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# **Stabilizing Arsenic in Copper Heap Leaching Residues**

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Abstract: The need to sustainably produce raw materials encourages mining companies to develop and incorporate new economically and environmentally efficient processes. Therefore, there is a need to investigate the behavior and stabilization of hazardous elements present in effluents from metal recovery processes such as arsenic. This study evaluates the incorporation of an effluent solution from a copper smelter that is to be treated in a copper hydrometallurgical plant (heap leaching). The treatment is applied to recover compounds of interest such as copper, acid and water, in addition to confining impurities as stable residues in the leach residues. Here, we assess the capacity of the mineral to retain arsenic. To do this, a mixed solution of effluent and process solution was prepared, with a concentration of 1 g/L of arsenic. The solution was irrigated in leach columns loaded with a heap mineral with varying pH levels (0.8; 1.5 and 2) and solution potentials (510 and 540 mV). The concentrations of arsenic and iron in the solution and in the solid residues were measured to determine the capacity of the mineral to retain arsenic and how it was retained. The pH level plays an important role since, at a higher pH, the presence of arsenic and iron in the solution decreases, therefore increasing in the solid residue. Finally, a retention of 57% of arsenic is reached at pH 2. The characterization of the residues by scanning electron microscopy (SEM) confirms that arsenic is associated with Fe, S and O, forming ferric arsenates, while an X-Ray analysis identifies the arsenic compounds as crystalline scorodite.

Keywords: leaching; hydrometallurgical process; arsenic stabilization; scorodite; inertization

## 1. Introduction

Mineral processing and metallurgical operations have taken a new turn according to the type of copper production being used. Innovation and new mineral processing alternatives are essential to maintaining copper production [1–3]. Production by hydrometallurgical processes has started to decline, and new techniques are required to overcome various processing challenges [4–7], one of which is the increasing arsenic content in copper deposits. According to government regulations, when arsenic cannot be recovered from a process and is eliminated as waste, it must be confined in a stable environment [8–10].

Arsenic is one of the most toxic and carcinogenic elements. In solution, it can be absorbed by vegetation and pass through the food chain to human beings [11–14]. Arsenic can be found in a natural state, as well as in sulphides such as realgar, enargite and orpiment, as arsenide in oxides and as arsenate. Arsenopyrite (FeSAs) is the most common arsenic mineral [15]. In copper ores, arsenic is often contained in tennantite ( $Cu_{12}As_4S_{13}$ ) and enargite ( $Cu_3AsS_4$ ) [16], which are respectively 20.2% and 19.0% arsenic [17]. This is why the final disposition of arsenic must be controlled, and to do this it

is necessary to establish the form of arsenic that is present in order to stabilize and confine it over the long term.

Numerous studies have considered the most stable arsenic form for final disposal. It has been concluded that  $As^{5+}$  is more stable than  $As^{3+}$  [18]. Studies by [19] have indicated that arsenate ( $As^{5+}$ ) can precipitate in the presence of ( $Mn^{3+}$ ) in oxidizing environments. Therefore, the presence of a high concentration of manganese can positively influence arsenic precipitation. Precipitation with lime is a widespread practice despite consensus about the low arsenic concentration content and low long-term stability of the resulting precipitates. Precipitation of  $As^{+5}$  with lime at room temperature results in the formation of various calcium arsenate compounds, including  $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$ ,  $Ca_5(AsO_4)_3OH$  and  $Ca_3(AsO_4)_2$ , as well as  $CaHAsO_4 \cdot xH_2O$  and  $Ca_5H_2(AsO_4)_4$ . These compounds depend on the concentration and oxidation state of arsenic, calcium and  $SO_4^{2-}$  and/or  $HSO_4^{-}$ . It should be noted that there is evidence that calcium arsenate compounds decompose upon contact with atmospheric  $CO_2$  or carbonate ions to form calcium carbonate and a soluble arsenic acid [18].

