

# DECOMPOSITION NATURE IN ALKALINE MEDIUM OF A THALLIUM JAROSITE.

Hernán ISLAS<sup>a</sup>, Francisco PATIÑO<sup>a</sup>, Antonio ROCA<sup>b</sup>, Iván A. REYES<sup>c</sup>, Mizraim U. FLORES<sup>d</sup>, Elia G. PALACIOS<sup>e</sup>, Martín REYES<sup>a</sup>.

<sup>a</sup> Universidad Autónoma del Estado de Hidalgo, Área Académica de Ciencias de la Tierra y Materiales. Carretera Pachuca – Tulancingo Km. 4.5, C.P. 42184 Mineral de la Reforma, Hidalgo, México.

<sup>b</sup> Universitat de Barcelona, Facultad de Química, Martí i Franques 1, 08028 Barcelona, Spain.

<sup>c</sup> Universidad Autónoma de San Luis Potosí, Instituto de Metalurgia. Av. Sierra Leona No. 550, Lomas 2da. Sección, C.P. 78210 San Luis Potosí S.L.P. México.

<sup>d</sup> Universidad Tecnológica de Tulancingo, Área de Electromecánica Industrial. Camino a Ahuehuetitla #301 Col. Las Presas, Tulancingo, Hidalgo, México 43642.

<sup>e</sup> Instituto Politécnico Nacional, Escuela Superior de Ingeniería Química e Industrias Extractivas, Unidad Profesional Adolfo López Mateos, C.P. 07738México Distrito Federal, México.

#### Abstract

Thallium is considered a highly toxic metal, and along with iron it is an undesirable element in the hydrometallurgical industry of zinc; these elements are precipitated in a solid jarosite type compound, which is then placed in open spaces exposed to environmental agents. This piece of work presents a comprehensive study on the decomposition nature in alkaline medium of a thallium jarosite with the formula  $TI_{0.86}$  ( $H_3O$ )<sub>0.14</sub> Fe<sub>3.11</sub> (SO<sub>4</sub>)<sub>2.11</sub> (OH)<sub>6.11</sub>( $H_2O$ )<sub>0.44</sub>. This compoud was synthesized by using 3.1x10<sup>-1</sup> molL<sup>-1</sup> Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 4.0x10<sup>-2</sup> molL<sup>-1</sup> Tl<sub>2</sub>SO<sub>4</sub>solutions in a 1 liter glass reactor at a temperature of 94°C with 600 min<sup>-</sup> mechanical stirring for 24 hours. The solid sample was characterized by X-ray Diffraction, Scanning Electron Microscopy, along with Energy Dispersive X-ray Spectroscopy, Inductively Coupled Plasma Spectrometry and gravimetry. The results confirm that the obtained product corresponds to a thallium jarosite, whose particles are semispherical, with a dominant size between 38 and 44 µm.

With the thallium jarosite decomposition in 0.01molL<sup>-1</sup>NaOH medium in a 1/2 liter glass reactor at a temperature of 30 with magnetic stirring, an S-type curve was obtained whose experimental points preferentially fit the decreasing core model of constant size spherical particles, where the chemical reaction controls the decomposition process. Partially decomposed solids were studied by Scanning Electron Microscopy along with Energy Dispersive X-ray Spectroscopy; an unreacted core, a reaction front and an ash halo can be observed. The total decomposition products correspond to an amorphous compound.

Keywords: Precipitated, Decomposition, Jarosite, Thallium

### 1. INTRODUCTION

Heavy metals such as thallium are considered hightly toxic, since they both as ions or as part of compounds, they are water-soluble, and can be easily absorbed by living organisms, causing serious damage to health. Thallium is one of the most toxic elements to human, compared to mercury, cadmium or lead [1,2]. This metal is usually related to sulfide minerals, and are often found among mineralized zones, so it is present in mining materials used in the recovery of zinc, gold, copper, lead and uranium [3,4].

