

Arsenic removal from electrolytic sludge generated in the production of copper

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Abstract

The electrolytic sludge (ES) is generated in the electrolyte treatment plant during the production of copper. Nowadays, this sludge is returned to the process due to their high copper concentration. However, it also contains high arsenic concentration that generates serious problems due to its accumulation in the industrial process, negatively affecting cathodic copper quality. Thus, the arsenic must be reduced or removed to acceptable level in the recovered electrolytic stream. In this work, arsenic removal from an electrolytic sludge solution by synthesis of crystalline scorodite ($\text{FeAsO}_4 \cdot \text{H}_2\text{O}$) is proposed. The precipitation of scorodite is performed following two different methodologies: (1) controlling the iron oxidation process; and (2) controlling the pH evolution by several stages of neutralization. In addition, two types of solutions were used in the experiments (an artificial and ES solution). Large crystalline scorodite particles (20 μm) are formed when artificial solution is used without pH control, but the arsenic precipitation efficiency was low (around 64 %). Nevertheless, smaller crystal size was obtained when pH control is carried out, but more than 90 % of arsenic precipitation efficiency was reached. When ES solution is employed, amorphous ferric arsenate is formed. The leaching tests indicated that the crystalline scorodite with a grain size of about 20 μm leaches around 3 mg/kg (< 0.0007 % As contained in the scorodite). So, the scorodite synthesis by several stages of neutralization could be an effective technique for removal and immobilization of the arsenic in dissolution.

Keywords: *Copper, electrolyte sludge, scorodite, atmospheric precipitation, arsenic.*

1. Introduction

New consumer societies and growing in industrial activity generate high amount of wastes that cause loss economy and severe problems in the human health and environment. In this scenario, the concept of circular economy emerges, which is based on close the cycle life of the products, services, waste, materials, water and energy. So, the new tendency is reuse, recycle and valorise the generated wastes. In this sense, the development of technologies and new applications to valorise wastes in order to reduce disposal costs and avoid environmental pollution is increasing importance. The suitable treatment of industrial wastes is able to generate co-products with economic value that can be used in broad application range [1].

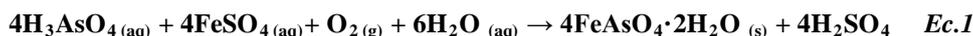
Atlantic Copper, located in Huelva (Spain), is one the biggest manufacturer of ultrapure copper cathodes in Europe (> 99.5% Cu), which produces more than 285.000 tons of cathodes per year. The industrial process begins with the smelting of copper ore concentrated (around 30 % Cu) in the Flash Smelting Furnace (FSF), in which the matte (64 % Cu) is obtained. Then, this intermedium product is carried to Converters where it is become in blister copper, with a 99 % of Cu. In the next stages, Fire Refining and Casting, the blister copper is transformed in copper anodes (99,7 % Cu). The smelter can produce 330.000 tons of anodes per year. Finally, the anodes undergo electrolysis in which the copper contained is refines to produce 99.99%-pure copper cathodes [2].

During the electrolytic copper refining, the concentration of impurities, such as arsenic, antimony and bismuth increase gradually in the electrolyte. The high concentration of these impurities produces floating slimes, which give rise to a severe nodulation of the cathodic copper, negatively affecting to current efficiency and cathode quality. Therefore, these impurities must be removed or reduced to acceptable levels. The conventional process used for controlling the level of the impurities in electrolyte involves the use of multistage electrolytic cascading cells [3], where sludge with high Cu and As content (around 10 %) is generated. Nowadays, this sludge is returned to the FSF, because of its high concentration of Cu (65 %). However, its recirculation involves serious problems of As accumulation in the process. For this reason the concentration of arsenic should be reduced substantially during copper production.

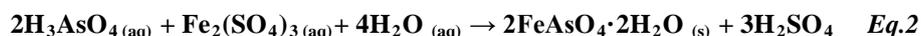
In the last decades, the removal and immobilization of arsenic present in a solution has been studied. The most common methods to reduce the arsenic concentration in solutions are: precipitation, adsorption, ion exchange resins, reverse osmosis and cementation process [4-5]. These methods can present some disadvantages such as a moderate or low efficiency, depending to the arsenic concentration solution, high costs due to regeneration and replacement of resins, high electrical consumption, etc. and in most cases, they require a pre-treatment. However, The United State Environmental Protection Agency (EPA) designated the co-precipitation with ferric ions as “The Best Demonstrated Available Technology (BDAT)” for disposal of arsenic in a solution [6]. For that reason, the most investigated method is the arsenic precipitation as ferric arsenate or scorodite [7-8].

