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Investigations on the selective arsenic reduction from copper concentrates by alkaline sulfide leaching and arsenic precipitation

Meiner, Karsten, TU Bergakademie Freiberg, Germany (corresp. author)

Berkh, Khulan, BGR-Federal Institute for Geosciences and Natural Resources, Germany

Weigelt, Aaron, Aurubis AG, Germany

Thiere, Alexandra, TU Bergakademie Freiberg, Germany

Vogt, Daniel, TU Bergakademie Freiberg, Germany

Stelter, Michael, TU Bergakademie Freiberg, Germany

Kassahun, Andrea, Wismut GmbH, Germany

Meima, Jeanette, BGR-Federal Institute for Geosciences and Natural Resources, Germany

Charitos, Alexandros, TU Bergakademie Freiberg, Germany

Abstract

Arsenic is a critical element in copper refining process which causes environmental and health risks and is therefore unfavorable if its content in the concentrates for smelters is too high. The best available technique on an industrial scale to remove arsenic from copper concentrates is partial roasting and subsequent immobilization as scorodite. With partial roasting a residual content of 0.3 wt.-% As or less can be ensured in the calcine. In comparison to partial roasting, the selective leaching of arsenic within an alkaline sulfide solution is investigated followed by the precipitation of arsenic sulfide / sodium tetrathioarsenate to immobilize the arsenic. Successful results considering sulfide leaching and challenges faced with regard to the precipitation step and subsequent elution steps after drying are presented and discussed.

1. Introduction

Arsenic is a critical element in the copper primary production due to the need of cost-intensive processes to reduce the concentration of this financially penalized impurity in copper concentrates alongside antimony and bismuth (Schlesinger et al., 2011; Nazari et al., 2017; International Copper Study Group, 2021). The feed materials for the first stage of primary pyrometallurgical copper production, smelting plants, are flotation concentrates. These may contain more than 1 wt.-% of arsenic depending on the ore deposit (Duckworth, 2016; Nazari et al., 2017). Therefore, it is necessary to bring the arsenic content to a threshold, which suits international smelting requirements. In China, the typical import limit is 0.5 wt.-% As in the feed concentrates to inhibit its enrichment in phases associated with pyrometallurgical copper production (Duckworth, 2016).

Currently, the most suitable technique to remove arsenic reliably from copper concentrates is partial roasting, whereby the arsenic is volatilized as As_2S_3 and afterwards oxidized (Nazari et al., 2017). The resulting arsenic concentration in the roasting calcine is around 0.3 wt.-%, independent from the arsenic in the feed stream (A. Charitos et al, 2016). Important for the industrial implementation is the necessary sulfur content in a range of 35-40 wt.-% and a low calcium content beneath 0.5 wt.-% to inhibit losses by formation of involatile $Ca_3(AsO_4)_2$ (Nazari et al., 2017). The collected arsenic-bearing waste from the roaster off-gas treatment will be neutralized, washed, oxidized and precipitated as ferric arsenate, scorodite or calcium arsenate (Nazari et al., 2017). These are known as landfilling solids, whereby scorodite is the-state-of-the-art deposit in terms of water resistance, i.e. stability against leaching (Fujita et al., 2009; García, 2016; Nazari et al., 2017).

The idea to leach selectively the arsenic in an alkaline sulfide solution (ASL), where the copper remains as sulfide residue, is described in the literature. Alkaline sulfide leaching aims at arsenic-and/or antimony-rich minerals in the concentrate, i.e., enargite, tennantite or tetrahedrite (Tongkamp et al., 2010; Nazari et al., 2017). The effect of adding elemental sulfur to precipitate arsenic as a sulfide compound (Na_3AsS_4) from alkaline sulfide leaching has already been investigated, including residue characterization (Tongamp et al. 2010; Nakon 2012; Li, 2013; Haga et al., 2015; Bedoya-Lora et al., 2019). The attendance of UV-absorbing polysulfides was discussed in some of the above cases, however their possible effect on the arsenic containing alkaline sulfide solution could be a matter of further inquiry. Moreover, the suitability of ASL as a possible industrial hydrometallurgical alternative, in contrast to partial roasting, followed by the subsequent precipitation as As_2S_3 or Na_3AsS_4 instead of scorodite or calcium arsenate has not yet been investigated. Hence, the above-mentioned route is the subject of this paper as a potentially viable option for pretreatment of copper concentrates. Parameters associated with both the leaching and precipitation steps are part of the experimental investigation considered here.

