EFFECT OF REACTION TEMPERATURE ON SCHWERTMANNITE SYNTHESIS,

FROM SIMULATED COPPER HEAP LEACH SOLUTIONS

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ABSTRACT

The work here, examines the effects of the reaction temperatures (25˚C and 65˚C) and co-existing metal ions (Cu^{2+} and Fe^{2+}) on schwertmannite, synthesized from the simulated copper heap leach solutions. It is observed that, schwertmannite can be synthesized at both 25˚C and 65˚C, from all the experimental conditions, excepting for the solution containing 100 mM Fe^{2+} at 65˚C, as goethite is generated under these conditions. Schwertmannite products, synthesized at both temperatures have similar chemical compositions; however, they differ in surface characteristics. The specific surface area of the schwertmannite, synthesized at 65˚C was much larger (147.4–176.9 $m^2 g^{-1}$) than the specific surface area of the schwertmannite, synthesized at 25˚C (14.1–21.4 $m^2 g^{-1}$). The efficiency of As(V) removal from acidic aqueous solutions (pH 3-4), by the synthesized products were also investigated. The results showed that, the maximum As(V) sorption capacities of the schwertmannite, synthesized at 65˚C was much higher (114-128 mg g^{-1}) than the maximum sorption capacities of the schwertmannite synthesized at 25˚C (17-23 mgg^{-1}).

KEYWORDS: Schwertmannite; Temperature; Copper Heap Leach Solution & As(V) Sorption

INTRODUCTION

Arsenic (As), a very toxic inorganic pollutant is a major contaminant in tailings of porphyry copper mines the principle source of copper production worldwide (John et al., 2010). Arsenic control remains as an important issue in the development of porphyry copper mine operations. Immobilization of As by Schwertmannite ($Fe_8O_8(OH)_{8-2x}(SO_4)_x$, with x typically (1–1.75) has attracted much attention in recent years, due to its strong binding affinity to toxic As species in acidic to neutral pH environments (Bigham et al., 1994; Fukushi et al., 2003; HoungAloune et al., 2015a; Regenspurg and Peiffer, 2005).

Schwertmannite, a poorly crystalline ferric-oxyhydroxysulfate mineral is commonly formed in, acidic iron- and sulfate-rich environments (Bigham et al., 1994, 1990; Bigham and Nord- strom, 2000). Generation of schwertmannite from copper heap leach solutions is of economic and environmental interest for As control at porphyry copper mines. Such leach solutions generally contain high concentrations of Fe^{3+} and SO_4^{2-}, the components of schwertmannite.

Schwertmannite can be synthesized by several techniques such as dialysis, by adding ferric chloride/nitrate to sodium/potassium sulfate solutions at 60°C (Bigham et al., 1990); oxidation of $FeSO_4$ solutions by H_2O_2 (Regenspurg et al., 2004); and biooxidation of $FeSO_4$ solutions by Acidithiobacillusferrooxidans (Liao et al., 2009). These techniques may

not be suitable for schwertmannite generation, at porphyry copper mines. For example, the dialysis technique requires a period of more than 30 days for dialyze against deionized water, which is a time-consuming and inefficient work for real operation at copper mine sites.

To overcome these obstacles, appropriate techniques for synthesis of schwertmannite, from copper heap leach solutions should be investigated. Our previous study indicated that, it is possible to synthesize schwertmannite from copper heap leach solutions, with high efficiency enabling As(V) removal, by a neutralization technique (HoungAloune et al., 2014, 2015a). This follow-up study, reports on the effect of reaction temperatures ($25°C$ and $65°C$) and co-existing metal ions (Cu^{2+} and Fe^{2+}), on the properties of the schwertmannite products formed.

METHODS

Solution Preparation

Solutions containing known concentrations of H_2SO_4, Na_2CO_3, Fe^{3+}, Fe^{2+}, Cu^{2+}, and As^{5+} were prepared by dissolving, reagent-grade H_2SO_4, Na_2CO_3, $FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3 \cdot nH_2O$, $CuSO_4 \cdot 5H_2O$, and $Na_2HAsO_4 \cdot 7H_2O$ (Wako Pure Chemical Industries, Ltd., Japan) in distilled/ion-exchanged water. The results, for the solid-phase analyses, are presented on a dry weight basis, unless noted otherwise.

