ammonium loss 633–713 K (360–440 °C)

\[
[(\text{NH}_4)_{0.72}\text{Na}_{0.06}\text{Fe}_{2.52}(\text{SO}_4)_{1.85}(\text{AsO}_4)_{0.15}\text{OH})_{4.20}] \rightarrow \text{Na}_{0.06}\text{Fe}_{2.52}\text{O}_{1.74}(\text{SO}_4)_{1.85}(\text{AsO}_4)_{0.15} + 0.72\text{NH}_3 + 2.46\text{H}_2\text{O} \tag{2}
\]

Desulfation 808–963 K (535–690 °C)

\[
[\text{Na}_{0.06}\text{Fe}_{2.52}\text{O}_{1.74}(\text{SO}_4)_{1.85}(\text{AsO}_4)_{0.15}] \rightarrow 1.09\text{Fe}_2\text{O}_3 + 0.28\text{Fe}(\text{SO}_4)_3 + 1.01\text{SO}_2 + 0.15\text{AsO}_4 + 0.06\text{NaFe}(\text{SO}_4)_2 \tag{3}
\]

Previous studies have reported that, when subjected to high temperatures after undergoing alkaline decomposition, jarosite-type compounds transform into a crystal compound identified as hematite with an amorphous oxide [23–25]. NH₄–Na jarosite with arsenic was stable up to 518 K (245 °C), after which dehydroxylation followed by ammonium loss (633–713 K) and subsequent desulfation (808 K) took place. Arsenate remained stable in the structure up to 853 K (580 °C), when it started to volatilize. This was, in fact, very convenient, as the aim of this study was the incorporation and inertization of arsenic in environments with extreme temperatures.

Three syntheses, each with a yield of 30 g of ammonium-sodium jarosite with arsenic were performed. In addition, with a pycnometer, using water as the immersion liquid, the density was determined; the result was 2.75 g cm³. This density was very similar to that reported in other studies on jarosite-type compounds [16,19]. Particle size distribution results showed that the main sizes were retained in the meshes with diameters of between 25 and 38 µm, with a retained weight of 48.5% and 33.1%, respectively (Table 4). According to the sieving results, most of the precipitate obtained was very fine. This could be related...
to the total reaction time of the synthesis. It would be possible to increase the particle diameter with an increase in the reaction time, however, this would lead to redissolution of the small jarosite particles formed due to increase in pH during the reaction, and therefore the yield of the reaction would have turned out to be very low. For this reason, it was decided to enhance the yield rather than increasing the size of the particle in the precipitate.

**Table 4.** Particle size distribution conducted by wet sieving of the synthesized product (weight %).

| Mesh Number | Diameter µm | Weight t/g | Weight % |
|-------------|-------------|------------|----------|
| +100        | 150         | 1.98       | 7.28     |
| −100 + 170  | 90          | 0.43       | 1.58     |
| −170 + 200  | 75          | 0.07       | 0.26     |
| −200 + 270  | 53          | 0.28       | 1.03     |
| −270 + 325  | 44          | 0.72       | 2.65     |
| −325 + 400  | 38          | 13.20      | 48.50    |
| −400 + 500  | 25          | 9.00       | 33.08    |
| −500        | -           | 1.53       | 5.62     |
| **Total**   | **27.21**   | **100**    |          |

4. **Discussion**

4.1. **Controlling Stage and Kinetic Model**

The decomposition solution was analyzed at different time intervals to determine the controlling stage that describes the decomposition of ammonium-sodium jarosite with arsenic in NaOH media. A kinetic model was also determined, and the solid residues were characterized by SEM-EDS whereby an image of a partially decomposed particle was produced (Figure 5), showing a reaction front, unreacted core, and an ash layer of solid byproducts (Figure 5a). EDS analyses showed that in the core Na, S, Fe, O and As were present, meaning that these had remained unreacted; Fe, O and As could be identified in the ash layer (Figure 5c). Figure 5d (X-ray mapping results) showed that Fe and O were present throughout particles, while S could only be seen in the core, indicating that they had diffused into the solution. Although NH$_4$ and Na were not detected in the mapping analyses due to their low concentration, the described behavior indicated that these species had also diffused into the solution. According to the results of the SEM-EDS analysis of partially decomposed particles, in this process arsenic was adsorbed as AsO$_4^{3-}$ by the solid residues made of Fe(OH)$_3$. The As adsorbed in the iron hydroxide was not released into the solution at times after the total decomposition of ammonium-sodium jarosite with As in alkaline media. This would reduce the bioavailability of arsenic in natural environments with alkaline pH, such as seawater and underground water.

