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A Process Mineralogy Based Approach for Arsenic Removal from Copper Concentrate in Cu – Mo Flotation Circuit

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Abstract

Due to anthropogenic activities of arsenic, its contamination has been widely recognized as one of the most consequential environmental pollutants. This study aims to investigate the possible controlling factors in the amount of arsenic in copper concentrate of the Sungun processing plant – located in northwestern Iran. For this purpose, via utilization of process mineralogy approach, an attempt is made to provide a mineralogical-based approach to reduce or remove As from copper concentrate. Chemical analysis of flotation circuit products shows changes of 0.13-1.00% for As in concentrate, and up to 0.003% for tailings. Arsenic is recovered to concentrate in the form of sulfosalt minerals including tennantite and enargite, along with copper sulfides. In order to reduce the arsenic in copper concentrate, flotation tests are performed in Eh values of +300, +200, +100, 0, -100, -200, and -300 mV. Based on the results, a re-flotation step on copper concentrate with a pulp potential range of -300 to +300 mV is conducted as an effective and optimal solution to reduce the amount of As. At a potential of -100 mV, Cu-As minerals (tennantite and enargite) tend to be depressed, and at +300 mV, these minerals tend to float. During the processing circuit, via flotation of particles with a size of -25 μm and adjusting the pulp potential to +300 mV, it is possible to produce two copper concentrates with low arsenic content (< 0.2%) and high arsenic content (> 0.2%). The first concentrate, which is flotation tailings, can be sold in the same way. The second one can be sold after complete removal of arsenic by leaching and then collection of harmful gases.

1. Introduction

Arsenic is one of the most important and toxic inorganic pollutants. Numerous studies have investigated the possibility of separating arsenic-bearing minerals (tennantite and enargite) from copper and iron sulfide minerals utilizing various methods [1-3]. Pyrometallurgical and hydrometallurgical processes are the most common methods used to remove arsenic from copper concentrate [3, 4]. These include alkaline sulfide leaching, hypochlorite leaching, sulfuric acid diluted with aluminum sulfate leaching, and combined pressure oxidation with the leaching of copper precipitate [4]. The efficiency of roasting as

one of the options for reducing the arsenic content in copper concentrates and preparing clean feed for copper smelters, has also been investigated [3, 5]. This method faces challenges such as copper losses with deposition of iron compounds, problems in electrowinning for chloride process, stabilization of toxic impurities, adsorption, separation, oxidation, and stabilization of produced gases. All the methods listed above are largely not commercialized [1, 2, 6-8]. Another method for refining arsenic-bearing copper concentrates is flotation. The flotation process is relatively simpler and less harmful than the pyrometallurgy and

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hydrometallurgy processes. Numerous studies have been conducted on the application of flotation to remove arsenic minerals from copper concentrate [9-13]. The main challenge in this method is strong floatability of arsenic minerals in the presence of conventional flotation collectors. Another problem is failure to depress arsenic minerals by conventional depressants (such as lime, sulfide cyanide, and permanganate) [13, 14]. The utilization of chemicals, selective oxidation or modifiers of minerals, and control of redox potential (Eh) have been studied by several researchers [9, 15-17]. Based on these studies, it was concluded that flotation redox potential (Eh) control is an effective strategy to develop the separation of copper-arsenic-bearing minerals from other copper sulfide minerals [16-18].

These studies have typically been performed on the flotation behavior of some single copper sulfide minerals and enargite, while the diversity of mineralogical composition and texture is a very important factor and play a significant role in the efficiency of flotation process. In the present study, a geometallurgical approach were applied to address the challenge of arsenic in copper ore processing products and introduce a method for arsenic removal from copper concentrate in the Cu-Mo flotation circuit of Sungun copper-molybdenum processing complex – located in northwestern of Iran. In the Sungun complex (mine and processing plant), arsenic is mainly produced as a by-product of extraction and processing. Examination of exploratory data from drilled boreholes for the Sungun copper deposit indicates the amount of more than 70 ppm of arsenic in ore. The entry of this feed into the Sungun processing plant, and the flotation process on it, will cause the concentration of arsenic with a grade of more than 0.25% in copper concentrate. This amount of arsenic in copper concentrate is more than the permissible standard (0.20%). Increasing arsenic

from 0.20% in copper concentrate leads to economic and environmental challenges in downstream processes such as smelting.

In the paper part I, the distribution of arsenic in different zones of the mine has been determined by examining the data and analysis of the selected core samples. In this paper (Part II), by implementing a mineralogical approach, comprehensive information about the texture, structure of copper minerals and their relationship with arsenic-bearing minerals, the presence of arsenic minerals in the feed, and their behavior during the flotation process, including floatability and arsenic recovery to copper concentrate, have been obtained. On the other hand, the operating conditions of the existing circuit are examined, and then by combining them with the mineralogical information of the process, the circuit is optimized to solve the challenge of the presence of arsenic in copper concentrate.

1.1. Sungun Cu-Mo Plant

The main mineralization of the Sungun deposit is copper and molybdenum sulfide minerals; since chalcopyrite is the main mineral of copper in Sungun deposit, the flotation method is utilized for its processing. In the concentration plants of phases 1 and 2 of the Sungun complex, copper concentrates are obtained from input ore with an average copper grade of 0.60% via the flotation method. The molybdenum grade in the input feed to the copper-molybdenum concentration plant is about 0.01-0.02%, which for the beneficiation of molybdenum, the concentrate of the copper concentration plant is transferred to the molybdenum processing plant. An overall schematic of copper and molybdenum processing in phase 1 and 2 copper-molybdenum concentration plants is shown in Figure 1.

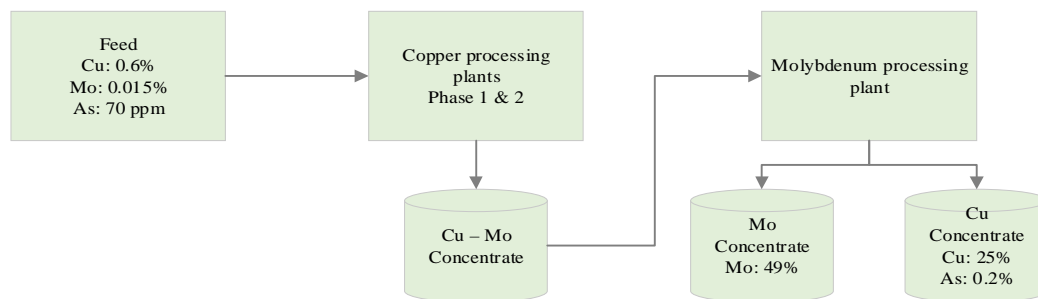


Figure 1. Copper and molybdenum processing stages in Sungun copper-molybdenum processing complex.

