



Kinetic modeling and experimental design of the sodium arsenojarsite decomposition in alkaline media: Implications



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ABSTRACT

The alkaline decomposition of a synthetic sodium arsenojarsite sample with formula $[\text{Na}_{0.87}(\text{H}_3\text{O})_{0.13}]\text{Fe}_{2.50}[(\text{SO}_4)_{1.95}(\text{AsO}_4)_{0.05}][(\text{OH})_{4.45}(\text{H}_2\text{O})_{1.55}]$ was studied in NaOH and $\text{Ca}(\text{OH})_2$ media. The experimental data on the progressive conversion period are consistent with the spherical particle model with decreasing core and chemical control. Partially decomposed particles observed by SEM confirm the presence of a non-reacting arsenojarsite core, a reaction front and an amorphous ash halo consisting of $\text{Fe}(\text{OH})_3$ with adsorbed AsO_4 , which coincide with the mentioned model. An experimental design was also developed to determine the effects of the variables and their interactions that are directly involved in the decomposition reaction. It was found that T , $[\text{OH}^-]$, and $[\text{OH}^-] \cdot T$ interactions are the factors with the greatest influence on the reaction. With the data obtained from the chemical kinetics and experimental design, we proposed a series of equations that satisfactorily describe the decomposition process in function of conversion and time.

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1. Introduction

Jarosite-type ores belong to the supergroup alunite, whose general formula is: $\text{MY}_3(\text{ZO}_4)_2(\text{OH})_6$, where $\text{M}=\text{Na}^+$, K^+ , Ag^+ , Rb^+ , H_3O^+ , Tl^+ , NH_4^+ , Hg^{2+} , Pb^{2+} ; and $\text{Y}=\text{Fe}^{3+}$, Al^{3+} , Cr^{3+} , Cu^{2+} , Zn^{2+} ; and $\text{Z}=\text{S}(\text{VI})$, $\text{As}(\text{V})$ or $\text{P}(\text{V})$. The supergroup alunite consists of three groups of ores (alunite, beudantite and crandallite) that in combination can make more than 40 different compounds (Jambor, 1999). The jarosite-type compounds where site Y is occupied by Fe^{3+} and site Z is occupied by $\text{S}(\text{VI})$, are of mineralogical interest, and especially of metallurgical interest. Although nine kinds of jarosite can be synthesized, only six of these compounds can be found in nature as ores; the most common are the sodium, potassium and hydronium jarosites (Dutrizac and Kaiman, 1975, 1976). Substitution of hydronium ions H_3O^+ for potassium or sodium in M-site showed that most of the natural jarosites were solid solutions of hydronium jarosite. Furthermore, other substitutions have been reported in the trivalent Y-site in synthetic jarosites [Al(III), In(III), Ga(III) and Cr(III)], as well as a complete substitution of the SO_4^{2-} in Z-site for SeO_4^{2-} and CrO_4^{2-} sites (Brophy and Sheridan, 1965; Dutrizac and Kaiman, 1976). From a geological point of view, their origin is related to alteration processes of sulfides and hosting rocks, both supergene and hydrothermal (Desborough et al., 2010). The formation processes of jarosite-type compounds with a human origin range from the deliberate precipitation

in hydrometallurgical processes, mainly in the zinc as a medium to control impurities such as Fe, S, As, Sb, P, Cu, Mn, Ni and Pb (Arregui et al., 1979), to those produced as residues in environments polluted by acid rock drainage (ARD) or acid mine drainage (AMD).

It has been previously reported that the jarosite-type compounds can incorporate elements of environmental importance into their structure, such as Pb^{2+} , As^{5+} , Cr^{3+} , Cd^{2+} , Hg^{2+} , F^- (Dutrizac, 1991; Dutrizac and Chen, 2005; Dutrizac and Jambor, 1987; Dutrizac et al., 1980, 1987, 1996; Gunneriusson et al., 2009). For instance, As^{5+} is widely precipitated in jarosite-type compounds (natural and synthetic), and the way it incorporates can influence its mobility and bioavailability in natural or controlled environments. The As incorporated in the structure might influence the solubility of the jarosite, stabilizing it in a wide range of conditions that are tolerated by pure jarosites. For this reason it is important to know the behavior of this kind of compounds under different environmental conditions, both for the residues produced by the hydrometallurgical industries and for the compounds that are naturally produced, because arsenic or other toxic species contained in these compounds may be released in a bioavailable form into the ecosystems after their dissolution or decomposition. Several studies have been carried out on the decomposition of jarosite-type compounds, whether for industrial interests, such as the recovery of metallic values as Ag and Zn (Patiño et al., 1994, 1998, 2003; Roca et al., 1993, 2006; Salinas et al., 2001), or to know the chemical composition, thermodynamical properties or the way in which they are solubilized (Das et al., 1995; Drouet and Navrotsky, 2003; Drouet et al., 2004; Frost et al., 2005; Majzlan et