2. Experimental

2.1 Material characterization

Three Chilean concentrates and one ore were investigated, defined as A, B, G and F respectively in dependence of delivery entrance for analyses. Their physical-chemical compositions are listed in table 1. Concentrates A and B are weathered samples, while F and G are the most fresh ones. The elemental analysis of the feed and leaching residues was realized in double determination by Thermo M6 AA6 System AAS from aqua regia solution; the sulfur determination by C/S analysis with an ELTRA CS- 580 analyzer (*), the Ca content (**) by ICP-OES from AnalytikJena PlasmaQuant PQ9000. Concentrates A and B are weathered concentrate samples, while ore F and concentrate G are fresh ones. The d80-values were measured for the feed samples and leaching residues by dry dispergation with the diffraction device of HELOS & RODOS from Sympatec within a 3 s measuring cycle. The particle size distribution of the concentrates was measured shortly after the homogenization runs to inhibit renewed agglomeration.

Table 1: physical-chemical composition of used copper concentrates by AAS in aqua regia, S-content (*) by C/S-analysis, Ca-content (**) in HF-HNO3 by ICP-OES.

	Conc. A	Conc. B	Ore F	Conc. G
	wt.-%			
d_{80}/µm	91.9	92.9	155.0	50.0
As	4.0	1.8	4.5	2.8
Cu	14.3	20.3	11.7	23.1
Fe	23.1	17.1	7.0	18.8
S*	40.8	25.0	17.0	35.0
Sb	0.3	0.2	0.1	0.2
Ca**	0.3	0.1	0.3	0.3

The investigated copper concentrates A and B are, coarser than the typical size range of 40-70 µm after flotation (Schlesinger et al., 2011). For qualitative and semi-quantitative elemental composition of the mineral grains, energy dispersive X-ray microanalyses were performed using two Silicon Drift Detectors (Flash Detector 5030) from Bruker Nano. Textural characteristic and mineralogical composition of all feed samples, leaching residues and precipitation residues were investigated with a high-resolution SEM (MLA 650F Quanta FEG ESEM) by BGR. Only the obtained results of the major phases of the feed samples are shown in table 2. All three concentrates contain considerable amounts of enargite Cu_3AsS_4 and tennantite $Cu_{12}As_4S_{13}$. In addition, the concentrates contain a high proportion of fine-grained matrix with a grain size of less than few microns. It

mostly consists of minerals like chalcanthite $CuSO_4 \cdot 5H_2O$, melanterite $FeSO_4 \cdot 7H_2O$ and brochantite $Cu_4[(OH)_6|(SO_4)]$, which are also present in the samples of A, B and G. Ore F shows a high amount of quartz SiO_2. Moreover, it contains unusual high amounts of enargite resulting in a high copper content.

Table 2: Mineralogical characterization (MLA) of major phases in feed samples .

|	Conc. A	Conc. B	Ore F	Conc. G
		Vol.-%		
Pyrite	41	20	11	25
Matrix	22	27	2	24
Chalcopyrite	3	12	--	11
Chalcocite	--	--	--	4
Covellite	1	4	--	2
Enargite	6	3	21	5
Tennantite	12	5	5	9
Quartz	3	3	51	3