In the curve shown in Figure 6, an induction period followed by a progressive conversion period and a stabilization zone can be observed. In the induction period, only traces of SO$_4^{2-}$ and Na$^+$ ions were found in the solution and the color and morphology of the solids remained unchanged. In this stage, difficulty in the diffusion of OH$^-$ ions into the surface of the particles of ammonium-sodium jarosite with arsenic and the formation of active sites until the establishing of a reaction front was observed. The end of the induction period was indicated by a color shift in the particles, going from a brownish yellow to orange; at the same time, concentrations of SO$_4^{2-}$ and Na$^+$ increased progressively (progressive conversion period) until reaching a stabilization zone, which marked the end of the decomposition process.
had also diffused into the solution. According to the results of the SEM-EDS analysis of partially decomposed particles, in this process arsenic was adsorbed as AsO$_4^{3-}$ by the solid residues made of Fe(OH)$_3$. The As adsorbed in the iron hydroxide was not released into the solution at times after the total decomposition of ammonium-sodium jarosite with As in alkaline media. This would reduce the bioavailability of arsenic in natural environments with alkaline pH, such as seawater and underground water.

**Figure 5.** (a) SEM-BSE image of a partially decomposed particle of ammonium-sodium jarosite with arsenic in NaOH media; pH = 12.85, 303 K (30 °C), $d_0 = 38 \mu m$, RPM = 500 min$^{-1}$, 8 min of reaction, (b) EDS analysis corresponding to the core, and (c) EDS analysis corresponding to the ash layer in Figure 5a. (d) Energy dispersive X-ray mapping of the elements in greater proportion according to the EDS spectrums. Results show that a shrinking core kinetic model satisfactorily describes the decomposition process in alkaline medium of the ammonium-sodium jarosite with arsenic studied.

**Figure 6.** Decomposition curve of ammonium-sodium jarosite with arsenic in NaOH media (pH = 12.85, 303 K (30 °C), $d_0 = 38 \mu m$, RPM = 500 min$^{-1}$).

Figure 7 shows XRD diffractograms at different reaction times and after total decomposition, corresponding to the data in Figure 6. Solid residues were identified as amorphous Fe(OH)$_3$, since they did not generate any crystal phases under the decomposition conditions studied for this paper.
The kinetic equation where the controlling stage that describes the process corresponding to the chemical reaction, is:

\[ f_1 = 1 - (1 - X)^{1/3} = k_{\text{exp}} t \] (4)

The kinetic equation that describes the diffusion through the ash layer as the stage controlling the process is:

\[ f_2 = 1 - (1 - X)^{2/3} + 2(1 - X) = k_{\text{exp}} t \] (5)

where \( X \) is a dimensionless number. Physically, it is the amount of decomposed ammonium-sodium jarosite with arsenic that has reacted; \( t \) is time and \( k_{\text{exp}} \) is the experimental rate constant [26,27].

For ammonium-sodium jarosite with arsenic, the assessment using Equation (4), which is more consistent with the linear requirement, corresponds to chemical control (Figure 8). From Figure 8, the slope of the straight lines represents the \( k_{\text{exp}} \) value and their intersection with the axis time represents the induction time (\( \theta \)). Therefore, the model that best describes the alkaline decomposition process of ammonium-sodium jarosite with arsenic after the induction period is the shrinking core model with chemical control. The \( k_{\text{exp}} \) for a chemical control is defined as:

\[ k_{\text{exp}} = \frac{2V_m k_q C_A^n}{d_0} \] (6)

where \( V_m \) is the molar volume, \( k_q \) is the chemical rate constant of the reaction, \( C_A \) is the reactant concentration ([OH \(^-\)]), \( n \) is the order of reaction, and \( d_0 \) is the initial particle diameter. The molar volume was obtained by means of the molecular weight of the compound (461.29 g/mol) and the calculated density (2.75 g/cm\(^3\)), resulting in \( V_m = 167.74 \times 10^{-6} \text{ m}^3/\text{mol} \).
where $X$ is a dimensionless number. Physically, it is the amount of decomposed ammonium-sodium jarosite with arsenic that has reacted; $d_0$ is the initial particle diameter. The molar volume was obtained by means of the molecular weight of the compound (461.29 g/mol) and the calculated density (2.75 g/cm$^3$), resulting in $V_m = 167.74 \times 10^{-6} \text{ cm}^3$. The dissolution reaction was strongly dependent on temperature and [OH$^-$]. For the particle size effect, the induction time was almost the same. For $k_{exp}$ the opposite happened—when temperature and [OH$^-$] increased, the value of the constant also drastically increased.

