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Possibilities for the Environmental Processing of Gold-Bearing Ores

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Abstract: This article will focus on the alkaline leaching of gold-bearing tetrahedrite concentrate in a solution containing sodium sulfide and sodium hydroxide. This selective leaching is followed by the leaching of heavy and waste metals into the solution, which may influence the physical properties and quality of the desired product, possibly causing environmental toxicity. At the same time, the amount of gold was observed during the leaching process to increase its content in the solid phase for the possibility of recovery and subsequent extraction of the precious metal. Sodium sulfide works very effectively on sulfide minerals which include tetrahedrite, and sodium hydroxide eliminates the hydrolysis of sulfur which slows leaching. The leaching kinetics were carried out with a duration of five hours, and based on volume sampling at certain time intervals from three samples, with the characteristic NaOH concentration, the leaching efficiency was observed from the results with atomic absorption spectrometry. The solid residue containing the tetrahedrite concentrate was analyzed through X-ray photoelectron analysis spectrometry, from which the % solids content was determined, and it is also known to deduce the leached amount of metals for each sample.

Keywords: gold; tetrahedrite; hydrometallurgy; leaching; heavy metals; environment

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1. Introduction

Gold mining is still very topical. Interest in gold mining is growing in many countries, while it has a major impact on the environment. The mining, recovery, processing, and extraction of gold-bearing ores cause the large consumption of dangerous chemicals and the generation of waste containing heavy metals, which are released in an uncontrolled manner and cause extensive contamination of the ecosystem [1–3]. Therefore, the whole process should be carefully regulated through global guidelines based on current knowledge of toxicity, principles, and modern environmental standards [4]. Based on this, alternatives to cyanide leaching are sought; even if cyanidation is very effective, it does not meet the requirements of environmental protection. The aim is to prevent toxic substances from entering waste and to minimize the impact on the environment [5,6].

The choice of a suitable method of processing gold-bearing raw materials is conditioned by the ratio of free-content gold to bound gold. Gravitational methods of separation, the essence of which lies in different densities of each component occurring in the raw material, are suitable for obtaining free gold. To obtain gold that is bound, chemical treatment methods are used, which include amalgamation, cyanidation, leaching in thiourea, and other types of reagents, or, possibly, combined physical and chemical separation methods such as flotation [7]. These processing methods of gold are directly related to affecting the environment. Innovative production methods and the processing of gold-bearing raw materials are aimed at reducing the environmental risks that are still present and just in development. Despite current technological advances, a large amount of waste is generated, and aggressive chemicals necessary for processing are also often used, based on which there are global criteria that must be observed in all countries due to reducing and limiting environmental risks and human health hazards [8].

Hydrometallurgical processing of gold-bearing ores represents an important group of methods used in gold mining and is formed by a combination of several elementary processes using aqueous solutions to recover metals from ores, concentrates, and recyclable or residual material [9,10]. Hydrometallurgy is a process which is usually divided into four general areas such as leaching, concentration, solution purification, and the regeneration of metals. The hydrometallurgical process usually involves the concentration of metals from the leaching ore process, dissolving the metal or metal compound in a solution where other reagents are present. Waste separation and leachate cleaning follow. In the next step, the metal or metal compound precipitates from the leachate are processed by chemical or electrolytic processes. The most used reagents are, for example, dilute H_2SO_4, NaOH, and others [11–13].

Leaching is the process by which gold found in a gold-bearing raw material passes into a solution, or conversely, it remains in the gold-bearing raw material and only unwanted metals or harmful admixtures are leached out [7]. Leaching is a technique of extraction metallurgy and consists of the application of acid or alkaline solutions which come into direct contact with the precious metal-containing material. The decisive parameters in leaching are the reduction potential, the pH of the solution, and the temperature, which are usually adjusted to optimize the dissolution of the desired metal in the liquid phase. The leaching process is considerably less toxic compared to pyrometallurgy, as it does not cause environmental pollution through gases and dust [11,12]. Choosing the right leaching process for gold depends on the ore texture, mineralogy, chemical requirements, leaching techniques, and environmental management. Hydrometallurgy is mainly considered a chemical dissolution in alkaline, neutral, and acidic systems. All systems require the oxidizing agent to oxidize gold and a ligand that forms a complex with the gold in solution. pH adjustment is usually necessary [14].

A suitable replacement for cyanide leaching is thiourea leaching. Thiourea in an acidic solution dissolves gold to form a complex. The addition of a catalyst, ferric sulfate, increases the oxidation of gold. The reaction proceeds according to the equation:

$$Au^0 + 2SC(NH_2)_2 \rightarrow Au[SC(NH_2)_2]_2^+ + e^- \quad (1)$$

The dissolution of gold in thiourea is faster than in cyanide, but the consumption volume of thiourea in the leaching process is high because it oxidizes rapidly into the solution. Laboratory experiments to accept this reagent have led to high consumption and increased production costs. There are also concerns about its impact on the environment. Despite claims that thiourea is less toxic than cyanide, it is a suspected carcinogen and should therefore be treated with caution [15].

Other suitable replacements could be leaching with sulfide, bisulfite, and hydrogen sulfide. Sulfur-based reagents other than thiosulfate and thiourea are sulfides, bisulfides, hydrogen sulfide (or sulfur dioxide), and polysulfides. Of these reagents, only bisulfite and hydrogen sulfide have practical applications [16]. Gold solubility has been shown to increase with hydrogen sulfide (H_2S) activity, suggesting that the major complexes involved in gold transport under reducing conditions are bisulfite complexes. Thus, for gold to be soluble, the solution must contain sulfur and the pH of the liquid must be such that the sulfur is in the form of sulfide. There are three main bisulfite complexes: $Au(HS)^0$, $Au(HS)_2{}^-$, and $Au_2(HS)_2S^{2-}$. The course of the reaction of gold with bisulfides to form complexes:

$$Au + H_2S^0 \rightarrow [Au(HS)]^0 + \frac{1}{2} H_2 \quad (2)$$

$$2Au + 2H_2S + 2HS^- \rightarrow 2\,[Au(HS)_2]^- + H_2 \quad (3)$$

$$2Au + H_2S^- + 2HS^- \rightarrow [Au_2(HS)_2S]^{2-} + H_2 \quad (4)$$

Under low-pH conditions, neutral gold hydrogen sulfide $[Au(HS)]^0$ is formed, at a neutral pH, gold hydrogen sulfide $[Au(HS)]^{2-}$ is formed, and under strongly alkaline conditions, $[Au_2(HS)_2S]^{2-}$ is formed [17]. Due to the similar stability of gold and silver bisulfite complexes, bisulfite leaching may be suitable for leaching gold-bearing ores with high silver content. The ions of the HS^- and H_2S molecules diffuse much more slowly than the cyanide ions and oxygen molecules; slower dissolution can be expected if the same concentrations of reactants are used.

The dissolution of gold can take place due to the adsorption of polysulfide on the surface of gold causing the oxidation shown in the following reactions:

$$Sx^{2-} + 2(x - 1)e^- \rightarrow xS^{2-} \quad (5)$$

$$2Au + S_2{}^{2-} + 2S^{2-} \rightarrow 2S^{-2} + 2AuS^- \quad (6)$$

Thus achieving 90% extraction of gold from the sulfide concentrate at 50 °C without the addition of an oxidizing agent. A relatively high concentration of polysulfide is required for successful operation [18,19]. In thiosulfate and polysulfide mixtures, the polysulfides act only as a leaching agent if no other oxidizing agents are present. For example, in the presence of copper, polysulfides precipitate with copper to form CuS [16].

