

Article

Depression of Arsenopyrite during Collectorless Flotation in Presence of Aqueous Metal Ions and Inorganic Compounds

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Abstract: Currently, the depression of arsenopyrite during the flotation of base metal mineral sulfides is being continuously studied to reduce its presence in sulfide concentrates of economic interest. In this work, the influence of aqueous metal ions (Fe^{2+} , Cu^{2+} , and Zn^{2+}) in concentrations of 5, 25, and $75 \text{ g} \cdot \text{ton}^{-1}$; mixtures of aqueous chlorides (ammonium and magnesium) and aluminum sulfate (AS)–sodium silicate (SS); and the use of only ordinary Portland cement (OPC) in all concentrations of 0.05 to $0.6 \text{ g} \cdot \text{ton}^{-1}$ during the collectorless flotation and depression of a single-phase majority of arsenopyrite was analyzed. The results revealed a decrease in the hydrophobicity; its depression was greater with the use of OPC. At the concentration of $0.4 \text{ g} \cdot \text{ton}^{-1}$ at alkaline pH and a pulp potential of $+0.067 \text{ V}$, in 0.5 min, its flotation was 15.4 % *w/w* and the cumulative recovery at 10 min was 46.4 % *w/w*. The arsenopyrite depression was as follows: $\text{OPC} > \text{mixed chlorides} > \text{ASSS}$. Fe^{2+} , Zn^{2+} , Cu^{2+} ions activate flotation arsenopyrite. The solids obtained during the flotation were characterized using FTIR, and the functional groups responsible for the depression of arsenopyrite were identified.

Keywords: depression; activation; arsenopyrite; collectorless flotation; infrared



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1. Introduction

Arsenopyrite (FeAsS) is an arsenic sulfide with a monoclinic crystalline structure; in its pure form, it contains 46.0% As, 34.3% Fe, and 19.7% S and is highly toxic [1]; it is the most common and abundant of minerals that contain arsenic (As) and is commonly found in base metal sulfide deposits (Cu, Pb, and Zn) [2]. Furthermore, its presence in flotation concentrates has economic repercussions as its content is penalized; this reduces its content price per ton [3].

Environmentally, mine tailings containing arsenopyrite are the source of As in acid mine drainage (AMD) due to arsenic oxidation, contaminating both surface and underground water bodies [4]. In addition, industrially, the depression of FeAsS during the flotation of valuable metal sulfides and the obtaining of a concentrate with low FeAsS content requires abundant mixtures of inorganic substances such as sodium cyanide and lime [5–7].

Environmental restrictions, contamination, and the government inference to regulate the consumption, reduction, and disuse of cyanide encourage the research to replace it with reagent depressants that are friendly to the environment as well as efficient in the

depression of arsenopyrite [8]. The separation of FeAsS by flotation from minerals usually uses aluminosulfate [9], tannin [10] sodium hydrosulfide, sodium sulfite, and magnesium–ammonium [10–13].

However, there are some factors that limit the industrial applications of most depressants, such as the fact that they are not friendly to the environment and because of technical issues and profitability. Recent studies have indicated that the use of carboxymethyl cellulose (CMC) along with calcium ions successfully depresses arsenopyrite [13].

It has been shown that infrared spectroscopy can be used to determine the adsorption of flotation depressants, for example, it has been indicated that CMC is chemisorbed on the arsenopyrite surface by the effect of the hydroxide ions of calcium adhered to the mineral, which serve as a bridge for the adsorption of CMC [11].

The combination of lime with sodium humate (SH) has been evaluated, and the results have indicated that this mixture can selectively depress arsenopyrite through chemical adsorption through carboxyl groups and Ca atoms [12]. In another case, calcium hypochlorite and sodium humate were used; this combination inhibits the flotation of arsenopyrite, Ca(ClO₂) oxidizes the surface, and then SH is adsorbed to the surface; this adsorption was verified by means of zeta potential measurements [13].

Arsenopyrite depression has been studied using organic compounds such as sodium thioglycollate (STG), demonstrating a selective depression. FTIR analyses have indicated that STG chemically binds to the iron (Fe) and As sites on the arsenopyrite surface through its –COO– group and forms a hydrogen bond with water molecules through the top of the molecule; this in turn forms a hydrophilic layer that causes the depression of arsenopyrite [14].

Organic reagents can be very attractive to depress arsenopyrite. For example, it has been reported that the depression of arsenopyrite is due to the adsorption of *m*-nitrobenzoate on the mineral surface through the –NOO– group of the organic, which forms covalent bonds with arsenopyrite causing a decrease in their flotation [15,16]. However, while organic depressants have selective effects in depressing arsenopyrite, they incur larger costs than conventional reagents.

It has been cited in the literature that soluble starch is a promising depressant of arsenopyrite: even at low concentrations, it is adsorbed on the mineral surface by chemical adsorption and hydrogen bonding, where the poor flotation of arsenopyrite is attributed to the formation of the hydrophilic, i.e., hydroxylated iron [17].

Another inorganic compound used in the depression of arsenopyrite during flotation is ordinary Portland cement (OPC), which has been indicated to be effective in the separation of galena with a low arsenic content. OPC is a material composed of four main phases: tricalcium silicate (Ca₃SiO₅), dicalcium silicate (Ca₂SiO₄), tricalcium aluminate (Ca₃Al₂O₆), and tetra calcium aluminoferrite (Ca₄Al₂Fe₂O₁₀) [9,18].