The crystalline ferric arsenate dihydrate or scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), is a very stable mineral. The synthesis of this mineral is suitable for arsenic stabilization and storage due to its low solubility and high stability under acidic to neutral pH condition [9-10]. The hydrothermal precipitation is one method to obtain scorodite at temperatures above 100 °C using an autoclaving [11-12]. Nevertheless, this method demands a large capital investment due to necessary a sealed vessel that are resistant to high pressure, heat, acid, abrasion and also requires some auxiliary installations [9, 13]. For that reason, the scorodite synthesis at temperatures below 100 °C and atmospheric pressure has been widely investigated in last decades [8-10, 18]. The formation of scorodite can be carried out mainly base on two methods:

- Controlling the iron oxidation process. In this method the synthesis of scorodite is produced when a solution of high arsenic (V) concentration ($\text{As} \geq 10 \text{ g/L}$) that also contains ferrous iron is in presence of oxygen. The oxidations of ferrous to ferric ions induce the arsenic precipitation, according to next reaction [9-10, 16].



- Controlling the pH evolution. In this method is usually used a ferric ions solution to the formation of scorodite which is performed by sequential neutralization stages. The synthesis is carried out in three stages of pH = 1.5, 2.0 and 2.5, range in which scorodite precipitation occurs [13-15], according to next reaction.



Moreover, in the precipitation of scorodite there are several factors that should be considered for instance, initial pH, the molar ratio of iron to arsenic and temperature [8].

Taking into account the previous facts, the central objective of this work has been to reduce the arsenic concentration from an electrolyte sludge solution by synthesis of crystalline scorodite through atmospheric precipitation. This study is performed in two steps: in the first step, an artificial solution is used to reproduce scorodite and the second step involves the use of electrolyte sludge solution.

2. Materials and Methods

2.1. Waste generation process and samplings

The electrolyte sludge (ES) is generated in the electrolyte treatment plant (ETP). In this plant, mainly Bi, Sb and As are removed by electrowinning. This process is carried out in three stages and is done in a set of electrowinning cells known as "liberator cells". In each stage is obtained a solid product while the copper concentration decreases in the copper electrolyte (Fig. 1). The ES is produced in the third stage, in which is used both anodes and cathodes manufactured with lead to the removal of the dissolved arsenic as Cu_3As . During this process a part of ES is deposited in the electrodes and another one is precipitated in the bottom of the cell. Finally, both materials are mixed. Nowadays, this sludge is returned to the FSF, because of its high concentration of Cu.

The samples used in this study, electrolyte sludge, were collected from the Copper smelter located in Huelva (south-western Spain) over the spring of 2017. After collection, the samples were dried at 60 °C until reaching a constant weight.

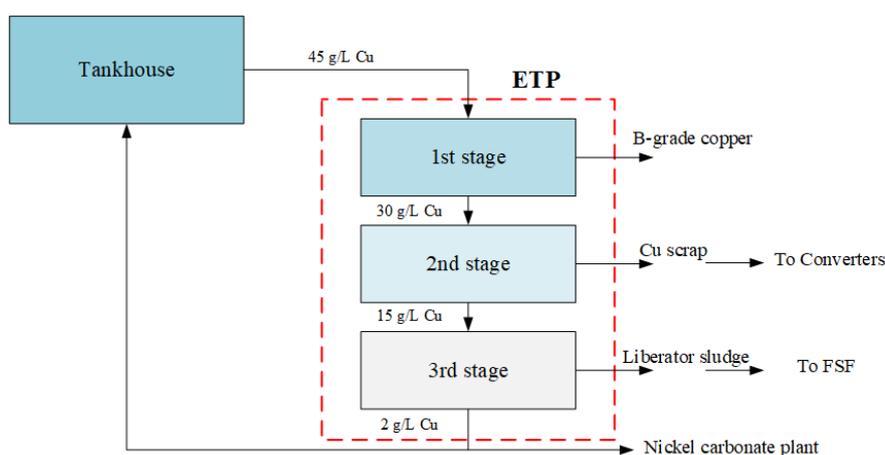


Fig. 1. Electrolyte treatment plant (ETP).

2.2. Experiments design for scorodite synthesis

The synthesis of scorodite is performed from arsenic solution. Two types solutions have been used in these experiments, an artificial solution prepared using arsenic (V) oxide pentahydrate (without interfering species) and solution from the electrolytic sludge. The second solution is obtained by dissolving the electrolytic sludge in a mix of sulphuric and nitric acid solution (1.4 M sulphuric acid and 1.8 M nitric acid) using a solid/ liquid ratio of 1:20 (initial pH < 0.5). In both cases, sulphate ferrous heptahydrate is employed.