In the hydrometallurgy of zinc, nucleation and growth of jarosite particles is used as a means to precipitate iron, alkaline metals, such as  $TI^+$ ,  $Pb^+$  and  $Hg^+$  among others, and to control sulfate ions. The jarosite type compound's general formula is **MFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>OH**<sub>6</sub>, where **M** is: H<sub>3</sub>O<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>,Rb<sup>+</sup>, Ag<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, TI<sup>+</sup>, 1/2Pb<sup>2+</sup>, 1/2Hg<sup>2+</sup>. This compound considerably improves the filtration process in hydrometallurgical circuits [5,6,7].



In Mexico this process is used in electrolitic zinc plants, where approximately 400 tons of jarosite waste are produced every day. Considering an uninterrupted jarosite production, it amounts to an average of 4 million tons [8].

Jarosite is considered a potentially dangerous industrial waste, and it is placed in storage areas directly exposed to atmospheric agents. These conditions have a decisive influence on the decomposition of jarosite and the probable release of the toxic metals contained in it.

Patiño and collaborators [9,10,11] have conducted studies on argentian jarosite type compounds, establishing the nature of the reaction and kinetic expressions of this kind of compounds. They have also atudied the mobilization of toxic metals, like the arsenic of jarosite type solids, by studying the decomposition kinetics of jarosite with arsenic in alkaline medium - NaOH and Ca(OH)<sub>2</sub> [12,13]. The non existent mobilization of arsenic contained in jarosite was found in these studies. They have reported that the solid products of the decomposition consist of an amorphous gel of absorbed FeOH<sub>3</sub> and AsO<sub>4</sub>. However, there are few studies on the thallium jarosite. Therefore, it is important to study the behavior of thallium contained in synthetic jarosite type compounds by the kinetics of the alkaline decomposition in NaOH medium in order to explain the mobilization of thallium contained in the jarosite into aqueous media.

### 2. EXPERIMENTAL PROCEDURE

### Synthesis of thallium jarosite:

The conditions and procedure used to synthesize thallium jarosite were determined based on research conducted on the formation of jarosites synthesized by Dutriczac et al. [7] and Patiño et al. [10,11].

Reagent grade Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Tl<sub>2</sub>SO<sub>4</sub> compounds were used for the synthesis. The formation temperature was 94 °C at 650 rpm mechanical stirring for 24 hours of reaction at 1 atmosphere of pressure. The laboratory equipment used for the synthesis of thalium jarosite were a conventional one liter glass reactor, a condenser, a temperature sensor, a propeller and a heating plate. The synthesized thalium jarosite was characterized by gravimetry for the determination of sulfate concentration, and by inductively coupled plasma spectrometry (ICP) for the quantification of iron, thalium and sulfur. The jarosite was characterized by X-ray diffraction (XRD), scanning electron microscopy together with energy-dispersive X-ray microanalysis (EDS).

### Nature of the reaction of the decomposition of thallium jarosite in NaOH medium:

To study the nature of the reaction, we employed the conditions and methodology used by Patiño and collaborators [11,12,13]. The experiments on the alkaline decomposition of thallium jarosite in NaOH were conducted at atmospheric pressure in a one liter glass reactor placed on a heating plate equipped with a temperature controller with magnetic stirring and a pH measuring system to monitor the reaction.

The experimental development of the alkaline decomposition of thallium jarosite consisted in adding to a reactor 1.0 g of the previously synthesized product with a particle diameter of 38  $\mu$ m at a 0.01 mol L<sup>-1</sup> NaOH ( pH 11.66) dissolution, at 30°C and rpm. During the alkaline decomposition, 5ml aliquots were taken at different decomposition times to determine, via ICP, the concentrations of SO<sub>4</sub><sup>2-</sup> and TI<sup>+</sup> ions. Residual solids were characterized by X-ray diffraction, SEM and EDS.