These cementitious materials have different rates of hydration and result in the production of various hydrates. Among them, the hydration of tricalcium aluminate (Ca₃Al₂O₆) has a higher rate of the hydration-producing ettringite (3Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) phase that selectively adsorbs to the mineral causing its depression [9,18].

Arsenopyrite depression is generally carried out at a high pH and in the presence of oxidants, such as hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), manganese dioxide (MnO₂), and hypochlorous acid (HClO) [19]. Furthermore, in the literature, it has been reported that strontium and barium ions promote the depression of arsenopyrite and inhibit the activation by copper ions [20].

It has been cited that the depression of arsenopyrite is based on the formation of a layer of oxidation products such as ferric hydroxide (Fe(OH)₃), also detecting arsenate species on the surface after oxidation [21]. Potassium permanganate has been used successfully as an oxidant on an industrial scale to depress arsenopyrite [22].

The use of oxidants modifies the pulp potential, for which it has been reported that arsenopyrite flotation is also affected by adjusting the redox potential of the pulp. With agents such as sulfide (S^{2−}), sulfite (SO₃^{2−}), and dithionite (S₂O₄^{2−}) ions [23,24]. Likewise,

arsenopyrite can be selectively depressed with a mixture of oxidant agent ammonium and magnesium chlorides [25].

However, despite the relevant information provided in the investigations described above, they do not analyze the surface speciation of arsenopyrite during the flotation–depression of the mineral in detail. This research paper analyzes the effect of aqueous metal ions in solution, such as Cu^{2+} , Fe^{2+} , and Zn^{2+} , as well as combinations of aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$ /sodium silicate Na_2SiO_3 , the use of a mixture of ammonium magnesium chlorides and ordinary Portland cement in the arsenopyrite activation–depression. The surface speciation was determined using Fourier transform infrared spectroscopy, and their influence on flotation.

2. Materials and Methods

2.1. Equipment and Reagents

To carry out the study on the depression of arsenopyrite during flotation, a mineral consisting of a majority phase of FeAsS , from the mining region of Zimapan, Hidalgo, Mexico, was used. Pieces of approximately 2.5 cm in section were mechanically prepared and ground in an agate mortar to a size of less than 75 microns. The particles were chemically and instrumentally characterized.

The instrumental analysis consisted of carrying out the characterization using X-ray diffraction (XRD) in an INEL Equinox 2000 model diffractometer with radiation $\text{Co } \alpha_1 = 1.789010 \text{ \AA}$. The phase was identified with Match software using the PDF 2 database for characterizing the morphology of the arsenopyrite particles, and to know their semiquantitative chemical composition, a JEOL JSM5900 scanning electron microscope (SEM) was used, and energy-dispersive microanalysis (EDS) and mappings were performed with an OXFORD detector.

The size of the FeAsS particles used for flotation were measured in a Bruker LSI3320 laser diffraction particle size analyzer. The mineral density was determined by the pycnometer method using Equation (1).

$$D = \frac{(MpM - MpV)(Dw)}{(MpW - MpV) - (MpWM - MpM)} \quad (1)$$

where D indicates the density (g/cm^3); MpM : mass of the empty pycnometer with plug plus mineral weight; MpV : mass of the empty pycnometer; Dw : density of water; MpW : mass of the pycnometer with water and plug; and $MpWM$: mass of the pycnometer with mineral, water, and stopper.

The mineral surface prior to the flotation tests was characterized via Fourier transform infrared spectroscopy (FTIR) in a Perkin Elmer equipment spectrum GX model by preparing a pellet containing 0.3 g of FTIR-grade KBr potassium bromide and 0.03 g of the sample, compressed with a hydraulic press at 40 psi.

Analytical-grade chemical reagents, deionized water, a Denver 1 L stainless steel laboratory flotation cell, and a polypropylene a diffuser and impeller were used for all tests. The pH of the flotation pulp and the oxidation reduction potential (ORP) were measured with a Thermo Scientific Orion potentiometer by using a platinum electrode with an internal solution of KCl. ORP measurements were expressed relative to the standard hydrogen electrode SHE by adding 0.241 V to the measured value [26,27].

The thermodynamic modeling of the behavior in aqueous medium of the metallic ions used was carried out in HSC chemistry version 5.2 by means of the construction of Eh–pH diagrams of the metallic aqueous systems studied for the different concentrations used— $5 \text{ g}\cdot\text{ton}^{-1}$, $25 \text{ g}\cdot\text{ton}^{-1}$, $75 \text{ g}\cdot\text{ton}^{-1}$ —and at a temperature of 17°C [28]. Flotation tests were generally carried out at this temperature.

2.2. Experimental Procedure

For chemical characterization, 0.1 g of mineral was weighed in triplicate and attacked with 0.01 L of aqua regia (AR) at 180°C until dry. Then, 0.01 L of AR was added, and the

samples were heated to boiling. The solutions were made to volume of 0.1 L, diluted, and analyzed on a Perkin Elmer Induction Coupled Mass Spectrometer (ICP), Model Optima 3000 XL.

To carry out the activation–depression analysis of arsenopyrite during the collectorless flotation, a variety of chemical systems and pulp potentials Eh (mV) were studied, verifying the surface speciation of the floated mineral using FTIR. The chemical conditions used were different concentrations of metal ions such as Fe^{2+} , Cu^{2+} , and Zn^{2+} using sulfate-type salts $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$, respectively.

