

Investigation of arsenic removal from copper concentrates by alkaline sulphur leaching

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Abstract: This study investigated the removal of arsenic from copper concentrates by alkaline sulphur leaching. The first set of mineralogical investigations was carried out as part of the study. It has been assessed that arsenic is present in the ore in the form of the tennantite and the minerals of the fahlerz group. Chemical analyses, SEM-EDS and XRD analyses support these mineralogical findings. As was observed to be associated with Cu-S. Mineralogical tests indicated that the arsenic in the concentrate could not be removed by flotation. Preliminary flotation tests also showed that arsenic could not be selectively separated from the copper concentrate. Na₂S and NaOH leaching (alkaline sulphur leaching) were carried out to selectively remove arsenic from the flotation concentrate. It was observed that the arsenic contained in the copper concentrate was recovered with high efficiency (>80%) after the alkaline sulphur leaching process. Furthermore, it was observed that arsenic recovery increased further (>90%) when the flotation concentrate was regrinded and alkaline leached under the same conditions. The leaching mechanism was investigated by chemical, ore microscopy, SEM-EDS and XRD analyses. Finally, elemental sulfur (S) precipitated the arsenic from the leach solution. The production of arsenic in solid salt form (Na₃AsO₄) by precipitation is an advantage of the process investigated in this study, as it is environmentally friendly and has the potential to be used in different areas.

Keywords: copper concentrates, arsenic removal, alkaline sulphur leaching, Na₂S, NaOH

1. Introduction

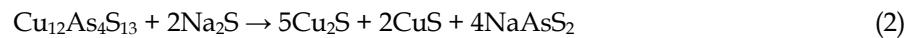
Arsenic is found in several different minerals in nature. Arsenopyrite (FeAsS) is perhaps the most significant of the group, with orpiment (As₂S₃) and realgar (As₂S₂) also being notable examples (Mandal and Suzuki, 2002). The present study investigates copper-iron-sulfide concentrates characterised by arsenic in enargite and tennantite. These minerals are the most commonly occurring copper-bearing minerals, characterised by their relatively high copper content. Nevertheless, it should be noted that a high arsenic presence also characterises this situation. The existence of this problematic element has a notable effect on the quality and fundamental characteristics of the copper product (Bujňáková et al., 2014).

The release of arsenic into the atmosphere represents a significant environmental concern at most copper smelting facilities worldwide, posing a substantial risk to surrounding ecosystems and human health. In the pyrometallurgical industry, metals containing arsenic require heating to approximately 500 °C. The oxygen flow is meticulously regulated. This process leads to the volatilisation of the resulting arsenic trioxide, followed by its recondensation (Espinosa, 1965). Nevertheless, the volatilised arsenic in this process may consequently constitute a further source of pollution. Furthermore, solidification and stabilisation are no longer considered the optimal approach for toxic waste with arsenic content (Leist et al., 2000). Therefore, it is necessary to develop alternative approaches for processing such materials (Türk, 2016).

In the composition of copper ores, arsenic is frequently found to be present within either tennantite or enargite. Analytical findings have revealed that particular copper-arsenic minerals contain 51.6%

and 48.4% copper, respectively, demonstrating a propensity to float similarly to other copper sulphide minerals, reporting to the concentrate. In light of the recent regulatory developments on the disposal of arsenic-based products, smelters are now obligated to exhibit heightened discernment in their approach to the procurement of concentrates. Furthermore, appropriate financial penalties are imposed for excessive concentrates arsenic levels (Long et al., 2012). Developing a cost-effective technique for removing arsenic-bearing minerals earlier in processing minerals is increasingly important.

Some hydrometallurgical approaches are available for the treatment of enargite and tennantite, including ammonia leaching (Gajam and Raghavan, 1983), bioleaching (Takatsugi et al., 2011), and acid leaching (Dutrizac and Morrison, 1984). Nevertheless, the preferred technique for extracting arsenic from these minerals would appear to be alkaline leaching (Curreli et al., 2009; Awe and Sandström, 2010). The extraction of arsenic from concentrates in sodium sulfide solutions using highly alkaline reducing conditions results from the alkaline leaching process. The processes of conversion or transformation of Cu_3AsS_4 or $(\text{Cu}_{12}\text{As}_4\text{S}_{13})$ to Cu_2S or CuS are shown in equations (1) and (2), respectively:



The leaching medium is composed of two primary constituents: sodium sulfide and sodium hydroxide. The application of Na_2S has been demonstrated to generate a markedly reducing environment, with a potential of approximately -500 mV being observed. This phenomenon is in marked contrast to the effect of NaOH on the pH values, which remain at a level greater than 12.5. The property of NaOH under investigation here has been shown to inhibit the hydrolysis of sulfide ions. The role of sulfide ions in the substitution of arsenic in enargite and tennantite has been proven (Tongamp et al., 2009). A crucial factor that has been demonstrated to significantly influence the efficiency of arsenic dissolution from enargite and tennantite is the impact of temperature. It has been found that an elevated temperature is associated with an enhancement in the efficiency of this process (Curreli et al., 2009).

In the process of pressure oxidation, the leaching of enargite, which occurs in the forms of $\text{Ca}_3(\text{AsO}_4)_2$ or $\text{Fe}_3(\text{AsO}_4)_2$ arsenic, is removed by dissolution in an alkaline solution (Na_2S - NaOH). For precipitation reactions to occur, the pH of the solution must be reduced to a level below 2. (Filippou et al., 2007). In contrast, Tongamp et al. (2010) have proposed an alternative process for removing dissolved arsenic from the Cu_3AsS_4 - NaHS - NaOH leaching system. In this process, arsenic is precipitated as Na_3AsS_4 without the need for pH adjustment.

This investigation proposes a solution to processes where arsenic cannot be removed from copper ores by flotation technique. Furthermore, mineralogical evaluations have been conducted to elucidate the mechanism by which physicochemical techniques cannot remove arsenic from such ores. The present paper proposes a methodology for treating arsenic-bearing copper concentrate, entailing the precipitation of the arsenic-containing filtrate obtained after selective alkaline leaching.

2. Materials and methods

2.1. Materials

The current study was performed on a run-of-mine ore and copper concentrate. The ore samples examined in this study were obtained from the sulphide copper deposit in Yomra, Trabzon. The ore is primarily composed of pyrite and chalcopyrite, accompanied by galena, fahlerz, bornite, and sphalerite. The main gangue mineral in the ore is quartz. The following chemicals were utilised in this study: calcium hydroxide ($\text{Ca}(\text{OH})_2$) (ACS, Sigma Aldrich, USA), sodium-diisobutyl dithiophosphinate (Aerophine 3418A, CYTEC), methyl isobutyl carbinol (MIBC, CYTEC), sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) (98% purity, Sigma Aldrich, USA), sodium hydroxide (NaOH) (>98% purity, Sigma Aldrich, USA), sulfur (S) (99.5% purity, Sigma Aldrich, USA), potassium iodide (KI) (≥99.5% purity, Merck, Germany), L-ascorbic acid (99% purity, Sigma Aldrich, USA), sulfate analyser kit (Palintest) and AAS standard solutions (Merck, Germany).

2.2. Methods

2.2.1. Sample preparation

A copper concentrate sample containing arsenic was subjected to fractional analysis, employing the standard sample preparation methods. The separation of the sample into six discrete fractions was achieved through the implementation of a sieve analysis technique, in which each fraction was separated using a specific sieve size. The fractions were -20 microns, 20-38 microns, 38-75 microns, 75-150 microns, and +150 microns. Thereafter, the polished sections of each fraction were prepared for mineralogical investigation.

The ore samples used in the flotation tests were dried in an oven. Due to the coarse size of the run-of-mine ore, a laboratory jaw crusher was used to reduce the particle size to -2 mm. Half of the crushed sample was retained as a reference. Wet grinding was performed using a laboratory-type rod mill with an internal diameter of 19.5 cm and an internal length of 30 cm. The ore sample was ground in a rod mill for different durations (5, 10, and 15 minutes), and the average particle size was calculated. In order to prevent oxidation of the ore, a grinding operation was carried out prior to each flotation test. Appropriate sampling and reduction techniques were employed to ensure that the flotation concentrate samples utilised in leach tests were reduced to the requisite quantity.

2.2.2. Flotation tests

The present study examined the performance of the traditional Denver D-12 type device by implementing flotation tests. In the experiment conducted, the pH value of the pulp was measured using a pH meter. Before the flotation experiments, the solid ratio of the ore subjected to wet grinding in the rod mill was adjusted to a range of 30-35%. Each reagent used in the flotation tests was transferred to a volumetric flask on a precision balance. The volume of the flasks to which 2.5 g of reagent had been added is 250 ml with distilled water. The reagents were prepared in this manner to achieve a concentration of 1% in 250 ml volumetric flasks. The amount of reagents used in the experiments was calculated in g/t. The conditioning step initiated pH adjustment (using $\text{Ca}(\text{OH})_2$) as the primary procedure. Subsequently, the flotation process was initiated by adding the collector (sodium-diisobutyl dithiophosphate) and frother (Methyl Isobutyl Carbinol). After completing the flotation tests, filtration was conducted using a vacuum pump. The solid residue was then dried in an oven at 105 °C. The dried materials were weighed on a high-precision scale. Finally, the metal contents of the solid samples were determined, and the flotation efficiencies of these samples were calculated.

