Thermodynamic Analysis of the Cu-As-S-(O) System Relevant to Sulfuric Acid Baking of Enargite at 473 K (200 °C)

M. SADEGH SAFARZADEH, JAN D. MILLER, and HSIN H. HUANG

While the growing demand for copper has compelled the industry to adapt new technologies for the treatment of copper-arsenic (enargite) concentrates, the refractory nature of such concentrates combined with the troublesome presence of arsenic has created a major metallurgical and environmental challenge. Preliminary results of the acid bake-leach process at the University of Utah have shown some potential advantages for the treatment of enargite concentrates. While the transformation of enargite to copper sulfate, arsenolite, and elemental sulfur has already been established experimentally, thermodynamic evaluation of the sulfuric acid baking process provides further understanding which should be useful. In this article, the available thermodynamic data for the species involved in the Cu-As-S-O system are compiled. These data were used to calculate the phase stability (Kellogg) diagrams as well as equilibrium compositions at 473 K (200 °C) using the STBCAL and HSC Chemistry® 5.1 software packages. The equilibrium composition calculations indicate that enargite can transform to copper sulfate either directly or through chalcocite and/or covellite. The major gaseous species during baking were found to be SO₂ and H₂O. The results of the thermodynamic calculations were further compared with two confirmatory baking experiments involving a high-quality enargite sample. The condensed reaction products from sulfuric acid baking based on XRD results include CuSO₄, As₂O₃, CuO-CuSO₄, and S₈ under both neutral and oxidative conditions. While all these compounds were predicted through equilibrium calculations, some of the predicted compounds were not detected in the sulfuric acid-baked enargite. None of the calculations indicated any appreciable amounts of arsenic-bearing gases at the baking temperature of 473 K (200 °C). Consistent with thermodynamic predictions, no H₂S gas was detected during the sulfuric acid baking experiment. Approximately, 80 pct of the baked enargite samples were leached in water.

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I. INTRODUCTION

THE elevated amount of arsenic found in some of the important copper deposits has rendered these resources to be of lower economic value. The increasing demands for copper and gold have prompted the metallurgical industry to develop sustainable processing options for challenging Cu-As ores/concentrates, notably for ores containing enargite (Cu₃AsS₄). Significant developments have been reported in the flotation separation of enargite-bearing ores with the purpose of producing a “clean” copper concentrate with less than 0.5 pct arsenic for smelting. However, now it seems that the time has come for the processing of high-arsenic “dirty” copper concentrates. To that end, there is going to be increasing interest in the treatment of Cu-As concentrates includ-

ing enargite and tennantite (Cu₁₂As₄S₁₃). Not only do these minerals contain more copper than chalcopyrite (48.4 pct in enargite and 51.5 pct in tennantite), but their concentrates also contain more gold than the chalcopyrite concentrates. There has been a dearth of literature on the treatment of Cu-As ores until about the year 2000, after which research activities have been intensified to design strategies to treat these problematic ores/concentrates. Interestingly, the entire body of enargite research published recently is the continuation of studies performed in the 1970s and 1980s. For example, development of alkaline sulfide leaching, pressure leaching, and roasting strategies for the treatment of enargite concentrates have been considered for some time.

A few thermodynamic studies of the Cu-As-S-(O) system have been reported, with little experimental validation of the theoretical calculations. Five well-known ternary compounds in the Cu-As-S system have been reported. These compounds include Cu₃AsS₄ with its high-temperature form (enargite) and the low-temperature form (luzonite), with the transition temperature between the two being in the range from 548 K to 573 K (275 to 300 °C). Other compounds include Cu₄As₂S₅, Cu₁₂As₄S₁₃ (tennantite), Cu₆As₄S₉ (sinnerite), and CuAsS (lautite). Not only are these compounds rich in copper, but also they are functional materials with

M. SADEGH SAFARZADEH, Ph.D. Candidate, and JAN D. MILLER, Professor, are with the Department of Metallurgical Engineering, College of Mines and Earth Sciences, University of Utah, 135 South 1460 East, Room 412, William C. Browning Building, Salt Lake City, UT 84112-0114. Contact e-mail: jan.miller@utah.edu
HSIN H. HUANG, Professor, is with the Department of Metallurgical and Materials Engineering, Montana Tech of the University of Montana, 215 ELC Building, 1300 West Park Street, Butte, MT 59701-8997.

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semiconducting and photoelectric properties.^[1] Babanly *et al.*^[1] estimated the standard Gibbs free energies of the formation of these compounds from electrochemical measurements using solid electrolytes. These values are tabulated in Table I.

The recent reviews on the treatment of enargite concentrates^[2,3] indicate that both conventional hydro-metallurgical and pyrometallurgical options fail to meet the required techno-economical and environmental criteria for the processing of enargite concentrates. While the only viable hydrometallurgical technique for the leaching of enargite appears to be pressure leaching (with all its complexities), generally the roasting of enargite does not expel all of the arsenic from the concentrate, contaminating smelting and electrorefining streams.