Proportional combinations of aluminum sulfate and sodium silicate $\text{Al}_2(\text{SO}_4)_3/\text{Na}_2\text{SiO}_3$ were also investigated in independent tests, evaluated in an aqueous solution containing 0.5 M of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), 2 M of ammonium chloride (NH_4Cl), and 1.5 M of ammonium hydroxide (NH_4OH), and ordinary Portland cement was used separately. The evaluated concentrations of these surface modifiers were 0.05, 0.1, 0.2, 0.4, and $0.6 \text{ g} \cdot \text{ton}^{-1}$.

For all of the tests of collectorless flotation, $60 \text{ g} \cdot \text{ton}^{-1}$ of the methyl isobutyl carbinol (MIBC) frother agent was used, provided by the company Alkemin S.A, S.R.L. The conditioning of the pulp was carried out inside the cell in 1 L of deionized water by first adding the frother agent, then the mineral, and later the surface modifying agent, leaving a conditioning time of 3 min for each modification.

The pH, oxide reduction potential (ORP) (mV), and electrical conductivity were measured at each stage. The measured ORP values were expressed in relation to the value of the standard hydrogen electrode (SHE) (V) by the addition of +0.241 V [26,27], as written above.

Once the conditioning time was completed, the test began, obtaining concentrates at flotation times of 0.5, 1, 2, 4, 6, 8, and 10 min. The valve that allows the entry of air and, therefore, the formation of bubbles was opened 15 s before each flotation time, and the spilled froth containing the floated particles was received in a previously weighed container of inert material. By weight difference, the quantity in grams of the floated arsenopyrite was obtained, and the percentage by weight of flotation (% *w/w* F) was obtained using Equation (2).

$$\% w/w F = \frac{C_c - C_v}{4} * 100 \quad (2)$$

where C_c is the weight of the container with the dry arsenopyrite mineral particles collected at each flotation time, C_v is the weight of the empty container, four (4) is the number of grams of mineral used in each test, and 100 is used to express the value in percentage. For the weighing of the containers, a precision analytical balance was used.

The arsenopyrite particles, floated at times of 0.5 and 10 min were mainly characterized using FTIR to determine the surface speciation and associate the bonds present with the depression or activation of the mineral during flotation. Only the IR spectra are presented for the particles flotation within 0.5 min.

3. Results and Discussion

3.1. Mineral Characterization

Table 1 shows the average quantitative chemical analysis of the majority elements contained in the arsenopyrite. Figure 1 shows the XRD spectrum of arsenopyrite identified with the PDF 96-900-0110. The arsenic species is the majority phase in the mineral.

Table 1. Mineral and chemical quantification of arsenopyrite via ICP.

% <i>w/w</i> Elements of Arsenopyrite						
As	Fe	S	Cu	Zn	Sn	Sb
44.35	33.13	18.01	0.013	0.003	0.009	0.006

The totality of the elements was not quantified.

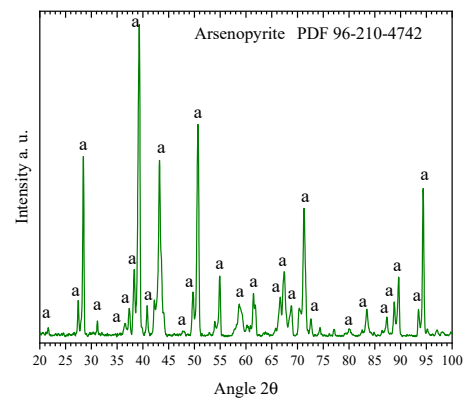


Figure 1. XRD diffractogram of arsenopyrite (FeAsS).

Figure 2 presents the micrographs obtained in SEM-EDS. Particles with irregular surfaces with subconchoidal fracture and angled edges were observed, showing the characteristic elements of arsenopyrite. The mineral sample ranged in size from 3 to 75 microns with a mean of 15.93 μm , providing an average value of density of 5.13 g/cm^3 , as reported in the literature [29].

