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Article

Kinetic Modeling of the Alkaline Decomposition of Potassium Arsenojarosite

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Uma amostra de arsenojarosita de potássio foi sintetizada e completamente caracterizada. A amostra obtida é uma solução sólida de arsenojarosita de potássio, cuja fórmula aproximada é $[K_{0,75}(H_3O)_{0,25}]Fe_{1,84}[(SO_4)_{1,82}(AsO_4)_{0,18}][(OH)_{2,34}(H_2O)_{3,66}]$. O processo de decomposição em meio alcalino foi estudado no período de indução e de conversão progressiva, e a ordem de reação e a energia de ativação foram determinadas para cada caso. Nas condições experimentais utilizadas, os resultados são consistentes com modelo de partícula esférica com núcleo decrescente e controle químico. Em ambos os processos, quatro modelos parciais e dois modelos globais foram desenvolvidos para descrever seu comportamento básico. Os modelos foram validados, e foi provado que descrevem favoravelmente o processo de decomposição em meio alcalino.

A sample of potassium arsenojarosite was synthesized and thoroughly characterized. The obtained sample is a solid solution of potassium arsenojarosite, whose approximate formula is $[K_{0.75}(H_3O)_{0.25}]Fe_{1.84}[(SO_4)_{1.82}(AsO_4)_{0.18}][(OH)_{2.34}(H_2O)_{3.66}]$. The decomposition process in alkaline medium was studied in the induction and progressive conversion periods, and the reaction order and activation energy were determined for each case. Under the used experimental conditions, results are consistent with the spherical particle model with decreasing core and chemical control. In both processes, four partial models and two global models were developed in order to describe their basic behavior. The models were validated, and it was proved that they favorably describe the decomposition process in alkaline medium.

Keywords: potassium arsenojarosite, alkaline decomposition, kinetic modeling, activation energy, reaction order

Introduction

In many parts of the world, potable water is polluted with arsenic. This element is disposed of by mining and chemical industries, refineries, etc.[1] The presence of arsenic in ground waters can be also natural because of the leaching of rocks and sediments that contain this element.[2] These ground waters contain great amounts of arsenic, and they are consumed by millions of people around the world, in countries like Bangladesh, Cambodia, China, India, Laos, Myanmar, Nepal, Pakistan and Vietnam in Asia.[3] This problem is also present in the American continent, in countries such as Argentina, Mexico, Chile, Peru, United States, Brazil and Canada.[4,5] For these reasons, the U. S. Environmental Protection Agency has set the amount of 10 μg L^{-1} as the maximum level of pollution allowed in potable water.[6] Thus, several alternatives have been studied in order to solve this problem.[7] Jarosite technology has been applied for 40 years in the zinc industry as a way to control Fe and other impurities, such as As. Therefore, arsenic can be incorporated into the structure of the jarosites, which work as an inerting medium for this toxic element. Regarding this, Dutrizac *et al.*[8,9] studied the incorporation of arsenic as AsO_4^{3-} in the lattice of potassium, sodium and lead jarosite at 97 and 150 °C. Patiño *et al.*[10-14] have thoroughly studied the alkaline reactivity of argentian jarosites in alkaline medium. Although there are several studies related to the alkaline decomposition of jarosite type compounds, only few ones are related to jarosite type compounds with arsenic.[15,16] These works are focused on the characterization of the dissolution residues and on the kinetic study of these compounds. However, regarding the latter,[16] the obtained kinetic models were not verified.

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For this reason, in this research work, a kinetic study, which allows to describe and to predict the behavior of this compound, was carried out at different experimental conditions. Reaction rates and dependencies were compared in a wide range of experimental conditions of concentration, temperature and particle size. Partial and global kinetic models of the induction and progressive conversion periods were developed for the alkaline decomposition of the potassium arsenojarosite in NaOH and $Ca(OH)_2$ media.

Experimental

The potassium arsenojarosite samples were synthesized using the parameters previously described by Dutrizac *et al*.[8,9] and characterized by different techniques.

