The Hydrothermal Reaction and Kinetic of Enargite

Gerardo Fuentes

Abstract The stoichiometry and kinetics of the hydrothermal reaction of enargite in copper sulphate solutions was investigated in the range 140–300 °C, and particle size under 15 and 50 μm. The stoichiometric experiment was performed at 300 °C, using one gram of sample (96% enargite, 4% tennantite) and 100 mL of copper sulphate solution (10 gpl) at 1.2 pH. Enargite reacted completely after 80 min. A solid product was obtained and characterized by XRD. The main product was chalcocite (M) and some traces of djurleite and chalcocite (Q). Tennantite did not react under these conditions. The kinetic experiments were conducted at 140 °C, 190 °C, 250 °C and 300 °C. From fitted data and Arrhenius equation the calculated activation energy (Ea) was 51 kJ/mol. According to the hydrothermal transformations studied, the reactivity of different phases found in the copper concentrates was bornite > chalcopyrite > covellite > sphalerite > pyrite > enargite > tennantite.

Keywords Hydrothermal reactions · Enargite · Kinetic

Introduction

It is known the fact, that the copper sulfides as the first treatment option, obey the natural flotation and then as concentrates are send to the smelter where metallic copper is obtained separated from the slag through a high temperature treatment and the sulfur is expelled as sulfur dioxide.

It is also known that as time passes, the copper grades have decreased substantially while the impurities grades are increasing steadily. Impurities containing copper concentrates have already been described [1] containing mainly Cd, Zn, Tl, As, Sb, Bi, Pb, Te and others.

Arsenic is an impurity that is associated with copper minerals forming enargite, tennantite, tetrahedrite, and that due to the pyrometallurgical treatment either in

G. Fuentes (✉)
Hydrometallurgical Consultant, Antofagasta, Chile
e-mail: gerardoerasmofuentes@gmail.com

conversion or roasting furnaces, it goes into the atmosphere together with the sulfur dioxide. A great quantity of literature can be found to eliminate arsenic or try to separate arsenic from copper. Most of these researches are carried out through hydrometallurgical procedures and have as their main objective the dissolution of arsenic minerals. Thus we can find studies on arsenic leaching from concentrates where one of the early investigation appears between 60–95 °C, in acid medium and Fe^{3+} [2], other authors used chlorine/ chloride mixture [3], leaching with sodium hypochlorite in oxidizing media and the arsenic is dissolved like arseniate [4], slow ammoniacal leaching works [5], complete leaching of enargite over 170 °C in acidic sulfate and chloride media [6], at low temperatures of 130–160 °C incomplete reaction by elemental sulfur that prevents the enargite dissolution [7], being investigations at 220 °C and 100PSI in reactor with sulfuric acid deliver a complete dissolution [8], others studies between 160–200 °C adding pyrite to force a galvanic effect [9] and lately the leaching between 140–200 °C, with sulfuric acid and oxygen adding ferrous sulphate [10].

On the other hand, in the subject of bioxidation, efforts have been made to treat sulfide minerals with leptospirillum [11], minerals and concentrates with Fe^{3+} and sulfolobus [12] and enargite treated with mesophiles and thermophiles at high temperatures [13].

There are also reviews of treatment of concentrates with enargite under pressure [14] as recent trends in the processes of enargite concentrates [15]. This latter one, separates the processes of copper and arsenic leaching, with those of selective dissolution of arsenic.

However, the dissolution of minerals or concentrates with arsenic does not seem to be the solution since, as we have seen, there is a lot of literature on this subject and very few practical applications, being the pyrometallurgical procedures the ones that are mostly used, being the roast the one that occupies a place important at present, despite the emanations into the atmosphere.

The hydrothermal reaction process [16] allows selectively to pass the impurities to solution and concentrate the solid phase in copper which means a separation easily through a solid-liquid filtration.

There is not much literature that studies this problem. Previous work by the authors [17] demonstrated the separation of 30% of arsenic using this technique. Tennantite and tetrahedrite have not been fully studied, possibly requiring extreme conditions for their transformation.