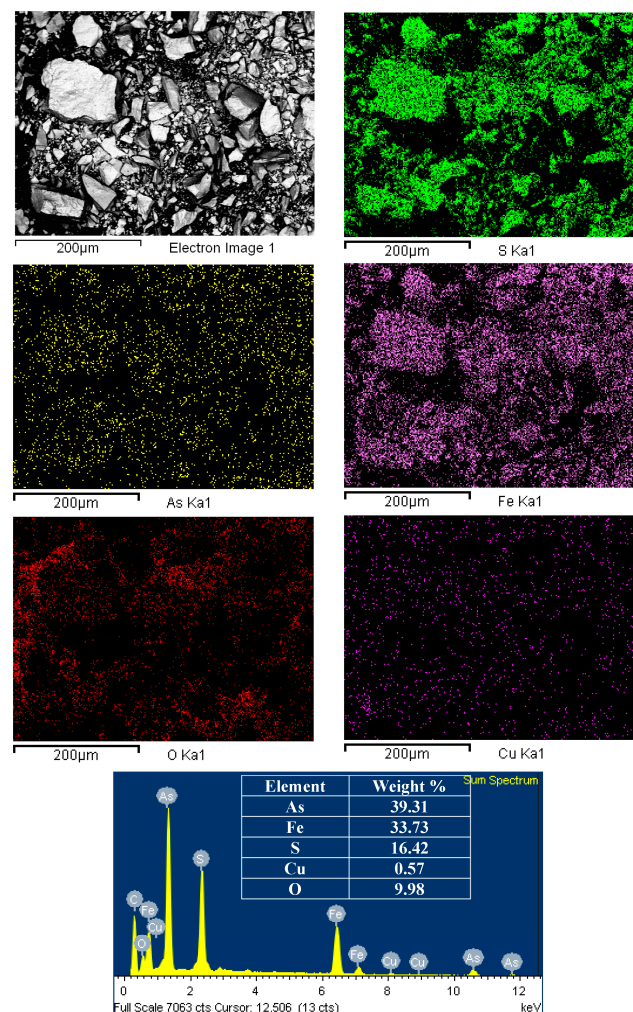


Figure 2. SEM micrograph, elemental mapping, and microanalysis (EDS) of arsenopyrite particles.

Figure 3 shows the infrared spectrum of arsenopyrite. The presence of four absorption bands located at 1034 cm^{-1} , 1058 cm^{-1} , 1114 cm^{-1} , and 1163 cm^{-1} indicate the coordination

of the sulfate ion with iron in a bidentate manner [30]. The Fe–O bond of iron oxide Fe_3O_4 was identified with the absorption band at 755 cm^{-1} [31,32].

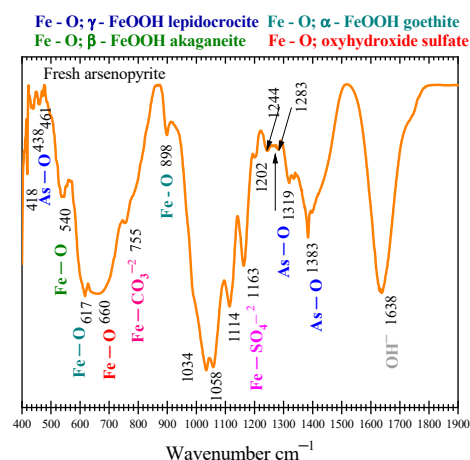


Figure 3. Infrared spectrum of pulverized arsenopyrite in agate mortar.

The absorption band at 540 cm^{-1} was associated with the Fe–O bond of akaganeite $\beta\text{-FeOOH}$, while the signal at 660 cm^{-1} was attributed to the Fe–O bonds of an oxyhydroxide sulfate. The vibration band at 617 cm^{-1} and 898 cm^{-1} showed the presence of the Fe–O bond, of the goethite $\alpha\text{-FeOOH}$ [29–31]. The arsenic oxidation of the sulfide formed As–O bonds and was associated with the bands at 438 cm^{-1} , 461 cm^{-1} , 1244 cm^{-1} , 1283 cm^{-1} , 1329 cm^{-1} , and 1383 cm^{-1} . The adsorption of water molecules represented by the vibration of the OH^- group corresponded to the band at 1638 cm^{-1} [30–35].

3.2. Flotation of FeAsS in the Presence of Ionic Aqueous Metals

The presence of aqueous metal ions and sulfur mainly as sulfate ions in the industrial flotation process is the result of the oxidation of mineral sulfide, present in polymetallic deposit, positively or negatively influencing the process [36]. This effect was part of the object of this investigation.

Figure 4 presents the results of the % *w/w* cumulative collectorless flotation (after 10 min) of arsenopyrite (FeAsS) in the presence of various case metal ion concentrations, Fe^{2+} , Zn^{2+} , and Cu^{2+} . When the ferrous ion and zinc concentration in the flotation pulp was $5\text{ g}\cdot\text{ton}^{-1}$, the maximum cumulative flotation of arsenopyrite was equal to or less than 34 % *w/w*, while the copper ions to activate the FeAsS surface obtained a 62 % *w/w*.

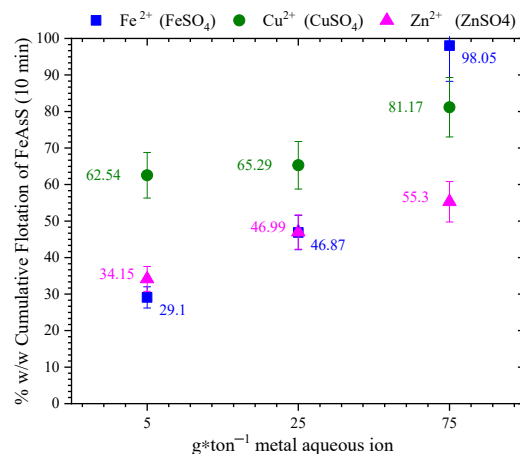


Figure 4. Cumulative flotation of arsenopyrite as a function of concentration and metal ion.

A higher concentration of aqueous metal ions in the pulp progressively increased the flotation of the mineral. The tests were carried out on average at an acid pH of around 5.5 and a pulp potential Eh of + 0.335 V. Under these conditions, thermodynamically zinc ions remained in solution as Zn^{2+} , and copper precipitates as $\text{Cu}(\text{OH})_2$.