2.2.3. Alkaline leaching tests

This study aimed to examine the applicability of alkaline leaching techniques for removing arsenic from the flotation concentrate. Leaching studies were conducted within a jacketed reactor, each with a nominal capacity of 250 millilitres and equipped with vortex preventers affixed to the inner walls. The temperature was controlled through the utilisation of a heating-cooling circulator, whereby water was circulated within the jacket of the reactor. During the leaching experiments, the reactors were sealed by applying suitable covers to prevent evaporation losses from the ambient temperature. The mixing process was conducted using a mechanical mixer configured with torque control and a digital speed monitor. In this study, a Teflon (PTFE)-coated impeller was utilised to ensure the impeller's resilience to leaching conditions, particularly elevated temperatures and alkalinity. The schematic representation of the leaching process is presented in Fig. 1. In the experimental process, the quantity of the initial solution was designated as 125 millilitres, and the solid ratio was established at 20% by weight/volume (w/v). The flotation concentrate sample was introduced into the reactor upon attaining the requisite temperature, triggering the experimental procedure. The mixing rate was constant and set at a speed of 500 rpm. The experiment was conducted at a temperature of 90 °C to ensure the optimal conditions for leaching. The leaching time was held constant at six hours. In addition, the impact of particle size on leaching process efficiency was investigated through the performance of distinct experiments utilising concentrate particle sizes (d_{80}) of 118 and 57.8 μm , respectively. At predetermined intervals (15, 30, 60, 120, 240, and 360 minutes) throughout the leaching process, samples were collected (2-3 mL) and subjected to centrifugation at 4100 rpm for three minutes. This procedure facilitated the separation of

solid and liquid phases. The extracted solution was then subjected to a process of dilution prior to undergoing a metal analysis. Following the conclusion of the leaching tests, the leach pulp was processed through a centrifuge at 4100 rpm for eight minutes. The objective of this step was to facilitate the separation of the loaded leach solution. After centrifugation, the transparent solution was transferred to sample storage bottles for further analysis. The solid phase was subjected to a hot purified water wash and oven-dried at 65 °C for 12 hours. The leaching performances were determined by analysis of the metal quantities present in the pregnant solution at the culmination of the leaching process, the metal quantities remaining in the waste material, and the metal quantities in the sample before leaching.

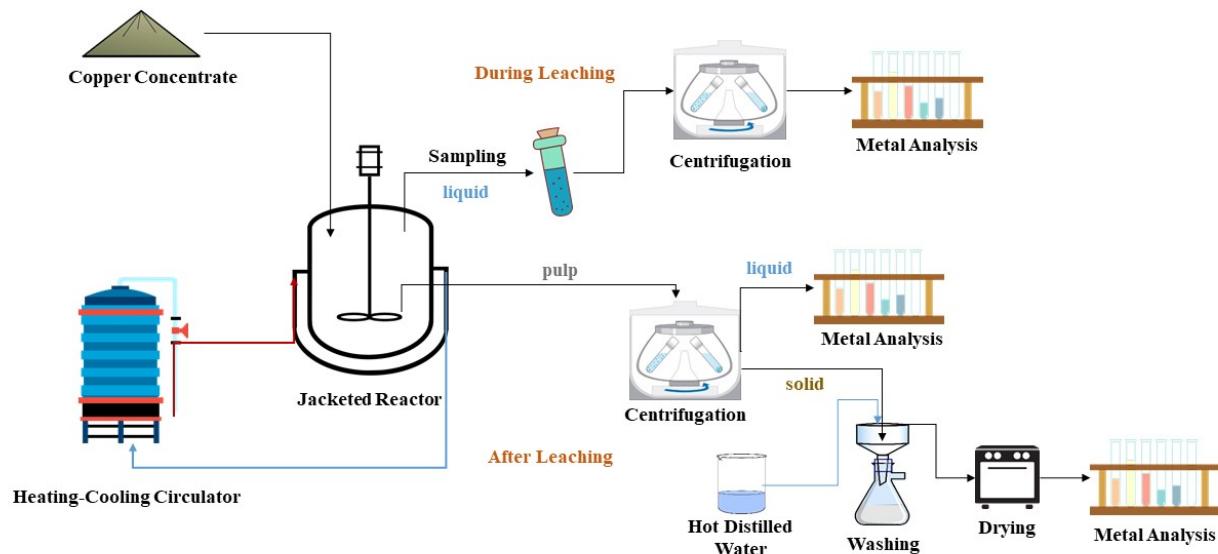


Fig. 1. Schematic diagram of the leaching system

2.2.4. Arsenic precipitation experiment

The precipitation of the arsenic from the pregnant leach solution can be achieved by means of a short and simple process. The arsenic concentration was increased to greater than 35 g/L to precipitate the arsenic using elemental sulphur (S) from the loaded alkaline leach solution. Double alkaline extraction experiments were performed to achieve this result under identical conditions, using the same leach solution. The findings of the experimental trials indicated that a leach solution with an arsenic concentration of 40.3 g/L was successfully produced. In this stage of the process, the solid (flotation concentrate) and liquid (arsenical alkaline leaching solution) phases were efficiently separated by solid-liquid separation following alkaline leaching. The pregnant leach solution was then conditioned at 90 °C for 20 minutes. The initial 10 minutes of the 20 minutes were used for the mixing stage. Concurrently, with the commencement of the second 10-minute period, elemental sulfur was incorporated into the solution at a concentration equivalent to 1.5 times that of the arsenic. After adding sulfur, the mixture was left undisturbed for 10 minutes. The conditioning phase was followed by initiating the precipitation process, which was carried out by slowly reducing the temperature in a laboratory setting.

2.2.5. Characterization

The samples were analysed using laser particle size analysis (Malvern Mastersizer 2000) to determine their size distribution. Microscopic examinations were conducted in the KTU Mining Engineering Department Laboratory using a Nikon Eclipse polarising microscope. In addition, the samples were characterised through scanning electron microscopy (Thermo Scientific Apreo 2S) and energy-dispersive X-ray spectroscopy (EDS; Thermo Scientific Ultradry EDS). X-ray diffraction measurements were conducted using the X'Pert3 Powder Diffractometer (PANalytical), which is equipped with a θ/θ goniometer, CuK α radiation (45 kV, 40 mA) and a Pixcel 1D detector. The scanning rate was set at

10 degrees per minute, ranging between 5 and 80 degrees. FE-SEM and XRD analyses were carried out at KTU Central Research Laboratory.

2.2.6. Chemical analysis

Before chemical analysis, the samples were dried in an oven. In order to identify the chemical composition of the samples, acid dissolution was carried out using a microwave digestion instrument (Milestone Ethos Easy). The metal contents of the samples were determined by atomic absorption spectrophotometry (PerkinElmer AAnalyst 400 AA). Arsenic analyses were conducted by integrating an atomic absorption spectrometer (AAS) and a hydride production device (Perkin Elmer FIAS 100 model). The calibration solutions were prepared using standard solutions with a concentration of 1000 (± 5) mg/L to determine metals with AAS. The standard solutions were prepared in a medium of 2M HCl. The analyses were carried out by calibrating the instrument with a blank solution containing 2M HCl. The standards were prepared in this way. In the calibration process, analyses were performed by providing a correlation coefficient of ≥ 0.999 for each metal. Each sample was analysed using a dual-reading method, with two readings obtained from each replicate sample.

Sulfur (S) analysis was carried out using a LECO CS744 carbon and sulfur analyser. In this device, carbon and sulfur are determined in inorganic substances by post-combustion infrared identification technique. Additionally, the analysis of soluble sulfates (SO_4^{2-}) in solution was conducted using a UV Spectrophotometer (Palintest 5000). In this method, a BaCl_2 tablet was added to the solutions within the appropriate pH range and mixed for two minutes. The tubes were subsequently subjected to a second mixing, after which a photometer measured the light transmittance (T) value at a wavelength of 520 nm. The sulphate ion concentration was then determined as milligrams per litre (mg/L) from the transmittance (T) value using the conversion table. Sulphate analyses were performed in duplicate, and the mean values of each analysis are presented herein.

3. Results and discussion

3.1. Ore characterisation

The current flotation tests were performed on a run-of-mine ore, with the chemical compositions of the samples presented in Table 1. The X-ray diffraction (XRD) pattern of the ore sample is shown in Fig. 2. As a result of the Rietveld analysis, it was determined that the dominant mineral in the sample was quartz. However, the ore also contained pyrite, chalcopyrite, barite, sphalerite and tennantite (Fig. 2).