The recovery of precious metals from lower-grade ores, waste material stockpiles, and residual waste through microbial species has recently generated a great deal of interest due to the decline in the quality of the deposits and at the same time high interest in gold. Also, biological processing is more environmentally friendly compared to physicochemical extraction processes, as the waste generated after the use of bacteria is biologically less reactive [20]. Biological processing method microorganisms have an important role in 1. the processing of low-grade gold-bearing ores (mining waste and tailings) using bioleaching for direct gold extraction, as conventional processing is too expensive, or in facilitating gold extraction and 2. pre-treatment of ores containing impurities, preventing leaching of the precious metal by bio-oxidation (e.g., arsenic found in gold-bearing ores) [21,22]. Bioleaching and bio-oxidation work (Figure 1) basically on the same principles and with the participation of microorganisms of the same species [22]. Bioleaching is a process in which bacteria help to dissolve gold from ores or waste. This process occurs commonly in nature under suitable conditions, which aids natural bacterial proliferation. Bio-oxidation is a pre-treatment process that reduces the use of solvents to leach gold in other parts of the operation, thereby promoting more efficient gold recovery. The bacteria release gold from the ores during the oxidation of sulfur or iron from sulfide ores. The bio-oxidation stage can increase gold recovery by up to five times [21].

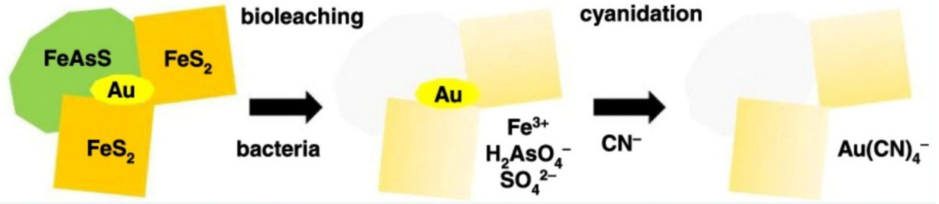


Figure 1. Treatment of gold-bearing ores by bio-oxidation before cyanide leaching [22].

The iron and sulfur-oxidizing bacteria are Acidithiobacillus ferrooxidans, the sulfur-only oxidizing bacteria are Acidithiobacillus thiooxidans, and the iron-only oxidizing bacteria are Leptospirillum ferriphilum and Leptospirillum ferrooxidans. These bacteria obtain energy via the oxidation of ferrous cation (Fe^{2+}) to ferrous cation (Fe^{3+}) or elemental sulfur (S^0) or by reacting with the reduced sulfur in a compound to acid sulfur (H_2SO_4). The released ferric cations and hydrogen ions then cleave the sulfide matrix [20]. The process of the reaction is summarized in the equation below using pyrite as a typical example of a gold-bearing ore:

$$FeS_2(Au) + 2Fe^{3+}\ 3Fe^{2+} + 2S^0 + (Au) \quad (7)$$

Microorganisms can also secrete ligands that can stabilize gold by forming complexes or gold-rich colloids. Microorganisms can also biologically produce amino acids, cyanide, and thiosulphate, which aid in the leaching of gold. Biological leaching has certain advantages over physicochemical methods. Microbial leaching procedures are more environmentally friendly in several aspects:

I. The absence of harmful gaseous emissions;
II. Low energy consumption (low temperature and pressure);
III. An increase in gold extraction from low-grade ores while reducing the consumption of chemical reagents;
IV. The tailings produced from bio-mining processes are less chemically and biologically active, as they are already biologically leached [23].

Tetrahedrite is a complex sulfide of antimony, arsenic, copper, silver, gold, or other metals such as iron, mercury, zinc, and others [24]. The general formula of tetrahedrite is $(Cu, Ag, Au)_6[Cu4(Fe, Zn, Hg, Cd)_2]\ (As, Bi, Te, Sb)_4(Se, S, Te)_{13}$ [25]. It is recognized as a specific sample of the mineral from the group of tetrahedrites, and we named it according to the predominant component. Naturally occurring specimens called tetrahedrites contain the predominant components of copper and antimony. If the predominant constituents are arsenic and antimony, we call such a sample tetrahedrite-tennantite, and if silver predominates, its name is tetrahedrite-freibergite [26,27]. Tetrahedrites with increased content of mercury (more than 17% Hg), bismuth (4% Bi), iron, lead, and nickel have their specific names. In addition to these elements, up to 8% can occur in tetrahedrite zinc or 2% cadmium [24,28].

In addition to toxic elements such as lead, antimony, and arsenic contained in the tetrahedrite mineral, it contains a significant amount of copper, silver, and gold, which represents this mineral as being very attractive in the field of mining [24]. The presence of these harmful elements significantly affects the quality and physical properties of the obtained product and causes serious toxicological and environmental problems. Therefore, it is necessary to investigate effective methods of preliminary treatment for the removal of harmful or undesirable components, such as arsenic, antimony, and other metals present, from gold ores. The hydrometallurgical processing of sulfide ores represents from an ecological point of view a suitable alternative to pyrometallurgical methods in which the air is contaminated with sulfur oxides, volatile and poisonous oxides (mainly antimony and arsenic) and mainly particles formed from dust [29–31]. Hydrometallurgical methods can be used to treat gold, arsenic, antimony, tin, and mercury contained in minerals, concentrates, and ores, as well as in complex compounds bearing any number of metals. Tetrahedrite leaching can be divided into two important dissolution mechanisms: alkaline and acid leaching [32,33].

During the acid leaching of tetrahedrite minerals with solutions of ferric chloride, sodium chloride, and hydrochloric acid, the crystal structure of the tetrahedrite breaks down at the same time and releases all its components without the formation of sulfate during the leaching reaction [24,34]. It is necessary to use a strong oxidizing agent because tetrahedrite is highly resistant. The most used oxidizing agents are copper cations (Cu^{2+}), iron cations (Fe^{3+}), oxygen (O_2), ozone (O_3), and hypochlorite (ClO^-). Tetrahedrites with high iron content dissolve faster than iron-poor tetrahedrites. For example, in acidic solutions of ferric chloride, copper and iron enter the solution, while antimony partially precipitates as a compound and this has the effect of slowing down leaching [35,36].

Alkaline leaching is a system of a mixture of sodium sulfide and sodium hydroxide. This unique hydrometallurgical system is a very selective solvent for the distinct leaching of tin, gold, antimony, arsenic, and mercury [37].

A high enough concentration of sodium hydroxide prevents the hydrolysis of sulfide ions (S^{2-}) and hydrogen sulfide (H_2S) slows down the effectiveness and progress of the reaction. Arsenic and antimony dissolve into thio-anions such as thioarsenate (${AsS_4}^{3-}$), thioantimonite (${SbS_3}^{3-}$), and thioantimonate (${SbS_4}^{3-}$) [35]. As an example, when the system is applied to materials containing arsenic, for example, orpiment, As_2S_3, a solution of sodium thioarsenite is formed. The course of the reaction is as follows:

$$Na_2S + As_2S_3 \rightarrow 2NaAsS_2 \tag{8}$$

$$NaAsS_2 + Na_2S \rightarrow Na_3AsS_3 \tag{9}$$

Dissolving elemental sulfur in sodium hydroxide is also used as a solvent for the alkaline sulfide leaching of arsenic. The combination of sodium hydroxide and elemental sulfur leads to the formation of sodium polysulfide (Na_2S_X) and sodium thiosulfate ($Na_2S_2O_3$) together with sulfides [37]. Sodium thiosulfate and sodium polysulfide are formed according to the following reactions:

$$4S^0\ (s) + 6NaOH\ (aq) \rightarrow 2Na_2S(aq) + Na_2S_2O_3(aq) + 3H_2O \tag{10}$$

$$(X - 1)S^0\ (s) + Na_2S(aq) \rightarrow Na_2S_x, \text{ where } x = 2\text{-}5 \tag{11}$$

Alkali sulfide technology is the most widely used because of its effective selectivity for the dissolution of antimony, arsenic, mercury, and tin and its easy application in full due to minimal corrosion problems associated with the acid leach system [35,37].