While iron remained in the aqueous phase as Fe^{2+} , $\text{Fe}(\text{OH})\text{O}_{(\text{aq})}$ or precipitate $\text{FeO} \cdot \text{OH}$ depending on the variation of the pulp potential, based on the information provided by the Eh–pH diagrams for metal–water systems. Figure 5 shows the Eh–pH (Pourbaix) diagrams of the metal– H_2O aqueous systems, built for a concentration of $5 \text{ g} \cdot \text{ton}^{-1}$, $25 \text{ g} \cdot \text{ton}^{-1}$, and $75 \text{ g} \cdot \text{ton}^{-1}$ to a temperature 17°C , using HSC software [28,37]; in the diagrams, the Eh and pH conditions are marked.

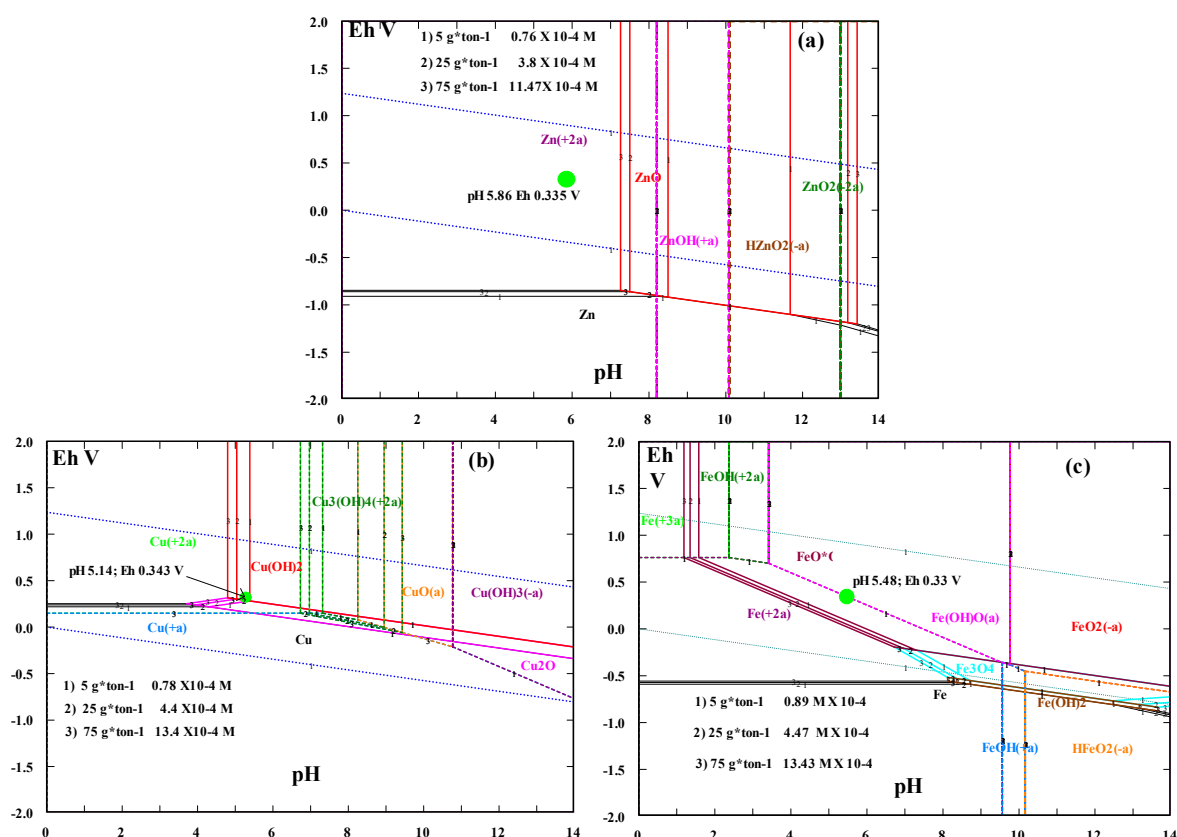


Figure 5. Eh–pH diagrams of the systems (a) Zn– H_2O ; (b) Cu– H_2O ; (c) Fe– H_2O for concentrations of 5, 25, and $75 \text{ g} \cdot \text{ton}^{-1}$ to a temperature 17°C [28,37].

The collectorless flotation tests were carried out, at positive oxidizing potentials of around +0.330 V. This indicated a tendency of the species to release electrons and the subsequent formation of metallic oxides, hydroxides, or oxyhydroxide sulfates of the arsenic and iron, or the metal (Fe, Zn, Cu) used in this study.

The interaction of the aqueous metallic species and the sulfate ions not only influenced the redox potential of the pulp but also affected the surface speciation of the arsenopyrite particles, decisively participated in the activation or depression of the mineral surface during flotation.

With an increase in the concentration of cupric ions and ferrous iron, the influence on the surface activation of FeAsS was greater, favoring the hydrophobicity and increasing the flotation of this mineral. Some authors have indicated that the activation of arsenopyrite proceeds because of an ion exchange mechanism [38]; in the present work, the superficial speciation of the arsenopyrite was obtained in the flotation using FTIR.

The highest pulp potential was obtained for Zn^{2+} followed by Cu^{2+} and Fe^{2+} with values at the beginning of the flotation test of +0.345, +0.336, and +0.323 V, respectively.

At the end of the test, the potential tended to increase, while the electrical conductivity remains unchanged throughout the flotation.