Experimental

Materials

A sample of "enargite" from Huencavelica Peru, was used for the experiments. This is a enargite sample of quite purity (∼96% enargite, ∼4% tennantite), ground and

sieved to minus 15 μm. This sample was used in an experiment whose objective was to characterize the product of the total conversion as well set the overall stoichiometry of the reaction.

The sample was characterized by X Ray Diffraction, analyzed chemically and was also used in the kinetic experiments.

Autoclave Experiments

Experiments were performed in a Teflon-coated stainless steel PARR-4563 stirring reactor with a programmable heating controller. The stirring speed was 800 min^{-1} in all experiments. The system was raised to the working temperature at a rate of ~5 °C/min, then maintained at this temperature for a fixed time (nominal time), until it was cooled to the ambient temperature, again at a rate of ~5 °C/min. After this treatment, the pH and the solution volume were measured. Copper and arsenic in the final solution were determined by A.A.S. Residual solids were characterized by XRD, reflected-light microscopy and SEM/EDS.

The nature of the reaction of enargite with copper ions was investigated in the range 140–300 °C. 1 g of 15 < μm enargite particles was treated with 100 cm^3 of slightly acidified (H_2SO_4, pH 1.2) copper sulfate solutions of known concentrations. Under these conditions, there is sufficient Cu^{2+} excess to assume practically constant copper concentration, pH and solution volume.

Experiment of Complete Reaction

Sample: 1.00 g

Size < 15 micrometers

Temperature: 300 °C
Time: 1 h
Initial volume of solution: 100 mL
Initial Cu^{2+} concentration: 10 gpL (in sulphate of copper form).
Initial pH: 1.2
Initial ORP: 434 mV (vs. Ag/AgCl)
Final pH: 0.4
Final ORP: 368 mV(vs. Ag/AgCl)

The Kinetics of the Process Was Studied in the Range of 140–300 °C

For study of kinetic 0.400 g of the sample 1 for each experience, was used and 0.200 L of 10 gpL of Cu^{2+}, using a pH = 1,26 at initial time. Solutions after experiment were analyzed for arsenic, copper by AAS, and solid phases were analyzed for As and Cu by AAS. The solid products were also analyzed for XRD and SEM/EDS.

Results and Discussion

X Ray Diffraction Study

In Fig. 1 appears the patterns of the sample. Apart a small amount of tennantite-4% according quantitative phase analysis by XRD- no other impurity is detected.

Chemical Analysis Study

The composition of the sample and the theoretical enargite (Cu_3AsS_4) is showed in Table 1. The presence of small amounts of antimony replacing arsenic is
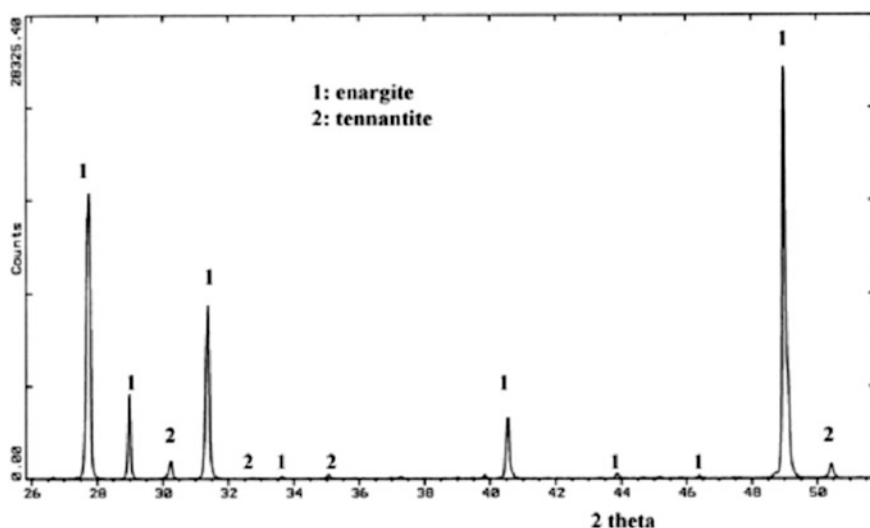

Fig. 1 XRD patterns of original sample

Table 1 Composition of sample and theoretical enargite

Element	Sample	Cu_3AsS_4
Cu	44.7	48.41
As	16.0	19.02
Sb	1.8	–
S	31.9	32.57

highlighted. The atomic relation Cu/(As + Sb) is equal to 3.08. This value is consistent, within experimental error, with the atomic relation of enargite. The molar relation Sb/As in the enargite used is 0.07.