The best alternative for arsenic stabilization is the formation of scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O) [20–22], which is capable of containing between 20–25% of As [23] and is stable under oxidizing conditions in the pH range of 2.0–6.0 [18,24]. The formation of scorodite at atmospheric pressure requires strict rigor with respect to the pH. It has been determined that  $As^{+5}$  precipitation at ambient pressure is directly affected by the pH level, with values over 4 resulting in the oversaturation of iron and arsenic in the solution, thus forming amorphous iron-arsenic compounds that are not stable for depositing [25]. Scorodite formation is reflected in the kinetics of its transformation, pH 1 is the established value, while at pH 2 it is moderate and at pH 4.5 the kinetics are slow [26]. Another factor to consider in the coprecipitation of As is the oxidation of  $As^{3+}$  to  $As^{5+}$ . Oxidation is important because the successful removal of arsenic requires that it be in the form of arsenate, especially when scorodite is formed [21,27].

This research analyzes the feasibility of incorporating the effluent solution from a metallurgical flue dust treatment plant (PLS-P) from a copper smelter to a copper hydrometallurgical plant. In this way, it is expected that the copper, acid and water, that are currently lost due to the high arsenic content, can be recovered and that the arsenic can be fixed in a stable form in the heap leaching residue, allowing for its disposal in a confined and environmentally safe area.

#### 2. Materials and Methods

To determine the behavior of arsenic and iron in the effluent flue dust solution (PLS-P) of a copper smelter when it is incorporated into an industrial copper leaching process, a set of six column-leaching tests were performed. Table 1 shows the details of the pH and solution potential (Eh) for the leaching columns (C-1, C2, C3, C4, C5 and C6).

Variable	C-1	C-2	C-3	C-4	C-5	C-6
pН	0.8	1.5	2.0	0.8	1.5	0.8
Eh (mV)	510	510	510	540	540	540

Table 1. Conditions and nomenclature in column leaching tests.

A representative sample of mineral used in the Lomas Bayas mining process was characterized by chemical analysis using inductively coupled plasma atomic emission spectroscopy (ICP-AES) via the model Optima 2000 DV (PerkinElmer, Überlinge, Germany), with a detection limit of 0.01 ppm for Cu and Fe and 0.5 ppm for As. A pulverized mineral sample was analyzed by X-ray analysis (Siemens model D5600, Bruker, Billerica, MA, USA), with an analysis time of one hour. The ICDD (International Center for Diffraction Data) database was used to identify the species that were present.

To perform the microscopy analysis, a polished briquette (Buehler Simplimet 2 briquetting machine) was made with transoptic powders and was characterized by scanning electron microscopy (SEM) using JEOL 6360-LV equipment (JEOL USA Inc., Peabody, MA, USA) and by an energy-dispersive

X-ray spectroscopy (EDX) microanalysis system (Zeiss Ultra Plus, Zeiss, Jena, Germany), operated at 30 kV under high vacuum conditions. Finally, the samples were also studied under a BX-51 reflected-light microscope (Olympus, Tokyo, Japan).

The size distribution was characterized in two stages, the first using mesh sizes of 1", 3/4", 3/8", 1/4", 6#, 10# and -10# mesh (Tyler). In the second stage, a 500 g (-10#) mineral sample was classified using 20, 30, 50, 70, 100, 140, 200, 270, 325 and 400# meshes (Tyler). Moisture was determined by the weight difference of a mineral sample before and after being dried at 95 °C in an oven for 14 h.

The ore from the heap leaching was loaded into columns 48 cm high and 9.5 cm in diameter. The columns were irrigated independently in duplicate with a mixed solution of PLS-P and Lomas Bayas heap leaching solution in a 1/10.74 ratio, with 1 g/L arsenic. The initial pH (0.8) and the solution potential (510 mV) with respect to the standard hydrogen electrode (SHE), were the natural values of the blend. Both the pH and the solution potential were conditioned according to Table 1, and NaOH and H<sub>2</sub>SO<sub>4</sub> (Merk, analytical grade) were used to control the pH of the solution. To regulate the solution potential up to 540 mV, ozone was injected into the solution for 5 min, using an ozonator model L21 (Pacific Ozone, Benicia, CA, USA), fed with oxygen through an oxygen generator system. The conditioned solution was irrigated in the columns, and the pregnant leach solution (PLS) was recirculated in the columns until completion of a 94-day leaching cycle.