The alkaline decomposition experiments in NaOH and $Ca(OH)_2$ media were carried out under the following conditions: 0.2 g potassium arsenojarosite (38 ± 2 μm) in an initial volume of 0.5 L, stirring rate of 500 min^{-1}, varying the concentration of OH^-, temperature and particle size. The pH value was kept constant during all the experiment in both media by adding small amounts of concentrated NaOH and $Ca(OH)_2$, respectively. The OH^- concentration was determined by considering the ionization constant of water and pH of the alkaline solution according to the temperatures used in a previous work.[17]

Figure 1 shows a scanning electron microscopy (SEM) image (JEOL JSM-5900 LV) of almost spherical particles, which are formed by soundly soldered rhombohedral crystals.

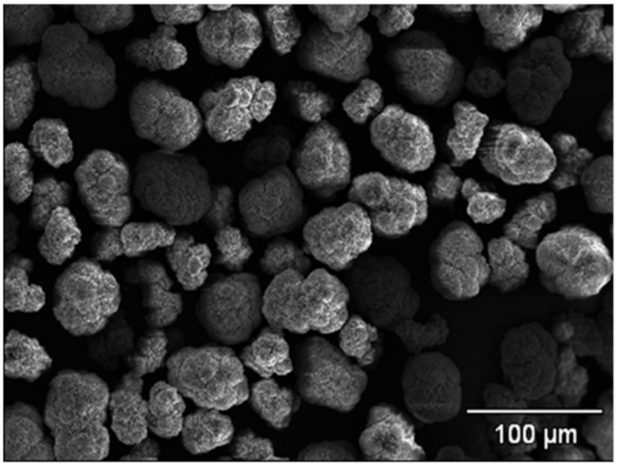

Figure 1. Particle size distribution of the synthesized potassium arsenojarosite.

The alkaline decomposition kinetics was monitored by atomic absorption spectroscopy (AAS) of potassium using a Perkin Elmer Analyst 200 equipment. For all of the performed experiments, the induction period (t_{ind}) was determined and the experimental rate constant (k_{exp}) was calculated. The kinetic modeling was carried out with the experimental results of the alkaline decomposition of potassium arsenojarosite. The solids at different decomposition times, as well as those submitted to high temperatures, were analyzed by X-ray diffractometry (SIEMENS D-500), SEM with an accelerating voltage of 20 kV and microanalysis by energy-dispersive X-ray spectroscopy (SEM-EDS in an Oxford Equipment). The objective was to determine their evolving process. Tables 1 and 2 summarize the experimental data that were used in the modeling.

Table 1. Decomposition of potassium arsenojarosite in NaOH medium: n = 2.65, E_a = 84.7 kJ mol^{-1} for the induction period; n = 1.86, E_a = 60.3 kJ mol^{-1} for the progressive conversion period

pH	$[OH^-]$ / (mol L^{-1})	T / °C	d_0 / μm	Induction time, t_{ind} / min	k_{exp} / min^{-1}
12.87	0.1081	30	38	0.04	0.088
12.53	0.0494	30	38	0.61	0.031
12.08	0.0175	30	38	5.00	0.004
11.96	0.0133	30	38	13.00	0.003
11.64	0.0064	30	38	87.72	0.001
10.93	0.0012	30	38	144.88	0.001
9.94	0.0001	30	38	217.86	0.001
12.92	0.0571	20	38	4.46	0.022
12.71	0.0519	25	38	3.00	0.026
12.46	0.0596	35	38	0.68	0.072
12.31	0.0586	40	38	0.57	0.112
12.16	0.0569	45	38	0.27	0.166
12.08	0.0638	50	38	0.17	0.278
11.90	0.0560	55	38	–	0.289
11.79	0.0570	60	38	–	0.369
12.77	0.0859	30	75	1.56	0.0133
12.80	0.0920	30	53	0.18	0.0189
12.78	0.0879	30	45	0.65	0.0222
12.83	0.0986	30	25	0.49	0.0400
12.81	0.0942	30	23	0.34	0.0435

Results and Discussion

Topology of the reaction

The decomposition of potassium arsenojarosite in NaOH and $Ca(OH)_2$ media presents an induction period (t_{ind}), during which the arsenojarosite does not react. Therefore, the SO_4^{2-} and K^+ concentrations are found at negligible levels in the solution (Figure 2). The induction period has been observed in the decomposition of jarosites synthesized in the laboratory, as well as in those coming from industrial plants.[18] The ion concatenation of the medium with the surface of the particle creates active sites until a reaction front is established, and through which the