This specific gold beneficiation process has been recognized as quantitative and selective for the extraction of gold from complex solutions of alkali sulfides containing a mixture of metals such as arsenic, tin, mercury, and antimony. These metals are selectively leached into the alkaline solution as impurities. The gold-bearing substrate solids present in the leaching process are cheap and readily available, and their direct processing is the cheapest and most efficient method of obtaining gold [37,38]. This article fills a crucial gap in the existing literature by investigating the alkaline leaching process of gold-bearing concentrates from tetrahedrite using sodium sulfide and sodium hydroxide. The study not only focuses on the selective leaching of heavy and waste metals and the enhancement of gold content in the solid phase but also provides insights into the leaching kinetics and the effectiveness of the leaching process. Additionally, the analysis of the solid residue and the determination of gold and heavy metal content contribute to a comprehensive understanding of the leaching behavior and potential for metal recovery.

2. Materials and Methods

The samples of tetrahedrite came from the Mária mine. Baňa Mária is located in the silver vein in Rožňava, Slovakia, where tetrahedrite is represented, which contains several different elements such as copper, silver, arsenic, bismuth, lead, zinc, and others [39]. Extensive investigation of the concentration of gold in tetrahedrite began to be followed in the late fifties, while the first mention of the presence of gold in the vein is recorded from the beginning of the twentieth century [40]. After several years of study, the occurrence of gold in tetrahedrite was proven in two forms, namely as an intermetallic younger Au-Hg-Ag alloy or as pure gold [39].

The samples were pre-treated before leaching in an alkali system. For the experiment, we used a sample of gold-bearing tetrahedrite flotation concentrate. The probable concentration of the elements represented in this concentrate after flotation is listed in Table 1.

Table 1. The content of elements in the tetrahedrite concentrate from the Mária mine by the AAS method.

Cu (%)	Ag (g.t^{-1})	Au (g.t^{-1})	Fe (%)	Sb (%)	As (%)	Bi (%)	Hg (%)	Co (%)	Cr (%)
1.8–3.5	4000–7050	5–10	8–10	12–14	0.6–0.9	0.2–0.4	0.6–0.9	0.1–0.2	0.05–1

To create a system for the alkaline leaching of metals such as arsenic, antimony, copper, and iron from sulfides, sodium hydroxide and sodium sulfide were used. The sodium sulfide was 1.14 M in a volume of 133 mL, and the sodium hydroxide was of different moles (0.75, 1.5, and 1.8) in a volume of 366 mL. The resulting solution was 500 mL. The sample weight of tetrahedrite was 4 g. For each experiment, liquid samples in a volume of 35 milliliters were taken at time intervals of 30 min, an hour, 2 h, 3 h, 4 h, and 5 h. These samples showed us the process of leaching arsenic, antimony, copper, and iron. The remaining volume of the solutions, with different concentrations of sodium hydroxide after 5 h of leaching, was filtered and dried.

The liquid samples were analyzed by atomic absorption spectrometry (AAS). The concentrations of heavy metals in the aqueous extracts were measured using AAS (iCE 3300 AA—ThermoFisher Scientific, Grand Island, NY, USA). They were determined in an extract consisting of 1 g of solid material and 25 mL of 0.5 mol.L^{-1} HCl.

The solid samples (filtrate from the leached tetrahedrite) were analyzed by X-ray photoelectron spectroscopy (XPS) (SPECS Surface Nano Analysis GmbH, Berlin, Germany). X-ray photoelectron spectroscopy (XPS) was performed using XPS instrument SPECS, equipped with a hemispherical energy analyzer PHOIBOS 100 SCD and a non-monochromatic X-ray source. The survey surface spectrum was measured at 70 eV pass energy and the core spectra was measured at 20 eV at room temperature. The basic pressure was 10^{-8} millibar with AlKα excitation at 10 kV (200 W).

3. Results

In the first experiment, a sample with 4 g of tetrahedrite concentrate was used, which was leached in a volume of 500 mL, which consisted of 133 mL of 1.14 M Na_2S and 366 mL of 0.75 M NaOH. The volume of 35 mL was taken during the leaching process in specifically determined time intervals. In Table 2, we can see the development of kinetic leaching, which includes the amount of leached metals over the time sequences.

Table 2. Kinetics of individual elements in a solution with a concentration of 0.75 M NaOH.

mg L^{-1}	0.75 M NaOH							
Time (h)	**0.5**	**1**	**2**	**3**	**4**	**5**	**12**	**24**
As	2.31	2.30	3.05	2.69	3.25	2.67	3.52	7.79
Sb	6.81	7.51	8.66	9.37	10.31	11.66	12.95	21.39
Cu	0.1	0.1	0.08	0.09	0.09	0.1	0.08	0.01
Fe	0.05	0.09	0.1	0.14	0.13	0.14	0.27	0.27

The remaining volume of the solution was filtered. The solid residue was analyzed by XPS. The analysis results show us in Figure 2 that the solid sample content consists of 4.07% antimony, 0.2% arsenic, 12.3% iron, 1.83% copper, and 0.2% gold in the leached tetrahedrite concentrate.