In addition, feed samples and the leaching residues were measured by powder X-ray diffraction using a Seifert-FPM URD 6.5 using the Bragg-Brentano geometry equipped with a sealed X-ray tube with Cu anode operated at 40 kV/30 mA and a graphite monochromator for filtering the diffraction beam to reduce the impact from Fe-fluorescence on the intensities. The qualitative phase analysis was done using the Search-Match routine of HighScore+ (Panalytical) restricted to the elemental composition by AAS in combination with the ICDD PDF-4+ database and the quantitative analysis was done with Rietveld refinement, implemented in the MAUD routine (L.M. Lutterotti, 1999). The resulting average error of all ASL-residue samples for each detected mineral phase was 17 %, due to the absolute error on phases at the lower detection limit of 2 Vol.-% being higher.

2.2 Leaching test conditions

The leaching tests were carried out in a 400 ml double-walled glass (DWG) vessel coupled with an external thermostat. An overhead stirring motor equipped with a Teflon stirrer ensured solid-liquid mixing. A design of experiments for the evaluated parameters and subdivided levels resulted in 25 (A/B) and 13 (F/G) duplicated experiments which are listed in table 3. The vessel lid contains a closable port for arresting the CrNi temperature sensor used to control the leaching temperature or the pH-Electrode (JuMO tecLine). The volume for all experiments was set to 200 ml. Each hour a 3 ml sample was taken by a pipette, transferred to a 5 ml centrifuge flask and centrifuged for solid-liquid-separation with 3000 rcf for 1 min in the Eppendorf centrifuge Type 5910R.

Table 3: All experimental conditions in ASL leaching tests for concentrate A, B, F and G.

Parameter	Unit	Used values
s/l-ratio	g concentrate / ml solution	1/2; 1/5; 1/10; 1/16; 1/20
Temperature	°C	60; 70, 80; 90
d80 (concentrate)	µm	25-155
[added $Na_2S \cdot 3H_2O$]	M	0; 0.5; 1.0; 1.5; 2.0; 2.5
[NaOH]	M	1.5; 2.5; 3.5
Stirring velocity	rpm	100; 200; 400
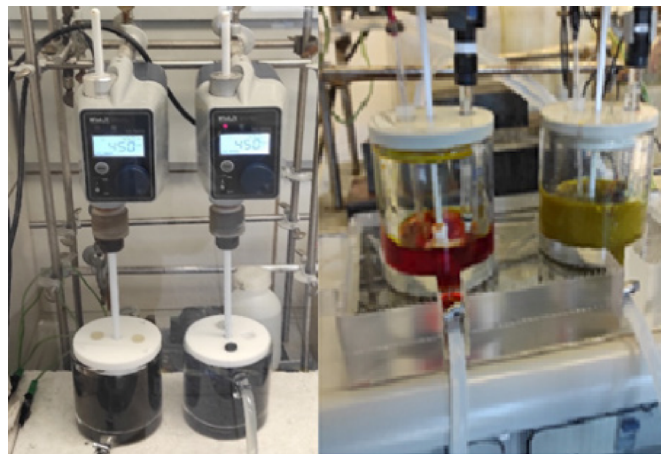
Figure 1: 400 ml DWG vessels with overhead Teflon stirrer-and Teflon or PVC plastic lids left) leaching setting, right) precipitation setting.

The concentration of the NaOH leaching solution was modified between 1.5 M / 2.5 M and 3.5 M NaOH (CAS- No.: 1310 – 73 - 2). Subsequently, up to 2 M $Na_2S \circ 3H_2O$ (CAS- No.: 16721 - 80- 5) was added to the solution. Before conducting an experiment, the lixiviants NaOH and Na_2S were pre-heated in a drying box (MEMMERT, Type UFE 500) to prevent remaining undissolved Na_2S-particles and to bring the solution close to reaction temperature. Afterwards the solution was added to the DWG vessel, which was filled with the weighed concentrate and heated to the reaction temperature by thermostat. The experimental setup of the DWG vessels used for leaching tests is shown in figure 1 on the left side and for precipitation of the arsenic sulfide from the leaching solution on the right side after solid-liquid separation. The separation of the leaching residue and the solution was realized by centrifugation for 10 min at 3000 rcf. The residue was washed with deionized water 3 times for 10-30 min at 3000-3500 rcf before drying for 24 h and crushing for analysis in a mortar with pestle made of porcelain. The experimental error was examined by correlation of the arsenic leaching