In keeping with the goal of effective copper recovery and minimum arsenic emission problems, a pyro-hydro-metallurgical treatment option was developed at the University of Utah, which renders the enargite water soluble while keeping most of the arsenic in solution. The process includes the baking of enargite concentrate with sulfuric acid at a low temperature [473 K (200 °C)], which transforms the enargite to copper sulfate and arsenic trioxide, followed by water leaching, which releases copper, arsenic, and iron into the solution. The details of the process can be found elsewhere.^[4–6]

A sound understanding of the thermodynamics of the sulfuric acid baking reaction is required to explain the observed experimental results. Thermodynamic information for Cu-As-S system in general, and for enargite in particular, has not been given much attention in the literature. Only two authors have independently reported the thermodynamic values for enargite. The first and the most reliable information was published by Craig and Barton,^[7] who estimated the values based on the studies of Wernik and Benson^[8] and Maske and Skinner,^[9] followed by the study of Seal II *et al.*^[10] who measured the heat capacity of enargite experimentally. Most researchers use the information from either of the mentioned articles to estimate the free energy of formation for enargite. It should be noted that tennantite (Cu₁₂As₄S₁₃) and sinnerite (Cu₆As₄S₉) are the other copper-arsenic sulfosalts that have been mentioned in the literature, with the former one being the second most abundant copper-arsenic feedstock in the copper industry. Listed in Table II is a summary of the thermodynamic information for enargite, tennantite, and sinnerite in chronological order. Taking into account the accuracy of the thermodynamic information, the data provided by Craig and Barton^[7] will be used in all our calculations.

Table I. Standard Gibbs Free Energies of Formation for the Compounds in the Cu-As-S System^[1]

Compound	ΔG_f° (kJ/mol)
Cu ₃ AsS ₄	-179.2 ± 0.6
Cu ₆ As ₄ S ₉	-429.4 ± 1.2
Cu ₄ As ₂ S ₅	-257.8 ± 0.8
Cu ₃ AsS ₃	-170.2 ± 0.6
CuAsS	-65.5 ± 0.3

These data were incorporated into the database of HSC Chemistry[®] 5.1^[12] and also STABCAL^[13] software for subsequent calculations. In view of the possible reactions that might occur during the sulfuric acid baking process, it is appropriate to see if the proposed reactions are thermodynamically favorable. To that end, a series of sulfuric acid baking reactions were proposed based on preliminary experimental results and also based on the results reported by Prater *et al.*^[14] The standard free energies of formation for the compounds involved in the reactions were obtained from HSC Chemistry[®] 5.1 software. Then, the standard free energies of reactions (ΔG_r°) at 298 K and 473 K (25 °C and 200 °C) (the latter one being the typical baking temperature) were calculated. The results are listed in Table III (Reactions [1] to [21]).

Reactions [2] and [3] represent the oxidation of enargite in an oxygen atmosphere. These reactions are highly exothermic. In terms of acid baking reactions, the most favorable reaction appears to be Reaction [4], where in the presence of oxygen, enargite converts into copper sulfate, arsenic trioxide, water, and sulfur dioxide. While oxygen favors the baking reaction to a great extent, the reaction can proceed in the absence of oxygen, as observed in Reactions [1] and [5]. In this case, the reaction is not favorable at room temperature, and therefore increasing the temperature is necessary.

Considering H₂S (g) as a reaction product, Reactions [7], [11], and [14] may be written. However, it is noted that none of these reactions is expected either at room temperature or at higher temperatures. According to Reactions [9] and [10], in the absence of oxygen, the production of S₂ (g) is not favorable but in the presence of oxygen, it is highly favorable (Reaction [12]). The generation of SO₃ (g) as a gaseous reaction product may be favored only in the presence of oxygen (Reactions [13] to [15]).

The key role of SO₃ (g) in the sulfation roasting of metal sulfides has been well established.^[15–17] One way to increase the partial pressure of SO₃ (g) in the roaster is through the introduction of sulfuric acid solution that will be decomposed at high temperatures and will generate SO₃ (g) according to the following reaction:

Reaction [22] is highly endothermic ($\Delta H_r^{298\text{K}(25^\circ\text{C})} = 132.39$ kJ/mol, $\Delta H_r^{473\text{K}(200^\circ\text{C})} = 129.35$ kJ/mol). $\Delta G_r^{473\text{K}(200^\circ\text{C})}$ is 52.77 kJ/mol, with ΔG_r° starting to become negative at 803 K (530 °C). Therefore, the minimum temperature of 803 K (530 °C) is necessary to get the benefit of Reaction [22]. This means that SO₃ (g) generated from the sulfuric acid decomposition may not contribute to the sulfuric acid baking reaction. However, there is another source of SO₃ (g) according to Reaction [23]:

This reaction is highly exothermic ($\Delta H_r^{473\text{K}(200^\circ\text{C})} = -198.34$ kJ/mol, $\Delta G_r^{473\text{K}(200^\circ\text{C})} = -108.74$ kJ/mol) below 773 K (500 °C). On the other hand, this reaction