The average amount of arsenic in the feed, concentrate, and copper tailings of the Sungun

copper – molybdenum processing plant were measured over 8 months period and the results are

shown in Figure 2-A. According to the diagrams in Figure 2, the changes in arsenic grade in the feed, concentrate, and final flotation tailings at different times show an almost similar trend, i.e. under constant operating conditions, the recovery of arsenic to copper concentrate is almost constant and affected by its amount in the feed. Graphs of copper and arsenic recovery in different months of the study period are also shown in Figure 2-B. Copper recovery changes fluctuate less during the study period, and its recovery changes are in the range of 4.80% (84-88%). In the case of arsenic, however, it is observed that the range of changes is wider, and arsenic recovery varies from 65 to 85% (changes in the range of 30.80%). Comparison of copper and arsenic recoveries does not show significant trends and dependencies for the recovery of these two elements. The reason for this can be attributed to the changes in arsenic minerals and copper-arsenic minerals in different zones of the Sungun deposit. In blocks where arsenic is

formed in the form of copper-arsenic minerals (such as tennantite and enargite), arsenic recovery has increased during flotation; but in cases where arsenic is in the form of arsenic minerals such as arsenopyrite. These minerals are likely to be depressed during flotation via adjusting the pH, and the final recovery of arsenic is reduced, i.e. changes in the amount, type and distribution of copper-arsenic minerals and arsenic-bearing minerals in different parts of the deposit is the main reason for the presence of arsenic in copper concentrate and changes in its recovery [19]. Since the current mining plan is based only on the regulation of copper grade and maximization of net present value (NPV), and no attention has been paid to its environmental (release of harmful elements) and metallurgical aspects, the development of a geometallurgical plan in addition to solving processing, environmental and metallurgical problems can also maximize economic productivity.

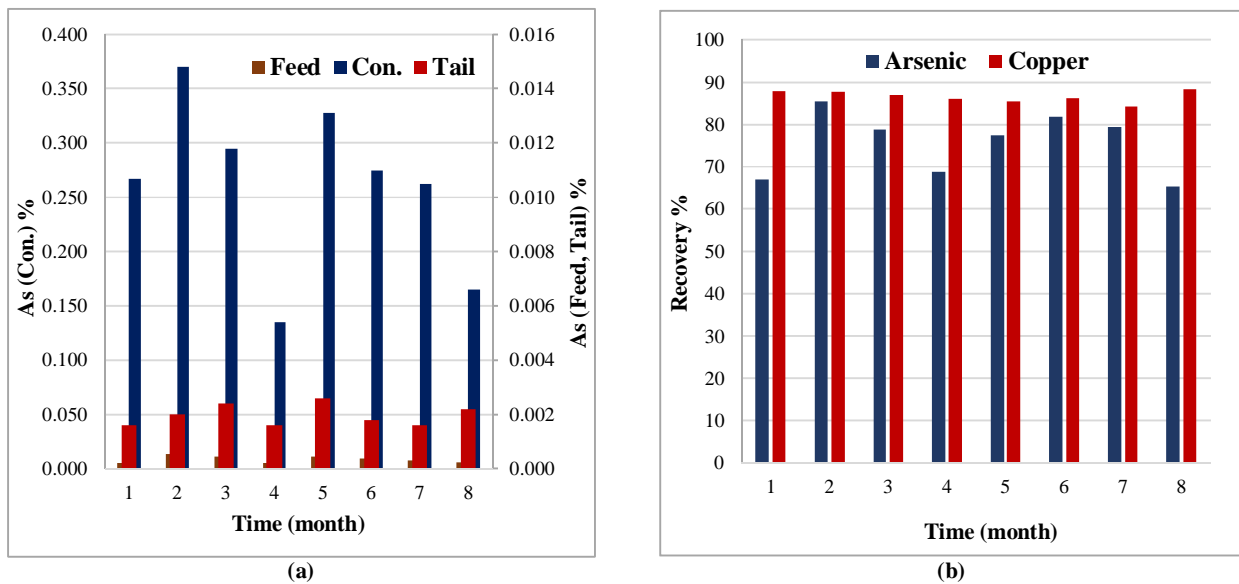


Figure 2. A) Changes in the average amount of arsenic in feed, concentrate, and tailings, B) Recovery of copper and arsenic elements to concentrate of Sungun copper in different months.

3. Materials and Methods

In the present study, by implementing mineralogy in the copper flotation process, an attempt has been made to obtain comprehensive information on the texture and structure of copper and arsenic minerals and their behavior during the flotation process. For this purpose, after reviewing the results of inductively coupled plasma mass spectrometry (ICP-MS) analysis for 8 months period (Figure 2), it was observed that the arsenic grade in the second month is higher than the other

months studied. Via examining the results of the analysis of the arsenic concentration in 31 days in this month, it was observed that the arsenic grade in 3 days of this month has higher values.

3.1. Mineralogical-based approach

In the next step, from samples of the mentioned 3 days (from the second month) polished sections were prepared in the size ranges of +25 μm and -25 μm . Microscopic study of polished sections is the most common method of studying the

mineralogical properties and textural association between minerals in mineral samples. Optical microscopic studies were performed to identify minerals, determine the degree of liberation, type and amount of arsenic minerals present in copper concentrate, interlocking of arsenic mineral in the matrix of other minerals and particles. For preparing polished sections, 30 g of the sample was prepared using a riffle sample splitter to preparation of polished sections and performing microscopic studies. Preparation of polished sections has been done in three stages of molding, abrasion and polishing. Al_2O_3 , Mg_2O_3 , Cr_2O_3 , and Fe_2O_3 have been used for polishing and preparation of sections. Microscopic studies were performed using the Leitz polarizing microscope of model SM-LUX-POL equipped with a digital imaging camera at the college of Mining Engineering, University of Tehran.

In the next step, the operating conditions of copper and molybdenum flotation circuits were determined. In this regard, the type and amount of chemicals in the circuits were investigated, and the values of Eh in different parts of the circuits were also measured. Finally, by combining mineralogical information and operating conditions of the circuits, flotation tests have been designed and performed to remove arsenic from copper concentrate.

3.2. Flotation tests

The alteration of pulp oxidation – reduction potential (Eh) to change the flotation behavior of

copper sulfide minerals associated with arsenic-copper and arsenic minerals were studied. For this purpose, flotation tests were performed using a self-aerated Denver laboratory flotation cell. First, based on the conducted research into redox potential control [9, 10, 15, 18] as well as measuring Eh values of Sungun copper-molybdenum processing plant flotation cells, 7 flotation tests were performed in Eh values of +300, +200, +100, 0, -100, -200, and -300 mV. In the next step, after determining the appropriate Eh, additional flotation tests were performed to determine the optimal conditions and flotation kinetics of arsenic-bearing minerals. The conditions are the same in all flotation tests and per Table 1. In each test, the pulp concentration is 25% and the rotor speed is 1200 rpm. NaOH was utilized to adjust the pH, and sodium sulfide (Na_2S) and hydrogen peroxide (H_2O_2) were used to adjust the Eh. In this way, after adjusting the pulp to a certain concentration, the pH value is adjusted first. The desired amount of Eh is then adjusted by adding sodium sulfide (to reduce the potential) and hydrogen peroxide (to increase the potential). It should be noted that in all tests, the preparation time for pulp and frothing was 60 and 120 seconds, respectively. In the first stage, frothing was done without adding chemicals, then by adding chemicals including polypropylene glycol (A65) and MIBC (A70) frothers, Sodium Isopropyl Xanthate (SIPX) and Thiono-Carbamate (Flomin) collectors.

Table 1. Operational parameters of flotation tests with pulp potential control.

pH	Eh (mV)	Na_2S (cc)	NaOH (cc)	H_2O_2 (cc)
11	-300	5	7	-
11	-200	3	5	-
11	-100	3	6	-
11	0	-	5	18
9.5	+100	-	5	9
8.5	+200	-	5	30
7.5	+300	-	7	80

After the initial flotation tests, it was determined that at a potential of +300 mV, there is a possibility of complete flotation of arsenic minerals. On the other hand, since the volume of copper-arsenic minerals is much less than other copper minerals, the best condition in terms of flotation is reverse flotation. In this way, smaller volumes of copper-arsenic minerals are floated, and other copper minerals are depressed. In this regard, additional flotation tests were performed to investigate the

flotation kinetics of arsenic minerals in the pulp potential of +300 mV and with the conditions stated in Table 2. Also the pulp concentration in this test is 20%. In this test, after the pulp was adjusted to the desired solid percentage inside the flotation cell, the pulp pH was first adjusted using NaOH at 11, and then the pulp potential at + 300 mV was adjusted utilizing H_2O_2 . In the next step, chemicals including collector and frothers were added to the pulp, and after 60 seconds of

preparation time, frothing was performed for 30 seconds. The air valve is then closed and chemicals are injected; after 60 seconds of preparation,

frothing was performed for 60 seconds. During the process using H_2O_2 , the pulp potential is maintained at +300 mV.