yield (Aly) of the liquid phase in dependence of the Aly of the residues, based on the arsenic content determination by AAS. The correlation lays within 10 % limits around the model fit line. The correlation coefficients for sample A, B, F and G (without outliers) concerning the evaporation loss of 15% in average were $R^2(A) = 0.96$, $R^2(B) = 0.90$, $R^2(F) = 0.96$, $R^2(G) = 0.97$.

2.3 Preliminary precipitation test conditions

Factors varied within the preliminary precipitation tests included the way of preparation of the utilized solution, the initial content of arsenic in the solution used for precipitation (As_{Feed}) and the added elemental sulfur. The temperature and duration of conditioning of the solution was 90 °C and 2 h, respectively. Subsequently, the temperature was reduced through natural cooling. Finally, precipitation was carried out at room temperature for 5 h for all experiments. The filtration of the precipitation residues was conducted within a vacuum pump and a Buchner funnel and afterwards with a PTFE membrane under vacuum filtration for the separation of finer grained residues. For the identification of the solid compounds a sample of each solution was taken by pipette on a Petri dish (10 ml) and dried overnight at 60 °C. The solid content of As, S and Sb in the precipitated solid was measured by SEM-EDX (CARL-ZEISS Ultra 55, EDAX, standardless quantification, 20 kV) at five different spots for every sample and as an average value over the sample.

2.4 Elution tests for precipitation residues

The elution tests of the precipitation residues were carried according to the DIN EN 12457- 4 standard Test using an 1:10 ratio of solid to liquid with 0.5 g of sample weight in a centrifuge tube with 5 ml distilled water in an overhead shaker Heidolph Reax2 for 24 h. The solutions were filtered over 0.45 µm. The solutions after the standard elution tests were diluted 1:100 and 1:1000 and acidified for the analytical determination by ICP-OES (Agilent 5100 ICP-OES) and ICP-MS (Agilent 7700 Series ICP-MS).

3. Experimental results

3.1 Alkaline sulfide leaching

Figure 2 shows the dependency of the resulting arsenic residue content in dependence on the added amount of sodium sulfide to NaOH solution during leaching for all feed materials.
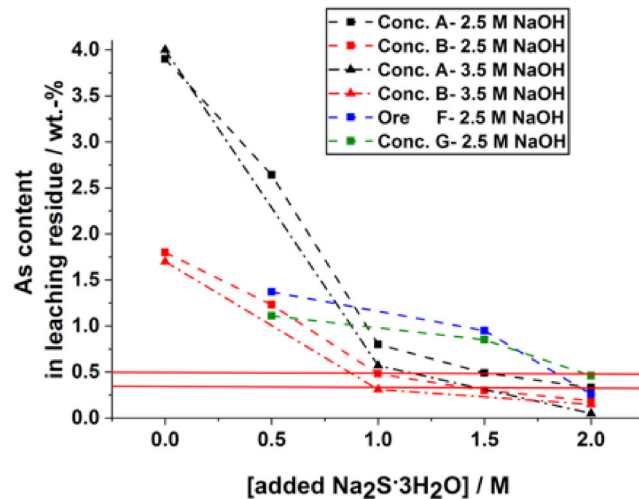
Figure 2: Arsenic leaching yield in dependence of Na₂S·3H₂O and NaOH with an s/l-ratio of 1:10 at 80 °C and 250 rpm with 4 h batch time with 0.5 and 0.3 wt.-% As lines.