Table II. Summary of Thermodynamic Information for Enargite

Mineral	Thermodynamic Function					ΔG° (T)	Temperature Range [K (°C)]	Reference
	ΔS_m^{298K} (25°C) (J mol ⁻¹ K ⁻¹)	ΔH_m^{298K} (25°C) (kJ mol ⁻¹)	$C_{p,m}^\circ(T) = a + 10^{-3}bT - 10^5cT^{-2}$ (J mol ⁻¹ K ⁻¹)					
			a	b	c			
Enargite (Cu ₃ AsS ₄)	—	—	—	—	—	-104,458 + 56.16T (cal mol ⁻¹)	298 to 873 (25 to 600)	[7]
Tennantite (Cu ₁₂ As ₄ S ₁₃)	—	—	—	—	—	-355,468 + 172.28T (cal mol ⁻¹)	298 to 873 (25 to 600)	[7]
Sinnerite (Cu ₆ As ₄ S ₉)	—	—	—	—	—	-236,340 + 136.83T (cal mol ⁻¹)	298 to 762 (25 to 489)	[7]
Enargite (Cu ₃ AsS ₄)	—	—	—	—	—	-437,160 + 235.0T (J mol ⁻¹)	298 to 873 (25 to 600)	[11]
Enargite (Cu ₃ AsS ₄)	257.7	37.4	196.7±1.2	49.9±1.6	19.18±0.84	—	298 to 944 (25 to 671)	[10]

is very slow at low temperatures, requiring catalysis to achieve acceptable rates of SO₃ (g) generation from SO₂ (g), and O₂ (g) mixtures.^[16] This situation is further demonstrated by looking at the equilibrium composition of sulfuric acid as a function of temperature (Figure 1), using the equilibrium module of the HSC Chemistry[®] 5.1 software. While no significant amount of SO₃ (g) is generated below 573 K (300 °C), the maximum amount of SO₃ (g) is found in the temperature range from 723 K to 773 K (450 °C to 500 °C), after which SO₃ (g) starts to decompose into SO₂ (g) and O₂ (g).

Therefore, it is less likely that SO₃ (g) can play a role in the sulfuric acid baking of enargite through this mechanism. Having said that, the effect of SO₃ (g) in the sulfation of enargite may not be ruled out, as described by Reactions [16] to [21]. In fact, these reactions are all highly favorable, considering the variety of reaction products. More importantly, Reactions [18] to [20] could resemble the baking of enargite with oleum, which is obtained by dissolving different amounts of SO₃ (g) in 100 pct sulfuric acid. If sufficient amounts of H₂S gas are generated in the baking reaction, then it can be used to produce elemental sulfur through the Claus process (Reaction [24]).^[18]

In view of the foregoing, the purpose of this article is to evaluate these enargite and associated reactions using phase stability diagrams and also equilibrium composition calculations. Finally, the results from two sulfuric acid baking experiments under neutral and oxidative atmospheres are reported to evaluate the credibility of the thermodynamic analysis.

II. METHODS AND MATERIALS

Thermodynamic calculations were performed using HSC Chemistry[®] 5.1 and also STABCAL software with a careful collection of the most reliable thermodynamic information for the species involved in the reactions. Most of the phase stability diagrams were constructed using STABCAL software unless otherwise stated. All the equilibrium calculations were performed using the free energy minimization module of the HSC Chemistry[®] 5.1 software. Both these softwares are available at the University of Utah. All calculations were performed in the absence and the presence of oxygen.

To confirm the results of the thermodynamic calculations, two baking experiments were performed. A high-quality enargite specimen from Butte, Montana, USA was purchased. Then, it was crushed and ground manually using a ceramic mortar and pestle, to avoid iron contamination from ball milling. The ground enargite was characterized using X-ray diffraction (XRD) and electron microprobe analysis (EMPA) methods. For EMPA and also optical microscopy (OM), the enargite powder was mounted in epoxy, polished to an extremely fine surface, and carbon coated. An optical image of the polished section is shown in Figure 2, which shows no impurity minerals are observed within the enargite particles.