4.4. Induction Period

In NaOH media, the induction period ($\theta$) increased as [OH$^-$] diminished and tended towards zero at high concentrations of [OH$^-$]. When representing the logarithm of $1/\theta$ against the logarithm of [OH$^-$], an order of reaction $n = 1.22$ was obtained. Figure 9a shows the dependence of the induction period with [OH$^-$]. The Arrhenius equation determines the dependence of $k_q$ with temperature (Equation (8)).

$$k_q = k_0 e^{(-E_a/R)} \quad (8)$$

![Figure 8](image_url)
Table 5. Decomposition of ammonium-sodium jarosite with arsenic in NaOH media. Conversion period: $E_a = 51.6 \text{ kJ/mol}$ and $n = 0.94$. Induction period: $E_a = 65.0 \text{ kJ/mol}$ and $n = 1.22$.

| pH   | [NaOH] mol/L | [OH$^-$] mol/L | T K  | $d_0$ µm | $\theta$ min | $k_{exp}$ min$^{-1}$ | $\text{tr}^a$ min |
|------|--------------|----------------|------|----------|--------------|--------------------|------------------|
| 11.46| 0.003        | 0.0042         | 303  | 38       | 40.16        | 0.0045             | 240              |
| 11.61| 0.005        | 0.0059         | 303  | 38       | 23.18        | 0.0057             | 210              |
| 11.79| 0.007        | 0.0089         | 303  | 38       | 16.00        | 0.0087             | 190              |
| 12.05| 0.010        | 0.01636        | 303  | 38       | 9.34         | 0.0138             | 90               |
| 12.39| 0.030        | 0.0358         | 303  | 38       | 2.41         | 0.0362             | 35               |
| 12.55| 0.050        | 0.0517         | 303  | 38       | 1.60         | 0.0544             | 25               |
| 12.69| 0.070        | 0.0714         | 303  | 38       | 1.19         | 0.0627             | 22               |
| 12.85| 0.100        | 0.1032         | 303  | 38       | 0.91         | 0.0755             | 20               |
| 13.26| 0.05        | 0.1250         | 293  | 38       | 3.65         | 0.0300             | 50               |
| 13.06| 0.05        | 0.1161         | 298  | 38       | 2.45         | 0.0414             | 40               |
| 12.86| 0.05        | 0.1056         | 303  | 38       | 1.86         | 0.0608             | 30               |
| 12.75| 0.05        | 0.1161         | 308  | 38       | 1.08         | 0.0787             | 25               |
| 12.65| 0.05        | 0.1282         | 313  | 38       | 0.75         | 0.0971             | 20               |
| 12.27| 0.05        | 0.0732         | 318  | 38       | 0.49         | 0.0998             | 18               |
| 12.16| 0.05        | 0.0767         | 323  | 38       | 0.34         | 0.1484             | 16               |
| 11.97| 0.05        | 0.0657         | 328  | 38       | 0.20         | 0.153              | 14               |
| 11.80| 0.05        | 0.0583         | 333  | 38       | 0.16         | 0.1805             | 12               |
| 11.65| 0.05        | 0.0535         | 338  | 38       | 0.12         | 0.2581             | 10               |
| 11.53| 0.05        | 0.0519         | 342  | 38       | 0.08         | 0.3189             | 8                |
| 12.85| 0.05        | 0.1032         | 303  | 90       | 2.11         | 0.0328             | 30               |
| 12.87| 0.05        | 0.1081         | 303  | 53       | 1.82         | 0.0496             | 30               |
| 12.86| 0.05        | 0.1056         | 303  | 45       | 2.05         | 0.0566             | 30               |
| 12.85| 0.05        | 0.1032         | 303  | 38       | 1.87         | 0.0638             | 30               |
| 12.84| 0.05        | 0.1009         | 303  | 25       | 1.83         | 0.0867             | 30               |

*a Total reaction time of the experiment.