The continuous red lines show the arsenic import limit threshold in China for copper concentrates (0.5 wt.-%) and the lower red line the typical As content of roasting calcine (0.3 wt.-% As) (Charitos et al., 2016). The arsenic content in the residue is decreasing with increasing sodium sulfide content due to the formation of thioarsenate. The usage of 2.5 M NaOH is effective for the dissolution of the arsenic by contributing the pH-value ≥ 12 for the dehydrogenation of the sulfide. At 2.5 M NaOH an ASL residue with an arsenic content of below 0.5 wt.-% and in some cases below 0.3 wt.-% has been achieved for conditions noted in the caption of figure 2. A concentration of 2.0 M Na₂S∘3H₂O was required to achieve above mentioned arsenic residue thresholds. Experiments realized at 3.5 M NaOH led to enhanced arsenic dissolution (compared to those with 2.5 M NaOH), resulting in lower arsenic residue content for all investigated feed materials. However, the higher amount of NaOH can lead to ineffective solid-liquid separation due to its higher salt freight. Moreover, NaOH is more expensive than Na₂S. Hence, a concentration of 2.5 M NaOH and added 2 M Na₂S is considered most suitable to obtain an arsenic-poor leach residue.

The temperature, stirring velocity, d_{80}-value, s/l-ratio were varied besides the concentrations of sodium hydroxide and sulfide, as already discussed in table 3. Increasing the s/l-ratio leads to decreased arsenic content in the residue due to more efficient mixing of the solid-liquid-pulp, which was determined from an s/l-ratio of 1/2, 1/5, 1/10 and up to 1/20 g concentrate/ml solution at two different temperatures of 80 and 90 °C. Increasing leaching temperature to 90°C with the other conditions the same as noted in the caption of figure 2, not only allows for an arsenic residue of below 0.3 wt.- % to be generated but yields arsenic concentrations as low as 0.13 wt.-%. In addition, experiments were carried out with coarse feed and ground particles (d_{80} = 92 µm, 71 µm, 44 µm and 24 µm) for concentrate A to examine leaching batch time in dependence of particle size of the concentrates. Considering the increasing leaching

kinetics by decreasing the particle size of the feed from the coarser (d_{80}(A)= 92 µm) to the finest-ground particles (d_{80}(A)= 24 µm), the fine-ground delivers the lowest arsenic residue content, measured at 80 °C. With a decreasing d_{80}-value the arsenic leaching yield is increased by 10 %. Else, the results with a medium d_{80} of 44 µm are satisfactory, considering the lower energy amount for grinding. Hence, within 2 h the arsenic concentration from copper concentrate A is decreased from 3.5 wt.-% (for d_{80} = 44 µm) to 0.13 wt.- % As in the leaching residue, whereas the leaching solution needs 4 h to decrease the arsenic content from 4 wt.-% to 0.3 wt.-% using the coarser feed concentrates (for d_{80} = 92 µm) and 2.5 M NaOH, 2 M Na_2S, 250 rpm at 90 °C. Based on the above laboratory scale experiments the ASL process is suitable to separate arsenic selectively from copper concentrates.

3.2 Leaching mineralogy

The corresponding changes with regard to the mineralogy of solids participating in the leaching reactions is elucidated in figure 3 for concentrate A as a function of the added sodium sulfide concentration. The main phases of the concentrate A are given in table 2.
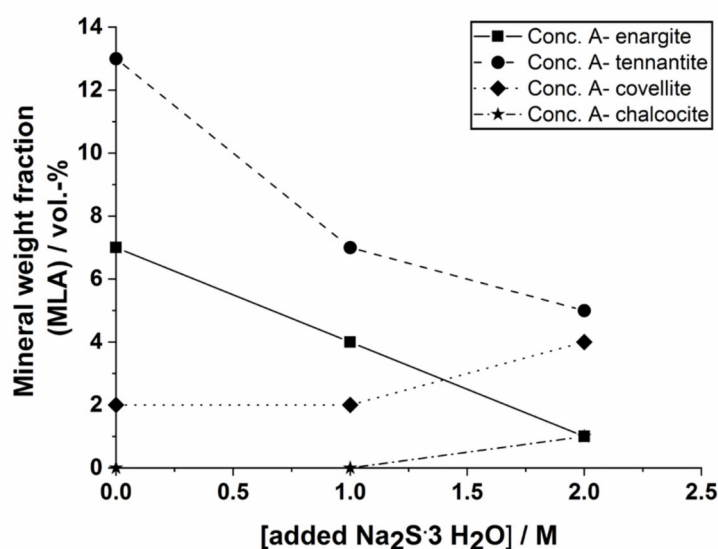