Table 2. Decomposition of potassium arsenojarosite in $Ca(OH)_2$ medium: n = 0.24, E_a = 88.3 kJ mol^{-1} for the induction period; n = 1.14, E_a = 74.4 kJ mol^{-1} for the progressive conversion period

pH	[OH$^-$] / (mol L^{-1})	T / °C	d_0 / µm	Induction time, t_{ind} / min	k_{exp} / min^{-1}
12.53	0.0494	30	38	28.5	0.006
12.48	0.0441	30	38	28.6	0.005
12.43	0.0393	30	38	28.6	0.004
12.33	0.0312	30	38	29.3	0.003
12.12	0.0192	30	38	33.2	0.002
11.87	0.0108	30	38	41.0	0.002
11.25	0.0026	30	38	56.0	0.002
11.06	0.0017	30	38	65.0	0.002
12.8	0.0434	20	38	52.0	0.002
12.55	0.0359	25	38	39.5	0.003
12.03	0.0221	35	38	22.0	0.003
11.95	0.0256	40	38	19.6	0.008
11.74	0.0216	45	38	16.6	0.009
11.58	0.0202	50	38	11.7	0.013
11.44	0.0194	55	38	9.2	0.018
11.24	0.0161	60	38	3.5	0.020
11.12	0.0158	65	38	0.9	0.041
10.93	0.0131	70	38	–	0.043
12.24	0.0254	30	75	40.0	0.0010
12.22	0.0242	30	53	31.5	0.0020
12.27	0.0272	30	45	29.7	0.0026
12.29	0.0284	30	28	23.2	0.0039
12.25	0.0259	30	23	17.3	0.0047

ions of the medium and the potassium arsenojarosite start to diffuse. This is followed by a progressive conversion period, when the concentrations of SO_4^{2-} and K^+ progressively increase until reaching stabilization (Figure 2), indicating the end of the reaction.

Figure 3a is an SEM image of a partially decomposed potassium arsenojarosite particle, showing an unreacted core surrounded by a reaction front, which is wrapped in an amorphous gel of iron hydroxide with arsenic. This can be confirmed in Figure 3b, which shows a linescan (indicated in Figure 3a) of the partially decomposed particle, from the core to the halo of the amorphous gel. This figure shows how the amount of sulfur and potassium decreased, indicating that these species have diffused from the core to the solution, while iron and arsenic are still distributed throughout the particle. The relative amounts of all the species are constant in the core, which means that it did not react. The residues do not evolve into new crystal phases, not even after reaching total decomposition (0-10 h). This was evidenced by the X-ray diffractograms in Figure 4, in which the decomposition product is observed

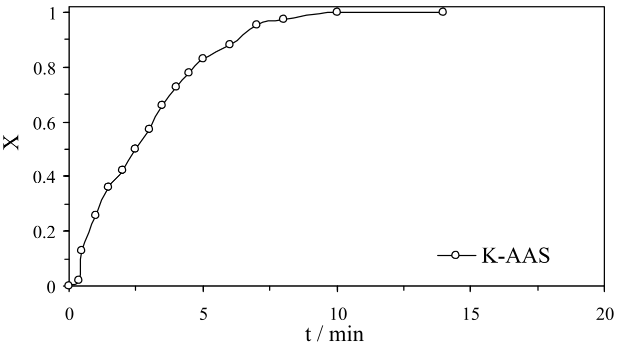

Figure 2. Alkaline decomposition curve of the potassium arsenojarosite, pH 12.78, 38 ± 2 µm, 30 °C.