# 3. RESULTS AND DISCUSSION

### Gravimetry and inductively coupled plasma Spectrometry (ICP).

The thallium jarosite was characterized by gravimetry to determine and quantify sulfates (SO<sub>4</sub><sup>2-</sup>), and by the inductively coupled plasma Spectrometry technique (ICP), using a Perkin Elmer-Optima 3000-XL, to quantify iron, thallium and sulfur (Fe, TI and S). The analysis results are shown in table I.



Species	Composition (Weight %)	Analysis technique
Fe <sup>3+</sup>	26.10	ICP
*S <sup>6+</sup> (SO <sub>4</sub> <sup>2-</sup> )	*10.14 (30.36)	ICP
TI <sup>1+</sup>	26.38	ICP
SO4 <sup>2-</sup>	30.46	Gravimetry
H <sub>3</sub> O <sup>+</sup> + OH <sup>-</sup> + H <sub>2</sub> O	17.06	Difference

Table	1	Chemical	composition	of the s	vnthesized	thallium	iarosite
	-	•			j		

### X-ray Diffraction.

In order to characterize the solids of the thallium jarosite synthesis, as well as the residual solids of the nature of the decomposition reaction, a SIEMENS D-50 diffractometer was used. The diffractogram in figure 1 corresponds to the thallium jarosite synthesis product, which adequately matches the PDF file (47-1768) of the crystal structure of thallium jarosite. The ICP and gravimetry analyses indicate that the product obtained from the synthesis experimental conditions corresponds to a thallium jarosite, also known as Doralcharite.



Fig. 1 Diffractogram of the thallium jarosite synthesis compared with the PDF file of Doralcharite (47-1768)

Based on the chemical analysis results presented in table I, and on the diffractogram in figure 1 of the synthesized thallium jarosite sample, we determined its approximate formula based on the theoretical formula of thallium jarosite. The  $H_3O^+ + OH^- + H_2O$  content was obtained by difference. According to the stoichiometric balance, the approximate formula is:

 $TI_{0.86}$  (H<sub>3</sub>O)<sub>0.14</sub> Fe<sub>3.11</sub> (SO<sub>4</sub>)<sub>2.11</sub> (OH)<sub>6.11</sub>(H<sub>2</sub>O)<sub>0.44</sub>, with an experimental density of 3.56 g cm<sup>-3</sup>.



#### Scanning Electron Microscopy (SEM).

A JEOL JSM- 5900LV low vaccum scanning electron microscope was used where the morphology, crystal habit and particle size distribution of thallium jarosite were observed. Figure 2 presents a general image (A) showing an even particle distribution of thallium jarosite, with particle sizes between 38 and 40  $\mu$ m and spherical morphology. A semi detailed image (B) of a thallium jarosite particle confirms the semi spherical shape of a particle of approximately 40  $\mu$ m diameter. The detail image (C) of a thallium jarosite particle indicates that it is made of soundly joined rhombohedral micro crystals.



**Fig. 2** (A) General image showing the particle size distribution of synthesized thallium jarosite, (B) semi detailed image of a thallium jarosite particle with semi spherical shape, and (C) detail image of a thallium jarosite particle comprised of rhombohedral micro crystals.

Figure 3 presents the energy-dispersive X-ray spectrum showing the typical elements of thallium jarosite and confirms once more the chemical analysis and X-ray results previously mentioned.



Fig. 3 EDS analysis of thallium jarosite

### Nature of the reaction of the decomposition of thallium jarosite in NaOH medium:

# Controlling stage.

The reaction rate was monitored via the sulfate ion  $(SO_4 \ ^2)$  in the solution, as seen in table II. This anion diffuses from the solid into the liquid's core; the concentration of the latter increases as the reaction progresses, until total decomposition of thallium jarosite is reached. The analysis method we employed to follow the process through sulfur was ICP.