Figure 9. (a) Order of reaction of the ammonium-sodium jarosite with arsenic in NaOH media. $1/\theta = [\text{OH}^-]^{1.22}$. (b) Dependence of induction time ($\theta$) on temperature, $E_a = 65.0 \text{ kJ/mol}$ in NaOH media.
4.5. Progressive Conversion Period

Figure 10 illustrates the dependence of $k_{exp}$ on the initial particle diameter $d_0$. The particle diameter was inversely proportional to the experimental constant ($k_{exp} \propto 1/d_0$). The model that best describes the alkaline decomposition process of ammonium-sodium jarosite with arsenic after the progressive conversion period is the shrinking core model with chemical control.

![Figure 10](image_url)

Figure 10. Dependence of $k_{exp}$ on particle size, $k_{exp} \propto 1/d_0$.

The order of reaction obtained with respect to the NaOH concentration was $n = 0.94$, for $[\text{OH}^-] \geq 3.00 \times 10^{-3}$ mol/L (Figure 11a). The reaction rate had a strong dependence on NaOH concentration under these conditions. With the $k_{exp}$ values from each of the experiments on the temperature effect, the Arrhenius plot (Figure 11b) for the progressive conversion period was obtained. The value of the obtained slope was $-6.2033$ in NaOH media. These values correspond to $-E_a/R$, and consequently the value of the activation energy was $E_a = 51.6$ kJ/mol. This value confirms that the decomposition process in NaOH media of the NH$_4$-Na jarosite with arsenic was controlled by the chemical reaction. All the kinetic parameters obtained for both media are summarized in Table 6.

![Figure 11](image_url)

Figure 11. (a) Dependence of $k_{exp}$ on OH$^-$ concentration for the decomposition of ammonium-sodium jarosite with arsenic in NaOH media. (b) Dependence of $k_{exp}$ on temperature, $E_a = 51.6$ kJ/mol in NaOH media.
Table 6. Kinetic parameters calculated for the decomposition of ammonium-sodium jarosite with arsenic in NaOH media.

| Kinetic Parameter | Induction | Progressive Conversion |
|-------------------|-----------|------------------------|
| $E_a$/kJ/mol       | 65.0      | 51.6                   |
| $n$                | 1.22      | 0.94                   |
| $k_0$              | $9.77 \times 10^{10}$ | $3.44 \times 10^6$ |

The energy dependence calculated for the induction period was considerably higher than the dependence of the progressive conversion period (see Table 6). The energy consumption was much higher due to the difficulty in chemical adsorption and in the subsequent establishment of a reaction front of OH$^-\,$ ions on the superficial cationic centers, which were very stable. The incorporation of arsenic in the structure of the ammonium-sodium jarosite, reduced the efficiency of the OH$^-\,$ attack on the particle surface. This may have been due to electrostatic repulsion towards the hydroxyls created for the arsenate bonds in the surface at elevated pH; furthermore, increase in the number of Fe-AsO$_4^{3-}\,$ bonds inhibits the dependence on [OH$^-\,$] in these systems [29]. The arsenic adsorbed in iron hydroxide is not released into solution, with alkaline pH reducing its bioavailability in natural environments, such as seawater and underground waters [17].

The kinetic expression for the induction period for de jarosite decomposition is:

$$\frac{1}{\theta} = \frac{r_0}{V_m} \times 9.7684 \times 10^{10} \times e^{-65,030/RT} [OH^-]^{1.22}$$

For the progressive conversion period the kinetic expression for NH$_4$-Na jarosite decomposition in NaOH media is:

$$1 - (1 - X)^{1/3} = 3.4395 \times 10^6 \times e^{-51,580/RT} [OH^-]^{0.94} t$$

5. Implications

Results of the elemental analysis of ammonium-sodium jarosite with arsenic showed an AsO$_4^{3-}\,$ incorporation of 3.19 W%, which was three times more than the sodium jarosite synthesized by Reyes et al. [13] and Patiño et al. [17] (1.0% WAsO$_4^{3-}\,$), and lower compared to the jarosite with arsenic synthesized by Patiño et al. [30] (3.8 W%). The obtained precipitates were of a brownish-yellow color, with a main size of 38 µm (48 W% retained) and a rhombohedral morphology.

According to the ICP results shown for the monitoring of each of the decomposition reactions, arsenic was not found in liquids, and was retained in the residual solid, which was made of iron hydroxide, according to the SEM-EDS analysis results of partially decomposed particles. This is very convenient, because after the decomposition of ammonium-sodium jarosite with arsenic in NaOH media, the arsenic appeared to be adsorbed in iron hydroxide and was not released to the solutions, which would reduce the bioavailability in natural environments of the studied media.