Synthesis of the Precipitates

The synthesis was carried out, using the procedure described by Houng Aloune et al. (2014). Briefly, 500 mL of solution containing 10 mM H_2SO_4 and 50 mM Fe^{3+} with or without Cu^{2+} and Fe^{2+} was prepared and added into a beaker under magnetic stirring at 350 rpm and at 25 or $65°C$. After discontinuing the magnetic stirring, 1 M Na_2CO_3 was titrated to the solution, to adjust the final pH to 3.0–4.0 (titration rate, 1500 µL/min). The resulting suspension was left to settle, and the supernatant was subsequently replaced with deionised water. This rinsing procedure was repeated 5 times to remove soluble ions. The precipitate in the beaker was then filtrated, dried at 40°C in a vacuum oven for 24 hours, and subjected to X-ray diffraction (XRD) analysis. To identify the composition of the synthesized products, 0.1 g of dried precipitates were dissolved in 100 mL of 0.1 M HCl and the Fe and S contents were determined with inductively coupled plasma atomic emission spectroscopy (ICP-AES). The dried precipitates were also subjected to specific surface area analysis, by multiple-point BET (Brunauer-Emmett-Teller).

Arsenic Sorption Experiments

Arsenic sorption experiments were conducted in a 200-mL flasks with 100 mg of dried synthesized products (as described above) and 100 mL of the solutions containing known concentrations of $Na_2HAsO_4 \cdot 7H_2O$ (As(V)), at the initial pH 3.0–4.0. The flasks were shaken for 24 h, in a water bath at $25°C$ at 120 rpm. After 24 h, the solution was filtrated through a membrane filter (pore size, 0.2 µm) and analyzed for arsenic, by ICP-AES. The amount of sorbed arsenic was calculated from the differences, between the initial (added) amount and final (remaining) amount of As, in the solutions.

Analytical Methods

A pH-meter and combined electrode with temperature compensation was used, to measure the pH and was calibrated regularly with standard buffer solutions of pH 1.68, 4.01, or 6.86. The concentrations of arsenic, iron, copper, and sulfur in the aqueous phase were measured, by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Seiko instruments SPS7800. Solid samples were ground to a homogeneous powder, in a mortar and subsequently

analyzed, by X-ray diffraction (XRD), using a RIGAKU powder diffractometer, with CuKα radiation (40 kV and 30 mA) to identify the minerals present in the samples. The specific surface area was measured by multiple-point BET using a NOVA 1000e surface area analyzer and N_2, as the adsorbate. Before the measurements, samples were heated at 120˚C, for 1 hour in glass tubes (to eliminate moisture) and then weighed.

RESULTS AND DISCUSSIONS

Mineralogy of the Synthesized Products

The synthesis was conducted at 25˚C and 65˚C, to investigate the effect of reaction temperature on the schwertmannite synthesis. Generally, both Cu^{2+} and Fe^{2+} are present in copper heap leach solutions, and it is also important to examine the behaviour of schwertmannite synthesis, in the presence of both Cu^{2+} and Fe^{2+}. The XRD analysis was used, to identify the formation of schwertmannnite.