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al., 2004, 2010; Smith et al., 2006b; Welch et al., 2008). However, very few studies are related to the behavior and stability of toxic species in the structure of these compounds (Baron and Palmer, 1996; Patiño et al., 2011; Savage et al., 2005; Smith et al., 2006a).

Therefore, the aim of this study is to present the kinetic study of the reactivity of jarosite-type compounds with arsenic in NaOH and Ca(OH)₂ in order to provide information on the stability of this compound in alkaline media, because, if the stages in which a reaction occurs are known, the conditions to inhibit or augment it will be available. The study provides the kinetics and the way in which the decomposition reaction occurs (nature, rate, dependence of the reaction on variables such as medium concentration, temperature and particle size). A complete statistical analysis by a factorial experimental design was also performed in order to examine the effects of the variables and their interactions that are involved in the decomposition reaction. Along with the chemical kinetics and the design of experiments, we determined a series of mathematical models that permit to obtain a good approximation on the behavior that jarosite-type compounds present with arsenic in media with an alkaline pH.

2. Experimental

2.1. Reagents and solvents

Iron(III) sulfate *n*-hydrate, anhydrous sodium sulfate, sodium arsenate dibasic heptahydrate, sulfuric acid (97.9%), hydrochloric acid (37.3%), sodium hydroxide and calcium hydroxide were used, all in ACS grade. For the quantitative analysis and decomposition experiments, standards (1000 mg dm⁻³) of Na, S, Fe and As were used. Reagents were purchased from J.T. Baker, and standards were purchased from PerkinElmer Pure. All of the solutions mentioned in this work were prepared with high-quality deionized water (18.0 MΩ cm).

2.2. Synthesis and characterization of sodium arsenojarosite

A sample of sodium arsenojarosite was synthesized with a similar method to that described by Dutrizac et al. (1987). A liter of solution containing 0.3 mol dm⁻³ Fe₂(SO₄)₃·nH₂O, 0.01 mol dm⁻³ H₂SO₄, 0.2 mol dm⁻³ Na₂SO₄ and 0.027 mol dm⁻³ Na₂HAsO₄·7H₂O, was prepared. Mass of the reagents was measured in an OHAUS-Analytical plus balance (±0.1 mg), and volume was measured in a Pyrex volumetric flask (±0.0003 L). The solution was placed in a glass reactor with a spiral condenser coupled on a heating plaque, with automatic temperature control (Super-Nuova/Barnstead-Thermoline) and three-bladed mechanical stirring. The solution was kept at a constant temperature of 94.5 °C (367.5 K) and a stirring rate of 500 min⁻¹ for 24 h. The obtained precipitate was filtered and repeatedly washed with hot deionized water (≈60 °C, 333 K) to eliminate Fe excess; it was dried in a stove at 65 °C (338 K) for 3 h.

The obtained sample was characterized by X-ray Diffraction XRD (Siemens D-500), Scanning Electron Microscopy SEM (JEOL JSM-5900LV) equipped with Energy-dispersive X-ray spectroscopy EDS (Oxford). The quantitative analysis was carried out by Inductively Coupled Plasma Spectroscopy ICP (PerkinElmer Optima-3000XL) to determine Na, Fe, S and As. In addition, the obtained solid was fractionated by particle size (wet sieving) through a series of Tyler sieves (USA Standard Testing Sieve, ASTM-11 specifications) with the following mesh number: 120 ($d_0 \geq 125 \mu\text{m}$), 170 ($125 < d_0 \geq 90 \mu\text{m}$), 200 ($90 < d_0 \geq 75 \mu\text{m}$), 270 ($75 < d_0 \geq 53 \mu\text{m}$), 325 ($53 < d_0 \geq 44 \mu\text{m}$), 400 ($44 < d_0 \geq 38$), and 500 ($38 < d_0 \geq 25 \mu\text{m}$).