In this work, the synthesis of scorodite is carried out by two methodologies. On the one hand, the arsenic precipitation is studied controlling the iron oxidation process [9-10] (Artificial solution: Case 1), and on the other hand, the precipitation is evaluated by several stages of neutralization using magnesium or calcium hydroxides as pH controller [13-15] (Artificial solution: Case 2, 3; Electrolytic Sludge solution: Case 4 and 5).

Table 1 shows the experimental conditions of the different cases studied for scorodite formation. In all experiments, Fe: As molar ratio is 1.5, the dissolution is heated at 85 °C, air is injected (1-2 L/min) and the reaction vessel is insulated with a thermal jacket in order to keep the temperature constant.

Case 1: Artificial solution is used and the iron oxidation process is controlled. The reaction takes place during 8 hours. Finally, the solution is filtered and the formed solid is dried at 50 °C until constant weight.

Cases 2 and 3: Artificial solution is employed and the pH is controlled using calcium hydroxide (Ca(OH)₂) or magnesium hydroxide (Mg(OH)₂), respectively. In both experiments the pH is adjusted every 3 hours. The following steps are the same as in the previous case.

Case 4 and 5: Electrolytic Sludge solution is used and the pH is controlled using calcium hydroxide (Ca(OH)₂) or magnesium hydroxide (Mg(OH)₂), respectively. The methodology followed is similar to previous cases (Case 2 and 3).

Table 1. Experimental conditions for synthesis of scorodite.

	Iron source	FeSO ₄ ·7H ₂ O
	Oxidizing reagent	Air
	Fe/As mole ratio	1.5:1
	Experimental temperature	85 °C
	Gas volume	1-2 L/min
Artificial solution (10 g/L As)		
Case 1	Prepared solution	500 mL
	Reaction time	8 h
Case 2	Reaction time by stage	3 h
	Prepared solution	100 mL
	Adjust of pH in three stages	Initial pH 1.5, 2.0 and 2.5
	Basic agent	Mg(OH) ₂
Case 3	Reaction time by stage	3 h
	Prepared solution	100 mL
	Adjust of pH in three stages	Initial pH 1.5, 2.0 and 2.5
	Basic agent	Ca(OH) ₂
Electrolytic Sludge Solution (5.5 g/L As)		
Case 4	Electrolytic sludge solution	200-500 mL
	Concentration of arsenic	5.5 g/L
	Adjust of pH in four stages	Initial pH 1.0, 1.5, 2.0 and 2.5
	Basic agent	Mg(OH) ₂
	Reaction time by stage	3 h
Case 5	Electrolytic sludge solution	100 mL
	Concentration of arsenic	5.5 g/L
	Adjust of pH in five stages	Initial pH 0.5, 1.0, 1.5, 2.0 and 2.5
	Basic agent	Ca(OH) ₂
	Reaction time by stage	3 h

The equipment used in the scorodite formation experiments is shown in Fig 2, which consists in: an air bomb, a rotameter, a mechanical stirrer, hot plate with the temperature control, a beaker with cover and a thermal jacket.

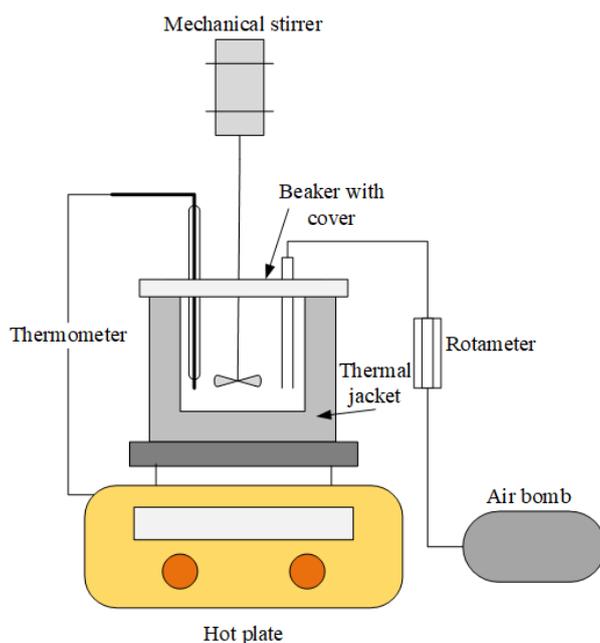


Fig. 2. Experimental equipment for synthesis of scorodite

2.3. Characterization techniques

The obtained solids were subjected to physico-chemical characterization, in which several techniques were used: X-ray fluorescence (XRF) for determining of major elements, X-ray diffraction (XRD) for determining the mineralogical composition, and scanning electronic microscopy (SEM) for determining the sample morphology. Moreover, leaching tests were also applied and the leaches were analysed by ICP-OES/MS.