The injection of air into the cell caused a strongly oxidizing chemical environment: with the increase in the concentration of the metal salt, the pulp potential also increases. These modifications alter the superficial nature of the arsenopyrite, leading to a variation in the speciation influencing the hydrophobicity and, therefore, the flotation of the mineral. The aqueous metal ions of copper and iron activate the arsenopyrite surface during collectorless flotation while the zinc ion depressed it, as shown in Figure 4. Even with a higher concentration of zinc ion in solution, arsenopyrite flotation was around 55 % *w/w*.

The surface speciation obtained using the FTIR of the arsenopyrite particles present in the 0.5 min flotation concentrate and in the presence of ferrous ion in concentrations of 5, 25, and 75 g*ton⁻¹ is shown as comparison in Figure 6; the % *w/w* of flotation for these conditions (0.5 min) are 3.5, 10.6, and 22.1 % *w/w*, respectively.

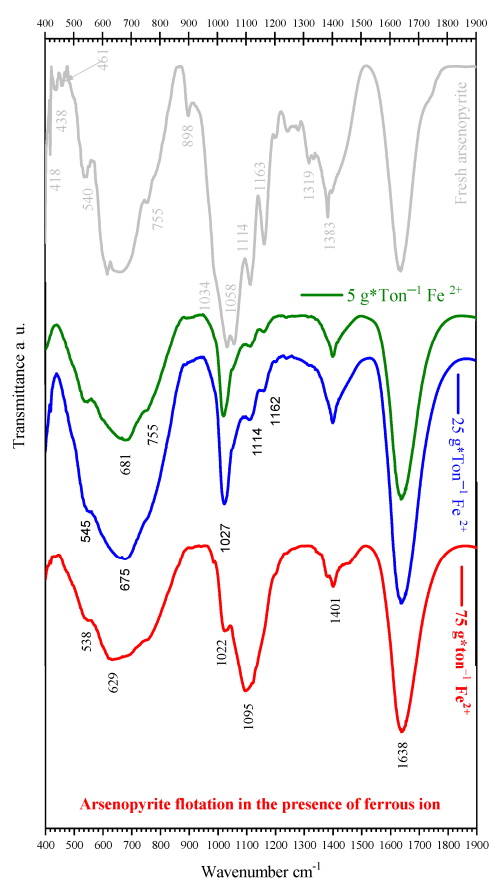


Figure 6. Infrared spectra of fresh and concentrated arsenopyrite at a time of 0.5 min of flotation in the presence of 5, 25, and 75 g*ton⁻¹ of ferrous ions.

This increase in flotation was attributed to the surface state, where the hydrophobicity of the mineral was favored by the presence of the free sulfate ion with a single vibration band at 1095 cm⁻¹ reported in other works [30]; this is due to the oxidation of the metals (iron and arsenic) of arsenopyrite.

The bands around 1022 cm⁻¹, 1027 cm⁻¹, and 1401 cm⁻¹ corresponded to the oxidation of surface arsenic forming As–O bonds [30] present in the three concentrations studied, while the iron from the arsenopyrite was associated with oxygen forming Fe–O bonds related to the absorption band at 629 cm⁻¹ of the previously reported akaganeite β-FeOOH species [31–34].

When the ferrous ion concentration in the flotation pulp was 75 g*ton⁻¹, the formation of these species improved the hydrophobicity of the mineral and floated to a greater extent,

obtaining 98 % *w/w* of accumulated flotation, indicating a surface poor in iron/arsenic and rich in sulfur and metal oxides.

The use of ferrous ion concentrations of 5 and 25 g*ton⁻¹ presented Fe–O bond bands at 681 cm⁻¹, 675 cm⁻¹ corresponding to the formation of oxyhydroxide sulfate on the surface of the arsenopyrite. The increase in the ferrous ion concentration dissolved this species, forming akaganeite β -FeOOH assigned to the band at 629 cm⁻¹. At all of the concentrations analyzed during flotation, arsenopyrite adsorbed the water molecules represented by the previously reported stretching vibration band of the 1638 cm⁻¹ [31–34].

The arsenopyrite particle flotation within 0.5 min and in the presence of dilute solutions of ferrous ion 5 and 25 g*ton⁻¹ showed the presence of three adsorption bands at 1162 cm⁻¹, 1114 cm⁻¹, and a weak shoulder at 1053 cm⁻¹, indicating the formation of coordinated compounds of the sulfate ion with iron in a monodentate manner with the three bands described in the literature [30]; these signals are the difference between a cumulative recovery of 46.87 % *w/w* in the presence of 25 g*ton⁻¹ of Fe²⁺ and 98.0 % *w/w* with a concentration of 75 g*ton⁻¹, as seen in Figure 6.

Contrast Figure 7 presents the infrared spectra obtained for concentrated arsenopyrite in the presence of 5, 25, and 75 g*ton⁻¹ of cupric ion Cu²⁺. Under this flotation conditions of pH (5.14) and pulp potential (+0.343 V) the copper ion tends to precipitate as cupric hydroxide as shown in Figure 5b. IR spectra show multiple adsorption bands indicating a variety of M–O bonds for iron, arsenic, and copper.