2.3. Decomposition in alkaline media: experiments

All the alkaline decomposition experiments were carried out in a 1.0 L glass reactor on a heating plaque with automatic temperature control and magnetic stirring. For the decomposition in NaOH and

Ca(OH)₂ media, 0.2 ± 0.0001 g of sodium arsenojarosite was used in an initial volume of alkali solution of 0.5 ± 0.0002 L, with an initial particle diameter of 38–44 μm and a stirring rate of 750 min⁻¹. In both media, the pH was kept constant by adding small amounts of a concentrated solution of NaOH or Ca(OH)₂ accordingly. The effects of OH⁻ concentration, temperature and particle size were studied by varying one parameter and keeping the other two parameters constant.

The pH of the solution in each experiment was constantly measured in the bulk of the solution with an Orion 3 Star pH meter equipped with a Thermo Ross Ultra Sure Flow pH electrode (precision ±0.01, pH range 0 to 14) and an Automatic Temperature Compensation probe (ATC, temperature accuracy ±0.5 °C). In order to obtain precise measurements, the electrode calibration was performed with three standards, 4.00 (potassium biphthalate solution), 7.00 (NaH₂PO₄–KH₂PO₄ solution) and 10.01 (H₃BO₃–KCl–NaOH solution) at 25 °C; the slope in all of the cases was 96.0 ± 5.0%. The used pH meter automatically adjusts the calibration and pH readings to the measured temperature. Interferences due to sodium ions can be considered negligible when measuring at pH values of less than 12, because the pH membrane of the electrode used is composed of special low sodium glass. For measures greater than 12, it is necessary to add a correction value to the observed pH reading; since [Na⁺] in the experiments was never greater than 0.1 mol dm⁻³, this correction was ≥0.01 in the temperature range of 20–60 °C (293–333 K) for all the cases (Thermo Scientific Orion ROSS, electrode user guide). Equipment and buffers were by Thermo Scientific.

In previous works on the decomposition of jarosite-type compounds without arsenic, it has been reported that the reaction is characterized by the release of ions occupied by sites *M* and *Z* of the structure and their quick diffusion towards the solution (Patiño et al., 1994, 1998, 2003, 2010; Roca et al., 1993, 2006; Salinas et al., 2001). Therefore, the progress of the reaction was followed by taking samples of the solution (5.0 ± 0.01 mL) at different times (established according to the reaction conditions of each experiment), and by determining sulfur by ICP for the reactions in NaOH medium. For the reactions in Ca(OH)₂ medium, the reaction was followed by determining sodium by means of Atomic Absorption Spectroscopy AAS (PerkinElmer Analyst 200).

The most useful variable to describe the evolution of a solid–fluid reaction is *conversion* *X*, which is a dimensionless number that represents the physical amount of substance that has reacted; in our case, it is possible to calculate *X* as follows:

$$X = \frac{A_t}{A_\tau} \quad (1)$$

where *X* is the fraction of sodium arsenojarosite that has reacted; *A_t* is the quantity of Na or S in the solution at any given time *t* and *A_τ* is the quantity of Na or S at the end of the reaction. On the other hand, in order to choose the kinetic model that describes the decomposition process, several experiments were performed beforehand to observe the evolution of the solids at different conversion values. These solids were characterized by XRD, SEM and EDS.

2.4. Experiment design

In order to use a statistical approach when designing and analyzing an experiment, special care has to be taken when choosing from these points: factors and their levels, variable of response, type of experimental design and data analysis (Montgomery, 1997). The decomposition of jarosite-type compounds in alkaline media has been previously studied (Baron and Palmer, 1996; Patiño et al., 1994, 1998, 2003, 2010, 2011; Roca et al., 1993, 2006; Salinas et al., 2001; Savage et al., 2005; Smith et al., 2006a); and there are several factors that affect the decomposition of jarosite-type compounds (natural and synthetic) with and without arsenic, such as pH of the medium (concentration and generator of OH⁻/H₃O⁺), temperature, type of

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