2.3.1. X-ray fluorescence (XRF)

X-ray Fluorescence analysis was performed using a Panalytical (AXIOS model) sequential spectrometer. The system is equipped with X-ray tube of 4 kW, Rh front window and anode, five analysing crystals (PX1, PE 002, LIF 200, Ge 111, and LIF220) and two X-ray detectors, flow and scintillation. Prior to the analysis, the samples were prepared as pressed tables of 40 mm diameter and 25 mm thickness.

2.3.2. X-ray diffraction (XRD)

The mineralogical study was performed a Bruker diffractometer (D8-Advance A25 with $\text{Cu}_{K\alpha}$ radiation). Diffractometer settings were 40 kV, 30 mA, a scan range $3\text{-}70^\circ$ (2θ) with a step size of 0.015° , a rotational speed of 30 rpm and a counting time of 0.1 s per step.

The phases crystalline were identified with the software Match! (Phase Identification from Powder Diffraction) using the COD database (Crystallography Open Database).

2.3.3. Scanning electron microscopy (SEM)

The morphology and microstructure of the solids were studied using an environmental scanning electron microscope (QUANTA-Fei 200). Moreover, it is equipped with an Energy Dispersive Spectrometer (EDS) which enable multi-elemental semi-quantitative analysis. Following this, a mineralogy database [19] was used to determine the mineralogical composition.

Prior to the analysis, the samples are covered with carbon by metallization process using an EMITECH K-550X system.

2.3.4. Inducting coupled plasma- optical emission or mass spectrometry (ICP-OES/MS)

The determination of the composition the leaches were carried out by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique for the elements with a high concentration (100 ppb-1000 ppm). It is used an ICP-OES Varian 735S spectrometer. While for the elements with a low concentrations, between 1 ppt to 10 ppb, the determination was performed by Inductive Coupled Plasma Mass Spectrometry (ICP-MS) using a Pekin Elmer ELAN 9000 spectrometer.

2.3.5. Leaching test

Leaching tests were performed according to the R.D. 1481/2001 of 27 December [20], which regulate the disposal of waste by landfill, which is in agreement with the provisions of the Directive 1999/31/EC on landfills. The leaching tests set out in the norm UNE-EN 12457-4:2003 [21] was adopted in our experiments. The extraction fluid used was distilled water at a liquid/solid ratio of 10 L/kg ($\pm 2\%$). Polyethylene bottles were used as extraction vessels, which were subjected to rotation with agitation equipment with Teflon-coated rod at 5-10 rpm during 24 ± 0.5 h. After extraction were vacuum filtered using membrane filters of 0.45 μm pore size.

3. Results and Discussion

3.1. Characterization of the electrolyte sludge (ES)

The ES contains high Cu concentration (54 %) (see Table 1), which is mainly in form of copper metal (Cu) and cuprite (Cu_2O). In addition, another significant copper fraction is associated to arsenic in form of Cu_3As (domeykite mineral) and sulphur as copper sulphates ($\text{CuSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Cu}_5(\text{SO}_4)_2(\text{OH})_6 \cdot 4\text{H}_2\text{O}$). These results suggest that copper could be treated for its recovery or recycle, if the arsenic is previously removed.

It stands out the low concentrations of Bi, Ni, Pb and Sb present in the sludge, because these impurities remain in the electrolytic solution during the ETP process. Nowadays, the concentration of these impurities in the electrolyte are reduced in other plants of the process, such as nickel carbonate plant [2] or new research pilot plants [22].

Table 2 Concentrations (%) of major elements measured by XRF in ES, and mineral phases identified. LOI = Loss on ignition; N.D = No detected.

ES Concentration (%) major elements				Mineral phases (%)	
As	9.5 ± 2.9	P	0.02 ± 0.01	Domeykite (Cu_3As)	27
Bi	0.41 ± 0.05	Pb	0.07 ± 0.03	Cuprite (Cu_2O)	22
Ca	0.02 ± 0.01	S	7.1 ± 1.8	Native copper (Cu)	19
Cl	0.03 ± 0.01	Sb	0.47 ± 0.16	Poitevinite ($\text{CuSO}_4 \cdot \text{H}_2\text{O}$)	5.2
Cu	54 ± 4	Si	0.02 ± 0.01		
Fe	0.03 ± 0.01	Zn	0.04 ± 0.01		
Ni	0.39 ± 0.10	LOI	N.D		

3.2 ES dissolution

In order to obtain a completely dissolution of the ES, several leaching experiments were performed using various acid solutions (sulphuric acid, nitric acid, hydrogen peroxide, etc.) and different solid/liquid ratios. The experiments revealed that the ES is successfully dissolved in a mix of 1.4 M sulfuric acid and 1.8 M nitric acid using a solid/ liquid ratio of 1:20 (g / mL). The Fig. 3 shows the concentrations of major element of ES in solution in relation with their concentration in the solid phase. The solution contains around 26 g/L of Cu, 5.5 g/L of As, and 50 g/L of S. These data have been estimated according the Cu, As and S concentration in the sludge and sulfuric acid added, and they were confirmed by ICP-OES/MS.