Hydrothermal Treatment Results in Stoichiometry Experiment

The solid product of the hydrothermal reaction to complete conversion of enargite is, essentially, chalcocite-(M) Cu_2S. Only traces of djurleite and chalcocite (Q) are detected. Figure 2 shows XRD patterns of the final product compared with the initial sample. Note the complete reaction of enargite and no reaction of tenantite. The XRD patterns intensity scale of the final product has been expanded in order to observe clearly the products formed which implies, obviously, to increase the intensity of peaks of non reactioned tennatite.
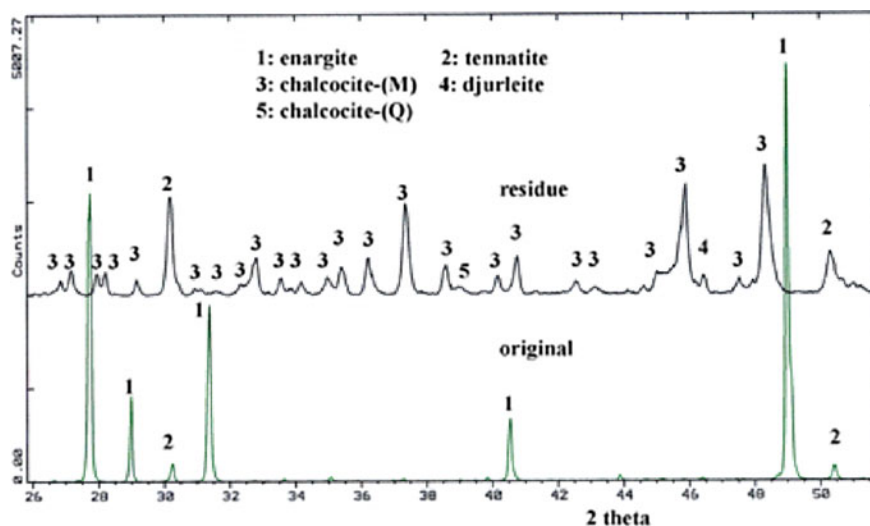

Fig. 2 XRD patterns of product from complete reaction of enargite, compared with original enargite

The results of experiment indicates 3.5 mol of Cu consumption from solution by mol of arsenic reactioned, that is approximately by mol of enargite reactioned. Also indicate the appearance of 0.79 mol of sulphate in solution by mol of enargite reactioned. The relation Sb/As in solution is 0.09, near to relation of 0.07 contained in initial enargite. This indicate that Sb from enargite passes also into solution besides the As.

Kinetics Experiments

Experimental results are presented in Table 2, at four temperature levels (140, 190, 250, 300 °C) and operating in steady state condition for 30, 60 and 90 min. These times were adjusted in Table 2 according to the necessary times to reach the working temperatures.

In Fig. 3, the extraction kinetic is plotted. The resultant plot corresponds to a 11 independent tests.

There is a significant effect of temperature on the arsenic extraction, and therefore the activation energy can be calculated from the Arrhenius equation. The reaction formed irregular thicks layers of product. This experimental observation indicates a kinetic control by solid layer diffusion. Consequently, kinetic data is modeled with the following shrinking core model:

$$F(\alpha) = 1 - (2/3\alpha) - (1 - \alpha)^{2/3} = k\,ex \tag{1}$$

and

$$k\,ex = k_{PL}/r_o^2 \tag{2}$$

where α is the fraction reacted of Enargite, t the time, $k\,ex$ the experimental rate constant, r_o the initial particle radius and k_{PL} the rate constant for product-layer diffusion control.