The columns were irrigated using a multi-head MasterFlex peristaltic pump at a rate of 10 (L/h)/m<sup>2</sup>. The drained solutions from the columns were collected separately, sampled every five days and analyzed with an Absorption Spectrometer, (SpectrAA-50/55, Varian, Santa Clara, CA, USA) for As(total), As<sup>3+</sup>, As<sup>5+</sup> using HG-FAAS (hydride generation with pH speciation), and using FAAS (flame atomic adsorption spectrometry with pH speciation) in the case of Fe<sub>(total)</sub>, Fe<sup>2+</sup>, Fe<sup>3+</sup> and Cu<sup>2+</sup>. Figure 1 shows a schematic of the system used. At the end of the cycle (94 days), the irrigation was discontinued and the columns were drained for three days and discharged. A sample was taken from the leaching residue that was obtained in each column for physical, chemical, X-ray and SEM analysis.



Figure 1. Experimental setup.

# 3. Results

#### 3.1. Sample Characterization

The mineral sample came from the operations of Minera Lomas Bayas. The sample had a copper content of 0.45%, which is characteristic of minerals from this deposit. The sample had 0.37% moisture, a granulometry with  $F_{80}$  of 19.29 µm and a low presence (5.4%) of fine material–100#. Table 2 shows the results of the chemical analysis of the sample.

Table 2. Chemical composition of the initial sample.

Element	ement As I		e <sub>(total)</sub> Fe <sup>2+</sup> Fe <sup>3+</sup>		Cu <sub>(total)</sub>	Cu <sub>(Soluble)</sub>	
Mass (%)	0.003	2.96	0.56	2.40	0.45	0.31	

The optical microscope showed that the copper was mainly secondary sulphur. The metal component content was low, constituting less than 0.5% of the sample, with a size that generally did not exceed 0.5 mm. Table 3 shows the relative abundance of mineral species and the mineralogical associations: chalcocite-bornite, chalcocite-covellite and chalcopyrite-covellite. The X-ray analysis determined that the sample was composed mainly of quartz (40.82%), albite (21.72%), orthoclase (16.5%), chlorite (7.72%), muscovite (7.37%) and lesser quantities of chalcocite, goethite, chalcopyrite, molybdenite and chrysocolla.

Table 3. Percentages of the minerals identified by optical microscopy.

Mineral	Volume (%)
Chalcocite (Cu <sub>2</sub> S)	50
Chalcopyrite (CuFeS <sub>2</sub> )	20
Covellite (CuS)	15
Bornite ( $Cu_5FeS_4$ )	10
Pyrite (FeS <sub>2</sub> )	3
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	2

The SEM-BSE (back-scattered electrons) observations confirmed the results of the optical microscope analysis, where the copper associated with sulphides was in the form of 50-µm particles. Figure 2a,b shows the particles (a) and (b) together with their elemental distribution spectrum, from which the presence of Cu-Fe-S phases like chalcopyrite and bornite could be determined.

The particles were analyzed to determine the Cu-Fe and S atomic and molar ratios. Table 4 shows the results of the EDX analysis of two Cu-containing particles. Particle (b) had an atomic ratio of Cu/Fe/S of 1/1/2, which is the atomic ratio of chalcopyrite (CuFeS<sub>2</sub>), while particle (a) approximated the ratio of bornite (Cu<sub>5</sub>FeS<sub>4</sub>).



Figure 2. Micrograph and spectrum of mineralized particles of (a) bornite and (b) chalcopyrite.