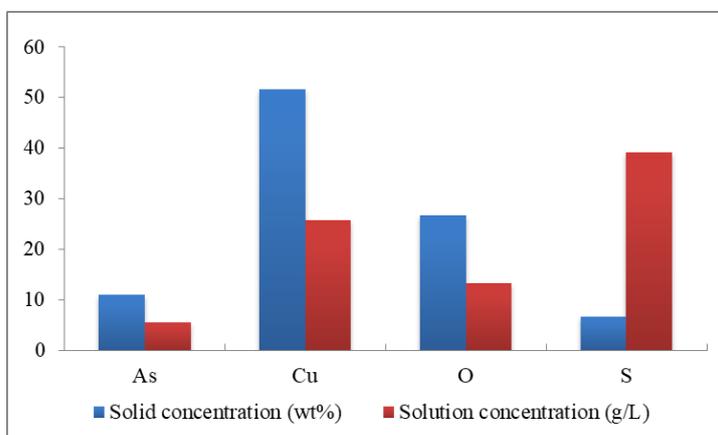


Fig. 3. Concentrations of major elements in the ES and after the leaching

3.2. Physical-chemical characterization of solids phase from scorodite experiments.

The concentrations of major elements (% dry weight) of the obtained precipitated solids are shown in Table 3. It is observed that the precipitates in the Cases 1 and 2 are mainly composed of 39 % As and 24 % Fe. These values are in agreement with the theoretical composition of scorodite (32 % As and 24 % Fe) [17-18]. Moreover, the losses on ignition (around 15 %) agree with the theoretical weight change associated with the loss of the two H₂O molecules of FeAsO₄·2H₂O (about 15.5 %) [11]. According to the diffraction pattern (Fig. 4) scorodite is the only mineral phase identified in both cases and their particles (Fig. 5) present a dipyramidal octahedron crystals form, according to their theoretical structure. In Case 1, the crystal size identified is around of 20 μm, however, the crystals are smaller and form aggregates in the Case 2, being less than 10 μm.

Table 3. Concentrations (%) of major elements by XRF of precipitates obtained at the different cases. LOI= Loss on ignition; N.D= No detect3

Test	As	Bi	Ca	Cu	Fe	O	S	Sb	LOI
Case 1	39.2	N.D	N.D	N.D	23.6	22.9	0.03	N.D	14.1
Case 2	38.1	N.D	N.D	N.D	24.0	22.6	0.07	N.D	15.3
Case 3	19.0	N.D	11.9	N.D	13.0	33.6	11.4	N.D	11.0
Case 4	32.1	2.17	N.D	4.23	24.1	25.4	2.14	0.59	9.1
Case 5	1.83	0.10	22.1	3.39	1.65	41.5	20.2	0.08	8.9

In Case 3, the solid formed contains 19 % As, 13 % Fe, 12 % Ca and 11 % S as major elements (Table 3). This composition is in agreement with the mineral phases found, scorodite and gypsum, by the XRD analysis (Fig 4). The presence of gypsum is due to the addition of Ca(OH)₂ to adjust the pH [14-15]. It is estimated that the precipitated is formed about 40 % of gypsum and 60 % of scorodite, according to As and Ca content. The morphology of solid particles is in Fig 5 can be observed, being this precipitate formed by two types of particles: fines particles (point 4, Fig 5) showing dipyramidal octahedron crystals (scorodite), which are adhered to large particles (point 3, Fig 5) with tabular structures (gypsum). These results confirm the crystal phases identified by XRD analysis. Besides it can be observed that the chemical composition of the particles determined by EDS is similar composition as measured using XRF analysis.