Table 2. Operational parameters of arsenic flotation kinetic test with pulp potential control.

pH	Eh (mV)	Conditioning time (s)	Concentrating time (s)	A65 (cc)	A70 (cc)	Z11 (cc)	Flomin (cc)	H_2O_2 (cc)	NaOH (cc)
11	+300	60	30	1.5	1.00	1	1	80	28
			60	1.25	0.80	0	0	10	0
			120	1.00	0.60	0	0	10	0
			240	0.75	0.50	1	1	4	0
			480	0.50	0.30	0	0	9	0
			960	0.00	0.00	0	0	0	0

4. Results and Discussion

4.1. Mineralogical studies

By examining the arsenic grade of feed, concentrate, and tailings of the copper flotation circuit (Figure 2), concentrate was selected (due to the high grade of arsenic) to study the properties of arsenic-bearing minerals. Examination of arsenic levels in the 8 months (Figure 2) indicates a grade of more than 0.35% for existing arsenic in copper concentrate in some months. Daily studies of arsenic grade in copper concentrates of the mentioned month indicate changes of 0.22 to more than 1.32% for the arsenic grade in copper concentrate. In this case, the copper grade in the concentrate varied from 22.64 to 27.60%. Sieve analysis was performed on three copper concentrates (corresponding to these days) of this month, which contained the highest amount of arsenic. The d_{80} value of copper concentrate for the three samples is 40.90, 39.82, and 38.52 μm . Therefore, it can be stated that there is no significant difference in the particle size distribution of copper concentrate on different days. According to the graph, in all three concentrates (different days), the amount of fine particles (< 25 μm) is about 40%.

To perform microscopic studies and study the degree of liberation, each of the mentioned concentrates was separated into two fractions of fine-grained and coarse-grained particles utilizing a 25- μm sieve. Then from each of them, polished sections (a total of 6 sections) have been prepared and mineralogical studies have been performed on it. All three samples are almost identical in mineralogy and diversity of available minerals, with only a slight difference in the frequency ratio of minerals.

Metallic minerals are the main constituents of the studied concentrates (Figure 3); about 85-90% of the total volume. These minerals are mainly sulfide and sulfosalts. Sulfide and sulfosalts phases include

chalcopyrite, pyrite, chalcocite, bornite, tennantite, enargite, covellite, molybdenite, sphalerite, galena, and digenite, respectively. Sulfosalts belong to the group of enargite – lawsonite and the tennantite – tetrahedrite group. The two minerals enargite and tennantite, which are among the responsible minerals containing arsenic, account for about 6% of the volume of floating metal minerals. From the mineral frequency distribution standpoint, chalcopyrite with a frequency of 40-50% by volume is the main responsible sulfide phase (Figure 3-B). Next is pyrite with a frequency of 20-25% by volume. Chalcocite in the amount of 5-8% by volume, bornite in the amount of 2-4% by volume, minerals of the sulfosalts group in the subgroup of enargite- lawsonite about 1-1.50% by volume, a subgroup of tennantite-tetrahedrite (mainly tennantite) in the amount of 2-3.50% by volumes. Also in small amounts, 0.01-0.10%, galena, sphalerite, molybdenite, and copper are significant elements.

Since SIPX and Flomin collectors are utilized in Sungun copper processing plants for flotation of copper sulfides, and also due to the similar surface properties of copper sulfides and sulfosalts minerals (tennantite and enargite), free tennantite and enargite minerals have found their way into concentrates. Therefore, the use of depressants, which depress arsenic minerals without affecting the flotation properties of copper sulfides, will significantly reduce the amount of this element in copper concentrate. On the other hand, CuAsS_4 (enargite) and $\text{Cu}_3\text{AsS}_{3.25}$ (tennantite) contain 48.40% and 51.60% of copper, respectively. As can be seen, the amount of copper in each of these two minerals is more than 48% and the amount of arsenic is about 19%. Considering the volume percentage of tennantite and enargite minerals in the final copper concentrate and also the amount of copper recovery in Sungun copper processing plant, via depressing these minerals, there will be a decrease of about 2.50-4% in the final copper

recovery. Therefore, it can be concluded that the best way to reduce arsenic is to remove it from the final copper concentrate; thus during the processing, all floated copper minerals containing arsenic (tennantite and enargite) and without arsenic (copper sulfides) finally enter the final

flotation cells as feed (to separate copper-arsenic minerals). The concentrate at this stage of flotation is referred to as the high arsenic content copper concentrate, and the tailings of this flotation will be referred to as the low arsenic content copper concentrate (target product).

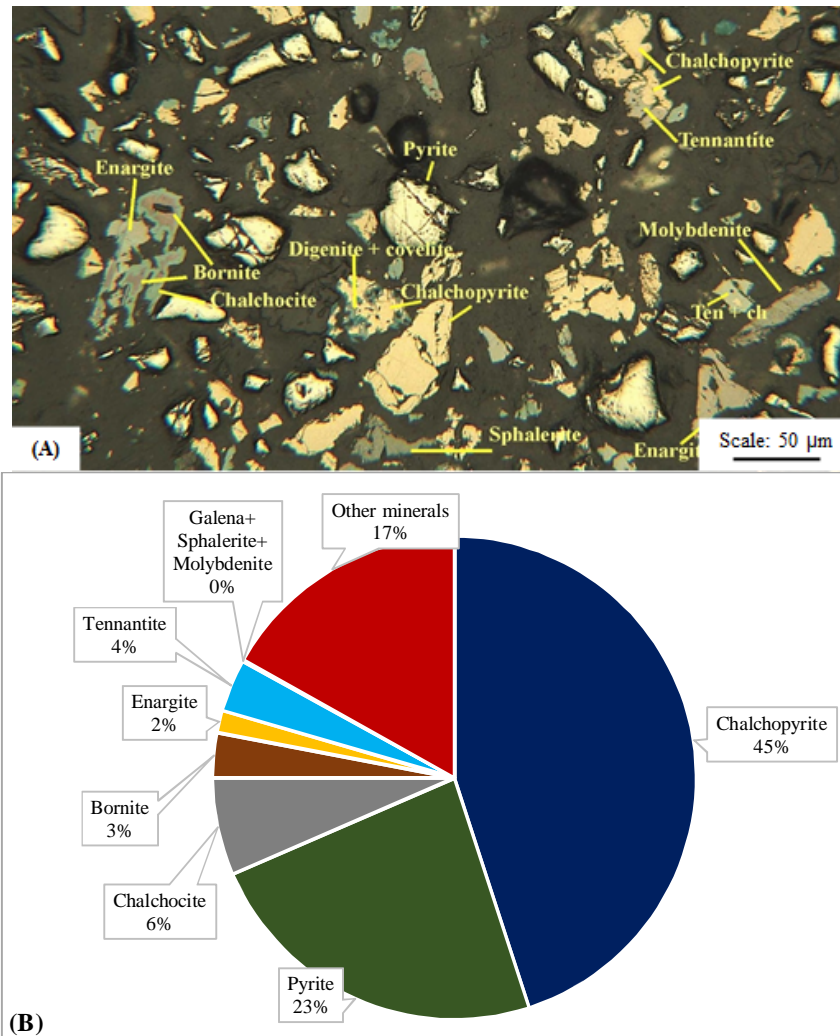


Figure 3. A) Metal minerals forming copper concentrate - Reflected light photomicrographs in plane-polarized light (PPL), B) Their frequency in concentrate of Sungun copper (particles with a size of +25 μm).