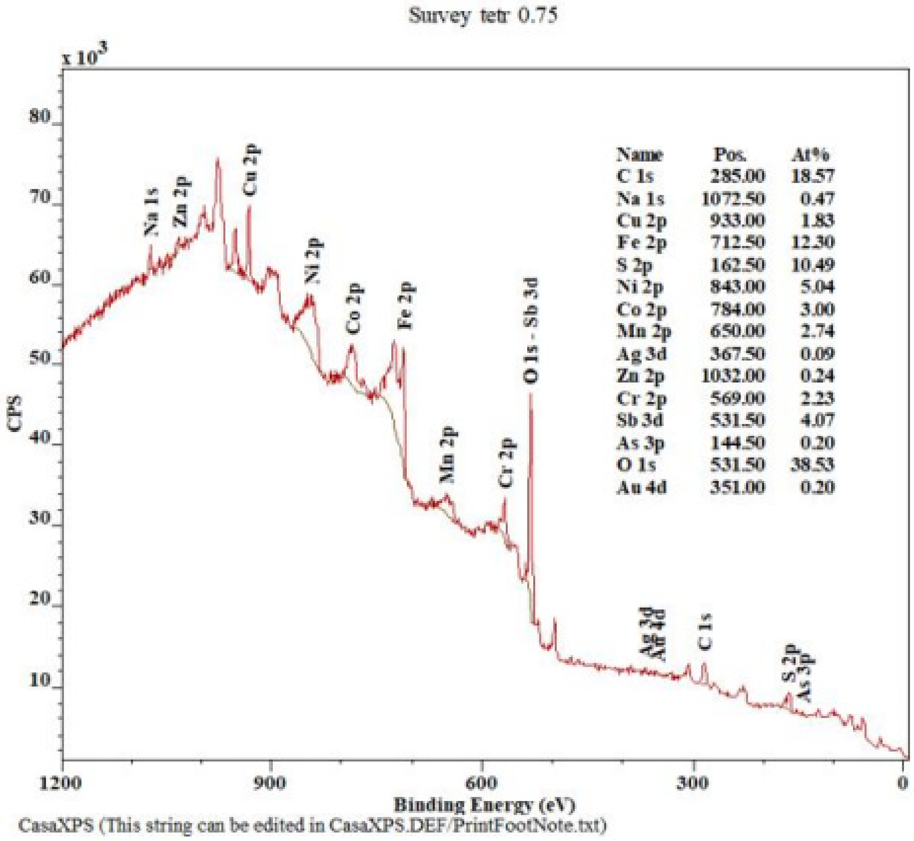


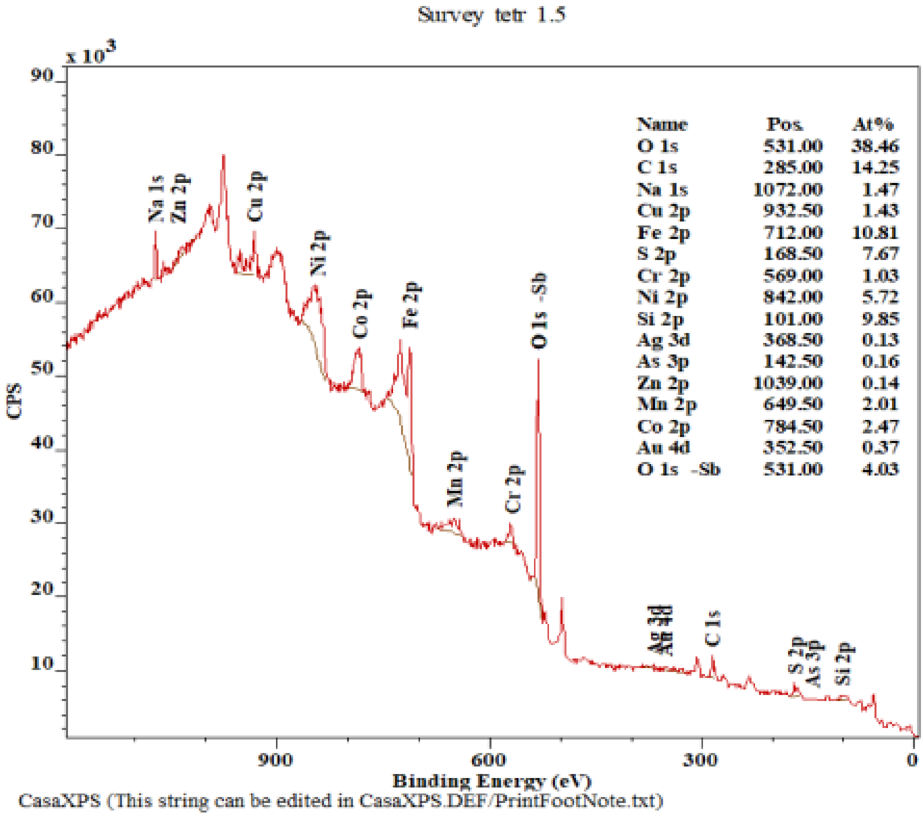
Figure 2. Spectral analysis of the sample leached with 0.75 M NaOH.

In the second experiment, a sample with 4 g of tetrahedrite concentrate was used, which was leached in a volume of 500 mL and consisted of 133 mL of 1.14 M Na_2S, and 366 mL of 1.5 M NaOH. The volume of 35 mL was taken during the leaching process in specifically determined time intervals. In Table 3, we can see the development of kinetic leaching, which includes the amount of leached metals over the time sequences.

Table 3. Kinetics of individual elements in a solution with a concentration of 1.5 M NaOH.

mg L^{-1}	**1.5 M NaOH**							
Time (h)	**0.5**	**1**	**2**	**3**	**4**	**5**	**12**	**24**
As	3.31	4.24	4.37	4.91	4.65	5.05	9.37	22.43
Sb	11.31	11.52	13.21	15.41	16.54	17.13	20.44	51.14
Cu	0.05	0.04	0.05	0.04	0.05	0.07	0.09	0.07
Fe	0.11	0.14	0.15	0.1	0.1	0.11	0.35	0.3

The remaining volume of the solution was filtered. The solid residue was analyzed by XPS. The analysis results show us in Figure 3 that the solid sample content consists of 4.03% antimony, 0.16% arsenic, 10.81% iron, and 1.43% copper, and the gold content is 0.37% in the leached tetrahedrite concentrate.



Name	Pos.	At%
O 1s	531.00	38.46
C 1s	285.00	14.25
Na 1s	1072.00	1.47
Cu 2p	932.50	1.43
Fe 2p	712.00	10.81
S 2p	168.50	7.67
Cr 2p	569.00	1.03
Ni 2p	842.00	5.72
Si 2p	101.00	9.85
Ag 3d	368.50	0.13
As 3p	142.50	0.16
Zn 2p	1039.00	0.14
Mn 2p	649.50	2.01
Co 2p	784.50	2.47
Au 4d	352.50	0.37
O 1s -Sb	531.00	4.03

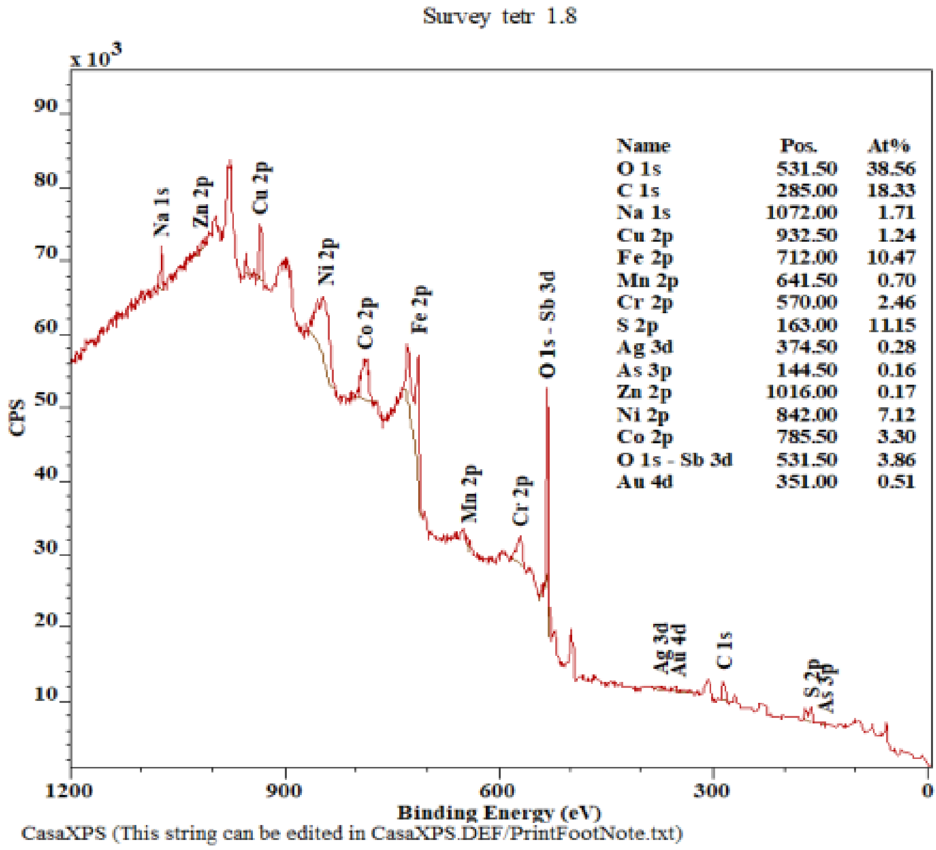
Figure 3. Spectral analysis of the sample leached with 1.5 M NaOH.