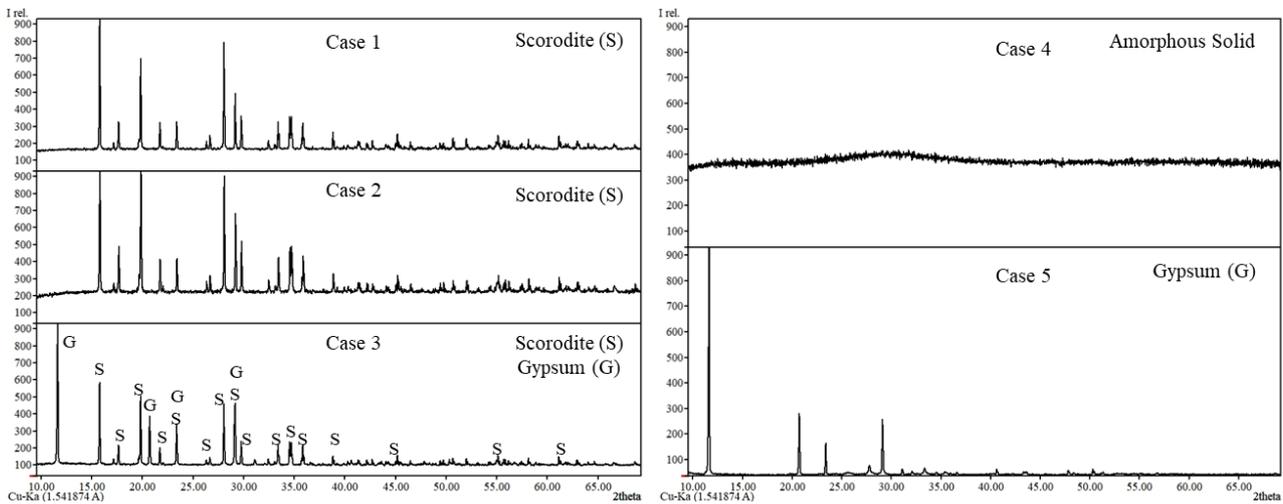
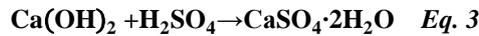


Fig. 4. XRD patterns of precipitates obtained at the different cases

The solid precipitated in the Case 4 is composed mainly of 32 % As and 24% Fe. Also, it contains Bi (~ 2 %), Cu (~ 4 %), S (~ 2 %) and Sb (< 1 %) in minor proportions, according to the XRF analysis (Table 3). The XRD results are shown Fig 4, where it can be seen that the solid obtained in this case is amorphous. However, its composition is similar to the theoretical composition of scorodite, so it is possible that this solid is some of the amorphous ferric arsenate phases described by other researchers [17-18, 12]. SEM image (point 1, Fig. 6) shows that the particles are forming aggregates, which are characterised by their amorphous morphology, in agreement with the XRD analysis. In addition, the EDS results confirm these agglomerated are mainly composed of Fe and As, in agreement with the data obtained by FRX analysis.

The solid formed in the Case 5 contains 22% Ca and 20 % S as major elements. Also, it contains Cu (~ 3 %), As (~ 2 %) and Fe (~ 2 %) in lower concentration, Table 3. In the XRD pattern (Fig. 4) is observed that gypsum is the only crystalline fraction found. As in previous experiments, the formation of gypsum is associated with the presence of calcium hydroxide added and sulfuric acid, which is in the electrolytic sludge solution (Eq. 3). These results are in agreement with the chemical composition determined by XRF analysis. The SEM pictures show that the solid presents heterogeneous morphology. It can be seen tabular crystals, which are in agreement with the theoretical structure of gypsum, with small particles deposited onto their surface (point 2, Fig. 6). These particles have high concentration of As and Fe and not present crystalline morphology, so it could be some of the amorphous ferric arsenates phases found by other authors [17-18, 12].