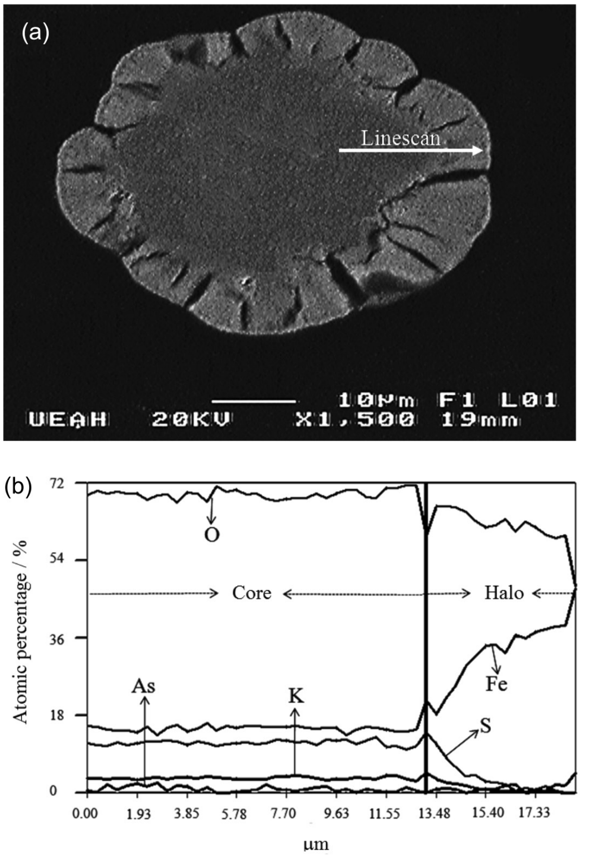

Figure 3. (a) Potassium arsenojarosite particle partially decomposed in NaOH medium, pH 12.78, 38 ± 2 µm, 30 °C and (b) linescan of the particle shown in figure 3A.

as an amorphous material. Therefore, the process is given by the following reaction:

$$[K_{0.75}(H_3O)_{0.25}]Fe_{1.84}[(SO_4)_{1.82}(AsO_4)_{0.18}][(OH)_{2.34}(H_2O)_{3.66}] + 3.43\ OH^-_{(aq)} \rightarrow 0.75\ K^+_{(aq)} + 1.82\ SO_4^{2-}{}_{(aq)} + 1.84\ Fe(OH)_3\ 0.18\ AsO_4^{3-}{}_{(gel)} + 4.16\ H_2O \quad (1)$$

The decomposition solids were exposed to high temperatures. At 110 and 400 °C, there is no formation of new crystal phases, but sharp diffraction peaks,

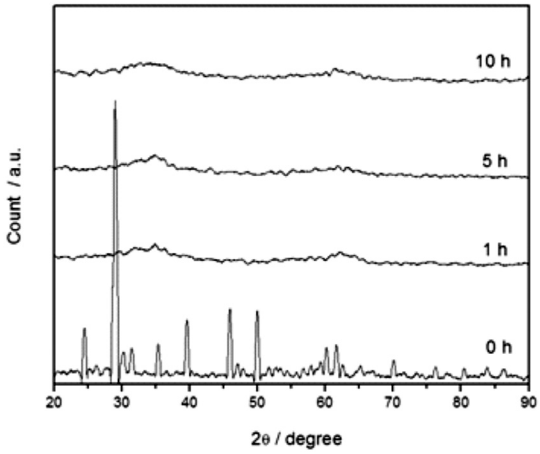

Figure 4. X-ray diffractograms of a potassium arsenojarosite sample at different decomposition times in NaOH: pH 12.78, 38 ± 2 µm, 30 °C.

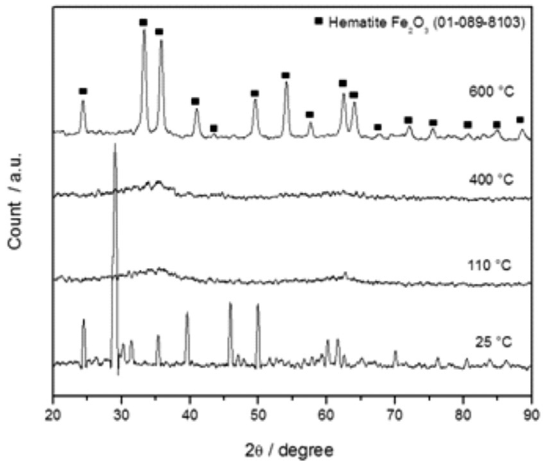

Figure 5. X-ray diffractograms of the total decomposition product heated at 110, 400 and 600 °C for 1 h, including the identification of the phase formed at 600 °C.