Table 2 Arsenic conversion

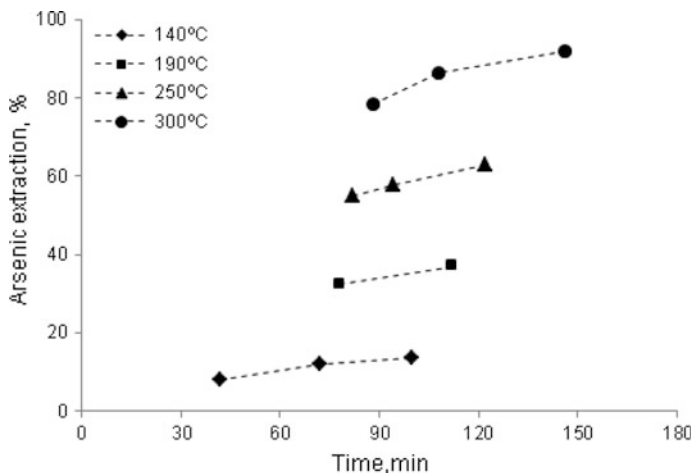| 140 °C		190 °C	
Time (min)	Conversion (%)	Time (min)	Conversion (%)
42	8.1	50	n/a
72	11.9	78	32.5
100	13.5	112	36.9
250 °C		300 °C	
Time (min)	Conversion (%)	Time (min)	Conversion (%)
82	55.1	88	78.6
94	57.8	108	86.4
122	63.0	146	91.9

Fig. 3 Kinetics of arsenic extraction

Temperature Effect

The temperatures studied were 140, 190, 250, 300 °C. The experimental condition were fixed to [Cu^{2+}] 5 g/L, pH 1.3–1.1, *p80* = 15 μm. Figure 4, illustrates the effect of temperature on kinetics, piloted as F(α) v/s time at four levels of temperature.

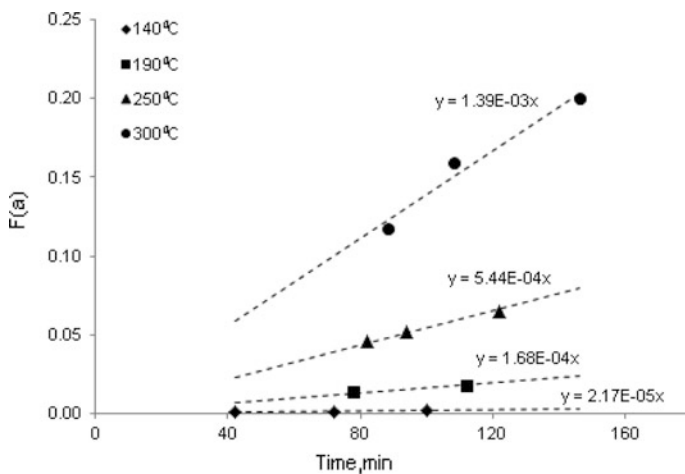F(a) is plotted to facilitate parameter estimation in an non explicit equation for conversion v/s time
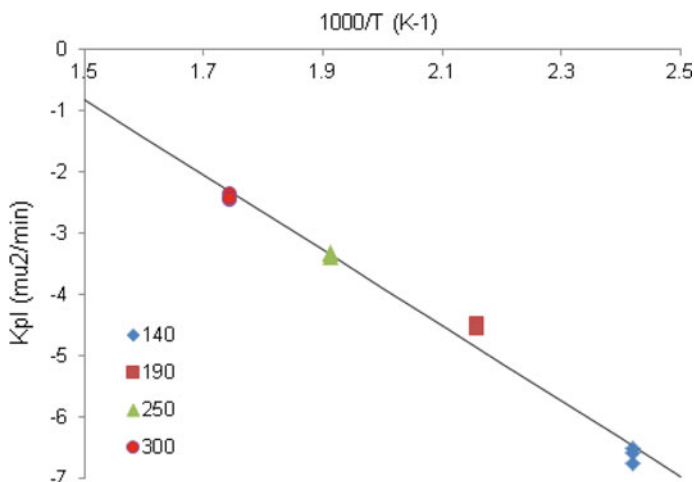

Fig. 4 F(α) v/s time

Fig. 5 Arrhenius plot

The Arrhenius plot is presented in Fig. 5. where Kpl is calculated from Kexp divided by square radius (7.5 microns), while K exp is obtained from F(α) divided by reaction time in minutes. For convenient representation it is plotted 1000 over temperature (Kelvin) v/s natural logarithm of KpL, The slope of the curve represented Activation Energy divided by gas constant, in this case Activation Energy is derived directly from the slope in KJ/mol.