Table 1. The elemental analysis values of a run-of-mine ore

Element	Unit	Cu	Zn	Pb	Fe	As	Ag (g/ton)	S
Ore	%	2.1	1.6	0.3	21.6	0.21	113	25.3

The SEM image and EDS analysis results of the ore sample are shown in Fig. 3. The major peaks in the EDS analysis have been identified as Si, S, Fe, K, Ca, Ba, Cu, Zn and As. The results of the SEM-EDS data and the chemical and XRD analysis confirm each other. The EDS analysis revealed that the prominent spectral peaks were indicative of Si with quartz, S with pyrite, chalcopyrite, sphalerite, tennantite, Cu with chalcopyrite, tennantite, As with tennantite, Zn with sphalerite and Ba with barite.

Microscopic examination of the fraction above 150 microns revealed that pyrite and chalcopyrite were the dominant minerals. It was found that the liberation was inadequate. The association of chalcopyrite, fahlerz and pyrite was determined in grain with dimensions of 290×150 microns. Different compounds were also observed, including pyrite, chalcopyrite, fahlerz and sphalerite (Fig. 4a-4b). Pyrite with a tectonic cataclastic texture of 55×150 microns was monitored. Fahlerz, chalcopyrite, and pyrite complex particles with a size of 75×55 microns are present in these grains; sphalerite and fahlerz formed separately from chalcopyrite. The fahlerz-chalcopyrite substitution was determined (Fig. 4c). The microscopic examination of the particles between 38-75 microns showed that the liberation was better than the upper sieve fractions. The relative grains of chalcopyrite and pyrite were observed to be lower, and most of the pyrites were free. However, the substituted fahlerz chalcopyrite textures were not

liberated (Fig. 4d). As a result of the examination of the relevant sections, it was found that the most common gangue mineral was quartz (Fig. 4).

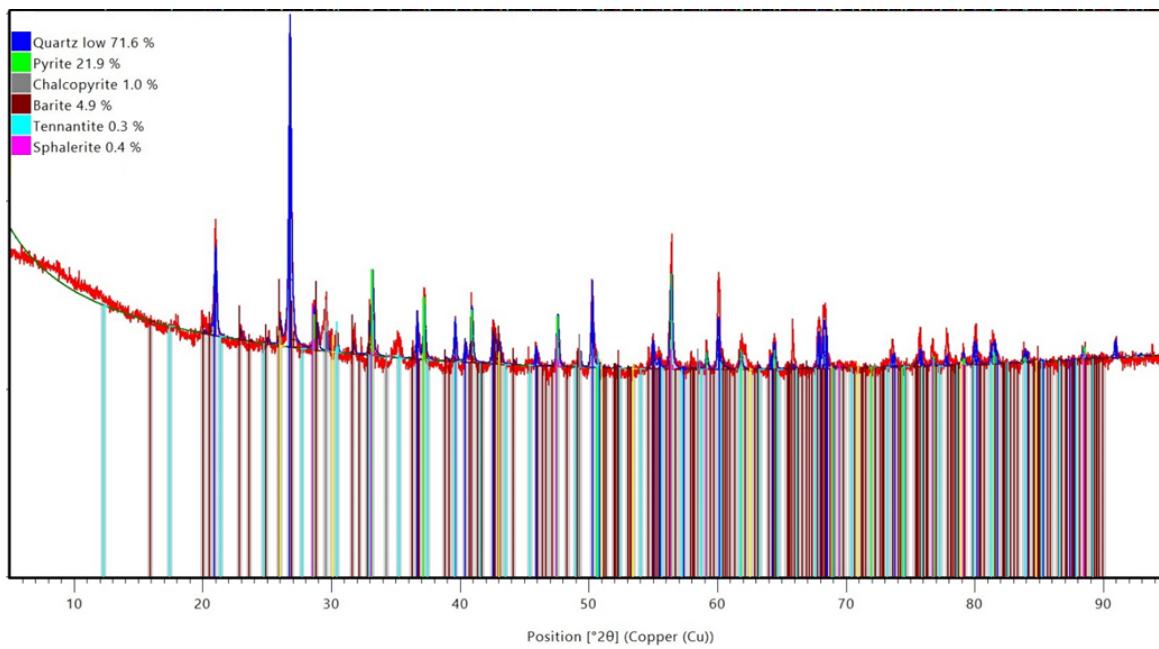


Fig. 2. X-ray diffraction pattern of the copper ore

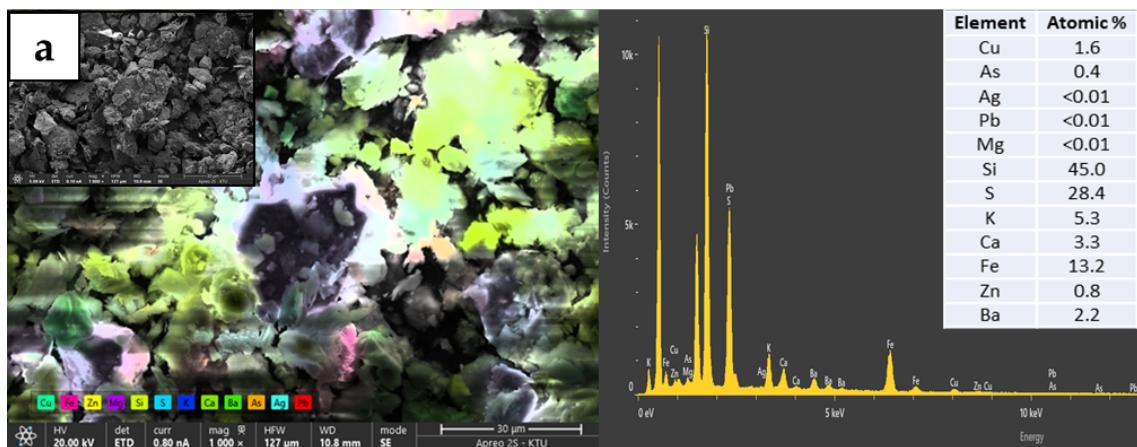


Fig. 3. SEM image (a), EDS spectra, elemental mapping and analysis of copper ore

3.2. The flotation behaviour of arsenic and other sulfide minerals

Economic considerations indicate that achieving a separation of minerals containing arsenic at an initial step in processing is favourable. In the flotation process, when the ore particle size (d_{80}) values were 148.6 μm , 81.2 μm , 64.8 μm and 53.2 μm , the Cu recoveries were 90.7%, 97.2%, 95.3% and 96.5% respectively (Fig. 5). As illustrated by the results obtained, the ore mineral particle size has a significant impact on the flotation process (Wang et al., 2023). Incomplete liberation diminishes the flotation efficiency for particles measuring above 80 μm . It has been observed that minerals, particularly arsenic, zinc (Zn), lead (Pb), iron (Fe), and silver (Ag), present in the ore, act in concert and are retained in the concentrate. Using flotation, a physicochemical technique, it was determined those minerals including As, Zn, Pb, Fe, and Ag remained in the concentrate due to their tendency to associate with Cu (Liu et al., 2025). Following a comprehensive mineralogical examination (Section 3.1) and a series of preliminary flotation tests, it was determined that the production of arsenic-free copper concentrate by flotation was not a viable option (Fig. 5). Moreover, in the recent past, research into the selective flotation

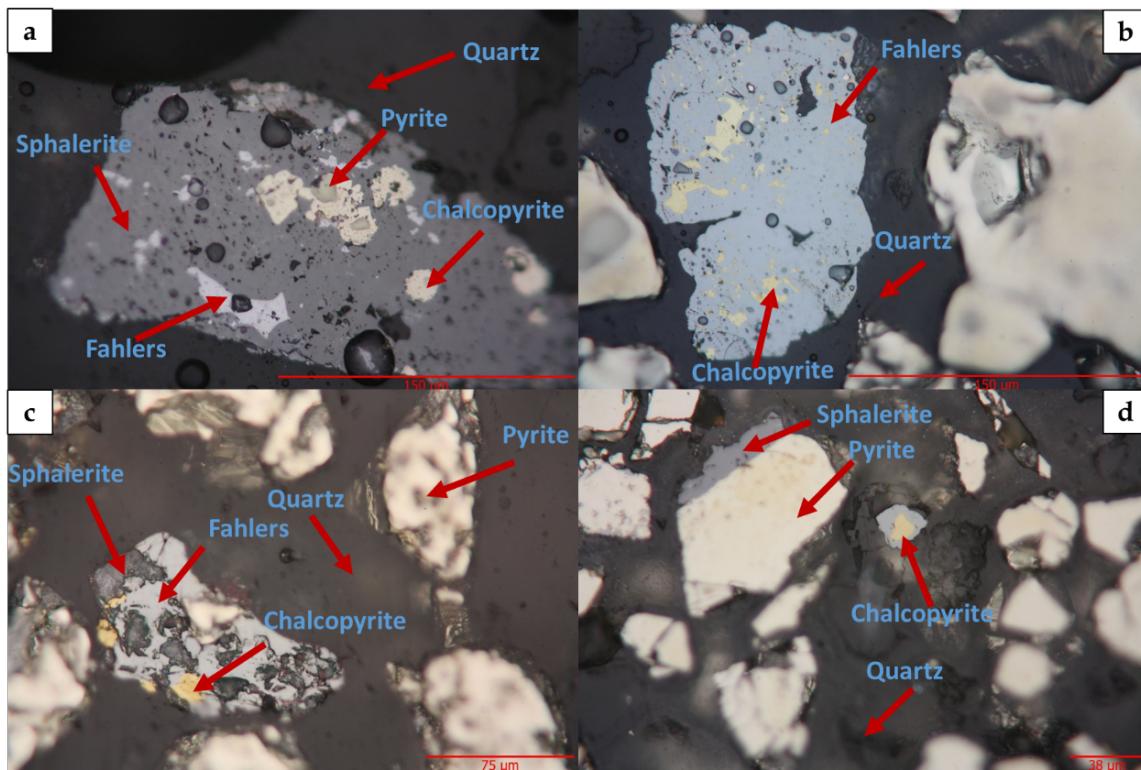


Fig. 4. Microscopic images of copper ore (a: +150 μm , b: +150 μm , c: +75 μm , d: +38 μm)