Element	Particle (a) % Atomic	Particle (b) % Atomic		
S	50.76	50.52		
Fe	14.86	24.72		
Cu	34.38	24.76		

Table 4. Semi-quantitative analysis of Cu-Fe-S phases in copper minerals.

#### 3.2. Column Leaching Test

The PLS-P and irrigation solutions were combined to obtain 1 g/L of arsenic. Table 5 shows the chemical composition of the mixture.

Element	Unit	Leach Sol.	PLS-P	Mix Sol.
$H_2SO_4$	g/L	5.86	109	11.8
As <sub>(total)</sub>	mg/L	29.0	12,040	988
As <sup>3+</sup>	mg/L	29.0	12,020	973
$As^{5+}$	mg/L	< 0.001	20.0	15.0
Fe <sub>(total)</sub>	mg/L	1383	2206	1630
Fe <sup>2+</sup>	mg/L	642	2192	752
Fe <sup>3+</sup>	mg/L	741	14.0	880
Cu <sup>2+</sup>	mg/L	140	9477	910

Table 5. Chemical analysis of the solutions used in the leaching tests.

The pH and natural solution potential of the Lomas Bayas irrigation solution were 1.5 and 650 mV, while for the PLS-P solution, they were -0.28 and 412.8 mV. The mixture of the two solutions had a pH of 0.8 and 510 mV. The pH and solution potential levels of the mixture of solutions fed to the columns were modified according to the operating conditions detailed in Table 1. The ore acid consumption was 3.3 kg<sub>acid</sub>/t<sub>ore</sub>, 5.8 kg<sub>acid</sub>/t<sub>ore</sub> and 22.5 kg<sub>acid</sub>/t<sub>ore</sub> at pH 2.0, pH 1.5 and pH 0.8, respectively. Thus, the pH can be considered relatively stable inside columns, especially for pH 2.

The arsenic concentrations in the product solutions (PLS) from the leaching column decreased in all the tests, as can be seen in Figure 3a,b. The influence of the pH level on the decrease in the arsenic content can be observed. There is a slight decrease at pH 0.8 for 510 and 540 mV. When the pH increases to 1.5 and 2, the decrease in the arsenic content in the solution is more notable, that is, more arsenic is retained by the mineral.



Figure 3. Arsenic concentration behavior in solution over time. (a) C-1, C-2, C-3, (b) C-4, C-5, C-6.

The arsenic concentration in the solution decreased by 200 to 500 mg/L by the end of the cycle in the tests at pH 0.8 and in the test at pH 2.0, respectively. Arsenic retention in the mineral was in



the range of 20% (pH 0.8), which increased to 57% with pH 2.0. This was the consequence of the precipitation of  $As^{5+}$ , since  $As^{3+}$  remained almost unchanged throughout the evaluation (Figure 4).

**Figure 4.** (a) As concentration in solution and (b) As retention in function of the pH (0.8 to 2) and Eh (510 to 540 mV).

Like the arsenic, the concentration of Fe in the solutions at the end of the cycle was dependent on the pH level. At a high acidity of pH 0.8, the Fe content was 2.2 g/L, higher than in the initial solution; that is to say, there was a negative retention of 40% (Figure 5), as a consequence of leaching iron minerals that were present in the mineral. At a low acidity of pH 2, the Fe concentration was 0.88 g/L, which is to say that 46% of the iron was retained by the mineral. The retention of Fe<sup>3+</sup> at pH 0.8 was practically nil, and at pH 2 it reached 80%, so it follows that the decrease in Fe was mainly a consequence of Fe<sup>3+</sup> precipitation. This was corroborated by reports in the literature [28,29].



**Figure 5.** (a) Fe concentration in solution and (b) Fe retention in function of the pH (0.8 to 2) and Eh (510 to 540 mV).

Assuming that the pH level increases in an industrial heap as the percolating solution of the mineral acid is consumed, the middle and lower zones of the heap will present the appropriate conditions to precipitate these elements as ferric arsenate (FeAsO<sub>4</sub>·H<sub>2</sub>O), an amorphous precursor of the scorodite [29,30].