Inductively Coupled Plasma Spectrometry (ICP)			
t (min)	X so <sub>4</sub> <sup>2-</sup>		
0	0		
1	0.0008311		
2	0.03577748		
3	0.0639857		
4	0.10098302		
5	0.15898123		
6	0.22779267		
8	0.27676497		
10	0.31590706		
12	0.4512958		
14	0.55272565		
16	0.64298481		
19	0.75558534		
21	0.78999106		
24	0.86907954		
27	0.91733691		
30	0.93610366		
33	0.98570152		
36	1		

Table 2 Data of the decomposition fraction of the sulfate ion SO42- with the reaction time

With these results, a type **S** decomposition curved was obtained, as observed in figure 4. It presents an induction period, a progressive conversion period and a stabilization zone of sulfate ions that indicates the end of the decomposition reaction.



Fig. 4 Decomposition curve in NaOH 0.01M, 30 °C, 38 µm and 650 rpm, monitored with ICP

Nine experiments were conducted at different reaction times. The reacted solids were characterized by X-ray diffraction. The spectra of each of the experiments are presented in figure 5, where it can be noted that the reflection intensity peaks of the reticular planes of thallium jarosite initially decrease until disappearing, leading to the formation of an amorphous solid probably comprised of iron hydroxide and thallium. These solids do not evolve into crystal phases even at times longer than total decomposition.





Fig. 5 Diffractograms of the synthesized thallium jarosite at different times of the decomposition reaction in NaOH medium 0.01 M.

The experimental results of the decomposition of thallium jarosite in NaOH medium are preferentially described by the constant size spherical particle model, where the chemical reaction controls the process. This experimental fact can be appreciated in table III and figure 6A. Clearly, the model of control by transport in figure 6B was disregarded, as the dispersion of the experimental points gives a regression coefficient of r = 0.95 as a result, while the regression coefficient for the chemical control is r = 0.98. Therefore, for further studies on the decomposition kinetics of thallium jarosite in NaOH medium, it is advisable to use the chemical control model.

Table 3 Applying of the chemical control model and model of control by transport to the experimental data

<i>Tim</i> e (min)	<b>X</b> \$04	Chemical control 1 - (1- <i>X</i> <sub>SO4</sub> ) <sup>1/3</sup>	Control by material transport 1-3(1- $X_{SO4}$ ) <sup>2/3</sup> + 2(1- $X_{SO4}$ )	
0	0	0	0	
1	0.0008311	0.00033458	3.3575E-07	
2	0.03577748	0.01446093	0.00062131	
3	0.0639857	0.02589489	0.00197691	
4	0.10098302	0.04107181	0.00492211	
5	0.15898123	0.0656051	0.01234735	
6	0.22779267	0.09595573	0.02585548	
8	0.27676497	0.11800897	0.03849154	
10	0.31590706	0.13573433	0.05026994	
12	0.4512958	0.20673798	0.11054957	
14	0.55272565	0.26729974	0.17615077	
16	0.64298481	0.32898924	0.25348617	
19	0.75558534	0.4259912	0.38979754	
21	0.78999106	0.45504475	0.43274884	
24	0.86907954	0.55431895	0.58115788	
27	0.91733691	0.63381573	0.69593121	



30	0.93610366	0.65499744	0.72504878
33	0.98570152	0.8684268	0.95262094
36	1	0.99999394	1
40	0.99821269	0.75921188	0.85398451
45	0.98257373	0.65408425	0.72380985
50	0.99642538	0.65792159	0.7290055

Figure 6. Applying of models: A) Chemical control, and B) control by transport, for the decomposition of thallium jarosite in NaOH 0.01 M, 30  $^{\circ}$ C, 38  $\mu$ m size and 650 rpm.

### CONCLUSIONS

Thallium jarosite was synthesized according to the following conditions:  $0.25 \text{ mol } L^{-1} \text{ Fe}_2(\text{SO}_4)_3$ ,  $0.032 \text{ mol } L^{-1} \text{ Tl}_2\text{SO}_4$ ,  $94^\circ\text{C}$ , 650 rpm and 24 hours. The obtained precipitate presents a semi spherical shape, comprised of rhombohedral crystals with a compact texture. The thallium jarosite has the following approximate formula:  $[\text{Tl}_{0.86} (\text{H}_3 \text{O})_{0.14} \text{ Fe}_{3.11} (\text{SO}_4)_{2.11} (\text{OH})_{6.11} (\text{H}_2 \text{O})_{0.44}]$ , with a resulting density of **3.56 g/cm^3**.