In the third experiment, a sample with 4 g of tetrahedrite concentrate was used, which was leached in a volume of 500 mL and consisted of 133 mL of 1.14 M Na_2S and 366 mL of 1.8 M NaOH. The volume of 35 mL was taken during the leaching process in specifically determined time intervals. In Table 4, we can see the development of kinetic leaching, which includes the amount of leached metals over the time sequences.

Table 4. Kinetics of individual elements in a solution with a concentration of 1.8 M NaOH.

mg L^{-1}	**1.8 M NaOH**							
Time (h)	**0.5**	**1**	**2**	**3**	**4**	**5**	**12**	**24**
As	3.44	4.12	4.40	4.53	4.77	5.08	9.11	14.59
Sb	9.78	14.11	14.80	16.69	19.52	21.24	55.85	66.21
Cu	0.07	0.08	0.04	0.07	0.07	0.03	0.03	0.03
Fe	0.04	0.08	0.08	0.09	0.14	0.20	0.45	0.49

The remaining volume of the solution was filtered. The solid residue was analyzed by XPS. The analysis results show us in Figure 4 that the solid sample content consists of 3.86% antimony, 0.16% arsenic, 10.47% iron, and 1.83% copper, and the gold content is 0.51% in the leached tetrahedrite concentrate.



Name	Pos.	At%
O 1s	531.50	38.56
C 1s	285.00	18.33
Na 1s	1072.00	1.71
Cu 2p	932.50	1.24
Fe 2p	712.00	10.47
Mn 2p	641.50	0.70
Cr 2p	570.00	2.46
S 2p	163.00	11.15
Ag 3d	374.50	0.28
As 3p	144.50	0.16
Zn 2p	1016.00	0.17
Ni 2p	842.00	7.12
Co 2p	785.50	3.30
O 1s - Sb 3d	531.50	3.86
Au 4d	351.00	0.51

Figure 4. Spectral analysis of the sample leached with 1.8 M NaOH.

In the following Figures 5 and 6, we can see the graphic process of leaching each metal. In Figure 5, the yield of arsenic and antimony increases significantly. Antimony increases its concentration in the solution throughout the experiments proportionally up to 66.21 mg L^{-1} in the mixture of 1.14 M Na_2S and 1.8 M NaOH after 24 h. The arsenic concentration was approximately stable, but after 24 h, it slightly increased to 22.43 mg L^{-1} in the mixture of 1.14 M Na_2S and 1.8 M NaOH.

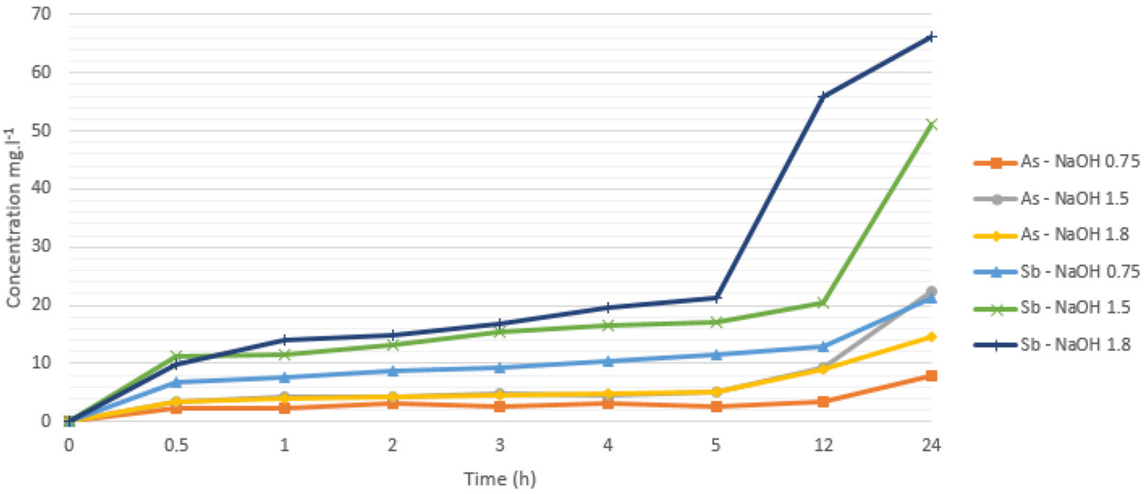


Figure 5. Leaching of Sb and As in the mixture of 1.14 M Na_2S and 0.75 M, 1.5 M, and 1.8 M NaOH.

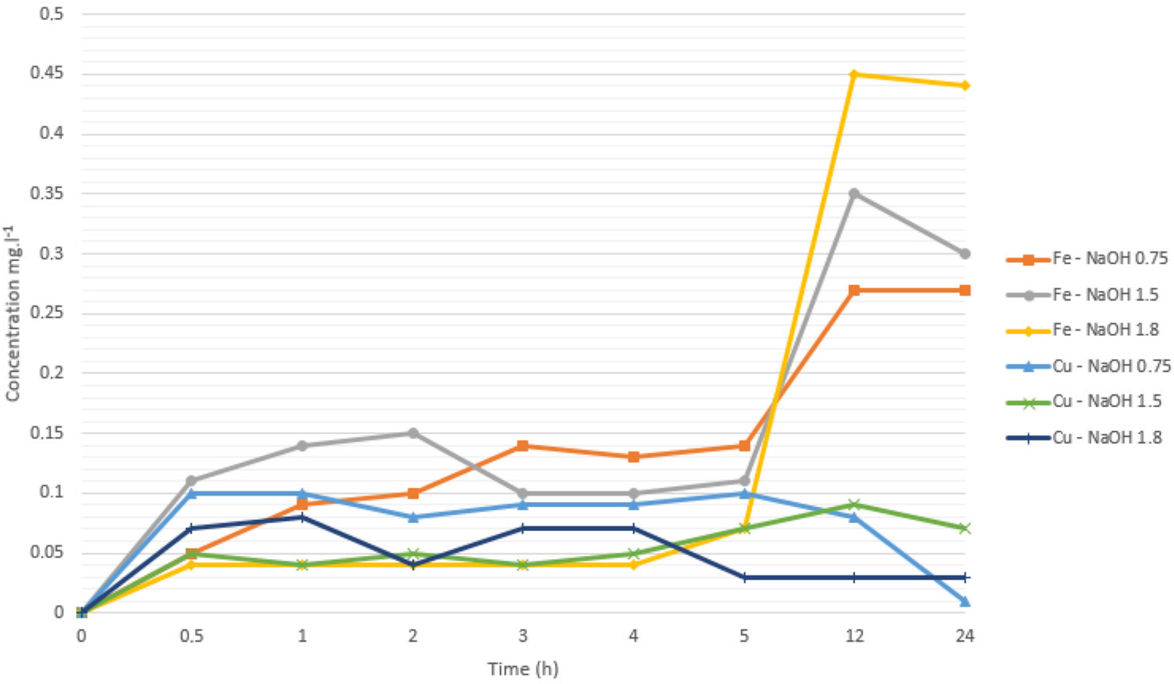


Figure 6. Leaching of Fe and Cu in the mixture of 1.14 M Na_2S and 0.75 M, 1.5 M, and 1.8 M NaOH.

In Figure 6, the yield of iron increases significantly by leaching for 12 h in each mixture. The highest growth of iron occurred with the mixture of 1.14 M Na_2S and 1.8 M NaOH up to 0.45 mg L^{-1}. The copper concentration is the highest at three hours of leaching in a mixture of 1.14 M Na_2S and 0.75 M NaOH and subsequently decreases in each mixture.

4. Comparison of the Results

According to the following Figures 7–10, we can compare the amount of leached metals of the three samples according to the amount of non-leached components after 5 h, which remained in a solid state according to the XPS analysis. Figure 11 shows us the gold content located in these three samples in a solid state.