Examination of existing minerals from the interaction and their degree of liberation standpoint, in the coarse size fraction (+25 μm), indicates that the available free components include pyrite, chalcopyrite, bornite, chalcocite, enargite-lawsonite, tennantite-tetrahedrite (Mostly tennantite and rarely tetrahedrite), molybdenite, galena, sphalerite, covellite and elemental copper (Figure 4). The predominant sulfide minerals are mainly in free form, and the overall degree of liberation of them (pure free parts or a combination of these minerals) was determined to be about 90-95%. Minerals of the sulfosalt group, including

tennantite and enargite, are found in the free and involved form. The overall degree of liberation of sulfosalt minerals was about 80-85%. The free parts of tennantite and enargite comprise about 75-80% of the total of these parts. Compounds consisting of two or more minerals some of them shown in Figure 4. It should be noted that in most cases, chalcocite, covellite, and digenite are involved with other copper sulfide minerals, especially chalcopyrite and bornite, and to a lesser extent with sulfosalts (tennantite and enargite) in the form of substitution and to a lesser degree isogonic growth, and chalcopyrite are also rarely

found in the form of exclusion and inclusion in a host of bornite and sphalerite. In addition to the interaction of arsenic-bearing minerals, they also are locked with copper sulfide minerals (especially chalcocites). Interaction of enargite and tennantite with chalcopyrite, the main copper mineral in the Sungun deposit, has also been observed. About 15-20% of sulfosalts are involved with copper-bearing sulfide minerals (chalcopyrite, bornite, chalcocite, covellite, and digenite). About 5-10% of them are involved with each other and a maximum of 10-15% of them are involved with copper sulfide minerals, especially chalcopyrite, bornite, and chalcocite. In these cases, the locking between enargite and tennantite with copper sulfide minerals is the main reason for these minerals to enter copper concentrate. The application of depressants in this case significantly reduces

copper recovery (due to interactions with copper sulfide minerals as well as copper in the structure of sulfosalts). Re-grinding (or increasing the comminution time in the previous stages of comminution) to obtain the appropriate degree of liberation and then utilizing depressants to depress arsenic ores can be an effective solution to this problem. However, considering the above and the degree of liberation of minerals, the production of two products of high arsenic content and the low arsenic content concentrate is a more effective solution from a technical and economic standpoint. Copper minerals with a suitable degree of liberation (more than 90%) produce a concentrate containing a minimum amount of arsenic; copper minerals involved with tennantite and enargite as well as free tennantite and enargite minerals from high arsenic content concentrate.

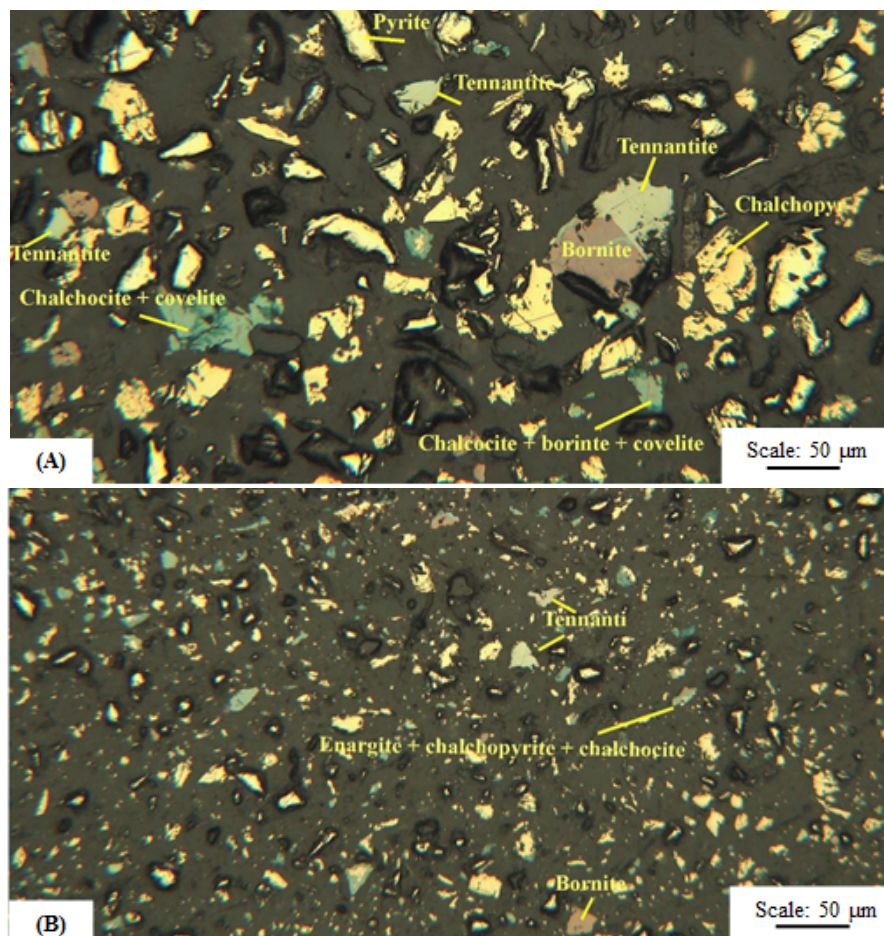


Figure 4. Free and involved minerals forming concentrate of Sungun copper, A) particles with size + 25 μm and B) particles with size - 25 μm; Reflected light photomicrographs in plane-polarized light (PPL).

4.2. Flotation tests with Eh control

4.2.1. Eh control in Sungun flotation circuit

Previous studies have shown promising results regarding the possibility of separation of arsenic-copper sulfides from copper sulfide minerals by controlling the pulp flotation potential [9, 10, 15, 18]. Accordingly these studies, to optimize the sulfide copper flotation circuit, and to determine the appropriate location for arsenic removal, Eh of different points of the circuit have been measured (Table 3). According to the measured values for flotation cells (phase 1 and 2 copper plants as well as molybdenum plants), the potential of all cells is decreasing. It should be noted that Sungun plant consists of two phases. The potential of phase 1 and 2 cells of the copper plant was in the range of -60

to -100 mV, and the molybdenum plant was in the range of -500 to -700 mV. In the molybdenum processing plant, to increase the pulp potential of the process and depress the copper minerals and float molybdenum, the injection of sodium sulfide starts from the first flotation cell and continues to the last cell in several different points. Therefore, the amount of pulp potential in the molybdenum plant (as expected) decreases from the first cell to the last cell. This action causes all copper sulfide minerals to be depressed (transferred to molybdenum or copper concentrate), and molybdenum to be floated and recovered to concentrate. Based on this, copper concentrate or molybdenum processing plant tailings were determined to be suitable for flotation tests by controlling the pulp potential.

Table 3. Eh values of flotation cells of Sungun copper-molybdenum complex.