characteristic of crystalline hematite, Fe_2O_3 (01-089-8103), were observed after thermal treatment at 600 °C (Figure 5).[13]

All results in NaOH and $Ca(OH)_2$ media, it can be explained using the spherical particle model with decreasing core, in which the process is controlled by the chemical reaction according to the following expressions:[19-21]

$$k_{exp}t = 1 - (1 - X)^{1/3} \qquad (2)$$

where

$$k_{exp} = \frac{V_M k_q c_A^n}{r_0} \qquad (3)$$

k_{exp} is the experimental rate constant, X is the fraction that reacted, V_M is the molar volume of the solid, c_A represents the reactant concentration, r_0 stands for the initial radius of the particle, k_q is the rate constant of the chemical reaction and n is the reaction order. Figure 6 presents the experimental results from Figure 2 after applying equation 2, and it can be observed that they are consistent with the chemical control expression as the stage that controls the reaction rate.

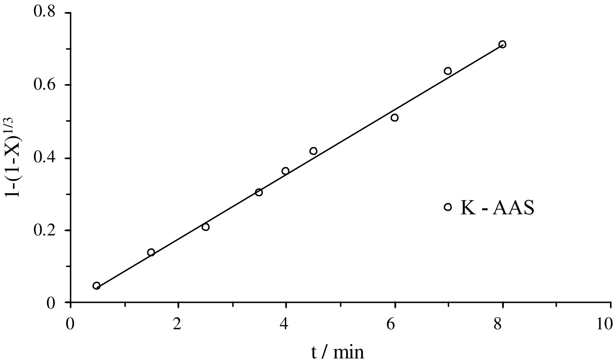

Figure 6. Representation of the decreasing core model with chemical control of the data in Figure 2.

Modeling

Arsenojarosite decomposition in alkaline medium

Tables 1 and 2 summarize the experimental results, in which the induction period (t_{ind}) and experimental rate constant are presented within a wide range of experimental conditions, such as NaOH and $Ca(OH)_2$ concentrations, temperature and particle size. The initial pH was kept constant along the reaction, and the $[OH^-]$ was calculated according to the ionic constant of water at the working temperature of each reaction, as previously mentioned in the Experimental section.[17]

Induction period (t_{ind})

For the induction period of the potassium arsenojarosite decomposition in NaOH medium with $[OH^-] > 6.4 \times 10^{-3}$ mol L^{-1}, a fractional reaction order of n = 2.65 was obtained. The calculated activation energy in NaOH medium is $E_a = 84.7$ kJ mol^{-1}. In the case of the $Ca(OH)_2$ with $[OH^-] > 3.1 \times 10^{-2}$ mol L^{-1}, the fractional reaction order is n = 0.24. The calculated activation energy in $Ca(OH)_2$ medium is $E_a = 88.3$ kJ mol^{-1}. According to these results, the induction period for NaOH is defined by the following expressions.

For $[OH^-] > 6.4 \times 10^{-3}$ mol L^{-1}:

$$1/\theta = \frac{1}{(r_0 v_M)} [OH^-]^{2.65}\, 5.6 \times 10^{17}\, e^{-84700/RT} \qquad (4)$$

For the induction period in $Ca(OH)_2$ medium with $[OH] > 3.1 \times 10^{-2}$ mol L^{-1}, the expression is the following:

$$1/\theta = \frac{1}{(r_0 v_M)} [OH^-]^{0.24}\, 3.4 \times 10^{13}\, e^{-88300/RT} \qquad (5)$$

Progressive conversion period

For the progressive conversion period corresponding to the potassium arsenojarosite decomposition in NaOH medium with $[OH^-] > 6.4 \times 10^{-3}$ mol L^{-1}, a fractional reaction order of n = 1.86 was obtained. The activation energy calculated in NaOH medium is $E_a = 60.3$ kJ mol^{-1}. Therefore, the kinetic expression for the progressive conversion period in NaOH medium is as follows.