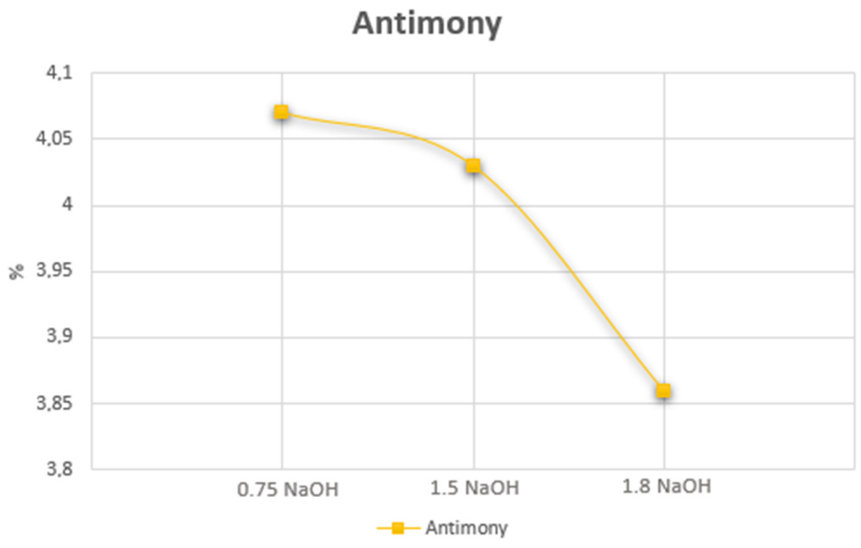


Figure 7. The amount of antimony in the leach residue after leaching at different NaOH concentrations.

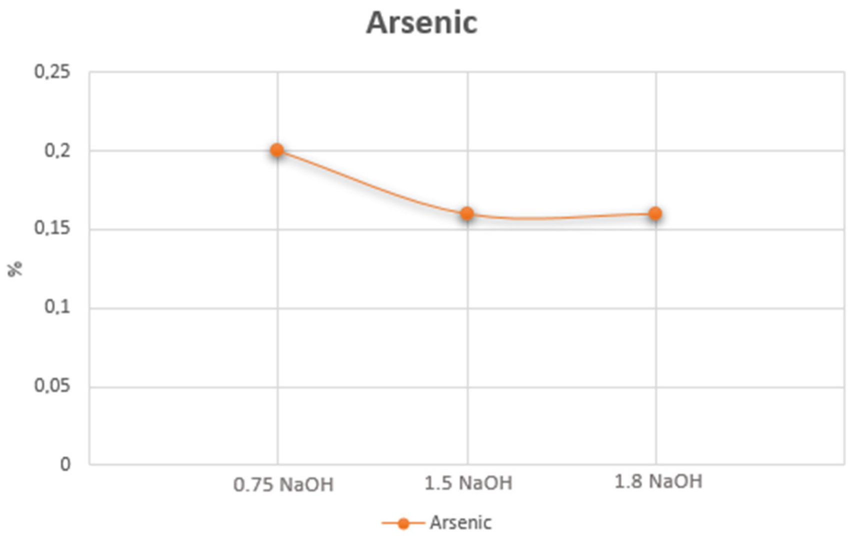


Figure 8. The amount of antimony in the leach residue after leaching at different NaOH concentrations.

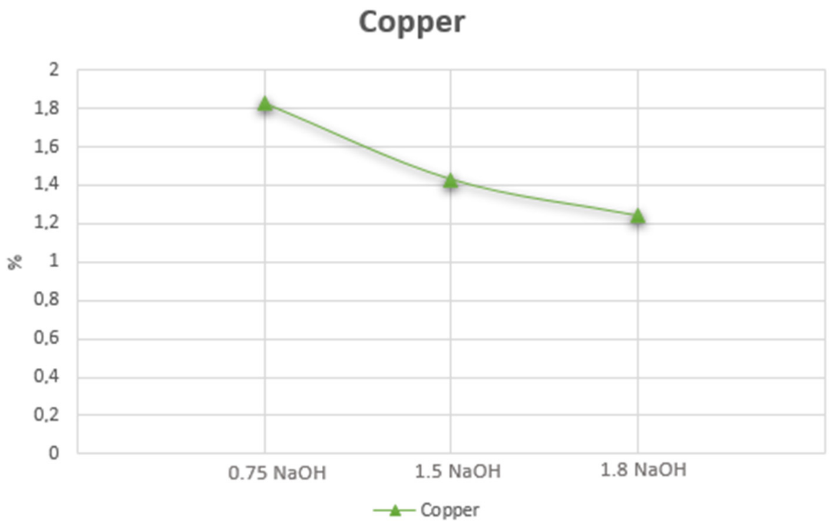


Figure 9. The amount of antimony in the leach residue after leaching at different NaOH concentrations.

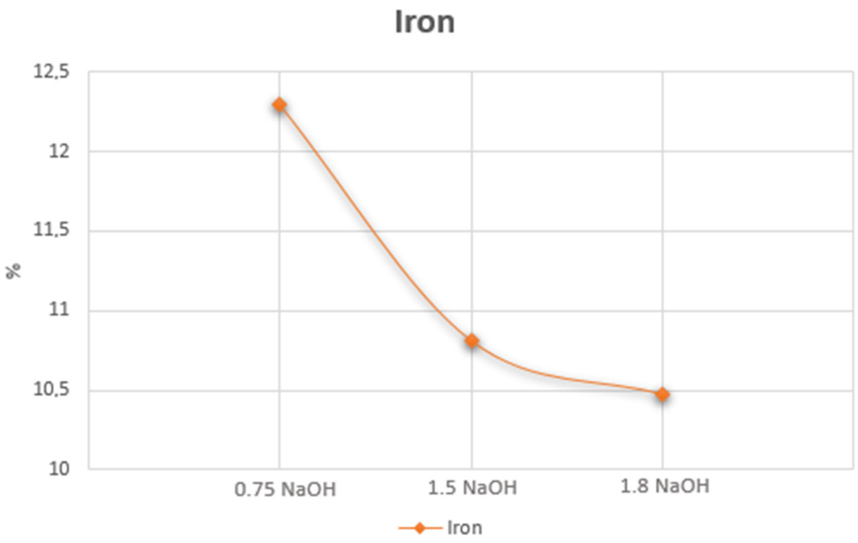


Figure 10. The amount of antimony in the leach residue after leaching at different NaOH concentrations.

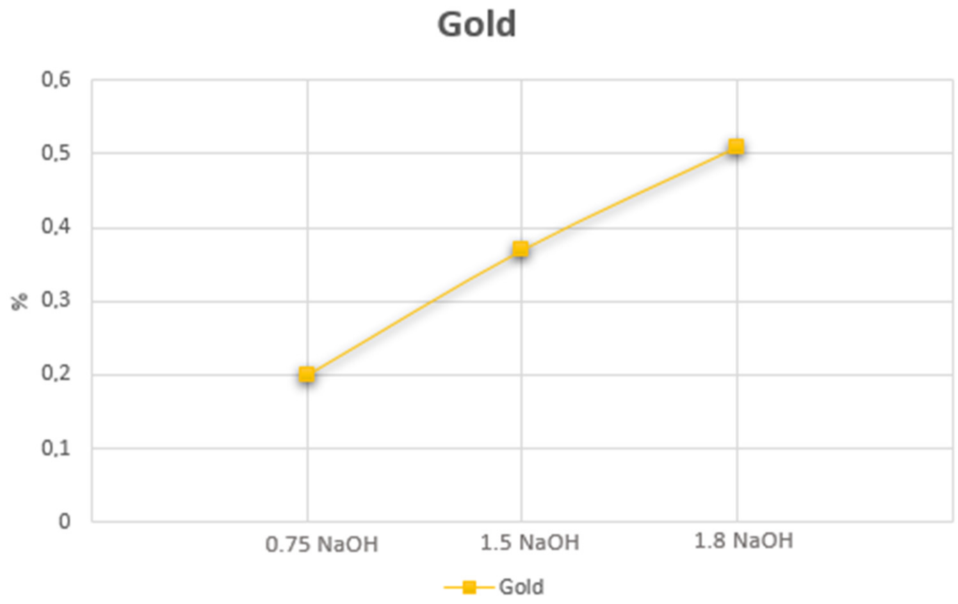


Figure 11. The amount of antimony in the leach residue after leaching at different NaOH concentrations.