The XRD patterns of a sample synthesized from 50 mM Fe^{3+} solution, with or without Cu^{2+} and Fe^{2+} at 65˚C are shown in Fig. 1(a). The results confirm that, schwertmannite appears as the dominant phase of the product synthesized, without Cu^{2+} and Fe^{2+}. Traces of brochantite $(Cu_4(SO_4)(OH)_6)$ could be inferred for samples, synthesized with 100 mM Cu^{2+}, and also here, schwertmannite is the major mineral component detected. Goethite $(\alpha FeOOH)$ appears as the main mineral phase formed, for samples synthesized at the initial Fe^{2+} concentration of 100 mM. Schwertmannite becomes the prominent mineral, with no goethite phase in the synthesized product in the presence of 100 mM Cu^{2+} and 100 mM Fe^{2+}. Fig. 1(b) shows the XRD patterns of the samples synthesized at 25˚C. As suggested by Fig. 1(b), schwertmannite appears as the main mineral phase for all products synthesized with or without addition of Cu^{2+} and Fe^{2+}.
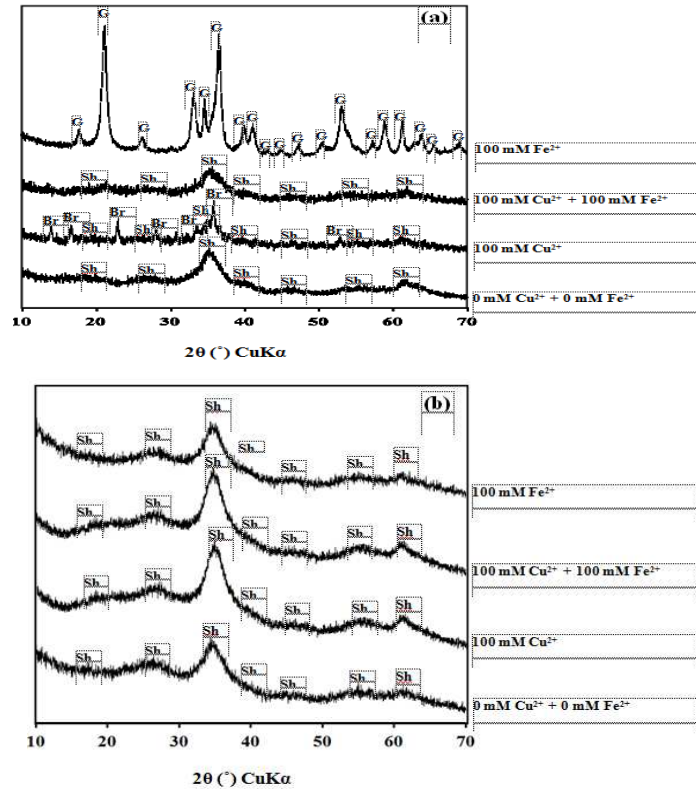
Figure 1: XRD Patterns for Samples Synthesized From 50 Mm Fe^{3+} Solution in the Absence or Presence of Cu^{2+} or Fe^{2+} At (A) 65˚C and (B) 25˚C. Schwertmannite is denoted As "sh", Brochantite As "Br", And Goethite As "G"

The mineralogy of the products synthesized at 65˚C suggests that addition of Cu^{2+} alone has no significnant effect on the schwertmannite synthesis, but that Fe^{2+} has a strong effect on the synthesis. However, Cu^{2+} has the ability to inhibit goethite formation in the presence of Fe^{2+}. However, the results for the products synthesized at 25˚C imply that the presence of Cu^{2+} and Fe^{2+} do not affect the schwertmannite synthesis. In conclusion, schwertmannite can be synthesized at both 25˚C and 65˚C, from all solutions except for solutions containing Fe^{2+} at 65˚C, as goethite is generated at this condition.

There are two possibilities for goethite formation processes in the presence of Fe^{2+}. One is co-precipitation with schwertmannite or direct formation of goethite from solution; and the other is the transformation of intermediate schwertmannite to goethite during the synthesis process. A previous study (HoungAloune et al., 2014) has suggested that, goethite would not be likely to form directly from the solutions; and it was also confirmed that Fe^{2+}-catalyzed the transformation of schwertmannite to goethite under pH 3-4 at 65˚C, suggesting that goethite is formed by transformation of intermediate schwertmannite, during the synthesis at 65˚C. On the other hand, Fe^{2+}-catalyzed transformation of schwertmannite did not occur at 25˚C (HoungAloune et al., 2015b). This suggests that the transformation rate may be dependent on temperature, and Jönsson et al. (2005) reported that, the transformation rate of schwertmannite to goethite is slower at lower temperatures. Yee et al. (2006) also found that, Fe^{2+}-catalyzed transformation of poorly ordered ferrihydrite into crystalline goethite is significantly faster at 60 °C than at 21 °C.