For $[OH^-] > 6.4 \times 10^{-3}$ mol L^{-1}:

$$1 - (1 - X)^{1/3} = 2.37 \times 10^{11}\, e^{-60300/RT}\, [OH^-]^{1.86}\, t \qquad (6)$$

For the progressive conversion period corresponding to the potassium arsenojarosite decomposition in $Ca(OH)_2$ with $[OH^-] > 1.92 \times 10^{-2}$ mol L^{-1}, a fractional reaction order of n = 1.14 was obtained. The activation energy calculated in $Ca(OH)_2$ medium is $E_a = 74.4$ kJ mol^{-1}, so the kinetic expression for the progressive conversion period in $Ca(OH)_2$ is as follows.

For $[OH^-] > 1.92 \times 10^{-2}$ mol L^{-1}:

$$1 - (1 - X)^{1/3} = 1.2 \times 10^{12}\, e^{-74400/RT}\, [OH^-]^{1.14}\, t \qquad (7)$$

Figure 7 is a plot of the development of the kinetic model according to equations 4 and 5, showing the experimental induction period ($t_{ind\text{-}exp}$ (min)) *vs.* the calculated induction period ($t_{ind\text{-}calc}$ (min)). Since the induction and progressive conversion periods are at different magnitude orders, the base 10 logarithms of the calculated and experimental induction periods were plotted.

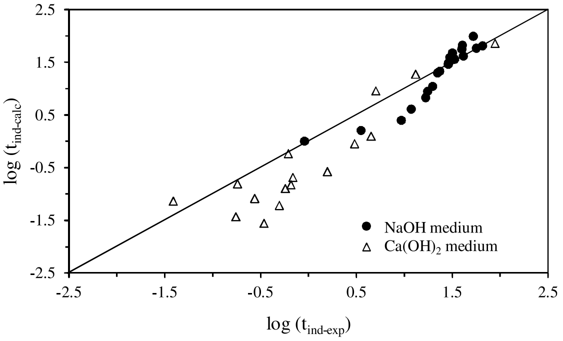

Figure 7. Induction period. Alkaline decomposition of the potassium arsenojarosite. Comparison between the calculated and experimental data in NaOH and $Ca(OH)_2$ media.

Figure 8 presents the development of equation 6, being a plot of the experimental rate constant *vs.* the calculated rate constant, e.g., k_{exp} (min^{-1}) *vs.* k_{calc} (min^{-1}) in NaOH medium. Likewise, Figure 9 depicts the development of equation 7, which represents the behavior of the progressive conversion period in $Ca(OH)_2$ medium.

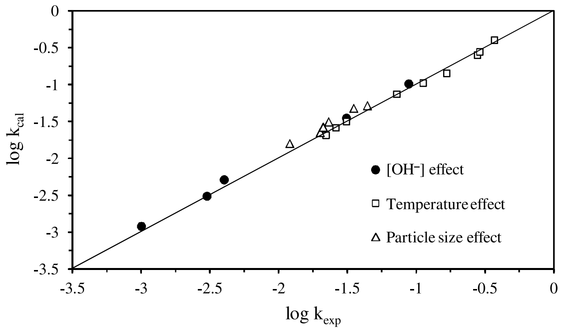

Figure 8. Progressive conversion period. Alkaline decomposition of the potassium arsenojarosite in NaOH medium. Comparison between the calculated and experimental data, $[OH^-] > 6.4 \times 10^{-3}$ mol L^{-1}.

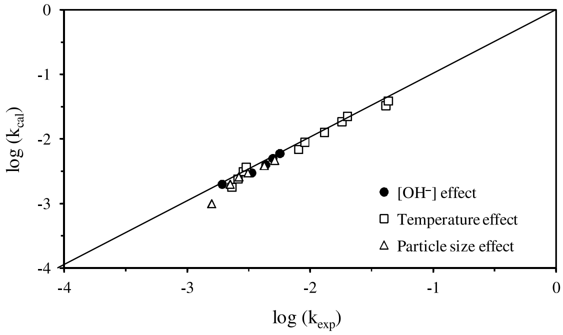

Figure 9. Progressive conversion period. Alkaline decomposition of the potassium arsenojarosite in $Ca(OH)_2$ medium. Comparison between the calculated and experimental data, $[OH^-] > 1.92 \times 10^{-2}$ mol L^{-1}.