Figures 7–10 show the amount of metal in the solid state monitored in three samples. In the first sample leached with 0.75 M NaOH, the antimony content is 4.07%, in the second sample leached with 1.5 M NaOH, it is 4.03% and in the third leached with 1.8 M NaOH, it is 3.86%. It was observed that the decrease in the solid state was associated with increasing mole sodium hydroxide. The best effect was achieved with 1.8 M NaOH, where the leaching was the highest amount of antimony in the solution.

Figure 8 shows the arsenic content in the solid state monitored in three samples. For the first sample leached with 0.75 M NaOH, the arsenic content is 0.2%, in the second sample leached with 1.5 M NaOH, it is 0.16%, and in the third leached with 1.8 M NaOH, it is 0.16%. A decrease in the solid state with increasing mol sodium hydroxide was observed. The best effect was achieved with 1.5 M and 1.8 M NaOH, where the highest amount of arsenic was in the solution.

Figure 9 shows the copper content in the solid state monitored in three samples. In the first sample leached with 0.75 M NaOH, the copper content is 1.83%, in the second sample leached with 1.5 M NaOH, it is 1.43%, and in the third sample leached with 1.8 M, NaOH is 1.24%. A decrease in the solid state as the mole of hydroxide sodium increased was observed. The best effect was achieved with 1.8 M NaOH, where the highest amount of copper was leached into the solution.

Figure 10 shows the iron content in the solid state monitored in three samples. In the first sample leached with 0.75 M NaOH, the iron content is 12.3%, in the second sample leached with 1.5 M NaOH, it is 10.81%, and in the third sample leached with 1.8 M NaOH, it is 10.47%. A decrease in the solid state with the increasing mole of sodium hydroxide was observed. The best effect was achieved with 1.8 M NaOH, where the leaching was the highest amount of iron in the solution.

Figure 11 shows the development of gold content in the solid state monitored in three samples. In the first sample leached with 0.75 M NaOH, the gold content is 0.2%, in the second sample leached with 1.5 M NaOH, it is 0.37%, and in the third sample leached with 1.8 M NaOH, it is 0.51%. An increase in the solid-state content of gold with the increasing mole of sodium hydroxide. The best effect was achieved with 1.8 M NaOH, where gold reached the highest quantity.

5. Conclusions

The aim of this study was to leach waste metals (Sb, As, Fe, and Cu) into a solution and increase the concentration of gold content in the solid. We can evaluate the results presented in the paper in that increasing the concentration of sodium hydroxide is suitable as an effective leaching agent for the mineral tetrahedrite and can effectively select the listed metals into the solution, and the gold concentration in the solid state increases.

For all of the selected metals, leaching was the most effective in the third experiment (the third sample), where the solution consisted of 1.14 M Na_2S and 1.8 M NaOH. The concentration of metals in the solid state decreased the most after five hours of leaching, specifically antimony to 3.86%, arsenic to 0.16%, iron to 10.47%, and copper to 1.24%. The highest concentration of gold reached 0.51%. We can therefore conclude that in the third experiment with a concentration of 1.8 M sodium hydroxide, the most increased solubility of antimony, arsenic, iron, and copper into the solution and the concentration of the solid form of gold grew, while the best and most effective result was achieved compared to the concentration of 0.75 M and 1.5 M NaOH. Thus, it was possible to achieve the desired result with theoretical knowledge of alkaline leaching. With these experiments, it was possible to replace cyanide leaching with alkaline leaching, which is what achieved the desired effective result for the recovery of gold and the leaching of heavy metals into the solution. The alkaline leaching method worked as a purifier, whereby the gold remained in a solid state, it increased its concentration, and unwanted substances were removed. At the same time, the environment was protected.

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References

1. Ali, S.H. Environmental Science and Policy. In *Mining, the Environment, and Indigenous Development Conflicts*; University of Arizona Press: Tuscon, AZ, USA, 2009; Volume 54, pp. 504–511.
2. Wijewardena, R.; Takama, T.; Wijesekara, R.S. Environmental and Social Impacts of Mining and Mineral Processing in the Western Province of Sri Lanka. *J. Clean. Prod.* **2015**, *84*, 732–742.
3. Hilson, G. The Environmental Impact of Small-Scale Gold Mining in Ghana: Identifying Problems and Possible Solutions. *Geogr. J.* **2014**, *168*, 57–72. [CrossRef]
4. Aylmore, M.G. Alternative lixiviants to cyanide for leaching gold ores. *Dev. Miner. Process.* **2005**, *15*, 501–539. [CrossRef]
5. Zhang, Y.; Cui, M.; Wang, J.; Liu, X.; Lyu, X. A review of gold extraction using alternatives to cyanide: Focus on current status and future prospects of the novel eco-friendly synthetic gold lixiviants. *Miner. Eng.* **2022**, *176*, 107336. [CrossRef]
6. Young, C.; Taylor, M.P. Alternative lixiviants to cyanide for leaching gold ores. *Dev. Miner. Process.* **2016**, *15*, 383–415.
7. Kratochvíl, M. Gold-Bearing Ore Treatment Technologies. Diploma Thesis, University of Mining—Technical University of Ostrava, Ostrava, Czech Republic, 2014.
8. Müezzinoğlu, A. A Review of environmental considerations on gold mining and production. *Crit. Rev. Environ. Sci. Technol.* **2003**, *33*, 45–71. [CrossRef]
9. Bhargava, S.K.; Pownceby, M.I.; Ram, R. Hydrometallurgy. *Metals* **2016**, *6*, 122. [CrossRef]