Table III. Proposed Reactions for the Sulfuric Acid Baking of Enargite

Reaction Number	Reaction	$\Delta G_r^{\circ, 298\text{K}} (25^\circ\text{C})$ (kJ/mol)	$\Delta G_r^{\circ, 473\text{K}} (200^\circ\text{C})$ (kJ/mol)
1	$2\text{Cu}_3\text{AsS}_4 + 3\text{H}_2\text{SO}_4 = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 3\text{H}_2\text{O} + 33\text{SO}_2 (\text{g})$	6.621	-947.815
2	$2\text{Cu}_3\text{AsS}_4 + 15.5\text{O}_2 (\text{g}) = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 2\text{SO}_2 (\text{g})$	-4726.514	-4269.112
3	$2\text{Cu}_3\text{AsS}_4 + 13.5\text{O}_2 (\text{g}) = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 2\text{S}$	-4126.328	-3667.262
4	$4\text{Cu}_3\text{AsS}_4 + 3\text{H}_2\text{SO}_4 + 15.5\text{O}_2 (\text{g}) = 12\text{CuSO}_4 + 2\text{As}_2\text{O}_3 + 3\text{H}_2\text{O} + 35\text{SO}_2 (\text{g})$	-4719.89	-5216.93
5	$2\text{Cu}_3\text{AsS}_4 + 27\text{H}_2\text{SO}_4 = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 27\text{H}_2\text{O} + 27\text{SO}_2 (\text{g}) + 2\text{S}$	-3.920	-774.520
6	$2\text{Cu}_3\text{AsS}_4 + 2\text{H}_2\text{SO}_4 + 12.5\text{O}_2 (\text{g}) = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 2\text{SO}_2 (\text{g}) + 2\text{H}_2\text{O} + 2\text{S}$	-3820.964	-3452.985
7	$2\text{Cu}_3\text{AsS}_4 + 6.75\text{H}_2\text{SO}_4 = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 6.75\text{H}_2\text{S} (\text{g}) + 2\text{S}$	305.673	237.877
8	$2\text{Cu}_3\text{AsS}_4 + 9\text{H}_2\text{SO}_4 = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 9\text{H}_2\text{O} + 11\text{S}$	-51.356	5.310
9	$2\text{Cu}_3\text{AsS}_4 + 9\text{H}_2\text{SO}_4 = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 9\text{H}_2\text{O} + 5.5\text{S}_2 (\text{g})$	386.974	295.622
10	$2\text{Cu}_3\text{AsS}_4 + 10.333\text{H}_2\text{SO}_4 = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 10.333\text{H}_2\text{O} + 5.167\text{S}_2 (\text{g}) + 2\text{SO}_2 (\text{g})$	363.757	220.077
11	$2\text{Cu}_3\text{AsS}_4 + 8.333\text{H}_2\text{SO}_4 = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 6.333\text{H}_2\text{O} + 4.167\text{S}_2 (\text{g}) + 2\text{H}_2\text{S} (\text{g})$	386.334	293.967
12	$2\text{Cu}_3\text{AsS}_4 + 2\text{H}_2\text{SO}_4 + 10.5\text{O}_2 (\text{g}) = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{S}_2 (\text{g})$	-3061.386	-2745.567
13	$2\text{Cu}_3\text{AsS}_4 + 2\text{H}_2\text{SO}_4 + 13.5\text{O}_2 (\text{g}) = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 2\text{SO}_3 (\text{g}) + 2\text{H}_2\text{O} + 2\text{S}$	-3962.802	-3561.728
14	$2\text{Cu}_3\text{AsS}_4 + 8.25\text{H}_2\text{SO}_4 = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 8.25\text{H}_2\text{S} (\text{g}) + 2\text{SO}_3 (\text{g})$	548.538	395.093
15	$2\text{Cu}_3\text{AsS}_4 + 11\text{H}_2\text{SO}_4 = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 11\text{H}_2\text{O} + 5.5\text{S}_2 (\text{g}) + 2\text{SO}_3 (\text{g})$	550.500	401.156
16	$2\text{Cu}_3\text{AsS}_4 + 3\text{SO}_3 (\text{g}) = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 3\text{SO}_2 (\text{g})$	-2528.031	-2583.597
17	$2\text{Cu}_3\text{AsS}_4 + 27\text{SO}_3 (\text{g}) = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 27\text{SO}_2 (\text{g}) + 2\text{S}$	-2211.521	-2199.233
18	$2\text{Cu}_3\text{AsS}_4 + 25\text{SO}_3 (\text{g}) + 2\text{H}_2\text{O} = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 25\text{SO}_2 (\text{g}) + 2\text{H}_2\text{S} (\text{g})$	-1945.722	-1967.025
19	$2\text{Cu}_3\text{AsS}_4 + 6.75\text{SO}_3 (\text{g}) + 6.75\text{H}_2\text{O} = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 6.75\text{H}_2\text{S} (\text{g}) + 2\text{S}$	-246.227	-118.301
20	$2\text{Cu}_3\text{AsS}_4 + 7.25\text{SO}_3 (\text{g}) + 5.25\text{H}_2\text{O} = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 5.25\text{H}_2\text{S} (\text{g}) + 2\text{S}_2 (\text{g})$	-207.056	-90.799
21	$2\text{Cu}_3\text{AsS}_4 + 23\text{SO}_3 (\text{g}) = 6\text{CuSO}_4 + \text{As}_2\text{O}_3 + 21\text{SO}_2 (\text{g}) + 2\text{S}_2 (\text{g})$	-1735.617	-1709.301

Fig. 1—The distribution of species at equilibrium as a function of temperature representing the heating of sulfuric acid under neutral conditions (input: 1 kmol sulfuric acid, total pressure: 1 bar).

Fig. 2—Polished surface of the high-quality enargite particles (100 $\times$).

The XRD spectrum of the enargite powder obtained using a Rigaku D-Max 2000 model confirmed that enargite is the only major mineral present in the sample (Figure 3).

EMPA analysis, using a Cameca-SX50 machine, from four different locations on the sample indicated that the sample composition is uniform and very close to the ideal composition of enargite (48.41 pct Cu, 19.02 pct As, and 32.57 pct S) with very good repeatability. As with most of the enargite specimens, there is some antimony in this enargite sample, ~2 pct. The detailed results are listed in Table IV.

A $-150 + 106 \mu\text{m}$ portion of the ground enargite was prepared by screening using standard sieves. This size fraction was used in the baking experiments. The sample contained ~41.5 pct Cu and ~13.86 pct As, based on wet

chemical assay. The first baking experiment was performed in a muffle furnace (Barnstead Thermolyne 1300 model) to examine the effect of oxygen on the oxidation of enargite. The second experiment was performed in a standard tube furnace (Thermolyne 21100 model), connected to a nitrogen gas cylinder equipped with flow meters. A Pyrex glass tube (76 $\times$ 5 cm) was used to allow for observation during the reaction. In both furnaces, the temperature was controlled within $\pm 1^\circ\text{C}$. Analytic grade sulfuric acid (Mallinckrodt Chemicals, 95 to 98 pct) was used in the baking experiments. Both experiments were performed at a constant temperature of 473 K (200 $^\circ\text{C}$).