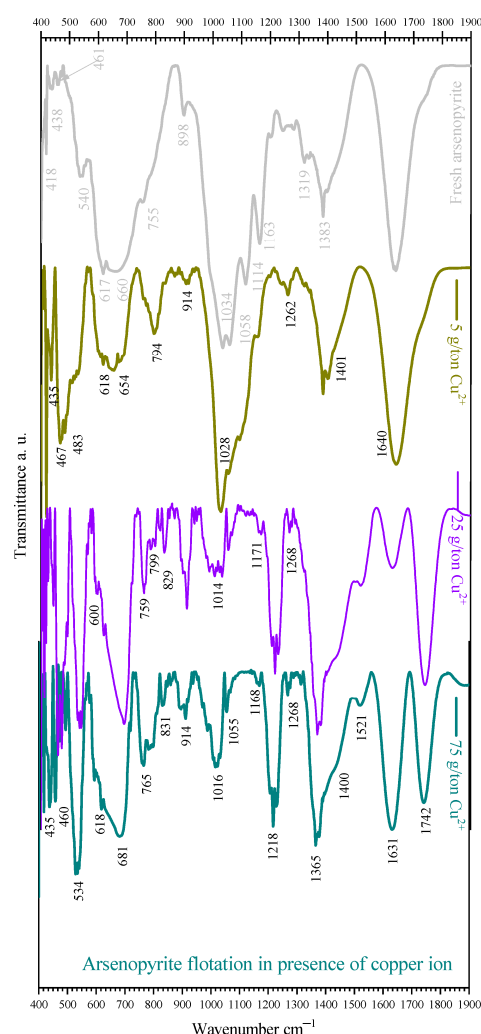


Figure 7. Infrared spectra of concentrated arsenopyrite at a 0.5 min flotation time in the presence of 5, 25, and 75 g*ton⁻¹ of cupric ion.

With the increase in the concentration of copper in solution, the adsorption bands of the sulfate ion detected on the surface of the arsenopyrite tended to dissolve; thus, with $5 \text{ g}\cdot\text{ton}^{-1}$ of Cu^{2+} , there were three adsorption bands at around 1053 cm^{-1} , 1093 cm^{-1} , and 1156 cm^{-1} , as previously reported [30], while with the use of 25 and $75 \text{ g}\cdot\text{ton}^{-1}$ of Cu^{2+} , a single band was formed at 1055 cm^{-1} , indicating the presence of free sulfate ion [30,34].

The As–O bonds identified with the vibration bands at 1521 cm^{-1} , 1401 cm^{-1} , 1365 cm^{-1} , 1268 cm^{-1} , 1218 cm^{-1} , 1016 cm^{-1} , 765 cm^{-1} , 460 cm^{-1} , and 435 cm^{-1} [33,38] gave the mineral a hydrophobic character, achieving a cumulative flotation of 81.7 % *w/w*. The oxidation of superficial iron formed Fe–O bonds at 618 cm^{-1} and 534 cm^{-1} , and the akaganeite $\beta\text{-FeOOH}$ at 914 cm^{-1} , 794 cm^{-1} and 618 cm^{-1} , corresponding to the Fe–O bond of the goethite $\alpha\text{-FeOOH}$. The Cu–O bonds were related to the signals at 681 cm^{-1} and 1742 cm^{-1} .

Regarding the influence of the zinc ion on the surface oxidation of the arsenopyrite, Figure 8 shows the infrared spectra of the arsenopyrite obtained in the first 0.5 min of flotation; here, it is necessary to mention that the aqueous ion Zn^{2+} depressed to a greater extent the particle obtaining a % *w/w* of cumulative flotation (10 min) of 34.1, 46.9, and 55.3 % *w/w* for Zn^{2+} concentrations of 5, 25, and $75 \text{ g}\cdot\text{ton}^{-1}$, respectively.

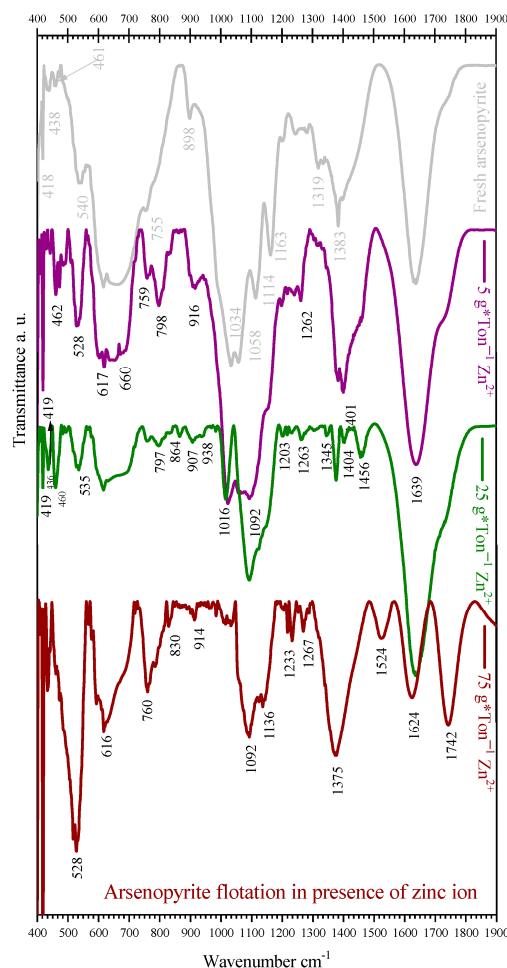


Figure 8. Infrared spectra of concentrated arsenopyrite at a flotation time of 0.5 min in the presence of 5, 25, and $75 \text{ g}\cdot\text{ton}^{-1}$ of zinc ion (Zn^{2+}).