Circuit Phase 1 – Cu processing		Circuit Phase 2 – Cu processing		Circuit Mo processing	
Flotation stage	Eh (mV)	Flotation stage	Eh (mV)	Flotation stage	Eh (mV)
Rougher cells (1 – 12)	(-77) – (-82)	Rougher cells (1 – 5)	(-77) – (-86)	Rougher cells (1 – 8)	(-600) – (-595)
Cleaner cells (1 – 2)	(-65) – (-66)	Cleaner cells (1 – 4)	(-102) – (-77)	Cleaner cells (1 – 8)	(-676) – (-622)
Recleaner cell	-64	Recleaner cell (1 – 3)	(-88) – (-76)		
Scavenger cells (1 – 4)	(-67) – (-73)	Scavenger cells (1 – 4)	(-88) – (-76)		

4.2.2. Arsenic removal with pulp Eh control

Research works have shown that the desired results for reducing the amount of arsenic in copper concentrates are in the range of positive potentials [10, 18]. But measuring the pulp potential values for the Sungun copper flotation circuit indicates a negative potential for all its cells. Therefore, the aim was to investigate the effect of changes in pulp potential to remove or reduce the amount of arsenic in copper concentrate by performing a re-flotation step on the final copper concentrate. For this purpose, by preparing a sample of the final copper concentrate (molybdenum plant tailings) as a feed for control flotations, flotation tests were performed in different values of Eh. The feed of the flotation tests is the final concentrate of the Sungun copper plant with the highest arsenic content. The arsenic grade in the selected feed (plant copper concentrate) for flotation tests at this stage was 0.21%, and the copper grade was 23.95%. Figure 5 shows the results of flotation tests with the conditions described in Section 3-2. It can be stated that at potentials less than +200 mV, almost all arsenic-bearing minerals have been depressed; and the amount of arsenic in low arsenic content concentrate is less than the permissible limit

(0.20%). On the other hand, according to the results obtained for the copper grade, in the potential of -100 mV, the grade of copper in the froth (high arsenic content concentrate) has increased, and it has the highest value, i.e. floated minerals in the potential of -100 mV also contain copper. In general, it can be said that the redox potential of -100 mV is the optimal point for flotation from the depressing copper-arsenic-bearing minerals and flotation of copper ores, standpoint. At a Eh of +300 mV, arsenic is the highest in the tests; this indicates that in this potential, copper-arsenic minerals tend to float. On the other hand, according to Figure 5, the copper grade, in this case, is reduced in the remaining part of the cell (low arsenic content concentrate) and is at its lowest value. It can be established that at this potential (+300 mV), copper sulfide minerals (including chalcopyrite, chalcocite, covellite, bornite) are less inclined to be float. Arsenic grade after injection of chemicals (collector and frother) has decreased compared to the first stage of frothing (without chemicals). However, the injection of chemicals has increased the grade of copper in the high arsenic content concentrate, which shows the positive effect of these chemicals on the flotation of copper-arsenic minerals.

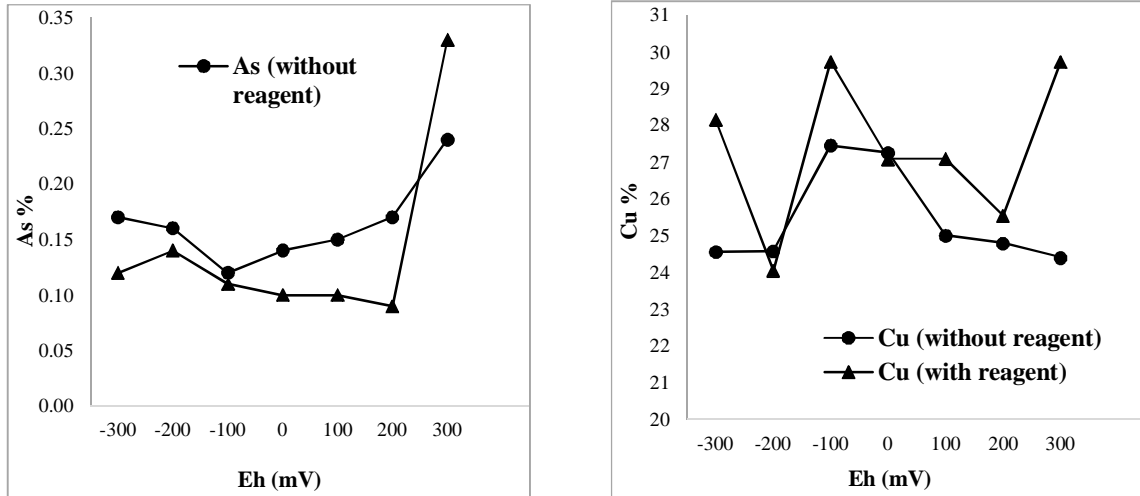


Figure 5. Arsenic and copper grade in concentrate of flotation tests with pulp potential control.

Figure 6 shows the changes in arsenic and copper tailings in flotation tests (low arsenic content concentrate) under different potentials. Changes in flotation pulp potential did not have a significant effect on arsenic grade at low arsenic content concentrate (especially in the Eh +200 to -300 mV). The lowest arsenic content is obtained in flotation with a potential of +300 mV. As mentioned and based on similar studies, in this flotation pulp potential, arsenic-bearing minerals tend to float and most of them have been transferred to high arsenic content concentrate [3, 20, 21]. According to the

graphs Figure 6, the highest copper grade of 23% was obtained in flotation with a potential of -100 mV. On the other hand, according to the results obtained for the copper grade, in the potential of -100 mV, the copper grade in the froth (high arsenic content concentrate) had the highest value. The reason for this can be attributed to the flotation of copper-arsenic minerals at a potential of -100 mV, i.e. in this potential, copper minerals are reduced to arsenic concentrate, and copper-arsenic minerals are floated.

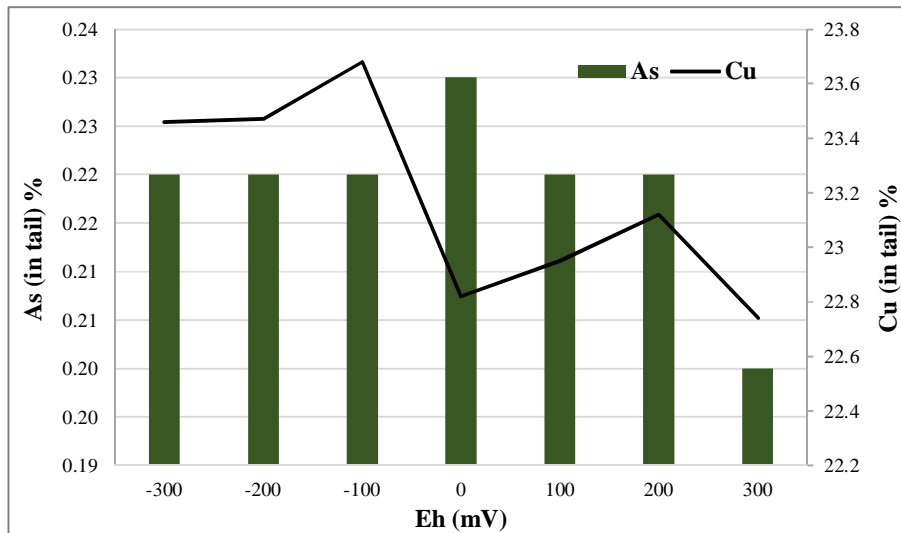


Figure 6. Arsenic and copper grades in low arsenic content concentrate in flotation tests (flotation tailing).