10. Adams, M. (Ed.) Advances in gold ore processing. In *Developments in Mineral Processing*; Elsevier: Amsterdam, The Netherlands, 2005; Volume 15, p. 346. [CrossRef]
11. Hydrometallurgy. Available online: https://chem.libretexts.org/@go/page/91360 (accessed on 23 April 2023).
12. Hydrometallurgy. Available online: https://medium.com/@bicspuc/hydrometallurgy-237ad568732d (accessed on 23 April 2023).
13. Cui, J.; Zhang, L. Metallurgical recovery of metals from electronic waste: A review. *J. Hazard. Mater.* **2008**, *158*, 228–256. [CrossRef]
14. Sparrow, G.J.; Woodcock, J.T. Cyanide and other lixiviant leaching systems for gold with some practical applications. *Miner. Process. Extr. Metall. Rev.* **1995**, *14*, 193–247. [CrossRef]
15. Hilson, G.; Monhemius, A.J. Alternatives to cyanide in the gold mining industry: What prospects for the future? *J. Clean. Prod.* **2006**, *14*, 1158–1167. [CrossRef]
16. Aylmore, M.G. Alternative lixiviants to cyanide for leaching gold ores. In *Gold Ore Processing*; Elsevier: Amsterdam, The Netherlands, 2016; pp. 447–484. [CrossRef]
17. Fisher, L. Hydrothermal Processes at the Osborne Fe-Oxide-Cu-Au Deposit, NW Queensland: Integration of Multiple Micro-Analytical Data Sets to Trace Ore Fluid Sources. Ph.D. Thesis, James Cook University, Douglas, QLD, Australia, 2007. Available online: https://researchonline.jcu.edu.au/4782/3/03Chapters4-6.pdf (accessed on 3 November 2008).
18. Li, J.; Miller, J.D. A review of gold leaching in acid thiourea solutions. *Miner. Process. Extr. Metall. Rev.* **2006**, *27*, 177–214. [CrossRef]
19. Liu, Z.W.; Guo, X.Y.; Tian, Q.H.; Zhang, L. A systematic review of gold extraction: Fundamentals, advancements, and challenges toward alternative lixiviants. *J. Hazard. Mater.* **2022**, *440*, 129778. [CrossRef]
20. Fashola, M.O.; Ngole-Jeme, V.M.; Babalola, O.O. Heavy metal pollution from gold mines: Environmental effects and bacterial strategies for resistance. *Int. J. Environ. Res. Public Health* **2016**, *13*, 1047. [CrossRef]
21. Kaksonen, A.H.; Mudunuru, B.M.; Hackl, R. The role of microorganisms in gold processing and recovery—A review. *Hydrometallurgy* **2014**, *142*, 70–83. [CrossRef]
22. Johnson, D.B. Biomining—Biotechnologies for extracting and recovering metals from ores and waste materials. *Curr. Opin. Biotechnol.* **2014**, *30*, 24–31. [CrossRef]
23. Reith, F.; Lengke, M.F.; Falconer, D.; Craw, D.; Southam, G. The geomicrobiology of gold. *ISME J.* **2007**, *1*, 567–584. [CrossRef]
24. Alp, İ.; Celep, O.; Paktunç, D.; Thibault, Y. Influence of potassium hydroxide pretreatment on the extraction of gold and silver from a refractory ore. *Hydrometallurgy* **2014**, *146*, 64–71. [CrossRef]
25. Silver and Gold-Bearing Tetrahedrite. Available online: https://www.mindat.org/min-26626.html (accessed on 10 May 2023).
26. Ghisani, F.; Timmo, K.; Altosaar, M.; Mikli, V.; Pilvet, M.; Kaupmees, R.; Krustok, J.; Grossberg, M.; Kauk-Kuusik, M. Characterization of tetrahedrite Cu10Cd2Sb4S13 monograin materials grown in molten CdI2 and LiI. *Thin Solid Films* **2021**, *739*, 138980. [CrossRef]
27. Miller, J.W.; Craig, J.R. Tetrahedrite-tennantite series compositional variations in the Cofer Deposit, Mineral District, Virginia. *Am. Mineral.* **1983**, *68*, 227–234. Available online: https://pubs.geoscienceworld.org/msa/ammin/article-abstract/68/1-2/227/41451 (accessed on 23 April 2023).
28. Biagioni, C.; George, L.L.; Cook, N.J.; Makovicky, E.; Moëlo, Y.; Pasero, M.; Sejkora, J.; Stanley, C.J.; Welch, M.D.; Bosi, F. The tetrahedrite group: Nomenclature and classification. *Am. Mineral. J. Earth Planet. Mater.* **2020**, *105*, 109–122. [CrossRef]
29. Xiao, F.; Mao, J.; Cao, D.; Shen, X.; Volinsky, A.A. The role of trivalent arsenic in removal of antimony and bismuth impurities from copper electrolytes. *Hydrometallurgy* **2012**, *125*, 76–80. [CrossRef]
30. Baba, A.A.; Ayinla, K.I.; Adekola, F.A.; Ghosh, M.K.; Ayanda, O.S.; Bale, R.B.; Sheik, A.R.; Pradhan, S.R. A review on novel techniques for chalcopyrite ore processing. *Int. J. Min. Eng. Miner. Process.* **2012**, *1*, 1–16. Available online: https://digitalknowledge.cput.ac.za/bitstream/11189/7612/1/A%20Review%20on%20Novel%20Techniques%20for%20Chalcopyrite%20Ore.pdf (accessed on 23 April 2023). [CrossRef]
31. Ling, H.; Malfliet, A.; Blanpain, B.; Guo, M. A review of the technologies for antimony recovery from refractory ores and metallurgical residues. *Miner. Process. Extr. Metall. Rev.* **2022**, 1–25. [CrossRef]
32. Awe, S.A.; Sandström, Å. Selective leaching of arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkaline sulphide solution. *Miner. Eng.* **2010**, *23*, 1227–1236. [CrossRef]
33. Aghazadeh, S.; Abdollahi, H.; Gharabaghi, M.; Mirmohammadi, M. Selective leaching of antimony from tetrahedrite rich concentrate using alkaline sulfide solution with experimental design: Optimization and kinetic studies. *J. Taiwan Inst. Chem. Eng.* **2021**, *119*, 298–312. [CrossRef]
34. Correia, M.J.N.; Carvalho, J.R.; Monhemius, A.J. The leaching of tetrahedrite in ferric chloride solutions. *Hydrometallurgy* **2000**, *57*, 167–179. [CrossRef]
35. Awe, S.A. Hydrometallurgical Upgrading of a Tetrahedrite-Rich Copper Concentrate. Doctoral Dissertation, Luleå Tekniska Universitet, Luleå, Sweden, 2010. Available online: https://www.diva-portal.org/smash/get/diva2:998811/FULLTEXT01.pdf (accessed on 23 April 2023).
36. Awe, S.A.; Samuelsson, C.; Sandström, Å. Dissolution kinetics of tetrahedrite mineral in alkaline sulphide media. *Hydrometallurgy* **2010**, *103*, 167–172. [CrossRef]
37. Anderson, C.G.; Twidwell, L.G. The alkaline sulfide hydrometallurgical separation, recovery and fixation of tin, arsenic, antimony, mercury and gold. *Lead Zinc* **2008**, *2008*, 121–132. Available online: https://www.saimm.co.za/Conferences/PbZn2008/121--132_Anderson (accessed on 23 April 2023).

38. Spasova, I.; Nicolova, M.; Veglio, F.; Groudev, S. Leaching of gold from a polymetallic sulphide ore. *Annu. Univ. Min. Geol. Sodia.* **2006**, *49*, 213–216. Available online: https://www.researchgate.net/profile/Stoyan-Groudev/publication/267788510_LEACHING_OF_GOLD_FROM_A_POLYMETALLIC_SULPHIDE_ORE/links/54ba25d40cf24e50e93dd7f3/LEACHING-OF-GOLD-FROM-A-POLYMETALLIC-SULPHIDE-ORE.pdf (accessed on 23 April 2023).
39. Sasvári, T.; Kondela, J.; L'uboslav, M.; Slowakiewicz, M. Indície Pt-PGE Mineralizácie na žile Strieborná av širšej Oblasti Rožňavského Rudného Pol'a (Spišsko-Qemerské Rudohorie, Západné Karpaty). 2003. Available online: http://gse.vsb.cz/2003/XLIX-2003--1-129--136.pdf (accessed on 23 April 2023).
40. Sasvári, T.; Mat'o, L. Charakteristika rožňavského rudného pol'a vo vzt'ahu k štruktúrno-tektonickej analýze a mineralizácie, na príklade ložiskových pomerov žily Strieborná. *Acta Montan. Slovaca* **1998**, *3*, 33–117. Available online: http://actamont.tuke.sk/pdf/1998/n5/6sasvari.pdf (accessed on 23 April 2023).