A porcelain crucible (diameter $\times$ height: 42 $\times$ 35 mm) was used for the muffle furnace experiment. The distance between the thermocouple and the surface of material was about 5 cm. Approximately 2 g of enargite powder was weighed and mixed with ~3.3 g of sulfuric acid and thoroughly mixed in the crucible. The crucible was weighed and transferred to the muffle furnace, which was preheated to the desired temperature. There was no atmosphere control, and the baking was done open to the ambient atmosphere. After 7 hours of baking, the crucible was taken out of the muffle furnace and cooled down in the ambient atmosphere to room temperature and weighed out. The baking time of 7 hours and the baking temperature of 473 K (200 $^\circ\text{C}$) were selected based on our experimental results published earlier,^[4] where it was established that under similar experimental conditions, the extractions of copper and arsenic upon water leaching did not change by baking the enargite concentrate for more than 6 hours. The baked material was removed from the crucible and ground using a mortar and pestle. A sample was taken for XRD.

In the tube furnace experiment, a porcelain boat (length $\times$ height $\times$ width: 100 $\times$ 15 $\times$ 10 mm) was employed. The thermocouple tip was placed right above the material's surface in the boat. Approximately 2 g of enargite powder was weighed and mixed with ~3.3 g of sulfuric acid and thoroughly mixed in the boat. Then, the boat was weighed and transferred to the tube

Fig. 3—XRD spectrum of the high-quality enargite specimen (scan rate 2 deg/min).

Table IV. EMPA Results for the High-quality Enargite Sample Used in the Current Study (Accelerating Voltage: 15 keV, Current: 30 nA, Beam Size: 10 μ m)

Spot No.	Wt pct Elements				Totals
	Cu	As	Sb	S	
1	47.5	18.8	0.55	32.1	99.1
2	47.9	18.2	1.50	31.6	99.1
3	47.8	17.1	2.57	31.6	98.9
4	47.5	16.8	3.57	31.5	99.2
Average	47.67	17.72	2.047	31.70	99.07

furnace, which was preheated to the desired temperature. The experiment was performed under a flow of nitrogen (flow rate $\sim$ 340 mL/min) to provide an oxygen-free atmosphere. Lead acetate test papers (Fisher Scientific) were used inside the tube to detect for the formation of H_2S gas. At the end of the experiment, the elemental sulfur formed inside the tube was rinsed with carbon disulfide (HPLC grade, Alfa Aesar). After 7 hours of baking, the sample was cooled down to room temperature under the flow of nitrogen to prevent any oxidation reactions at high temperatures outside the furnace. The baked material was removed from the boat and ground using a pestle and mortar. A sample was taken for XRD.

The baked and ground enargite samples from both experiments were subjected to two two-step leaching experiments. In the first leaching step, $\sim$ 2 g portions of the baked and ground enargite samples were leached in about 160 mL DI water. The water leaching experiments were performed in a 500 mL Erlenmeyer flask. The samples were leached for 45 minutes at 343 K (70 $^\circ\text{C}$) using a stirring speed of 400 rpm. At the end of each leaching experiment, the suspension was filtered, and solid residues were rinsed with DI water, and dried in a furnace at 343 K (70 $^\circ\text{C}$) over night. The residues were then weighed. The dried leach residues were then taken to a second leach step in 0.5 M sulfuric acid to ensure complete dissolution of soluble components. All other leaching conditions were the same as the first

water leaching step. The leach residues from the second leaching experiments were rinsed with DI water, dried, weighed, and sampled for XRD.

III. RESULTS AND DISCUSSION

A. Phase Stability and Equilibrium Composition Diagrams

The phase stability diagrams for the Cu-As-S system at 473 K (200 $^\circ\text{C}$) are constructed under neutral conditions. While enargite, tennantite, and sinnerite are the three copper-arsenic sulfosalts considered in constructing these diagrams, the phase sinnerite has not been reported to exist in copper-arsenic feedstocks or otherwise formed as an intermediate phase during the thermal treatment of enargite in neutral and oxidative atmospheres. This could be due to the rapid formation and transition of sinnerite that does not allow for identification at room temperature.

1. Cu-As-S system

The phase stability diagram for the Cu-As-S system at 473 K (200 $^\circ\text{C}$) (Figure 4(a)) indicates that enargite could be at equilibrium with sinnerite, tennantite, covellite (CuS), and chalcocite (Cu_2S), depending on the partial pressure of S_2 (g) and As_4 (g). The relative amount of these phases as a function of temperature can be calculated by a free energy minimization program

(a)

(b)

(c)

Fig. 4—(a) Predominance area (Kellogg) diagram for the system Cu-As-S at 473 K (200 °C) (S_2 vs As_4), (b) equilibrium composition as a function of temperature for enargite in a neutral atmosphere (input: 1 kmol enargite, total pressure: 1 bar), and (c) predominance area (Kellogg) diagram for the system Cu-As-S at 473 K (200 °C) (S_2 vs As_2S_3). Mineral key: CuS = covellite, Cu_2S = chalcocite, Cu_3AsS_4 = enargite, $Cu_{12}As_4S_{13}$ = tennantite, $Cu_6As_4S_9$ = sinnerite, and Cu_3As = domeykite.