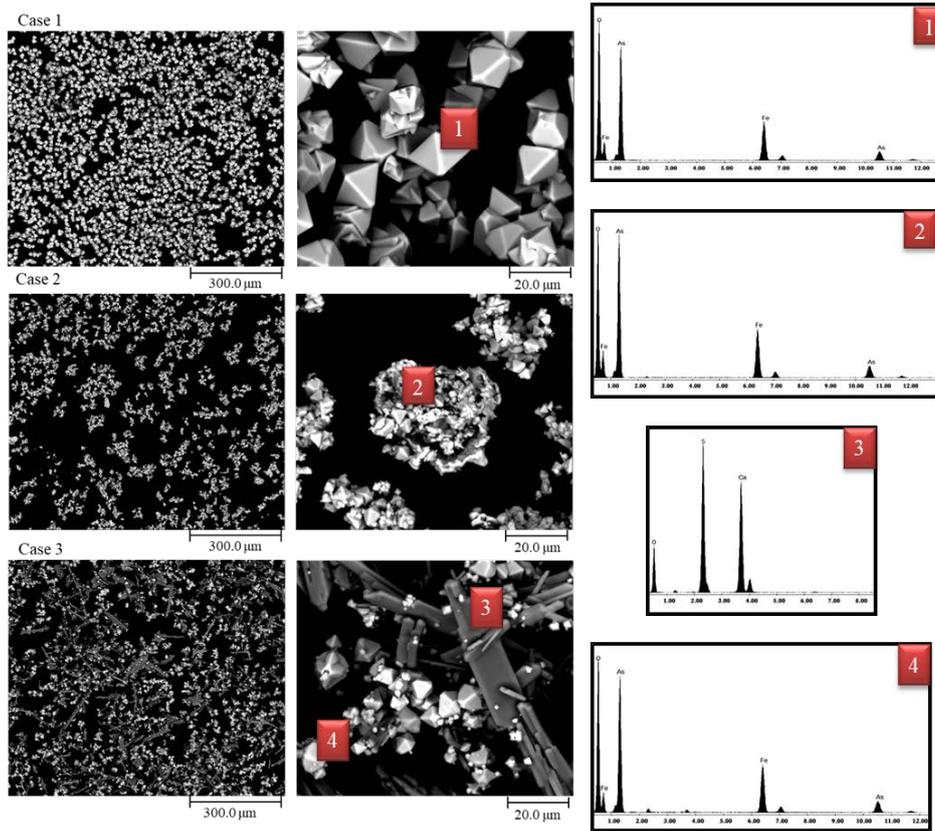


Fig. 5. SEM images of precipitates obtained using artificial solution.

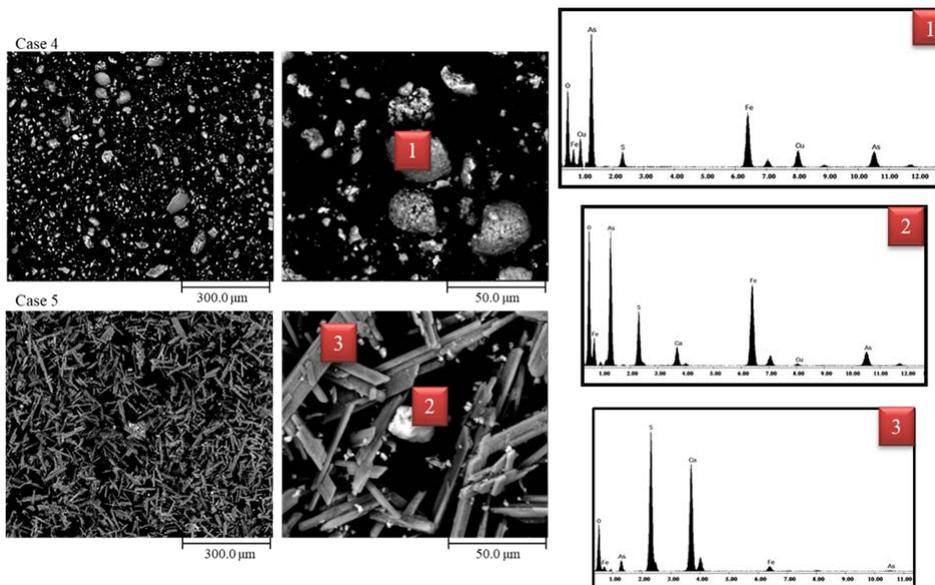


Fig. 6. SEM images of precipitates obtained using ES solution.

Finally, UNE leaching tests [21] according to the R.D 1481/2001 of 27 December [20], were performed to the solids obtained in each case to determine if their disposal on landfill would implied any environmental risk. The data of the UNE test and the thresholds concentrations both for non-hazardous and hazardous material, expressed as mg of elements leached per kg of original dry material in Table 4 are shown.

It can be seen that the concentration of As in all leachates is above the established limits in the R.D 1481/2001 (As: 2 mg/kg and 25 mg /kg, for both non-hazardous and hazardous waste, respectively). In addition, the results of the leaching test show that the particles fines of scorodite (Cases 2 and 3) leach more arsenic than larger particles (Case 1) [23-24]. Also, it can be observed that the solid formed in Case 2 leaches less arsenic than the obtained in Case 3, according to other researchers this fact is due to the agglomeration of the crystalline particles [24]. Hence, the arsenic mobility depends of the crystal size, agglomeration and sulphate ion substitution in the structure of scorodite, according to other reports [17-18, 24].

Furthermore, it can be seen that solids formed by using the ES solution (Cases 4 and 5), leach copper exceed above references limits for non-hazardous and hazardous material (50 mg/kg and 100 mg/kg, respectively). In agreement with other studies, this is due to inclusion or substitution of the copper or sulphate ions in the structure of scorodite that can produce phases amorphous and easily leachate [16-18, 24]. In addition, in the Cases 3 and 5 it can be seen a notable calcium and sulphur concentration in the leached, however do not exceed the reference limit values.

Table 4. Results of the leaching test on the samples obtained in the different cases. C_i = element concentration in the leaching liquid; i = number of case.