of As-minerals has concentrated on enargite. The primary mechanisms by which to achieve enargite selectivity comprise the implementation of selective flotation reagents (Tapley and Yan, 2003), selective oxidation processes (Guo and Yan, 2005; Li et al., 2019; Gan et al., 2022), and the modulation of pulp potential (Bruckard et al., 2007; Panayotova, 2023). Nevertheless, no commercially viable and universally applicable separation method at the flotation step has been developed (Plackowski et al., 2012).

As a result of mineralogical studies, the presence of copper minerals such as chalcopyrite and bornite, as well as secondary copper minerals such as covellite and chalcocite, were determined in the ore structure (Section 3.3). Secondary copper minerals dissolve in water to form CuSO_4 , which has been shown to activate the sphalerite found in the ore (Wan et al., 2023). In order to prevent this situation, the objective was to prevent the activation of sphalerite by adding Na_2S to the rod mill. For this purpose, flotation tests were carried out by Na_2S to the rod mill at a different dosage using optimum grain size (d_{80} : 64.8 μm) and reagent (collector & frother) amounts. It has been established that utilising Na_2S

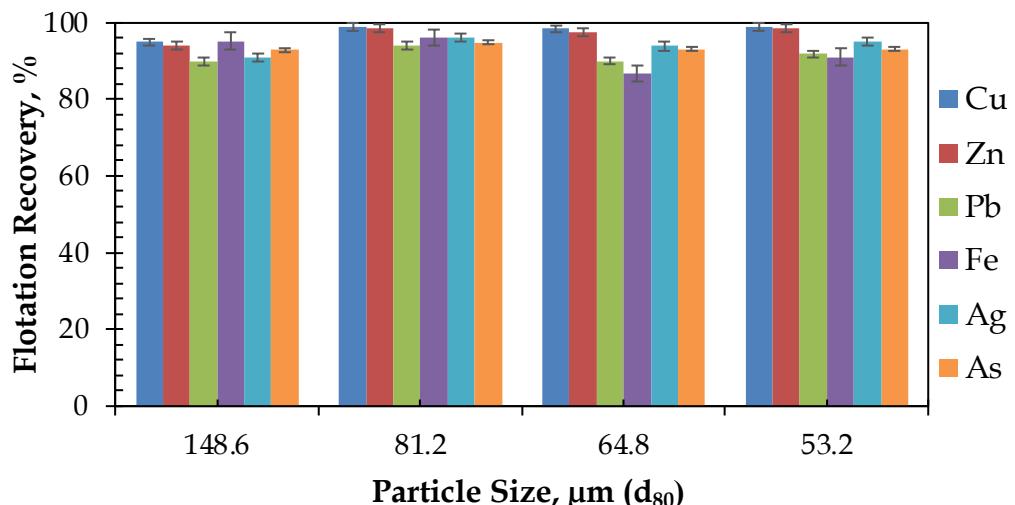


Fig. 5. The flotation efficiencies obtained at different ore particle sizes

results in a certain degree of inhibition of the revitalisation process of sphalerite. In these tests conducted for the separation of Cu and Zn minerals, no change in Cu recovery was observed, while a significant decrease in Zn recovery was noted (Fig. 6). Selective oxidation processes have been identified as a viable application for these types of ores (Guo and Yan, 2005; Gan et al., 2022). The chalcopyrite and other minerals must be separated for this process to be applied selectively. In this section, it was observed that sphalerite and pyrite could not be wholly separated from chalcopyrite (Fig. 6). Also, the use of Na_2S did not affect the arsenic in the ore. In light of the findings regarding the flotation technique, it is recommended that alternative processes be investigated for the separation of arsenic minerals from copper concentrate.

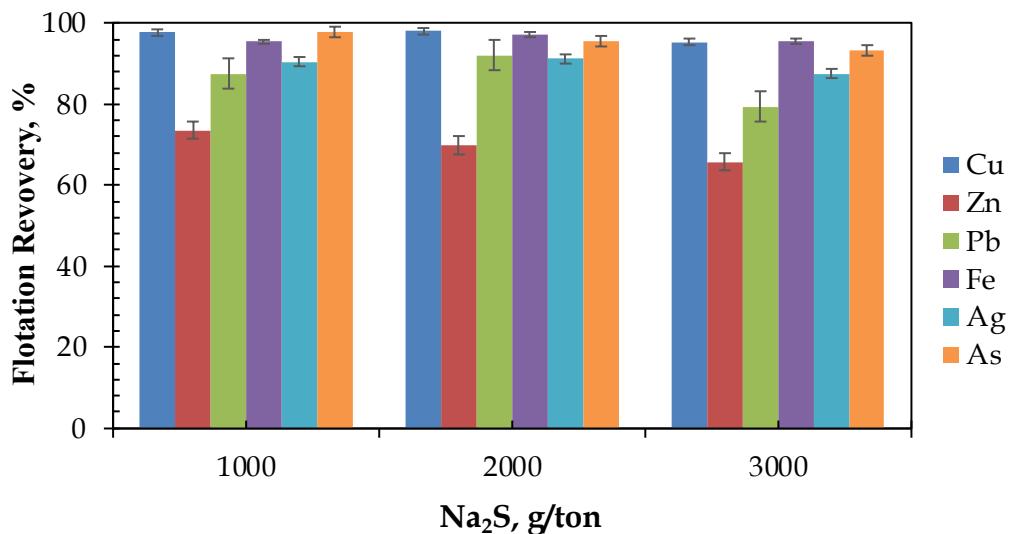


Fig. 6. The impact of utilising Na_2S as a modifier on the flotation performance

3.3. Microscopic structure of copper concentrate

A sieve analysis was implemented on the concentrate, calculating an average particle size (d_{80}) of 118 microns. The analysis of the collected data indicates that 9.9% of the sample displays a size above 150 microns, whereas 29% of the sample exhibits a size below 20 microns. Upon examination of particles measuring 150 microns and above, it was observed that chalcopyrite was the prevalent mineral. Following this, the density of pyrite, bornite, sphalerite and chalcopyrite were analysed. The presence of such mineral phases as bornite, sphalerite, pyrite and chalcopyrite were identified, with the latter reaching a size of 300×140 microns. In addition, compositions comprising fahlerz and chalcopyrite are available, with a size of 300×75 microns. The pyrite mineral is typically seen as a granular material within larger crystals. Within this specific range of particle sizes, the texture of the substitution is characterised by a high degree of complexity or multifaceted nature (Fig. 7a). Although the replacement texture is abundant in this grain size range, it was also observed that the number of interlocked grains is significant. Tennantite-tetrahydrate minerals were present in this particle size range. It was also observed that enargite and luzonite were present in the fahlerz structure (Fig. 7b).

Replacement minerals have been identified in fractions of grains measuring between 75 and 150 microns. It was determined through observation that an extensive quantity of chalcopyrite was present within this specific particle size range. Conversely, only a portion of the sphalerite was observed to be liberated. It has been observed that the sphalerite, fahlerz, bornite and covelin minerals exhibit an interlocking relationship (Fig. 8a). In addition, it has been noted that gangue minerals, mainly quartz, are not commonly found. A thorough analysis determined that these sections primarily contain ore minerals. A microscopic examination of particles measuring between 38 and 75 microns revealed the presence of chalcopyrite, fahlerz and sphalerite. Following a thorough examination of the relevant mineral particle, it was determined that grinding below 20 microns was required for liberation (Fig. 8b). Furthermore, it was observed that compositions of fahlerz and chalcopyrite, interpreted as replacement textures are prevalent occurrences. It is widely acknowledged that releasing these replacement tissues poses significant challenges. A microscopic evaluation of particles measuring between 20 and 38

microns was conducted. It was observed that free chalcopyrite and pyrite granules were prevalent in this particular section.