In all the kinetic expressions: $v_M = 153.07$ cm^3 mol^{-1}, R = 8.3144 J mol^{-1} K^{-1}, r_0 in cm, T in Kelvin, $[OH^-]$ in mol L^{-1} and t in minutes.

From equations 4 and 6, corresponding to the alkaline decomposition in NaOH medium with $[OH^-] > 6.4 \times 10^{-3}$ mol L^{-1}, a general expression can be established in order to determine the total reaction time needed for obtaining a definite conversion of the potassium arsenojarosite. The kinetic model is the following:

$$t_X = \frac{1}{\left(\frac{1}{r_0 v_M}\right) [OH^-]^{2.65}\, 5.6 \times 10^{17}\, e^{-84700/RT}} + \frac{1 - (1 - X)^{1/3}}{2.37 \times 10^{11}\, e^{-60300/RT}\, [OH^-]^{1.86}} \qquad (8)$$

Figure 10 shows the total reaction time needed for obtaining a potassium arsenojarosite conversion of X = 0.75 (calculated according to equation 8) *vs.* the same experimentally obtained parameters. It can be concluded that equation 8 is consistent with the experimental results because the experimental and the calculated data do not show any considerable differences.

For equations 5 and 7, corresponding to the decomposition in $Ca(OH)_2$ medium, an expression was

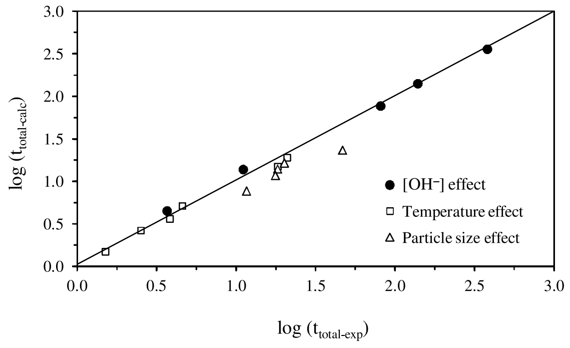

Figure 10. Alkaline decomposition in NaOH medium. Plot of the reaction total time obtained at an X = 0.75 conversion (experimental *vs.* calculated).

established in order to determine the total reaction time needed for obtaining a definite conversion of the potassium arsenojarosite. The kinetic model is the following:

$$t_X = \frac{1}{\left(\frac{1}{r_0 V_M}\right)[OH^-]^{0.24}\, 3.4 \times 10^{13}\, e^{-88300/RT}} + \frac{1-(1-X)^{1/3}}{1.2 \times 10^{12}\, e^{-74400/RT}\, [OH^-]^{1.14}} \qquad (9)$$

Figure 11 shows the total reaction time needed for obtaining a conversion of X = 0.75 (calculated according to equation 9) *vs.* the same parameter (experimentally obtained). It can be concluded, therefore, that equation 9 is consistent with the experimental results of the decomposition in $Ca(OH)_2$ medium.

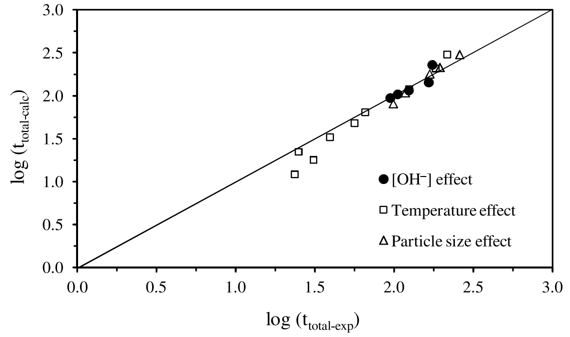

Figure 11. Alkaline decomposition in $Ca(OH)_2$ medium. Plot of the reaction total time obtained at an X = 0.75 conversion (experimental *vs.* calculated).