According to Figures 5 and 6, flotation by adjusting Eh to values above +300 mV has had the most suitable result in controlling the amount of arsenic-bearing minerals in copper concentrate. Therefore, additional flotation tests have been performed to investigate the flotation kinetics of

arsenic-bearing minerals in this Eh. The diagrams in Figure 7 indicate the grade and recovery of arsenic and the recovery of copper by changing the concentration-time at the redox potential of the pulp +300 mV. According to the figure, with increasing frothing time, recovery of both copper

and arsenic elements (to high arsenic content concentrate) has increased. The arsenic content has decreased with increasing frothing time. The amount of arsenic recovered during similar frothing periods is higher than that of copper. According to bar graphs representing the arsenic

grade-frothing time, the best time based on the arsenic grades recorded with the goal of selective separation of copper-arsenic minerals is about 500 seconds. In this case, the arsenic content in low arsenic content concentrate will be less than 0.20%.

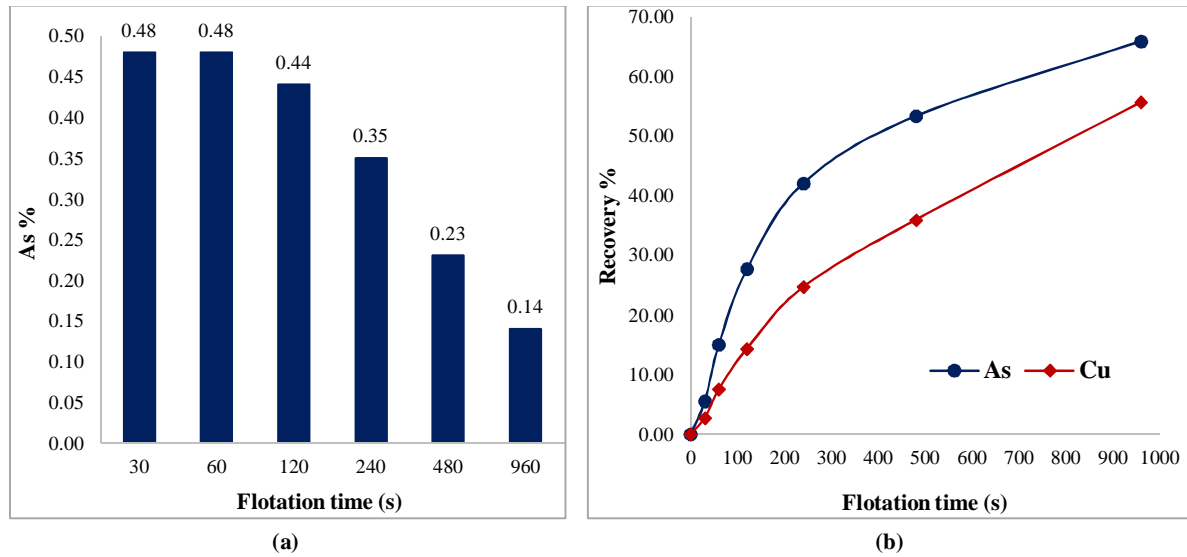


Figure 7. Grade and recovery of As and Cu - flotation time, in electrochemical potential of +300 mV.

The results of additional flotation tests at a potential of +300 mV indicate that, by adjusting the pulp potential to +300 mV, the arsenic content in the flotation concentrate decreases over time (Figure 7). Arsenic grade in flotation feed with pulp potential of +300 mV was 0.18%, and copper grade was 20.57%. According to Figure 8, during the flotation process with a potential of +300 mV, the arsenic content in the first stages of frothing has increased to 0.48% (high arsenic content fraction). This indicates the floatability of copper-arsenic minerals. On the other hand, the arsenic content in the tailings reached 0.12%, which had a significant decrease (low arsenic content fraction). Therefore, it can be said that low arsenic content copper concentrate (residue in the cell) with a potential of +300 mV, has the lowest amount of arsenic and can be sent to the smelter. On the other hand, the grade of copper in high arsenic content concentrate has increased to more than 27% in the first 120 seconds. This indicates the flotation of valuable copper minerals with arsenic. Also, the copper

grade in low arsenic concentrate has decreased to some extent, which can be attributed to the increase in copper grade in high arsenic content concentrate.

4.2.3. Mineralogy of flotation process with Eh of +300 mV

On the feed, concentrates, and tailings, flotation tests with +300 mV pulp, ICP-MS analysis, and microscopic mineralogy studies were performed in two size ranges of +25 μm and -25 μm . Figure 9 shows the grade analysis of arsenic in feed, different times of flotation concentrates (high arsenic content products), and tailings (low arsenic content product). In the feed, the arsenic content in the size range of -25 μm is more than +25 μm , i.e. arsenic-bearing minerals are more concentrated in the fine-grained fraction. It can be concluded that flotation of the final copper concentrate in the potential of +300 mV and for feed with a size of -25 μm for 500 seconds, has the most favorable result.

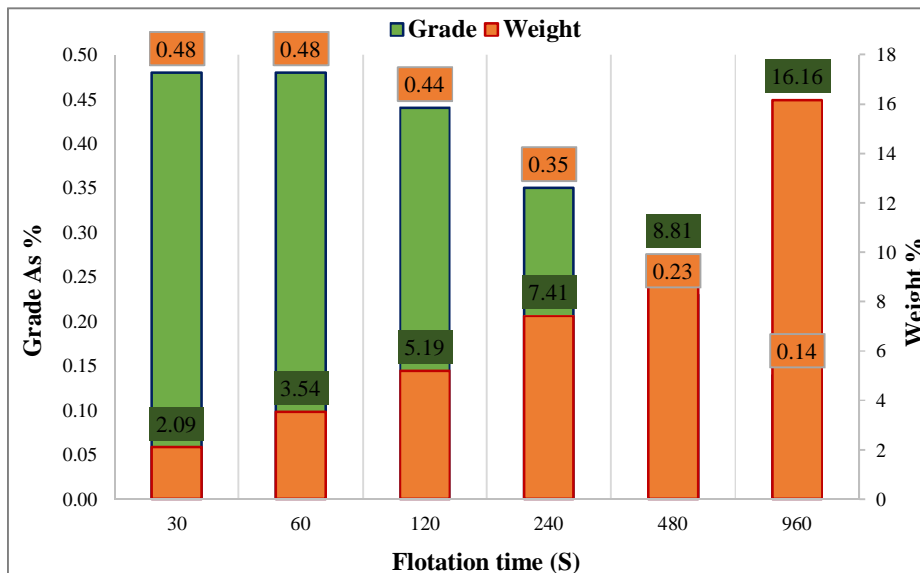


Figure 8. Weight and grade of arsenic in high arsenic content concentrate - flotation test with Eh +300 mV.

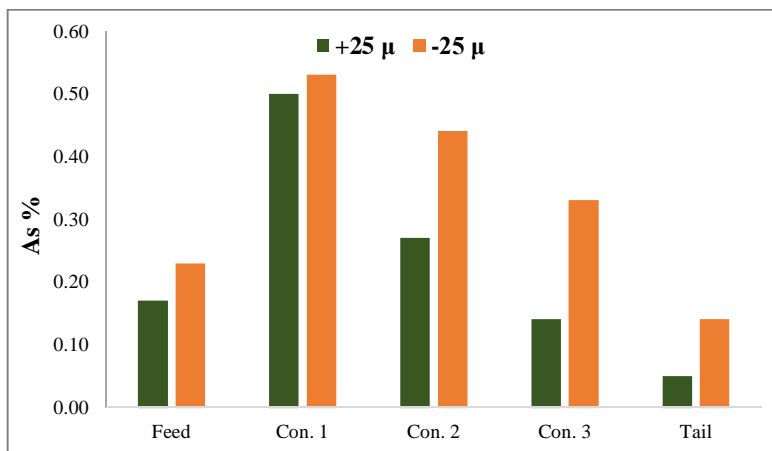


Figure 9. Arsenic values in feed and flotation products at + 300 mV for + 25 μm and -25 μm particles.