Although, the results showed the possibility for schwertmannite synthesis at both temperatures, the properties of the products synthesized at 25˚C and 65˚C may be different. Therefore, the characteristics of all synthesized products were investigated and are discussed in the following section.

Elemental and Surface Analyses of the Synthesized Products

The elemental compositions of the products synthesized with or without Cu^{2+} and Fe^{2+} at 25˚C and 65˚C are shown in Table 1. The results show that, the molar Fe/S ratios, determined from the Fe and S molar proportions, were 4.9-6.4 and 5.5-5.7 for the schwertmannite products synthesized at 25˚C and 65˚C, respectively. These values agree well with the molar Fe/S ratios reported previously, for natural and synthesized schwertmannite (Table 2).

There was a relatively high molar Fe/S ratio of 13.9 of the goethite product synthesized with the solution containing Fe^{2+} at 65˚C. Generally, goethite does not contain sulfate, however the solutions used for the synthesis in the present study contain high concentrations of sulfate. Goethite may adsorb SO_4^{2-}, especially at low pH (pH 3-4) where the net surface charge of goethite is positive (Juang and Wu, 2002). Here the total quantity of SO_4^{2-}, associated with goethite is small compared to schwertmannite products (Table 1).

Table 1: Elemental Composition and The Molar Ratios of
Products Synthesized at 25˚C and 65˚C

Samples			Elemental Composition (Mmol G^{-1})		Fe/S	Chemical Formulation
	Cu^{2+} (mM)	Fe^{2+} (mM)	Fe	S		
65˚C	0	0	9.11	1.59	5.7	$Fe_8O_8(OH)_{5.20}(SO4)_{1.40}$
	0	100	10.23	0.74	13.8	$Fe(OOH)$
	100	0	7.37	1.33	5.5	$Fe_8O_8(OH)_{5.10}(SO4)_{1.45}$
	100	100	7.25	1.31	5.5	$Fe_8O_8(OH)_{5.10}(SO4)_{1.45}$
25˚C	0	0	8.31	1.57	5.3	$Fe_8O_8(OH)_{4.98}(SO4)_{1.51}$
	0	100	8.83	1.82	4.9	$Fe_8O_8(OH)_{4.74}(SO4)_{1.63}$

| 100 | 0 | 8.06 | 1.53 | 5.3 | $Fe_8O_8(OH)_{4.98}(SO4)_{1.51}$ |
| 100 | 100 | 8.47 | 1.32 | 6.4 | $Fe_8O_8(OH)_{5.50}(SO4)_{1.25}$ |

The specific surface area of the products, synthesized with or without Fe^{2+} and Cu^{2+} at 25°C and 65°C is shown in Fig. 2. Here, the specific surface area of the schwertmannite synthesized at 65°C is much larger (147.4–176.9 $m^2 g^{-1}$) than the specific surface area of the schwertmannite, synthesized at 25°C (14.1–21.4 $m^2 g^{-1}$). This may imply that, the temperature of the synthesis has a significant effect on surface characteristic of the products.
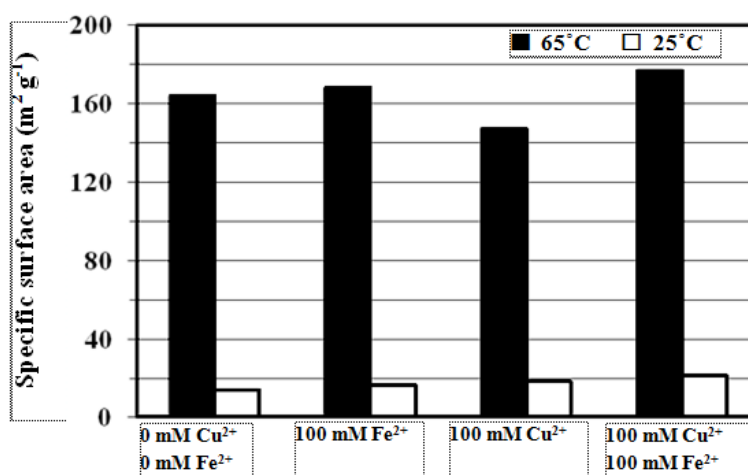
Figure 2: Specific Surface Area of the Products Synthesized with or without Fe^{2+} and Cu^{2+} At 25°C and 65°C