Fig. 5—The equilibrium composition as a function of temperature for enargite in oxidative atmospheres (input: 2 kmol enargite, 5 kmol O_2 , and total pressure: 1 bar).

such as SOLGASMIX^[19] that is used to calculate the equilibrium composition for multiphase systems.^[17] The result of such a calculation for enargite is shown in Figure 4(b). According to Figure 4(b), major decomposition of enargite starts at around 673 K (400 °C) with the most dominant gas species being S_2 and As_2S_3 . These results indicate that a more accurate phase stability diagram should be built considering these gaseous species as the major gaseous products of roasting in neutral atmospheres. The resulting phase stability diagram is shown in Figure 4(c), which indicates a greater stability domain for covellite than for chalcocite, being opposite to the trend observed in Figure 4(a). It is postulated from Figure 4(b) that at 473 K (200 °C), enargite converts into CuS, AsS, and Cu_2S as the major conversion products.

2. Cu-As-S-O system

The direct application of Kellogg diagrams to explain the enargite-sulfuric acid system is not possible because such diagrams are built for solid-gas systems. However, the study of the Cu-As-S-O system can provide some useful information for the sulfuric acid baking reaction. Considering this fact, constructing Kellogg diagrams for a quaternary system such as Cu-As-S-O at 473 K (200 °C) is complex. In fact, such a diagram would be an isothermal section of the Cu-As-S-O system at a constant molar ratio of Cu/As. Therefore, the equilibrium compositions in the Cu-As-S-O system will be discussed. Figure 5 shows the equilibrium composition of enargite in oxidative atmospheres. When the molar ratio of oxygen/enargite is 2.5, enargite can completely react at temperatures less than 501 K (228 °C) to give CuS, SO_2 (g), As_2O_3 (A)-Arsenolite, As_4O_6 , $CuSO_4$, and Cu_2S . While the formation of copper sulfate is favored at temperatures below ~463 K (190 °C), the formation of solid arsenic oxides (As_2O_3 (A) and As_4O_6) is expected at temperatures up to ~598 K (325 °C). Higher temperatures result in increased formation of chalcocite

and a reduction in the formation of covellite. At this specific oxygen potential, the only arsenic-bearing gas evolved from the oxidation process is As_4O_6 (g), which starts to form in significant amounts at ~523 K (250 °C).

To examine the effect of oxygen potential on the oxidation of enargite, the equilibrium state was established as a function of the oxygen potential at a constant temperature of 473 K (200 °C) (Figure 6). According to Figure 6, complete reaction of enargite at 473 K (200 °C) would require an oxygen/enargite molar ratio of at least 2.5, after which copper sulfate starts to form. Chalcocite starts to take over covellite at oxygen/enargite molar ratios greater than 3. The major arsenic species in the product are As_2O_3 (A) and As_4O_6 up to an oxygen/enargite molar ratio of greater than ~2.5, after which they decrease owing to the formation of the solid phase $Cu(AsO_2)_2$. The major gaseous reaction product is SO_2 which continues to form up to an oxygen/enargite molar ratio of ~8, after which SO_3 starts to predominate. Based on the information obtained from Figures 5 and 6, enargite can theoretically be completely oxidized to produce a variety of reaction products, depending on the conditions, specifically temperature and oxygen potential. Of course, these diagrams provide no information regarding the kinetics of enargite oxidation.

It is evident that effective conversion of enargite to copper sulfate requires a very high oxygen/enargite molar ratio. Also the formation of copper sulfate and arsenic oxides is highly favorable and can be expected under certain conditions for the treatment of enargite concentrates. To that end, it is worthwhile to examine the effect of sulfuric acid on the oxidation of enargite as discussed in the next section.

3. Equilibrium distribution of the species for the enargite-sulfuric acid system

As can be expected, the equilibrium state in the enargite-sulfuric acid system would be more complex

Fig. 6—The equilibrium composition as a function of oxygen potential for enargite [input: 2 kmol enargite, total pressure: 1 bar, and temperature 473 K (200 °C)].

Fig. 7—The equilibrium composition as a function of temperature for enargite in sulfuric acid in the absence of oxygen (input: 1 kmol enargite, 8 kmol H_2SO_4 , and total pressure: 1 bar).

than the enargite-oxygen system. The equilibrium distribution of species as a function of temperature in the absence of oxygen is shown in Figure 7. The sulfuric acid to enargite molar ratio is 8. While the main gaseous reaction products are SO_2 and H_2O , hydrated copper sulfates tend to form at low temperatures [298 K to 573 K (25 °C to 300 °C)] along with anhydrous copper sulfate, which continues to form even at higher temperatures. As_2O_3 (A) and As_4O_6 are the major condensed arsenic species, which their formation is facilitated at around 473 K (200 °C). Chalcocite and covellite continue to be major reaction products with the former taking over at temperatures greater than ~443 K (170 °C). At temperatures greater than ~423 K (150 °C), $\text{Cu}(\text{AsO}_2)_2$ is a major reaction product.

Cu_2O starts to form in appreciable amounts at temperatures greater than ~573 K (300 °C). No significant amount of arsenic gases are generated.