The reaction front, an ash layer of iron hydroxide with adsorbed arsenate, and an unreacted core of jarosite with arsenic, were the main characteristics of the progressive conversion period. The experimental data were consistent with chemical control in the shrinking core model. The decomposition of ammonium-sodium jarosite with arsenic in NaOH media had an order of reaction of $n = 0.94$ for $[OH^-] > 3 \times 10^{-3}$ mol/L, which showed that, after formation of the reaction front, the consumption of OH$^-\,$ ions decreased considerably. Additionally, low concentrations of OH$^-\,$ slowed down the start of the decomposition reaction. For the induction period, the order of reaction was $n = 1.22$, which indicated that there was higher consumption of OH$^-\,$ ions to support the reaction at the beginning of the decomposition process. The arsenate bonds in the structure of ammonium-sodium jarosite with arsenic generated an electrostatic repulsion towards the hydroxyls.
under highly alkaline conditions, which limited the OH\(^-\) attack on the particle surface; in addition, the increase in AsO\(_4^{3-}\) bonds inhibited the dependence on [OH\(^-\)].

The activation energy of the reaction in NaOH media for the progressive conversion period was 51.6 kJ/mol, and 65.0 kJ/mol for the induction period. To start the decomposition process, high concentrations of OH\(^-\) and temperature were needed. If these variables have low values, the start of the reaction becomes kinetically slow, with long induction times. Furthermore, arsenic was retained in the residual solids, even at times after the total decomposition of this jarosite.

Finally, in a comparison with other synthesized jarosites with arsenic, the order of reaction of ammonium-sodium jarosite with arsenic was 0.94, the dependence on OH\(^-\) being slightly higher than of the Na jarosite with arsenic synthesized by Reyes et al. [13] \((n = 0.70)\), and considerably below that of the potassium jarosite with arsenic synthesized by Patiño et al. [30] \((n = 1.86)\). The apparent activation energy of ammonium-sodium jarosite with arsenic was \(E_a = 51.6 \text{ kJ/mol}\), which was lower than the jarosite with arsenic synthesized by Reyes et al. [13], \(E_a = 57.1 \text{ kJ/mol}\) and the jarosite studied by Patiño et al. [30], \(E_a = 60.3 \text{ kJ/mol}\).

6. Conclusions

The synthesis of ammonium-sodium jarosite with arsenic was achieved, incorporating 3.19 W% of AsO\(_4\). The precipitate was of a brownish yellow color, with particle sizes ranging from 10 to 50 \(\mu\)m and the morphology of the aggregates was of a spherical type. Through chemical analysis, the approximate formula of the synthesized compound was determined to be:

\[
[(\text{NH}_4)_{0.72} \text{Na}_{0.06} (\text{H}_3\text{O})_{0.21}]\text{Fe}_{2.52}[(\text{SO}_4)_{1.85}(\text{AsO}_4)_{0.15}]\{(\text{OH})_{4.41}(\text{H}_2\text{O})_{1.59}\}
\]

Thermogravimetric study indicated that the ammonium-sodium jarosite with arsenic was stable up to 518 K (245 °C), after which dehydroxylation took place, followed by sulfate and ammonium loss. Arsenate was stable in the structure up to 883 K (610 °C), when it began to volatilize.

The decomposition curves of ammonium-sodium jarosite with arsenic showed an induction period and then a progressive conversion period. When temperature and OH\(^-\) concentration increased, the induction period decreased considerably. The progressive conversion period appeared after the formation of a reaction front; an ash layer of iron hydroxide with adsorbed arsenate formed around an unreacted core of ammonium-sodium jarosite with arsenic. The experimental data are consistent with the shrinking core kinetic model with chemical control. When the temperature and OH\(^-\) concentration increased, the induction period decreased exponentially and was independent of particle size under the conditions studied.

The induction period depended on high concentrations of the reaction media and high activation energy, indicating that, for the decomposition reaction to start, high [OH\(^-\)] and T conditions were necessary; conversely, if the value of these variables was low, the start of the reaction became kinetically slow (long induction times).

Finally, it is possible to consider the ammonium-sodium jarosite with arsenic compound as an alternative in the removal of arsenic from water, since, even after decomposition, the arsenic is retained in the residual solid.

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