Leaching residues samples were taken from the columns and characterized by chemical, SEM/EDX, X-ray, size distribution and moisture analyses. Figure 6 shows the granulometric profile of the residues from the six columns, which had a  $P_{80}$  of 20 mm. Moisture was around 7% (minimum 5.6% and maximum 8.03%). The granulometry was finer than the feed because of chemical fracturing during leaching.



Figure 6. Granulometric analysis of the feed and residues in the leaching columns.

Table 6 shows the Fe and As concentrations in the residues. It can be observed that the arsenic concentration is much higher than the initial concentration of the mineral (0.03 g/kg), that is, 0.03 g of arsenic per kilogram of mineral.

Column	As <sub>(total)</sub> g/kg	Fe <sub>(total)</sub> g/kg
C-1	1.52	28.76
C-2	1.56	35.61
C-3	6.16	45.84
C-4	1.52	28.96
C-5	1.19	34.20
C-6	1.43	30.00

Table 6. Fe and As concentrations in the leaching residue.

As expected, the concentrations of arsenic increased in the residues as a consequence of the decrease of this element via the precipitation in the solutions. The arsenic content increased in the mineral with a higher pH (Figure 7). At pH 2, the arsenic content in the mineral increased from its initial concentration by almost 200 times (0.003% As), while Fe increased 1.5 times, mainly as a result of  $Fe^{3+}$  precipitation; the  $Fe^{2+}$  present in the residues was 20% of the original quantity, which agrees with the solution analysis. The presence of iron in the residue increased in all tests, except those carried out at pH 0.8 (almost the same as the initial presence, 29.6 g/kg).

According to Equation (1), and in view of the mass balances proposed by [18], these results are consistent with [20], who determined the scorodite formation from flue dust when arsenic and iron were like arsenate and  $Fe^{3+}$ . The results also concur with what was reported by [21], who showed that the  $Fe^{3+}$  and  $As^{5+}$  precipitate in the presence of hematite and pyrite in the mineral as crystalline scorodite at 25 °C.

$$2H_3AsO_4(aq) + Fe_2(SO_4)_3(aq) + 4H_2O(aq) = 2FeAsO_4 \cdot H_2O(s) + 3H_2SO_4(aq).$$
 (1)



Figure 7. Changes in Fe and As concentrations in the leach residues as a function of the pH (0.8 to 2.0).

A sample of column leach residues with ochre-colored precipitates was selected for SEM/EDX electron microscopic analysis at pH 2 and 510 mV. Calcium sulphate crystals can be observed in Figure 8, as well as a second zone (lighter in color) with fine dust with high atomic weight elements, which were analyzed semiquantitatively by EDX.

Table 7 shows the semiquantitative EDX analysis; this analysis correspond to an ochre-colored precipitate that was analyzed by SEM (Figure 8), which had an atomic Fe/As ratio of 2/5. However, it was not possible to determine any species, since the iron is shared with other elements [12,20,30]. A sample of residue from every column (-100 #) was analyzed by X-ray diffraction to identify crystalline species. Table 8 shows the results of the analysis.



# Compact fine material with arsenic content

**Calcium sulphate** 

Figure 8. Micrographic (×350) sample of residue at pH 2 and 510 mV (C-3).

<b>Fable 7.</b> Percentage in	weight of	precipitates with	arsenic content (	EDX analy	vsis)
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0	Fe	S	Ca	Si	Cu	As	Al	К	Na	Р	Cl
55.13	9.96	9.34	1.97	4.63	0.40	5.31	3.47	1.10	2.95	0.45	1.24

Table 8 shows the results of the X-ray analysis. Scorodite is present in all the columns. The decrease in the concentration of As and Fe in the solution (mixture of PLS-P solution with the Lomas Bayas irrigation solution) can result in the formation of ferric arsenate [29], which is deposited in the leaching residues. With time, they reach a degree of crystallinity from contact with the mineral and solutions with a high potential; with exposure to ambient oxygen, they form scorodite [21]. Iron minerals like

jarosite and chlorite were also present, and these have the capacity to absorb not only arsenic but also other elements [28].