The specific surface areas of schwertmannite product, synthesized at 65°C are similar to these obtained by the dialysis technique at 60°C (Table 2). The specific surface areas of schwertmannite product synthesized at 25°C are similar to these obtained by oxidative or biosynthesis techniques carried out at room temperature. The large difference in surface area of these schwertmannite specimens, may be related to the particles morphology. As suggested by several studies that, particles formed by the dialysis technique are long needle-shaped crystals (hedge-hog like schwertmannite); and the oxidative synthesis method generated spheroids with a diameter of 250-500 nm (Bigham et al., 1990; Paikaray et al., 2011; Regenspurg et al., 2004; Vithana et al., 2014).

The specific surface area of goethite product (168.4 $m^2 g^{-1}$) synthesized in the presence of Fe^{2+} at 65°C agrees well with the specific surface area of natural goethite formed by acid mine drainage (100-200 $m^2 g^{-1}$, Murad and Rojik, 2004).

Table 2: Elemental Compositions and Surface Analyses of Schwertmannite Obtained by other Studies

Synthesis Method	References	Fe/S Mole Ratio	Chemical Formulation	BET (M^2/G)
Dialysis	Antelo et al. (2013)	8.15	$Fe_8O_8(OH)_{5.94}(SO4)_{1.03}$	-
	Fukushi et al. (2003)	5.3	$Fe_8O_8(OH)_{4.98}(SO4)_{1.51}$	154
	Regenspurg et al. (2004)	-	-	175-220
	Paikaray et al. (2011)	6.4	$Fe_8O_8(OH)_{5.50}(SO4)_{1.25}$	210
Oxidative	Vithana et al. (2014)	4.3	$Fe_8O_8(OH)_{4.3}(SO4)_{1.85}$	-
	Paikaray and Peiffer (2012)	6.3	$Fe_8O_8(OH)_{5.94}(SO4)_{1.03}$	14.7
	Regenspurg et al. (2004)	-	-	4-14
	Burton et al. (2010)	5.0	$Fe_8O_8(OH)_{4.8}(SO4)_{1.6}$	4-14
	Paikaray et al. (2011)	4.7	$Fe_8O_8(OH)_{4.60}(SO4)_{1.70}$	5.3

| Table 2: Contd.,				
Natural	Regenspurg et al. (2004)	-	-	72
	Jonsson et al. (2005)	5.4	$Fe_8O_8(OH)_{5.02}(SO4)_{1.49}$	42.9
Biosynthesis	Paikaray et al. (2011)	5.3	$Fe_8O_8(OH)_{4.98}(SO4)_{1.51}$	14.7
	Lioa et al. (2009)	4.31-4.48	-	3.4-23.4
Neutralization	HoungAloune et al. (2014)	5.3	$Fe_8O_8(OH)_{4.98}(SO4)_{1.51}$	-

Arsenic(V) Sorption Capacity

In the present study, As(V) sorption was fitted with the Langmuir adsorption isotherm, using the following equation (Liao et al., 2011):

$$q = \frac{q_m K_L C}{1 + K_L C} \quad (1)$$

Where q (mg g^{-1}) is the amount of adsorbed As (V), C (mg L^{-1}) is the equilibrium solute (As) concentration, q_m (mg g^{-1}) is the maximum adsorption capacity, and K_L is the equilibrium constant for the overall adsorption process.