Element	Detection Limit (mg/kg)	C1 (mg/kg)	C2 (mg/kg)	C3 (mg/kg)	C4 (mg/kg)	C5 (mg/kg)	Threshold Level Non-Hazardous material (mg/kg)	Threshold Level Hazardous material (mg/kg)
As	0.03	2.6	47	54	2527	174	2	25
Ba	0.02	<LD	<LD	<LD	<LD	<LD	100	300
Bi	0.02	<LD	<LD	<LD	<LD	1.2	-	-
Ca	0.1	<LD	0.5	5988	<LD	6033	-	-
Cd	0.002	<LD	<LD	<LD	<LD	<LD	1	5
Cr	0.02	<LD	<LD	<LD	<LD	<LD	10	70
Cu	0.002	<LD	<LD	<LD	3985	1745	50	100
Fe	0.01	5.2	5.8	28	9.5	2.3	-	-
Mg	0.1	<LD	42	<LD	904	5.0	-	-
Mo	0.005	<LD	<LD	<LD	<LD	<LD	10	30
Ni	0.005	0.4	0.3	0.1	3.8	3.2	10	40
Pb	0.01	<LD	<LD	<LD	<LD	0.2	10	50
S	1	110	55	5235	2942	5486	20000	50000
Sb	0.01	<LD	<LD	<LD	0.1	0.5	0.7	5
Se	0.02	<LD	<LD	<LD	<LD	<LD	0.5	7
Zn	0.005	<LD	0.1	<LD	0.15	<LD	50	200

3.3. Precipitation efficiency

The arsenic precipitation efficiencies in Table 5 are shown. According to the chemical composition data (Table 3), the degree of arsenic precipitation is around 100 % in cases 2, 3 and 5, in which the scorodite synthesis was performed by several stages of neutralization. Lower efficiencies were obtained in Case 1 and 4, reaching 64 % and 85 %, respectively. On the other hand, the iron could not be recovered more than 80 % in any cases.

Nevertheless, arsenic and iron precipitation yield was about 85 % and 49%, respectively, when ES solution and magnesium hydroxide were used. These values are similar found in other studies [17-18]. In addition, it can be seen that more than 90% of the calcium added precipitates in the two solutions

employed, while the magnesium remains in solution [14]. Also it is observed that the quantity of solid precipitated is higher when $\text{Ca}(\text{OH})_2$ is used (Cases 2 and 3). This difference in the mass amount is higher with the ES solution, due to a higher sulphates concentration.

Table 5. Precipitation efficiencies and amount of solid formed in each case.

Test	Initial Fe/As molar ratio	Solid mass obtained (g)	Precipitation (%) efficiency			
			As	Fe	Ca	Cu
Case 1	1.5	8.3	64	35	-	-
Case 2	1.5	3.2	100	69	-	-
Case 3	1.5	6.1	100	71	90	-
Case 4	1.7	2.9	85	49	-	2.4
Case 5	1.7	34	100	80	97	44

4. Conclusions

This study is focused on the arsenic removal from the sludge generated in the electrolyte treatment plant by atmospheric scorodite formation, and the experiments were carried out according to the oxidation of ferrous iron to ferric one, and pH evolution control. From this research, the following can be highlighted:

- i. Electrolyte sludge is characterized by a high concentration of Cu (around 54 %), As (around 10 %) and S (around 7%) as major elements. This composition is in agreement to the mineral phases found: cuprite (Cu_2O), domeykite (Cu_3As), native copper (Cu) and copper (II) sulphate hydrate ($\text{CuSO}_4 \cdot \text{H}_2\text{O}$). According to its composition, the ES is an important secondary resource of Cu and its reprocessing would have remarkable economic and environmental benefits.
- ii. ES is successfully dissolved in an aqueous medium with 1.4 M sulfuric acid and 1.8 M nitric acid by using a solid/liquid ratio of 1:20 (g/mL). The ES solution obtained contains 26 g/L Cu, 5.5 g/L As and 50 g/L S.
- iii. Crystalline scorodite is successfully obtained when artificial solution is used. However, when ES solution is employed, the formation of amorphous iron arsenate takes place.
- iv. The degree of arsenic precipitation is around 100 % in the most cases, in which the synthesis of scorodite is performed by stages of neutralization.
- v. Leaching tests reveal that scorodite with high grain size leachates less than fine or amorphous particles.

In summary, the scorodite synthesis by several stages of neutralization could be an effective technique for removal and immobilization of the arsenic contained in the sludge coming from the third step of the electrolytic purification plant. However, more researches are needed to find the optimal conditions in order to produce crystalline scorodite when the ES solution is employed in the experimental process.

Acknowledgements

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