Name	Formula	C-1 (%)	C-2 (%)	C-3 (%)	C-4 (%)	C-5 (%)	C-6 (%)
Quartz	SiO <sub>2</sub>	24.9	31.5	31.7	26.7	23.6	32.4
Orthoclase	KAlSi <sub>3</sub> O <sub>8</sub>	17.3	19.8	21.7	18.5	15.39	18.2
Pyrite	FeS <sub>2</sub>	0.00	0.28	1.11	0.61	0.25	0.46
Muscovite	KAl <sub>2</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH,F) <sub>2</sub>	10.2	5.93	17.3	14.0	16.6	11.3
Kaolinite	$Al_2Si_2O_5(OH)_4$	5.51	3.60	0.00	0.00	0.00	2.32
Albite	NaCaAlSi <sub>3</sub> O <sub>8</sub>	11.1	10.2	6.52	9.86	13.2	9.18
Chalcocite	Cu <sub>2</sub> S	0.95	1.43	1.08	1.18	1.12	0.00
Chlorite	(Mg,Fe) <sub>3</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (Mg,Fe) <sub>3</sub> (OH) <sub>6</sub>	3.95	6.74	8.20	7.50	3.87	10.5
Jarosite	KFe <sup>+3</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	3.22	1.39	0.20	1.26	0.94	1.22
Alunite	$KAl_3(SO_4)_2(OH)_6$	0.17	0.76	1.58	1.89	2.94	0.81
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	13.9	8.07	7.19	8.17	8.92	9.46
Scorodite	Fe <sup>3+</sup> AsO <sub>4</sub> ·2H <sub>2</sub> O	0.26	0.62	0.92	1.53	2.40	0.78
Nontronite	Na <sub>0.3</sub> Fe <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ·4H <sub>2</sub> O	8.57	9.69	2.50	5.76	9.10	1.72
Bassanite	$CaSO_4 \cdot 0.5H_2O$	0.00	0.00	0.00	3.12	1.74	1.69

Table 8. X-ray analysis of the leaching residues.

#### 4. Conclusions

Arsenic and iron in solution decreased during the leaching cycle (94 days). The decrease was directly related to the solution pH level. At pH 0.8, 20% of the arsenic and -40% of iron were retained (the iron increased due to ore acid leaching), while at pH 2 As decreased by 57% and Fe by 40%; As<sup>5+</sup> precipitation drove the decrease in As <sub>(total)</sub>, due to As<sup>3+</sup> remaining constant (in the range of 200 mg/L). The decrease in the concentrations of As<sup>5+</sup> and Fe<sup>3+</sup> was due to the precipitation of ferric arsenate (FeAsO<sub>4</sub>·H<sub>2</sub>O), an amorphous precursor of scorodite.

The concentration of As in the leaching residue increased (0.03 g/kg ore content) to 1.5 g/kg at pH 0.8 (increment of 50 times). At pH 2, the concentration of arsenic in the leaching residue reached up to 6.1 g/kg, an increase of 200 times.

At pH 0.8, the iron concentration was not modified by the simultaneous dissolution and precipitation and remained in the range of 2.9%. At pH 2, its content increased to 4.5%, that is, it increased 1.55 times.

The SEM analysis of the precipitates showed the presence of Fe, As and O, which could be ferric arsenate or arsenic ferrihydrites. The X-ray analysis of the leaching residue indicated the presence of crystalline scorodite in all the leaching residues, which was formed from ferric arsenate at room temperature and in the presence of iron minerals (hematite and pyrite).

Effluent solution treatment could be incorporated into hydrometallurgical plants: the arsenic content was stably retained in the leaching residues (confined area) as scorodite, providing the benefit of recovering water, acid and copper.

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