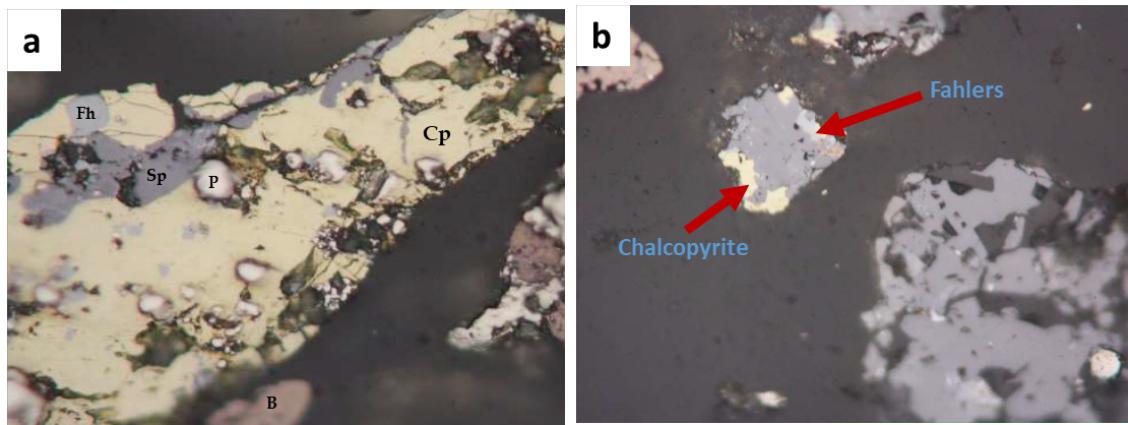


Fig. 7. Unliberated pyrite-chalcopyrite-sphalerite-fahlerite-bornite grain (Cp: Chalcopyrite, P: Pyrite, Sp: Sphalerite, B: Bornite, Fh: Fahlerz) (a) Fahlerz-enargite-luzunite-chalcopyrite granules (b)

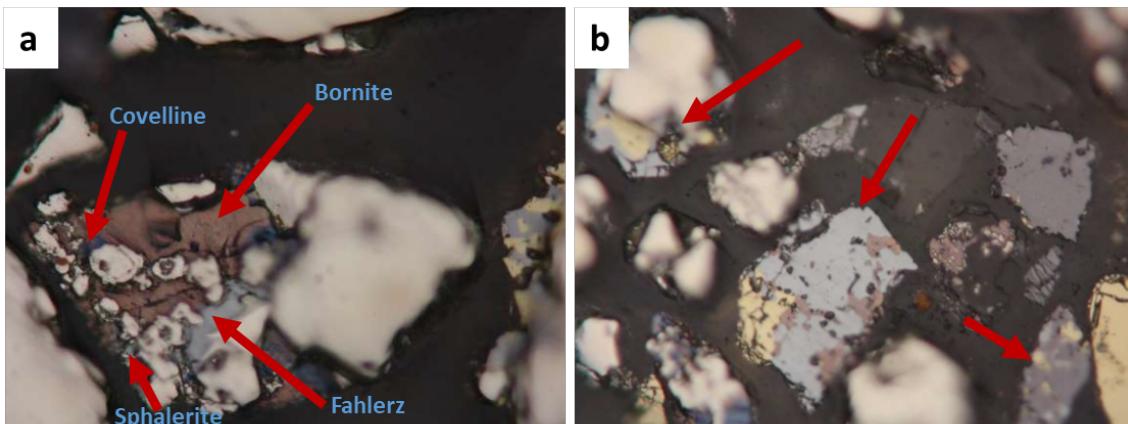


Fig. 8. Interlocking (bonded) sphalerite, fahler, bornite and covellite minerals (a) Interlocking sphalerite, fahlerite and bornite minerals (b)

Furthermore, the observation of the interlocking of chalcopyrite, fahlerz, sphalerite and pyrite, which had been previously noted in larger grain sizes, was confirmed at this specific particle size. Following comprehensive analysis, it was determined that certain complex-bound grains (bornite, fahlerz, sphalerite, and pyrite) contained disseminated grains of pyrite measuring less than 5 microns in size (Fig. 9a). Microscopic examination of the fraction below 20 microns revealed that the majority of the pyrite and chalcopyrite had been liberated. It was also noted that various free-bornite and fahlerz minerals were present. Despite the prevalence of bound particles, a limited number of chalcopyrite, sphalerite, and chalcopyrite amalgamated particles was detected (Fig. 9b).

A detailed mineralogical examination of the copper concentrate was conducted using a polarised microscope. The mineral composition of the copper concentrate was determined through comprehensive analytical procedures conducted on the fractions obtained (Fig. 7-9). The minerals that could be associated with the arsenic in the chemical composition of the concentrate were evaluated using a polarising microscope. As a result of these evaluations, it was understood that the concentrate contained fahlerz group minerals such as tennantite containing arsenic. In the SEM-EDS examinations conducted to verify this situation, the presence of sections containing elevated concentrations of Cu (32.8%–36.6%), As (12.3%–13.9%) and S (41.4%–43.5%) was determined by the point analysis technique (Fig. 10). The results obtained in this section are compatible with the XRD analysis results (Fig. 2), determining the mineralogical composition of the run-of-mine ore.

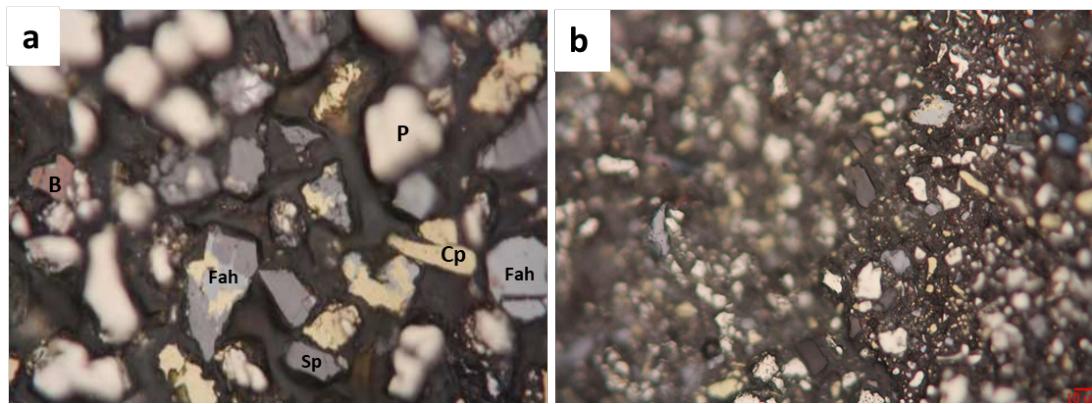


Fig. 9. Free pyrite-chalcopyrite granules and bound fahlerz-chalcopyrite-sphalerite-bornite granules (a)
Predominantly free minerals and limited bound chalcopyrite and fahlerz (<20 μm) (b)

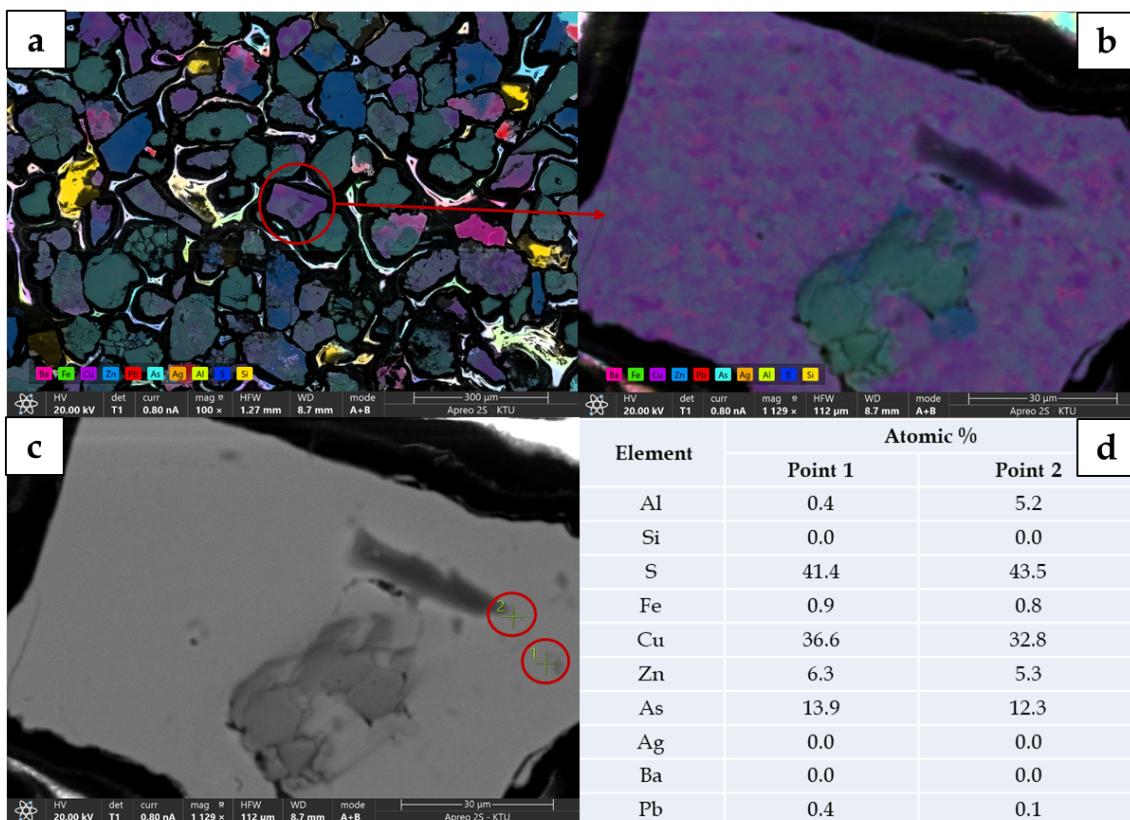


Fig. 10. Elemental mapping (a-b) and EDS-point analysis of copper concentrate (75-150 μm) (c-d)