Figure 3: Leaching mineralogy in dependence of added sodium sulfide concentration for concentrate A (d80 = 44 µm, 2.5 M NaOH, 250 rpm, 4 h, s/l-ratio 1:10).

According to MLA, copper minerals such as chalcocite and covellite are formed during ASL, whereas Enargite and Tennantite are reduced in the residues. In addition, unknown copper sulfide phases with a stoichiometry between covellite and chalcocite are formed. The reaction takes place with increasing sodium sulfide concentration to dissolve the arsenic as AsS45- ions, because of a higher accessibility to the arsenic and sulfur atoms in the crystal. It is also apparent from figure 3, that enargite can be probably more amenable to leaching in comparison to tennantite, besides the higher tennantite content. Most of the residues show a similar behavior, because tennantite

is often remaining in higher quantities, whereas enargite is completely missing in the leaching residues. This can be explained due to the higher tennantite content in the feed. The results from MLA lead to a probable assumption of the chemical reaction according to the proposed equation 1 (formulated by means of the mineralogy information from XRD and MLA).

$$5\ Na_2S_{(aq)} + 2\ Cu_3AsS_{4(s)} \quad \rightarrow \quad 2\ Na_5AsS_{4(aq)} + Cu_2S_{(s)} + 4\ CuS_{(s)} \qquad 1)$$

3.3 Sample characterization of arsenic sulfide precipitation and elution tests

Table 4 shows preliminary precipitation results, including the elution tests of precipitated sodium tetrathioarsenate (in contrast with the original goal to precipitate arsenic sulfide), which was determined qualitatively in the samples by XRD. The ASL solution resulting from leaching of fresh feed material (ore F) and from ground weathered concentrate A (d_{80} = 44 µm) were utilized in experiment 1 and 3, respectively. The solution in experiment 2 was prepared by dissolving orpiment powder As_2S_3 (Kremer Pigmente) in 2.5 M NaOH and in experiment 4 only a sulfide free solution with As_2O_3 in 2.5 M NaOH was used.

Table 4: Summary of precipitation results and conditions.

Exp. Nr./ Conditions	Unit	1	2	3	4.1	4.2	4.3
Type of solution		ASL/ Ore F	NaOH/ $As_2S_{3(orpiment)}$	ASL/ Conc A	NaOH/ As_2O_3		
[AsF$_{eed}$]	g/l	20.0	20.0	4.6	44.0		
Added S^{el}/[As$_{feed}$]	gS/g$_{As}$	2/7	2/7	1/1	1/2		
[As$_{solidEDX}$]	wt.-%	13.3	30.5	5.4	13.8	21.2	2.5
[S$_{solidEDX}$]	wt.-%	22.3	31.3	24.0	76.5	45.3	7.4
As-precipitated yield	%	4.8	1.4	3.2	7.3	1.4	7.1
[As$_{Elution}$]	g/l	3.0	8.9	0.8	3.6	15.9	3.6