The obtained activation energy in the interval 140°–300 °C was 51 kJ/mol, a value that through of an electrochemical model, can explains the hydrothermal conversion of the enargite [18].

Conclusions

According the stoichiometry experiment, Enargite reacted completely after 80 min. A solid product was obtained and characterized by XRD, and the main product was chalcocite (M) and some traces of djurleite and chalcocite (Q).

Experimental stoichiometry of the reaction is consistent with the Cu_2S formation and the step of As passing to As(III).

DRX study confirm that tennantite it is not apreciable attacked.

From fitted data of the kinetics experiment and Arrhenius equation the calculated activation energy (Ea) was 51 kJ/mol.

According to the hydrothermal transformations studied, the reactivity of different phases found in the copper concentrates was bornite > chalcopyrite > covellite > sphalerite > pyrite > enargite > tennantite.

References

1. Viñals J et al (2003) Topochemical transformation of enargite into copper oxide by hypochlorite leaching. Hydrometallurgy 68(1–3):183–193
2. Dutrizac J, Mac Donald R (1972) The kinetics of dissolution of enargite in acidified ferric sulphate solutions. Can Metall Q 11(3):469–476
3. Herreros O, Fuentes G, Quiroz R, Viñals J (2003) Lixiviación de concentrados de cobre con alto contenido de arsénico en medio cloro/cloruro. Revista de Metalurgia 39:90–98 (in spanish)
4. Curreli L et al (2005) Beneficiation of a gold bearing enargite ore by flotation and As leaching with Na hypochlorite. Miner Eng 18(8): 849–854
5. Gajam S, Raghavan S (1983) A kinetic study of enargite dissolution in ammoniacal solutions. Int J Miner Process 10:113–129
6. Riveros P, Dutrizac J, Spencer P (2001) Arsenic disposal practices in the metallurgical industry. Can Metall Q 40(4):395–420
7. Riveros P, Dutrizac J (2008) The leaching of tennatite, tetrahedrite and enargite in acidic sulphate and chloride media. Can Metall Q 47(3):235–244
8. Padilla R, Rivas C, Ruiz MC (2008) Kinetics of pressure dissolution of enargite in sulphate-oxygen media. Metall Mater Trans B 39(3):399–407
9. Ruiz MC, Vera M, Padilla R (2011) Mechanism of enargite pressure leaching in the presence of pyrite. Hydrometallurgy 105(3–4) (January): 290–295. https://doi.org/10.1016/j.hydromet.2010.11.002
10. Padilla R, Jerez O, Ruiz MC (2015) Kinetics of the pressure leaching of enargite in $FeSO_4$-H_2SO_4-O_2 media. Hydrometallurgy 158:49–55
11. Watling H (2006) The bioleaching of sulfide minerals with emphasis on copper sulfides-a review. Hydrometallurgy 84:81–108
12. Escobar B, Huenupi E, Godoy I, Wiertz J (2000) Arsenic precipitation in the bioleaching of enargite by Sulfolobus BC at 70 °C. Biotechnol Lett 19(8):719–722
13. Muñoz J et al (2006) Electrochemical study of enargite bioleaching by mesophilic and thermophilic microorganisms. Hydrometallurgy 84(3–4):175–186
14. Kimberley C, Anderson C (2013) Enargite treatments and pressure oxidation of concentrates. J Metall Eng (ME) 2(4):115–123
15. Safarzadeh S et al (2014) Recent trends in the processing of enargite concentrates. Miner Process Extr Metall Rev 35(5):283–367. https://doi.org/10.1080/08827508.2012.723651
16. Viñals J, Fuentes G, Hernandez MC, Herreros O (2004) Transformation of sphalerite particles into copper sulfide particles by hydrothermal treatment with Cu(II) ions. Hydrometallurgy 75:177–187
17. Fuentes G, Viñals J, Herreros O (2009) Hydrothermal purification and enrichment of Chilean copper concentrates. Part 2: The behaviour of the bulk concentrates. 95:113–120
18. Jang JH, Wadsworth ME (1994) Kinetics of hydrothermal enrichment of chalcopyrite, vol 550. ACS Symposium Series, pp 45–58