In flotation feed, copper sulfide minerals are abundant in chalcopyrite (90% by volume with 95% degree of liberation), bornite (2-3%), covellite, and chalcocite (2-3% in total). The interaction between arsenic-bearing minerals is mostly related to tennantite. Examination of the frequency and degree of liberation of minerals containing arsenic (tennantite and enargite) in the flotation feed (Figure 10), shows that in the size range of +25 μm, the frequency of these two minerals was about 1% with a degree of liberation of 85-90%; tennantite is the main mineral and its amount is about 3 times that of enargite. The number of sulfosalts in particles with a size of -25

μm had a relative increase compared to particles with a size of +25 μm, and their amount reached 1-1.50%. The degree of liberation of these two minerals in the size range of -25 μm was determined to be about 90-95%. Therefore, it can be said that arsenic is recovered to copper concentrate in two ways; in fine-grained fractions (-25 μm), arsenic-bearing minerals have a high degree of liberation and have been recovered to concentrate due to having similar flotation to copper sulfide minerals and in particles with a size of +25 μm, most of which contain arsenic-bearing minerals with chalcopyrite; this interaction has caused them to recover to the concentrate.

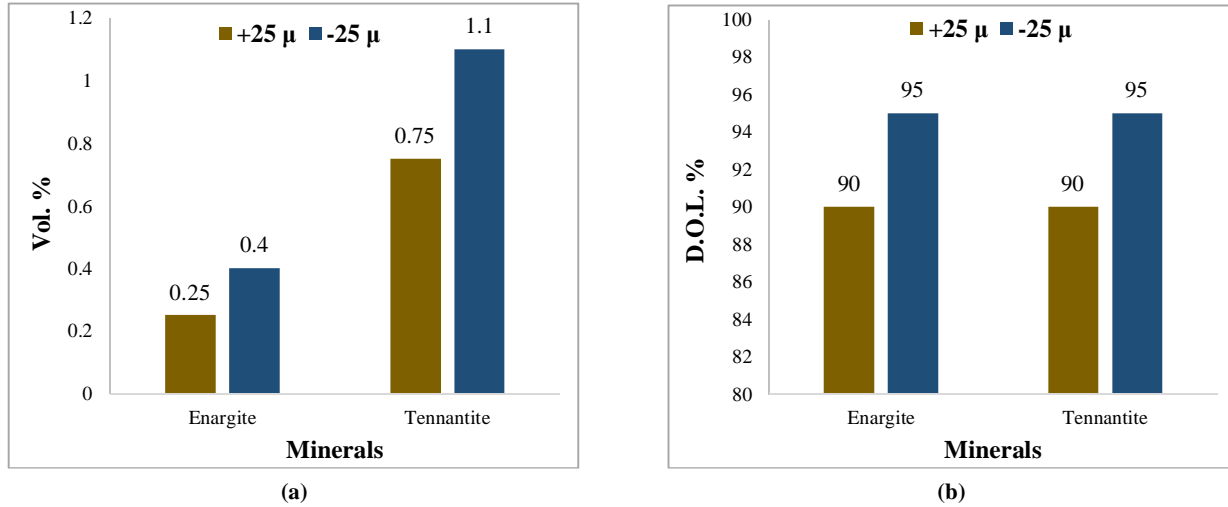


Figure 10. A) Frequency and B) degree of the liberation of tennantite and enargite minerals in the flotation test feed.

Examination of changes in the frequency of minerals and their degree of liberation in the first 120 seconds of flotation concentrate in the size range of +25 μ and -25 μ indicates that the type and order of frequency of sulfide minerals are very similar to the flotation feed. The degree of liberation of chalcopyrites floating in this concentrate is about 98%. The diagrams in Figure 11 show the frequency and degree of liberation of tennantite and enargite minerals in the first flotation concentrate. Tennantite and enargite together make up 2.5-3% of the first high arsenic content product, which is much more frequent in particles with a size of -25 μ. In both size ranges of +25 μ and -25 μ, the amount of tennantite is up to 3 times that of enargite. The degree of

liberation of sulfosalts is about 95% for +25 μ particles and approximately 98% for -25 μ particles. In particles with a size of +25 μ, tennantite and enargite are often found to be involved with chalcopyrite, in which the share of tennantite is higher than chalcopyrite (tennantite with a small fraction of chalcopyrite). It should be noted that in particles of -25 μ, particles involved in tennantite and chalcopyrite can also be seen. Therefore, one of the reasons for the increase in copper grade in high arsenic content concentrate is the interaction of chalcopyrite with minerals containing arsenic. Another reason is the amount of more than 48% copper in the structure of tennantite and enargite.

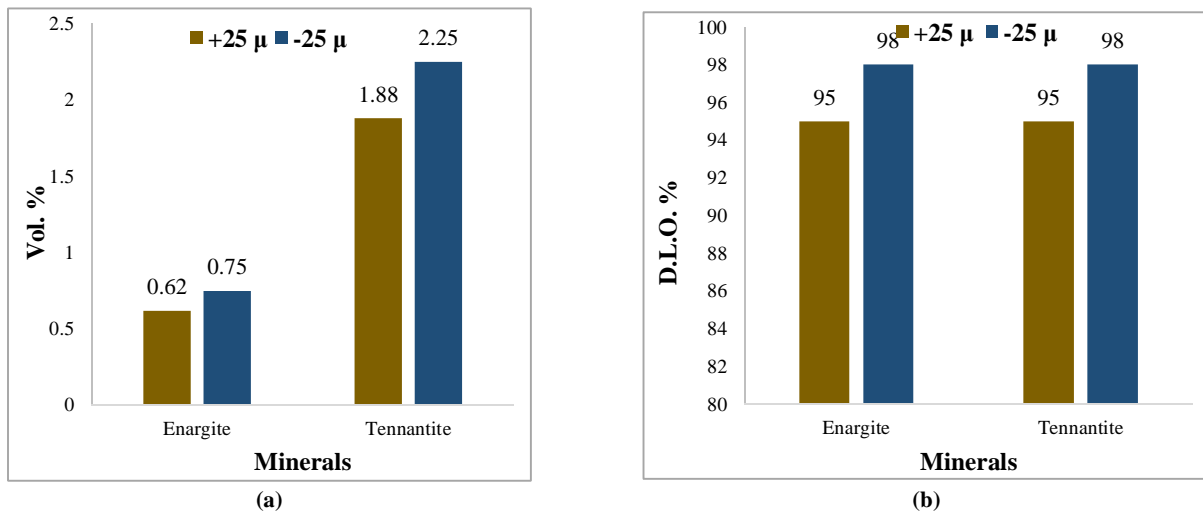


Figure 11. A) Frequency and B) degree of liberation of tennantite and enargite minerals in 120 seconds concentrate of flotation test with a potential of +300 mV.

In the second concentrate, which is related to the 240-second time of the frothing process, the heterogeneity and variation in particle size of sulfide and sulfosalt minerals increased in particles with a size of +25 μm . In this product, the amount of tennantite and enargite minerals has been relatively reduced and determined to be at about 1.50-2%, because most of the minerals are floated in the previous stage. The degree of liberation of these two minerals is not much different from the first concentrate, and only the amount of minerals involved in tennantite and enargite with chalcopyrite has increased. Therefore, it can be stated that free minerals containing arsenic are floated early, and over time, more of the arsenic-bearing minerals interacting with copper sulfides are floated. In the 480 seconds concentrate, variation, and heterogeneity are also observed in particles of +25 μm copper sulfide minerals, tennantite, and enargite. The amount of tennantite and enargite has decreased to about 0.50-1% and their interaction with copper sulfides has also increased. In particles with a size of -25 μm of this concentrate, the amount of tennantite and enargite is more than +25 μm particles and is about 1-1.5%; the frequency of tennantite is 3 times that of enargite.