Samples 4.1, 4.2. 4.3 are obtained from the same solution (exp. 4) sequentially by using different methods. In part 4.1. the precipitate is achieved on the Buchner funnel (Filtrak 391, Ø 11 cm), in 4.2 the precipitate is part after filtration on the Microfilter with the PTFE-filtering paper and in 4.3 the precipitated solid under the remaining filtrate, which are separated by pipetting the solution and drying on petri dish. In experiment 1 and 3 no precipitation occurred, hence solids utilized for elution tests were obtained as a result of drying overnight on the Petri dish. Moreover, in experiment 1 and 3, the SEM-EDX measurement of the solid residues shows an abundance of arsenic and a small amount of Sb from the leached Sb originating from feed materials F and A, respectively. Elution tests, realized at an s/l ratio of 1/10, with use of the precipitates

obtained through experiments is listed in Table 4. The resulting arsenic concentration in these solutions [As$_{Elution}$] reveal significant arsenic solubility than described in literature for sodium tetrathioarsenate. It was observed in this experimental case, that a marked color change in experiment 1 and 3 occurred after addition of elemental sulfur from yellowish orange (leaching solution) to dark red. It can be assumed, that the addition of the elemental sulfur to the arsenic and sulfide ions in the ASL can lead to the formation of longer polysulfide chains bonded to the tetrathioarsenate anions, forming arsenic sulfide clusters, leading to the observed color change and higher As solubility than expected. The low cooling rate could also be a reason for poor precipitation effect in this case. This can influence the solubility and stability of the resulting precipitates in the elution tests. I can also explain, why adding elemental sulfur did not automatically lead to effective precipitation, as shown by the low As-precipitated yield values achieved. Furthermore, precipitates attained (to be investigated further by XRD) showed qualitatively compositions of Na$_3$AsS$_4 \circ$11H$_2$O and/ or Na$_3$AsS$_2$O$_2 \circ$7H$_2$O with high amount of crystal water in all measured samples. According to literature the pentavalent arsenic is present in tetrathioarsenate and also measured qualitatively by XRD in the preliminary precipitation study. However, it is most probable that the trivalent arsenic is abundant under strong reducing conditions of the sulfide. Therefore, the trivalent arsenic is assumed according to equation 1, cause of the high reduction potential of sulfide on arsenic and antimony during formation of covellite and chalcocite. The differences to the literature should be further investigated with regard to the forming precipitate.

4. Conclusions

Three samples of copper concentrates and one copper containing ore were investigated, to study the removal of arsenic by alkaline sulfide leaching (ASL). The ASL works well for concentrates of different aging degree, for feed materials of low sulfur content (17 wt.-% S tested) and is insensitive to calcium presence in contrast to partial roasting. The optimal conditions for double walled glass vessel leaching were 90 °C at 1:10 solid/liquid-ratio and a concentration of 2.5 M NaOH/2.0 M Na$_2$S$\circ$3H$_2$O for reducing the arsenic content below 0.3 wt.-% As for all feed samples within 4 h batch time. Regarding to the best result achieved within the current study, the arsenic content of the grinded copper concentrate A, d$_{80}$ = 44 µm, is reduced within 2 h from 3.5 wt.-% to 0.13 wt.-% As. Moreover, precipitation was attempted in four preliminary runs by adding elemental sulfur to the ASL and cooling down, however low precipitation yields were obtained. The resulting elution rates of the As-S containing solids were prone to As elution. It should be considered that the addition of the elemental sulfur influences the solubility of the precipitates from ASL by changing the maximum load capacity due to formation of longer polysulfide chains interacting with the tetrathioarsenate anions.

5. Recommendations

A better harmonization between ASL and the precipitation of arsenic-rich sulfide solid should be achieved. The precipitation yield and arsenic solubility upon elution should be improved to allow landfilling of the residue. Outgoing from the preliminary precipitation tests, the maximum load capacity of arsenic in the ASL solution before precipitation in dependence of sulfide concentration and elemental sulfur addition at different temperatures should be investigated. In an ongoing study, the effect of the abundant polysulfides on the arsenic solubility in the ASL should be determined with UV-VIS measurements to elucidate above-mentioned interactions with tetrathioarsenate anions.

Acknowledgements

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