The As (V) sorption data for the synthesized products are plotted in Fig. 3, and the thermodynamic parameters calculated for Langmuir adsorption model are listed in Table. 2. The results show that the maximum As(V) sorption capacities of the schwertmannite, synthesized at 65˚C was much higher (114-128 mg g^{-1}) than the maximum sorption capacities of the schwertmannite, synthesized at 25˚C (17-23 mgg^{-1}). As detailed above, the temperature of the synthesis has a significant effect on the surface characteristics of schwertmannite products, and this may be a cause of the differences in As (V) sorption capacities.
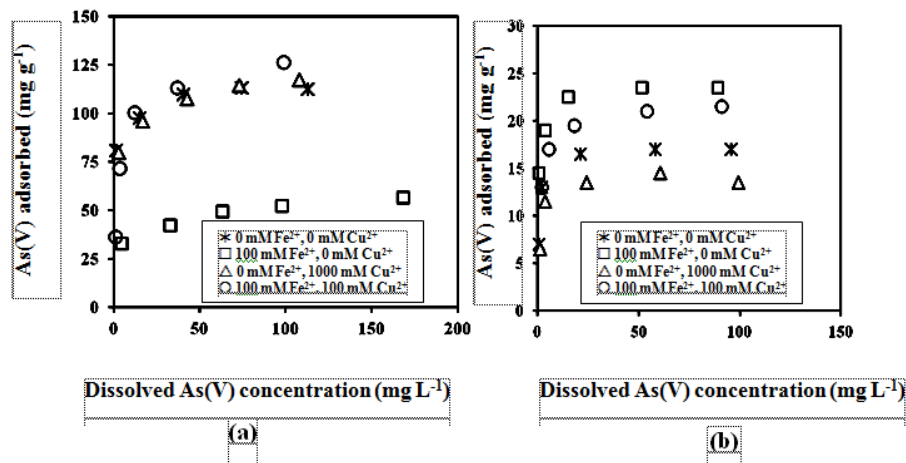
Figure 3: Sorption Isotherms of As(V) onto Synthesized Products in the Absence or Presence of Cu^{2+} and Fe^{2+} At (A) 65˚C and (B) 25˚C. Experimental Conditions: Ph = 3-4, Adsorbent = 1.0 G L^{-1}, Equilibrium Time: 24 Hrs

Table 2: Langmuir Parameters Obtained from the Modelling of Arsenate Sorption Isotherms on Synthesized Products in The Absence or Presence of of Cu^{2+} and Fe^{2+} At 25˚C And 65˚C. Experimental Conditions: Synthesized Product 1.0 G L^{-1}, Ph 3-4, 120 Rpm, and Equilibrium Time 24 Hrs

Samples				Langmuir Model		
	Cu^{2+} (Mm)	Fe^{2+} (Mm)		R^2	Q$_m$ (Mg G^{-1})	K$_L$
65˚C	0	0		0.99	114	0.71

	0	100		0.90	58	0.10
	100	0		0.90	120	0.29
	100	100		0.98	128	0.39
25°C	0	0		0.99	17	1.4
	0	100		0.94	23	3.5
	100	0		0.98	14	0.8
	100	100		0.99	21	0.8

The maximum As(V) sorption capacity is approximately 58 mg g^{-1} for goethite product synthesized from the solutions containing Fe^{2+} at 65°C, similar to the maximum As(V) sorption capacity of goethite reported previously by Lehmann et al. (2005) and Matis et al. (1997).

CONCLUSIONS

This study reports on the effect of the reaction temperatures (25°C and 65°C) and co-existing metal ions (Cu^{2+} and Fe^{2+}) on schwertmannite, synthesized from simulated copper heap leach solutions, by neutralization technique. It is shown that, Cu^{2+} and Fe^{2+} play an important role for the schwertmannite synthesis, at 65°C. However, Cu^{2+} and Fe^{2+} did not affect the synthesis, at 25°C. It was observed that, schwertmannite is formed at both 25°C and 65°C at all experimental conditions, except for the solution containing 100 mM Fe^{2+} at 65°C, as goethite was generated at this condition. Although, it is possible to synthesize schwertmannite at both temperatures, their surface characteristics are different. The specific surface area of the schwertmannite synthesized at 65°C was much larger (147.4–176.9 m^2 g^{-1}), than the specific surface area of the schwertmannite synthesized at 25°C (14.1–21.4 m^2 g^{-1}). The results showed that, the maximum As(V) sorption capacities of the schwertmannite synthesized at 65°C was much higher (114-128 mg g^{-1}), than the maximum sorption capacities of the schwertmannite synthesized at 25°C (17-23 mgg^{-1}).

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