Conclusions

The decomposition solids do not evolve into new crystal phases after reaching total decomposition. However, after being heated at 600 °C, the decomposition product evolves into a new crystal phase, which was identified as hematite (Fe_2O_3). The general mathematical models for the decomposition of potassium arsenojarosite in NaOH and $Ca(OH)_2$ media during the induction and progressive conversion periods are presented as follows:

$$t_X = \frac{1}{\left(\frac{1}{r_0 V_M}\right)[OH^-]^{2.65}\, 5.6 \times 10^{17}\, e^{-84700/RT}} + \frac{1-(1-X)^{1/3}}{2.37 \times 10^{11}\, e^{-60300/RT}\, [OH^-]^{1.86}} \qquad \text{NaOH}$$

$$t_X = \frac{1}{\left(\frac{1}{r_0 V_M}\right)[OH^-]^{0.24}\, 3.4 \times 10^{13}\, e^{-88300/RT}} + \frac{1-(1-X)^{1/3}}{1.2 \times 10^{12}\, e^{-74400/RT}\, [OH^-]^{1.14}} \qquad Ca(OH)_2$$

These models describe the process of alkaline decomposition of the potassium arsenojarosite. They will also allow to predict its behavior at different temperature (20-60 °C) and concentration conditions ($0.1\text{-}2.7 \times 10^{-4}$ mol L^{-1} for NaOH and $2.3 \times 10^{-2}\text{-}7 \times 10^{-4}$ mol L^{-1} for $Ca(OH)_2$).

References

1. Korngold, E.; Belayev, L. A.; *Desalination* **2001**, *141*, 81.
2. Thomas, S. Y.; Choong, T. G.; Chuah, Y. R.; Gregory K.; Azni, I.; *Desalination* **2007**, *217*, 139.
3. Brammer, H.; *Environ. Int.* **2009**, *35*, 856.
4. Mandal, B. K.; Suzuki, K. T.; *Talanta* **2002**, *58*, 201.
5. Ning, R. Y.; *Desalination* **2002**, *143*, 237.
6. EPA Office of groundwater and drinking water. *Implementation guidance for the arsenic rule*. EPA 2002, report-816-D-02-005-, Cincinnati, USA.
7. Katsoyiannis, I. A.; Zouboulis A. I.; *Water Res.* **2004**, *38*, 17.
8. Dutrizac, J. E.; Jambor, J. L.; *Can. Metall. Q*. **1987**, *26*, 91.
9. Dutrizac, J. E.; Jambor, J. L.; Chen, T. T.; *Can. Metall. Q*. **1987**, *26*, 103.
10. Patiño, F.; *J. Mex. Chem. Soc*. **1993**, *37*, 51.
11. Patiño, F.; Cruells, M.; Roca, A.; Salinas, E.; Perez, M.; *Hydrometallurgy* **2003**, *70*, 153.
12. Patiño, F.; Salinas, E.; Cruells, M.; Roca, A.; *Hydrometallurgy* **1998**, *49*, 323.
13. Patiño, F.; Roca, A.; Reyes, M.; Cruells, M.; Rivera, I.; Hernández, L. E.; *J. Mex. Chem. Soc*. **2010**, *54*, 216.
14. Patiño F.; Reyes, I.; Rivera, I.; Reyes, M.; Hernández, J.; Pérez, M.; *J. Mex. Chem. Soc.* **2011**, *55*, 197.
15. Smith, A. M. L.; Dubbin, W. E.; Wright, K.; Hudson-Edwards, K. A.; *Chem. Geol.* **2006**, *229*, 344.
16. Reyes, I. A.; Patiño, F.; Rivera I.; Flores, M. U.; Reyes, M.; Hernández, J.; *J. Braz. Chem. Soc.* **2011**, *22*, 2260.
17. Lide, D. R; *Handbook of Chemistry and Physics*, 89th ed.; CRC Press: Boston, 2009, ch. 8.
18. Roca, A.; Cruells, M.; Patiño, F.; Rivera, I.; Plata, M.; *Hydrometallurgy* **2006**, *81*, 15.
19. Levenspiel, O.; *Ingeniería de las Reacciones Químicas*, 3th ed.; Reverte: Barcelona, 2010, ch. 25.
20. Ballester, A.; Verdeja, L. F.; Sancho, J.; *Metalurgia Extractiva Fundamentos*, vol. 1; Editorial Síntesis: Madrid, 2000, ch. 7.
21. Sohn, H. Y.; Wadsworth, M. E.; *Cinética de los Procesos de la Metalurgia Extractiva*; Trillas: México, 1986, ch. 1.

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