3.4. Arsenic removal from copper concentrate by hydrometallurgical process

The investigation revealed that the copper concentrate utilised in this study exhibited high concentrations of arsenic (Table 2). It is acknowledged that copper concentrates with a commercial value must contain a maximum of 0.5% arsenic. As demonstrated in Section 3.1.1, microscopic analysis indicated that the arsenic present in the concentrate could not be removed by flotation. Consequently, Na_2S and NaOH leaching (alkaline leaching) were utilised to selectively remove arsenic from the flotation concentrate, and the leaching test results are addressed in this section. The leaching mechanism of tennantite is shown in equation (2). In the context of the alkali leaching process, the presence of Na_2S generates a reducing environment with a potential of <-500 mV. On the other hand, NaOH hinders the hydrolysis of arsenic-sulfur ions within the enargite mineral structure, thereby maintaining a pH level above 12.5 (Tongamp et al., 2009; Blanco-Vino et al., 2024). Bujňáková et al. (2014) demonstrated that increased temperature during the alkaline leaching process enhanced arsenic dissolution efficiency.

Furthermore, they ascertained that the maximum arsenic dissolution occurred at 90 °C in atmospheric conditions. Consequently, the application of hot (90 °C) alkaline leaching tests, employing a flotation concentrate containing 17969 ppm (1.8%) arsenic at 200 g/L Na₂S and 50 g/L NaOH concentrations, resulted in an As content of 4700 ppm (0.47%) in the concentrate, achieving an 82.1% As removal efficiency. While the arsenic in the concentrate was eliminated to a substantial degree, the time-leach efficiency curve in Fig. 11 demonstrates that the other metals remained entirely unleached. The concentrated sample contained 17969 ppm (1.8%) of arsenic. It is hypothesised that the sample, which is mechanically activated, possesses a reduced particle size, an enhanced specific surface area, and an improved level of reactivity (Welham, 2001).

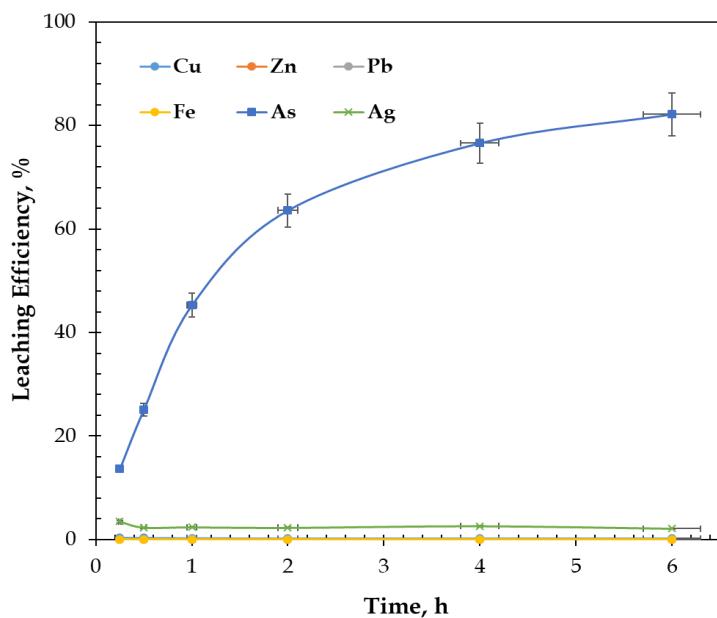


Fig. 11. Alkaline Leach Efficiency (unground concentrate) at 200 g/L Na₂S and 50 g/L NaOH concentrations and 90 °C

The enhancement of leaching processes in extractive metallurgy when high-energy milling is employed is primarily attributable to increases in specific surface area, decreases in mineral crystalline phase content and reductions in particle size (Baláž, 2000). Subsequently, the material was subjected to milling (d_{80} : 57.8 µm), and the leaching test was replicated within the original conditions. Following six hours, the arsenic content of the concentrate was found to be 1802 ppm (0.18%), while the arsenic removal efficiency increased to 90% (Fig. 12). It was observed that the chemical analysis results of the copper concentrate before and after leaching and the chemical analysis of the loaded leach solution were in agreement (Table 2). In addition, it is evaluated that the sulfur (S) passing into the solution after leaching is caused by NaAsS₂ passing into the solution phase due to the reaction (Equation 2) of tennantite and Na₂S. This mechanism explains the decrease in S percentage in the solid sample after leaching.

It was determined that the minerals forming the concentrate composition did not undergo morphological change after leaching in an intense alkaline environment (Fig. 13). In addition, arsenic is transferred to the solution phase with Na₂S from most arsenic minerals, particularly tennantite (Cu₁₂As₄S₁₃) and enargite (Cu₃AsS₄), which are found in the copper concentrate. This situation has also

Table 2. The distribution percentage of concentrate elements when subjected to alkaline leaching is determined through chemical analysis using the atomic absorption spectrophotometer (AAS)

Element	Unit	Cu	Zn	Pb	Fe	As	Ag (ppm)	S
Before Alkaline Leaching	%	13.02	8.41	1.98	22.04	1.80	561	48.1
After Alkaline Leaching	%	12.84	8.15	1.85	22.01	0.18	526	45.6
Leaching Solution	mg/L	0.3	0.6	1.3	0.55	3200	2.1	4850

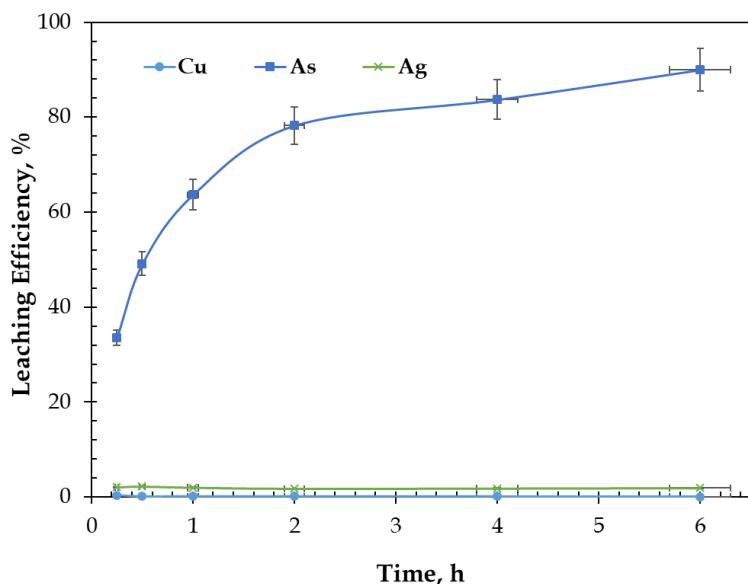


Fig. 12. Alkaline Leach Efficiency (ground concentrate) at 200 g/L Na₂S and 50 g/L NaOH concentrations and 90 °C