The results of the nature of the decomposition reaction in NaOH medium indicate the presence of an induction period, where the sulfate ions are at negligible levels, followed by a progressive conversion period where the sulfate ions diffuse into the solution and, finally, a stabilization zone of sulfate ions, which indicates that the decomposition reaction has ended. X-ray diffraction of the total decomposition solids indicates the formation of an amorphous gel that does not evolve into crystal phases, even at times following total decomposition.

The experimental data are preferentially adapted to the kinetic model of constant size spherical particles, where the alkaline decomposition process of thallium jarosite is controlled by the chemical reaction.

#### REFERENCES

- [1] Yarto, M. Los efectos de la contaminación: el caso de las sustancias tóxicas persistentes. México : Instituto Nacional de Ecología, 2004.
- [2] Cheam, V. Thallium contamination of water in Canada, Water Qual Res J. Can. 2001, 36(4), 851-77.
- [3] John Peter, A.; Viraraghavan, T. Thallium: a review of public health and environmental concerns, Environment International. 2005, 31, 493–501.
- [4] Twidwell, L. Potential technologies for removing thallium from mine and process wastewater, Eur. J. Miner Process Environ Prot. 2002, 2(1), 1–10.
- [5] James, S.; Watson, J.; Peter, J. 2000. Zinc production—a survey of existing smelters and refineries. In: Dutrizac, J.; Gonzalez, J.; Henke, D.; James, S.; Siegmund, A. (Eds.), Lead–Zinc 2000. The Minerals, Metals and Materials Society, Warrendale, PA, U.S.A., 205–225.
- [6] Dutrizac, J. The Behavior of Thallium during Jarosite Precipitation, Metallurgical and Materials Transactions B, 1997, vol 28B, 765-776.
- [7] Dutrizac, J.; Kaiman, S. Rubidium jarosite and thallium jarosite-new synthetic jarosite-type compounds and their strutures, Hidrometallurgy 1975, 1, 51-59.
- [8] Patiño, F.; Arenas, A.; Rivera, I.; Córdoba, D.; Hernández, L.; Salinas, E. Descomposición de plumbojarosita argentífera en medio CaO, Revista de la Sociedad Química de México, 2002, 1(46), 67-72.
- [9] Roca, A.; Patiño, F.; Rivera, I.; Hernández, L.; Pérez, M.; Salinas, E.; Reyes, M. Decomposition and cyanidation kinetics of the argentian ammonium jarosite in NaOH media, J. Mex. Chem. Soc. 2007, 51(2), 47-54.
- [10] Patiño, F.; Roca, A.; Reyes, M.; Cruells, M.; Rivera, I.; Hernández, L. Kinetic modeling of the alkaline decomposition and cyanidation of arjentojarosite, J. Mex. Chem. Soc. 2010, 54(4), 216-222.



- [11] Patiño, F.; Reyes, I.; Rivera, I.; Reyes, M.; Hernández, J.; Pérez, M. Decomposition kinetics of the argentian lead jarosite in NaOH media, J. Mex. Chem. Soc. 2011, 55(4), 208-213.
- [12] Patiño, F.; Flores, M.; Reyes, I.; Reyes, M.; Hernández, J.; Rivera, I.; Juárez, J. Alkaline decomposition of synthetic jarosite with arsenic, Geochemical Transactions. 2013, 14:2.
- [13] Patiño, F.; Reyes, I.; Flores, M.; Pandiyan, T.; Roca, A.; Reyes, M.; Hernández, J. Kinetic modeling and experimental design of the sodium arsenojarosite decomposition in alkaline media: Implications, Hydrometallurgy. 2013, 137, 115–125.