The effect of sulfuric acid dosage on the equilibrium composition at 473 K (200 °C) is illustrated in Figure 8, which shows that complete decomposition of enargite requires a sulfuric acid/enargite molar ratio of at least 5. The amount of sulfuric acid has a meaningful effect on the formation of copper sulfate, so that copper sulfate keeps increasing up to sulfuric acid/enargite molar ratio of 16, while the amounts of SO_2 (g) and H_2O (g) remain almost unchanged. At this point, the entire amounts of chalcocite and covellite are consumed, and copper sulfates predominate. Also, note that the stable form of arsenic becomes As_2O_4 .

Fig. 8—The equilibrium composition as a function of sulfuric acid amount for enargite [input: 1 kmol enargite, total pressure: 1 bar, and temperature 473 K (200 °C)].

Fig. 9—The equilibrium composition as a function of temperature for enargite in sulfuric acid in the presence of oxygen (input: 1 kmol enargite, 8 kmol H_2SO_4 , 1 kmol O_2 , and total pressure: 1 bar).

Examination of Figures 5 through 8 indicates that sulfuric acid is most significant for the decomposition of enargite to produce water-soluble copper sulfates and arsenic trioxide. More importantly, the SO_2 produced in the reaction can be used in a sulfuric acid plant to regenerate some of the acid required for the acid baking reaction.

The effect of the addition of oxygen to the enargite-sulfuric acid system can be observed from Figure 9, which shows the equilibrium composition as a function of temperature. The major difference from the previous case in the absence of oxygen is that there is no

significant amount of covellite formed and chalcocite predominates.

The effect of oxygen dosage on the oxidation of enargite in the presence of sulfuric acid at 473 K (200 °C) is shown in Figure 10. It is understood from Figure 10 that at oxygen/enargite molar ratios up to 4, all the sulfuric acid is consumed. At ratios greater than 4, no chalcocite and covellite exist, and these minerals convert into copper sulfate. At the ratio of 8, SO_3 (g) starts to form along with SO_2 (g); however, at oxygen/enargite ratios greater than 9, SO_3 (g) takes over as the only major gaseous species.

Fig. 10—The equilibrium composition as a function of oxygen potential for enargite [input: 1 kmol enargite, 8 kmol H_2SO_4 , total pressure: 1 bar, and temperature 473 K (200 °C)].

Fig. 11—XRD spectra of (a) high-quality enargite, (b) baked sample in muffle furnace, (c) final leach residue of the baked sample in muffle furnace, (d) baked sample in tube furnace, and (e) final leach residue of the baked sample in tube furnace (scan rate 2 deg/min). Baking conditions-muffle furnace: initial weight of enargite ($-150+106\ \mu\text{m}$) = 1.97 g, weight of sulfuric acid = 3.35 g, baking temperature: 473 K (200 °C), baking time = 7 h. Tube furnace: initial weight of enargite ($-150+106\ \mu\text{m}$) = 2.00 g, weight of sulfuric acid = 3.41 g, baking temperature: 473 K (200 °C), baking time = 7 h, nitrogen flow rate: $\sim 340\ \text{mL/min}$. First step leaching conditions in DI water: 45 min at 70 °C with a stirring speed of 400 rpm. Second step leaching conditions in 0.5 M sulfuric acid: same as the first step. The results indicated correspond to the leach residues from the second step leaching experiments. Powder diffraction file (PDF) numbers used for the identification of the phases are as follows: As_2O_3 00-036-1490, CuSO_4 00-015-0775, S_8 00-008-0247, and $\text{CuO}\cdot\text{CuSO}_4$ 01-074-1590.

IV. BAKING EXPERIMENTS

Before doing the acid baking experiments, two experiments were performed to see if any phase transformations occur to enargite at 473 K (200 °C) in the absence of sulfuric acid. The results indicated that no phase transformation took place, and enargite was

found to be stable at 473 K (200 °C). The baking experiments were performed under neutral (tube furnace experiment under a flow of nitrogen) and oxidative (muffle furnace experiment) conditions at a constant temperature of 473 K (200 °C). In the acid baking experiments in the muffle furnace, the temperature was increased to 481 K (208 °C) within 3 minutes from the

Fig. 12—Backscattered SEM micrographs from the polished section of the high-quality enargite sample baked in (a)–(c) tube furnace and (d) muffle furnace. Baking conditions-muffle furnace: initial weight of enargite ($-150+106\ \mu\text{m}$) = 1.97 g, weight of sulfuric acid = 3.35 g, baking temperature: 473 K (200 °C), baking time = 7 h. Tube furnace: initial weight of enargite ($-150+106\ \mu\text{m}$) = 2.00 g, weight of sulfuric acid = 3.41 g, baking temperature: 473 K (200 °C), baking time = 7 h, nitrogen flow rate: $\sim 340\ \text{mL/min}$.

start of the experiment and remained at 481 K (208 °C) for 2 minutes, and cooled back down to 473 K (200 °C) in 11 minutes. In the tube furnace experiment, the temperature increased to 505 K (232 °C) within 6 minutes and remained at this temperature for 2 minutes, and cooled back down to 473 K (200 °C) within 12 minutes. The difference in temperature increase is most probably associated with the distance of the thermocouple from the material bed. At the end of 7 hours of heat treatment, the sample coming out of the tube furnace was completely dry, corresponding to 15.5 pct weight loss at the end of experiment, while the sample coming out of the muffle furnace which had some moisture content due to residual sulfuric acid, showed 9.4 pct weight loss upon baking. Approximately 0.6 g elemental sulfur was formed inside the tube; this was not measured for the

sample baked in the muffle furnace even though its formation was observed on the furnace door. No H_2S was detected based upon the fact that the color of the lead acetate paper remained unchanged.