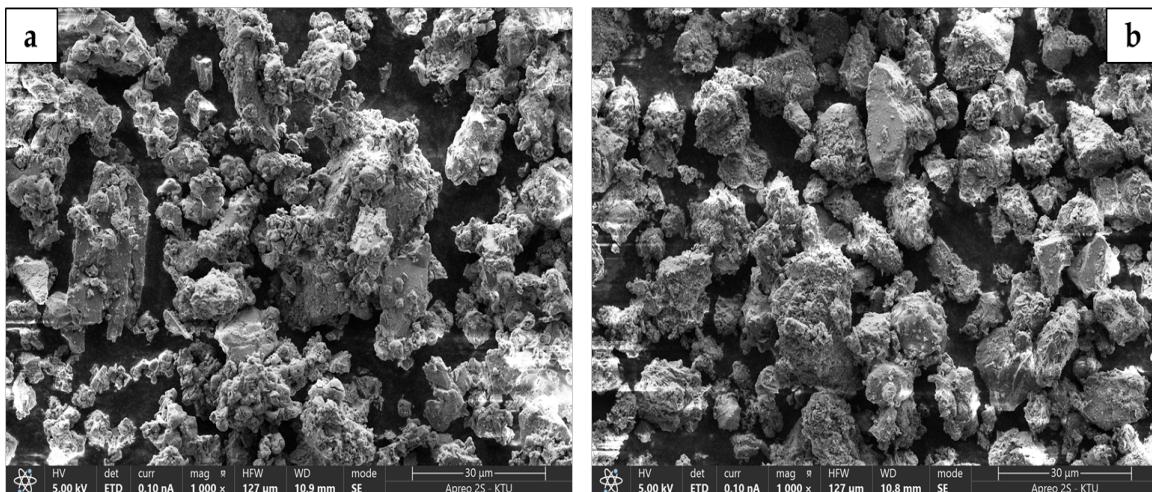


Fig. 13. SEM image of copper concentrate before (a) and after (b) alkaline leach treatment

been verified using SEM-EDS analysis and chemical analysis. When the EDS spectrum was examined, it was found that the arsenic peak in the concentrate prior to alkaline leaching had almost disappeared in the concentrate after leaching (Fig. 14). In addition, EDS elemental analysis results showed that the arsenic content decreased from 1.6% (Fig. 14a) to 0.3% (Fig. 14b) with alkaline treatment. These data confirm the results of atomic absorption spectroscopy (AAS).

Fig. 15 presents the results of the X-ray diffraction analysis of the initial copper concentrate with an arsenic content of 1.80 wt% alongside the leach residues obtained after leaching. The analysis of the obtained leach residues indicates a near-total absence of the distinctive diffraction peaks of tennantite (Cu₁₂As₄S₁₃). As can be seen from the Rietveld plot of the samples before and after the alkali treatment, the tennantite mineral almost disappeared with the alkali treatment and covellite (CuS) peaks formed instead (Fig. 15). It is evident that these data correspond with a high degree of similarity to the arsenic leaching profile of the sample as illustrated in Fig. 12. In addition, the presence of typical peaks of covellite (CuS) was identified in the leach residue obtained following a six-hour extraction process. These results support the conversion of tennantite (Cu₁₂As₄S₁₃) to Cu₂S in Na₂S media, as shown by the reaction (Equation 1) above. Tongamp et al. (2009) removed arsenic from the mineral enargite (Cu₃AsS₄) using NaHS. Their study also found that the mineral structure changed with alkaline leaching, forming Cu-S mineral. The researchers confirmed this change by employing XRD analysis.

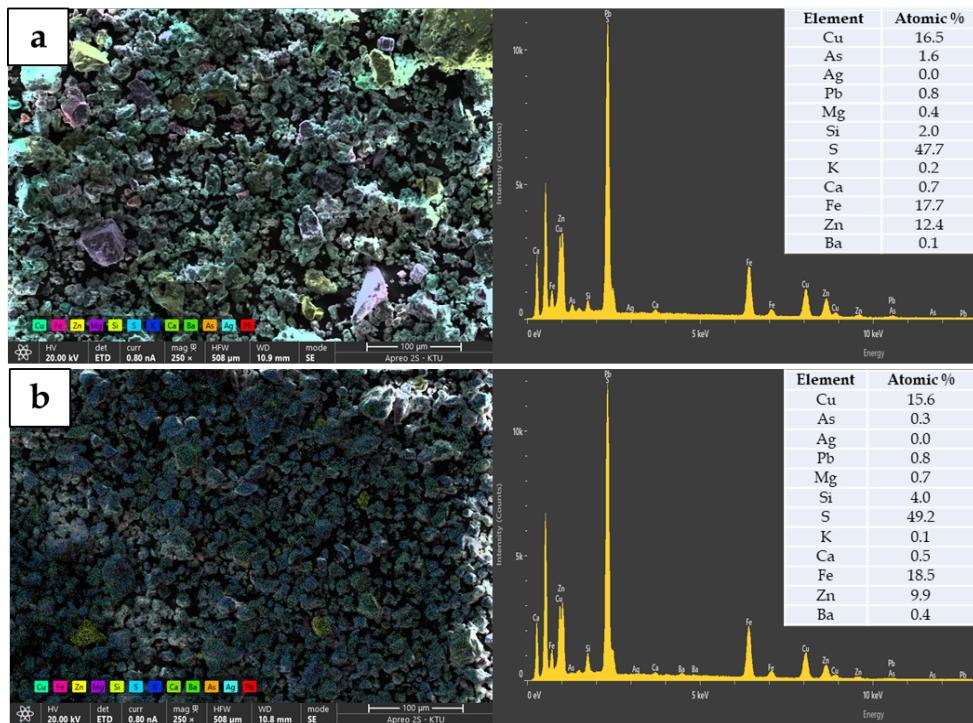


Fig. 14. EDS spectra, elemental mapping and analysis of copper concentrate samples before (a) and after (b) alkaline leaching

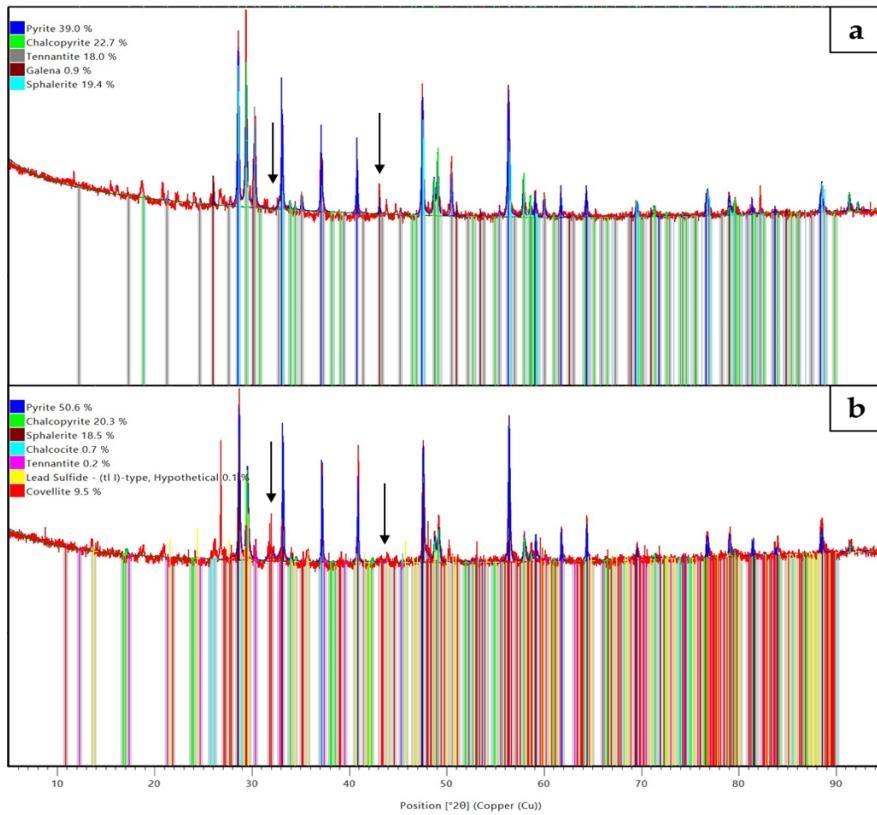


Fig. 15. X-ray diffraction pattern of the copper concentrate before (a) and after (b) the alkaline leach treatment

3.5. Arsenic precipitation

The study demonstrated that approximately 80% of the arsenic was precipitated from the loaded alkaline leach solution following the arsenic precipitation process, as outlined in the test procedure. The

alkaline solution from the precipitation process, which contains negligible arsenic, can be reused in the leaching stage. The precipitation of arsenic from solutions containing dissolved arsenic from the mineral enargite (Cu_3AsS_4) by alkaline NaHS leaching was investigated by Tongamp et al. (2010). This process facilitates the recycling of the alkaline solution and simplifies the management of the arsenic present. The pH and Eh of the media during all performed experiments were kept consistently above 13 and below -700 mV, respectively. Under such conditions of significant alkalinity, the dissolution of arsenic trisulphide (As_2S_3) was observed to occur. The Na_3AsS_4 salt, which is characterised by low solubility (Equation 5), is precipitated as a solid salt as a result of the reduction of added elemental sulfur (Equation 3) and the associated oxidation of thioarsenite (AsS_3^{3-}) to thioarsenate (AsS_4^{3-}) (Equation 4) (Tongamp et al., 2010b). As illustrated in Fig. 16, the process flow chart for the precipitation of arsenic from the solution is as follows.