In flotation tailings or low arsenic content concentrates, the amount of tennantite and enargite minerals is significantly reduced compared to feed and concentrates. The amount of these two minerals in particles with a size of +25 μm is about 0.10% and in particles with a size of -25 μm is approximately 0.20%. Due to the significant reduction of arsenic-bearing sulfosalt minerals such as tennantite and enargite, and arsenic grade, it is revealed that the amount of arsenic in the concentrate (high arsenic content product) is controlled by sulfosalt minerals in the first place. Comparing the frequency of tennantite and enargite minerals in low arsenic content products with ICP-MS analysis (Figure 9), it can be said that due to the difference in their amounts, there is a possibility of arsenic presence in most minerals (other than sulfosalts) such as arsenopyrite (several suspected particles of arsenopyrite have been observed, which need to be investigated with Electron probe micro-analyzer (EPMA)). In this product, some pyrite particles show optically weak anisotropy, and small amounts of arsenic may be present in their composition. Therefore, it can be stated that the arsenic content in Sungun concentrate is in the first place controlled by the presence of copper-arsenic sulfosalt minerals of the tennantite type and to a lesser degree enargite; in

small amounts, the presence of arsenopyrite or arsenic-bearing pyrite can also play a small role.

5. Conclusions

- Mineralogical studies have shown that tennantite and enargite are the two main minerals containing arsenic in Sungun copper concentrate. The flotation properties of these minerals in the flotation process are similar to those of copper sulfide minerals, and therefore will enter the concentrate, together. On the other hand, these minerals have been observed to be in interaction with copper sulfide minerals, especially chalcocites. Thus, as the chalcocite floats, the enargite and tennantite also float and enter the copper concentrate. Due to the constant operating conditions in the plant, changes in the arsenic grade at the feed to the plant is the main reason for the change in the arsenic grade of copper concentrate; and by increasing the grade of arsenic in the feed, its grade in the concentrate will increase.
- The utilization of flotation with pulp potential control as an effective way to reduce the amount of arsenic in copper concentrate showed that, at potentials around -100 mV, it is possible to depress arsenic-bearing minerals, and at +300 mV potential, arsenic-bearing minerals are completely floated.
- Increasing the flotation time did not result in significant changes in the arsenic content in the flotation concentrate with a potential of -100 mV. However, by adjusting the pulp potential to +300 mV, the arsenic content at high arsenic content concentrate increases with flotation time. It should be noted that with increasing frothing time, the copper grade has increased significantly.
- The lowest arsenic content is obtained in low arsenic content concentrate with a pulp potential of +300 mV.
- In general, two suggestions can be made that by conducting flotation on the final copper concentrate via setting the pulp potential at +300 mV, two concentrates can be obtained. The first concentrate, or low arsenic content, is flotation tailing with a weight percentage of 90% of the input feed. In this concentrate, the arsenic grade compared to feed has been reduced by about 66%. The second

concentrate, or high arsenic content, is also the flotation concentrate with a weight percentage of 10% of the input feed; which has a smaller volume than the first concentrate. The copper grade in this product is high and more than 27%. High arsenic content concentrate after complete removal of arsenic via roasting or utilization of alkaline sulfide leaching method, can be mixed with low arsenic content concentrate and sent to the smelter.

- The second proposal is almost identical to the first. In this case, due to the concentration of arsenic-bearing minerals in the size range of $-25\ \mu\text{m}$ and also the high flotation efficiency in this size, it is suggested that the copper-arsenic concentrate enter the hydrocyclone clusters before entering the flotation cells by controlling the pulp potential. Cut size should be $25\ \mu\text{m}$. The hydrocyclone overflow then enters the flotation cell by controlling the pulp potential and its underflow enters the ball mill in a closed circuit with the hydrocyclone.

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ارائه راهکاری مبتنی بر کانی‌شناسی فرایند مدارهای فلوتاسیون مس - مولیبدن، برای حذف آرسنیک از کنسانتره مس

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چکیده:

فرایندهای معدنکاری، فرآوری و متالورژیکی به ترتیب سبب استخراج آرسنیک از عمق زمین، آزاد شدن و ایجاد شرایط مناسب برای انجام واکنش‌های شیمیایی آن می‌شوند. هدف از این تحقیق، کنترل میزان As در کنسانتره مس با استفاده از راهکار مینرالوژیکی — ژئومتالورژی است. در این راستا مطالعه حاضر بر روی کارخانه فرآوری مس — مولیبدن سونگون (واقع در شمالغرب ایران) انجام گرفته است. آنالیزهای شیمیایی محصولات مدار فلوتاسیون نیز حاکی از تغییرات 1 – 0/13 درصدی برای As در کنسانتره، و تا 0/003 درصد در باطله مس، هستند. آرسنیک در قالب کانی‌های گروه سولفوسالت شامل تنانتیت و انارژیت، همراه با سولفیدهای مس به کنسانتره بازیابی شده است. خواص شناوری مشابه کانی‌های آرسنیک‌دار با سولفیدهای مس، درگیری سولفیدی مس با کانی‌های آرسنیک‌دار، همچنین نوع مواد شیمیایی و محدوده پتانسیل الکتروشیمیایی پالپ در سلول‌های فلوتاسیون، از عمده‌ترین دلایل بازیابی آرسنیک به کنسانتره مس هستند. انجام فلوتاسیون مجدد بر روی کنسانتره مس، با تغییر در پتانسیل پالپ (در محدوده 300- تا +300 mV) بعنوان راهکاری موثر و بهینه در کاهش مقدار آرسنیک مورد بررسی قرار گرفت. بر اساس نتایج، در پتانسیل تقریباً 100 mV- کانی‌های حاوی Cu-As (تنانتیت و انارژیت) تمایل به بازداشت شدن، و در پتانسیل‌های مثبت (300 mV+) این کانی‌ها تمایل به فلوته شدن دارند. در پتانسیل 300 mV+ حدود 10 درصد وزنی خوراک، با عیار آرسنیک < 0/45 درصد و مس < 27 درصد، به کنسانتره پرعیار آرسنیک بازیابی می‌شود. در این حالت عیار As و Cu در کنسانتره آرسنیک پایین به ترتیب < 0/2 و < 22/70 درصد است. بطور کلی تدوین برنامه استخراج معدن با دیدگاه کنترل مقدار آرسنیک در بار ورودی به کارخانه توام با تنظیم عیار حد مس در آن، می‌تواند راهکاری موثر در کاهش مقدار آرسنیک در کنسانتره مس باشد. در طی پروسه فرآوری نیز، با فلوتاسیون ذرات با اندازه 25 μm- و تنظیم پتانسیل پالپ در مقدار 300 mV+، می‌توان دو کنسانتره مس آرسنیک پایین (آرسنیک کمتر از حد مجاز 0/2 درصد) و بالا تولید نمود. کنسانتره مس آرسنیک پایین مستقیماً به ذوب ارسال شده و کنسانتره مس آرسنیک بالا نیز پس از طی فرایندهای هیدرومتالورژی، قابل ارسال به کارخانه ذوب خواهد بود.

کلمات کلیدی: فلوتاسیون مس - مولیبدن، کانی‌های آرسنیک‌دار، راهکارهای مبتنی بر کانی‌شناسی، حذف آرسنیک، سونگون.