The results of XRD for both the enargite (pattern (a)) and the baked samples (patterns (b) and (d)) are shown in Figure 11. While no significant difference is observed in the spectra of the baked enargite samples, the sample baked in the tube furnace (pattern (d)) shows stronger copper sulfate and elemental sulfur peaks, perhaps because it was dry. Enargite peaks are not labeled because the high-quality enargite pattern is inserted (pattern (a)), which was already identified. Considering the reaction products and the molar ratio of sulfuric acid/enargite which was used in the experiments (~ 7), the results can be tentatively compared to Figures 7 through 10.

Table V. The Results of Cu and As Extraction Following Water Leaching

Sample	Metal Extraction (Pct)	
	Cu	As
Tube furnace	83.9	77.5
Muffle furnace	86.0	76.9

The results from the experiments agree reasonably well with the thermodynamic calculations where the major reaction products were predicted to be CuSO_4 and As_2O_3 . Other phases predicted by thermodynamics may have formed, but were not detected due to their low percentage in the baked enargite. The amount of enargite reacted can be easily measured by the subsequent leaching experiments, which are reported in the next section. Characterization of the leach residues may show some of the phases which were not detected in the baked enargite as they are concentrated in the leach residue.

Polished sections of the baked samples were subjected to further scanning electron microscopy (SEM) studies. The results show a very similar microstructure for both baked samples, with a mixed arsenolite-copper sulfate association. Figure 12 shows the SEM images of both enargite samples baked in the tube and muffle furnace. The EDAX analysis of the mixed white-gray region showed that it is composed of Cu, As, S, and O. On the other hand, the EDAX spectrum of the areas free from the white phase indicates that the gray phase is most probably copper sulfate. Spot analysis of the white phases reveals that they are most probably arsenic trioxide.

V. LEACHING EXPERIMENTS

As a result of first step leaching in DI water, ~81 pct of the sample baked in the tube furnace was leached in DI water. Approximately 9 pct of the leach residue from the first leach step was leached in the second acid leaching experiment. Also, about 80 pct of the sample baked in the muffle furnace was leached in the first step leach followed by ~7 pct weight loss in the second leach step. The results for the second step leach in 0.5 M sulfuric acid may not be accurate because of the very small amount of material (<0.5 g) that was used in both experiments.

The results from leaching are very similar; indicating that ~80 pct of both baked enargite samples were leached in the simple water leaching experiments. The XRD results for the final leach residues are indicated in Figure 11. While the final residues are composed mainly of enargite and elemental sulfur, it is noted that the leach residue of the sample baked in the muffle furnace (pattern (c)) shows stronger elemental sulfur peaks as compared with the leach residue of the sample baked in the tube furnace (pattern (e)). It is also inferred from the spectra of the leach residues that neither covellite nor chalcocite was formed in appreciable amounts as

expected from the thermodynamic analysis. In terms of Cu and As extraction, the results are summarized in Table V. The pH and E_h of the pregnant leach solution (PLS) for both solutions were ~2.2 and ~625 mV (vs SHE), respectively. According to the results reported in Table V, Cu and As extractions were almost same for both the samples.

VI. CONCLUSIONS

A thermodynamic analysis was performed to further our understanding of the sulfuric acid baking of enargite in neutral and oxidative atmospheres. It was found that the major reaction products include CuSO_4 , As_2O_3 , SO_2 (g), and H_2O (g). Sulfuric acid was found to be a stronger sulfating agent than oxygen at low temperatures. No significant amounts of H_2S (g), SO_3 (g), and As_4O_6 (g) were found to form in the baking reaction, as predicted by thermodynamic calculations.

Sulfuric acid baking experiments of a high-quality enargite sample under oxidative and neutral atmospheres resulted in the formation of CuSO_4 , As_2O_3 , $\text{CuO}\cdot\text{CuSO}_4$, and S_8 , all of which were predicted based on equilibrium composition calculations. No H_2S was detected in the tube furnace experiment, adding credit to the calculations listed in Table III and also equilibrium composition calculations.

Two-step leaching of the baked enargite samples, first in DI water and then followed by leaching in 0.5 M sulfuric acid solution, resulted in more than 80 pct of the material leached for both samples, leaving behind enargite and elemental sulfur in the leach residues. Neither chalcocite nor covellite was detected in the leach residues. No significant amounts of the water-leached samples were leached in 0.5 M sulfuric acid solution, indicating that most reaction products (CuSO_4 , As_2O_3 , $\text{CuO}\cdot\text{CuSO}_4$) are completely leached in the water leach step.

A preferred operating window can be selected based on the current study to maximize the formation of water-soluble copper and arsenic compounds. Not only are the results of the current study useful for the analysis of the baking reaction, but they can also be useful for predicting enargite behavior during the roasting process.

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