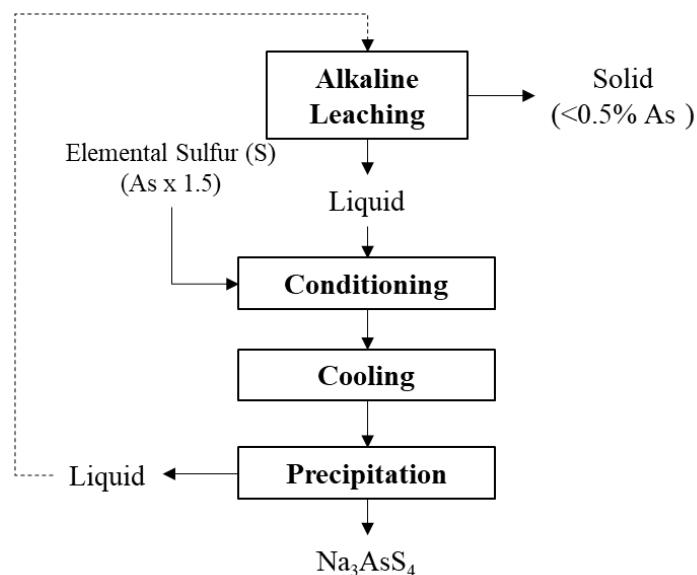
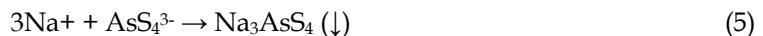
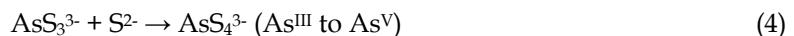
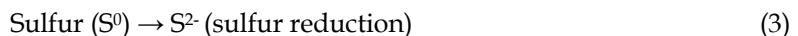


Fig. 16. The process of removing arsenic from the leach solution

4. Conclusions

It was assessed that arsenic in the copper concentrate investigated in this study was in the form of enargite mineral and fahlerz group minerals. No more than 0.5% arsenic is permitted in saleable copper concentrate. Due to its mineralogical structure, the arsenic contained in the copper concentrate is not expected to be removed by methods such as flotation. As a result, Na_2S and NaOH leaching were used to selectively remove arsenic from the copper concentrate, and at the end of the process, the arsenic concentration in the concentrate was reduced to below the acceptable level in the saleable copper concentrate. Further analysis suggests the mechanism of selective leaching of As in combination with its mineralisation state. Alkaline sulphur leaching is a promising process for removing arsenic from copper concentrates, offering numerous benefits such as improved environmental performance, increased smelter efficiency, economic benefits, lower operating costs and greater sustainability. It supports the production of higher-quality copper while minimising the risks and challenges associated with arsenic contamination.

The arsenic extracted from the flotation concentrate through alkaline leaching assumes a solution form. Due to the difficulty of storing the leach solution in systems such as tailings dams, recovery of arsenic in solid form from the leach solution is required. Moreover, there has recently been a demand for arsenic as a raw material. Consequently, it is imperative to recover high arsenic concentrations in solution and solid form. A solid precipitate was produced due to the arsenic precipitation test carried out in the present study.

Further research is required to conduct detailed studies on removing arsenic from the pregnant leach solution. Different arsenic precipitation techniques will be investigated, particularly the characterisation of the precipitates formed. In addition, future research is needed to evaluate the arsenic sediments from an environmental and economic perspective.

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References

- AWE, S. A., SANDSTRÖM, Å., 2010. *Selective leaching of arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkaline sulphide solution*. Minerals Engineering, 23(15), 1227-1236.
- BALÁŽ, P., 2000. *Extractive Metallurgy of Activated Minerals*. Elsevier, Amsterdam.
- BLANCO-VINO, W., ZAMORA, G., ORDÓÑEZ, J.I., 2024. *Selective Removal of Arsenic and Antimony from Pb-Ag Sulfide Concentrates by Alkaline Leaching: Thermodynamic and Kinetic Studies*. Mining, 4(2), 284-301.
- BUJNÁKOVÁ, Z., BALÁŽ, P., ZORKOVSKÁ, A., 2014. *Enargite concentrate processing by the combination of mechanochemical, hydrometallurgical and precipitation methods*. International Journal of Mineral Processing, 127, 28-36.
- BRUCKARD, W.J., KYRIAKIDIS, I., WOODCOCK, J.T., 2007. *The flotation of metallic arsenic as a function of pH and pulp potential – a single mineral study*. Int. J. Miner. Process. 84 (1-4), 25-32.
- CURRELI, L., GARBARINO, C., GHIANI, M., ORRÙ, G., 2009. *Arsenic leaching from a gold bearing enargite flotation concentrate*. Hydrometallurgy, 96(3), 258-263.
- DUTRIZAC, J.E., MORRISON, R.M., 1984. *The Leaching of Some Arsenide and Antimonide Minerals in Ferric Chloride Media*. In: Bautista, R.G. (eds) *Hydrometallurgical Process Fundamentals*. NATO Conference Series, vol 10. Springer, Boston, MA.
- ESPINOSA, M.H.V., 1965. Process for the removal of arsenic or arsenic compounds, United States Patent 3220796, Madrid, Spain.
- FILIPPOU, D., ST-GERMAIN, P., GRAMMATIKOPOULOS, T., 2007. *Recovery of Metal Values from Copper – Arsenic Minerals and Other Related Resources*. Mineral Processing and Extractive Metallurgy Review, 28(4), 247-298.
- GAJAM, S., RAGHAVAN, S., 1983. *A kinetic study of enargite dissolution in ammoniacal solutions*. International Journal of Mineral Processing, 10(2), 113-129.
- GAN, Y., DENG, R., LIU, Q., 2022. *Flotation Separation of Covellite and Enargite via Oxidation Treatment*. Minerals, 12(8), 970.
- GUO, H., YEN, W.T., 2005. Selective flotation of enargite from chalcopyrite by electrochemical control. Minerals Engineering, 18(6), 605-612.
- LEIST, M., CASEY, R.J., CARIDI, D., 2000. *The management of arsenic wastes: Problems and prospects*. J. Hazard. Mater. 76, 125-138.
- LI, T., ZHANG, Y., ZHANG, B., JIAO, F., QIN, W., 2019. *Flotation separation of enargite from complex copper concentrates by selective surface oxidation*. Physicochem. Probl. Miner. Process, 55(4), 852-864.
- LIU, X., DU, Z., SUN, C., ZHANG, N., 2025. *A review on the electrochemical analysis of sulfide minerals – Pyrite, chalcopyrite, and galena*. Green and Smart Mining Engineering, 2(1), 18-31.
- LONG, G., PENG, Y., BRADSHAW, D., 2012. *A review of copper-arsenic mineral removal from copper concentrates*. Minerals Engineering 36-38, 179-186.
- MANDAL, B. K., SUZUKI, K. T., 2002. *Arsenic round the world: A review*. Talanta, 58(1), 201-235.
- PANAYOTOVA, M., 2023. *Control of Non-Ferrous Metal-Sulfide Minerals' Flotation via Pulp Potential*. Minerals. 13(12), 1512.
- PLACKOWSKI, C., NGUYEN, A.V., BRUCKARD, W.J., 2012. *A critical review of surface properties and selective flotation of enargite in sulphide systems*. Minerals Engineering, 30, 1-11.
- TAKATSUGI, K., SASAKI, K., HIRAJIMA, T., 2011. *Mechanism of the enhancement of bioleaching of copper from enargite by thermophilic iron-oxidising archaea with the concomitant precipitation of arsenic*. Hydrometallurgy, 109(1-2), 90-96.
- TAPLEY, B., YAN, D., 2003. *The selective flotation of arsenopyrite from pyrite*. Minerals Engineering, 16(11), 1217-1220.
- TONGAMP, W., TAKASAKI, Y., SHIBAYAMA, A., 2009. *Arsenic removal from copper ores and concentrates through alkaline leaching in NaHS media*. Hydrometallurgy, 98(3-4), 213-218.

- TONGAMP, W., TAKASAKI, Y., SHIBAYAMA, A., 2010. *Selective leaching of arsenic from enargite in NaHS–NaOH media*. Hydrometallurgy, 101(1-2), 64-68.
- TONGAMP, W., TAKASAKI, Y., SHIBAYAMA, A., 2010b. *Precipitation of arsenic as Na₃AsS₄ from Cu₃AsS₄–NaHS–NaOH leach solutions*, Hydrometallurgy, 105, 42-46.
- TÜRK, T., 2016. *Optimisation of arsenic removal from pyrite ash by NaOH leaching using central composite design*. Desalination and Water Treatment, 57, 8575–8582.
- WAN, H., A. N. Y., LUUKKANEN, S., QU, J., ZHANG, C., XUE, J., WANG, S., BU, X., 2023. *New insights into the sphalerite activated by copper sulfate in lime systems*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 667, 131397.
- WANG, J., JÍNG, G., ZHENG, R., HUANG, Z., SUN, W., GAO, Z., 2023. *Ethylenediamine tetramethylenephosphonic acid as a selective collector for the improved separation of chalcopyrite against pyrite at low alkalinity*, International Journal of Mining Science and Technology. 33(7), 873-882.
- WELHAM, N.J., 2001. *Mechanochemical processing of enargite (Cu₃AsS₄)*. Hydrometallurgy, 62, 165–173.