When the zinc concentration in the flotation pulp was $75 \text{ g}\cdot\text{ton}^{-1}$, an intense vibration band occurred at 1624 cm^{-1} because of the adsorption of water molecules to the mineral surface. A similar situation occurred for the bond As–O detected in 1524 , 1375 , 1267 , 1233 , 1016 , and 760 cm^{-1} , as reported in the literature [33], and for the Fe–O bonds corresponding

to the akaganeite β -FeOOH species present at around 528 cm^{-1} and 616 cm^{-1} . The free sulfate ion at the surface form a single, strong adsorption band at around 1092 cm^{-1} .

3.3. Collectorless Flotation and Depression of FeAsS with Ratio of $\text{Al}_2(\text{SO}_4)_3/\text{Na}_2\text{SiO}_3$

Figure 9 shows the % *w/w* of FeAsS cumulative flotation (10 min) as a function of equal proportions (0.05, 0.1, 0.2, 0.4, and $0.6\text{ g}\cdot\text{ton}^{-1}$) of aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$ and silicate sodium Na_2SiO_3 (ASSS). The use of $0.4\text{ g}\cdot\text{ton}^{-1}$ depressed the arsenopyrite particles to a greater degree, achieving 49.5 % *w/w* cumulative flotation (10 min). In this test, at 0.5 min, there was 26.3 % *w/w*. The use of 0.1 and $0.2\text{ g}\cdot\text{ton}^{-1}$ of the ASSS ratio depressed the mineral particles to a lesser degree and the 53.8 and 55.6 % *w/w* cumulative were obtained, respectively.

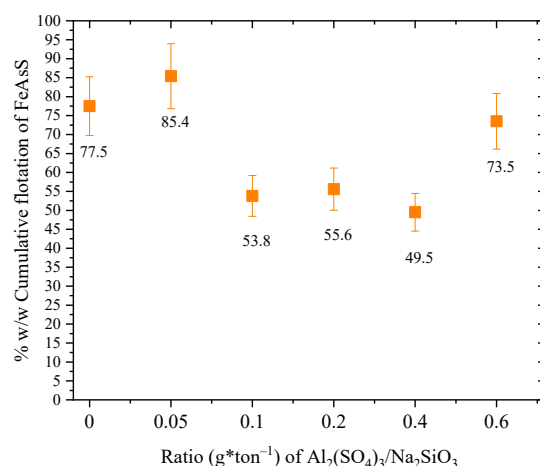


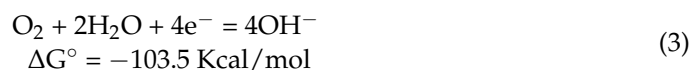
Figure 9. Cumulative flotation of arsenopyrite as a function of the $\text{Al}_2(\text{SO}_4)_3/\text{Na}_2\text{SiO}_3$.

Figure 9 also shows that the efficiency of flotation without a collector using only $60\text{ g}\cdot\text{ton}^{-1}$ of the MIBC frother without a depressant is 77.5 % *w/w*; it is known that semiconductor sulfides such as arsenopyrite and other sulfides and flotation because of the free sulfur bonds generated during fracturing and pulverizing [39,40]. This explains the high percentage of FeAsS flotation with only frother. The use of 0.05 and $0.6\text{ g}\cdot\text{ton}^{-1}$ of the ASSS depressant did not contribute to depressing the arsenopyrite.

The use of the ASSS depressant in the analyzed proportions allowed for the carrying out of the flotation—depression of arsenopyrite at a slightly acidic pH between 5.5 and 5.8, except for the test of collectorless flotation, which was carried out at a pH of 6.8. It has previously been mentioned that this mineral exhibits a good recovery by flotation in acidic chemical environments and decreases at an alkaline pH [41]; however, in this study, the use of the ASSS depressant at an acidic pH managed to depress arsenopyrite.

During the conditioning of the pulp, aluminum sulfate was first added; this provided an acidic character to the pulp with a pH of around 4, and strongly oxidizing pulp potentials of +0.35 to +0.4 V. Subsequently, the sodium silicate was placed, and this tended to increase the pH, returning values between 5.5 and 5.8, and the pulp potential decreased to values of +0.05 V. pH at the end of the test was 6.3; the pulp potential increased its oxidizing character, being +0.29 V on average.

This increase in pH was attributed to the formation of hydroxyl ions as indicated by Equation (3). In addition, its value of the Gibbs free energy calculated based on the thermodynamic information provided in the bibliography [37] is presented.



The variation pulp potential indicates changes in the surface composition of the arsenopyrite mineral particles, forming hydrophilic species such as oxides and hydroxides,

among others, which decrease the flotation of the mineral. surface presence of free sulfur promotes collectorless flotation of arsenopyrite [6].

Arsenopyrite depression is performed at pulp potentials slightly oxidizing potentials such as the one obtained in this investigation Eh +0.05 V, a potential at which the depression of arsenopyrite was considerably high. It has previously been indicated that the use of sodium sulfide as a reagent decreases the pulp potential and the flotation of the species is not carried out and is only achieved when the pulp potential reaches a more positive value [18].

The surface speciation of the concentrated arsenopyrite at a flotation time of 0.5 min was analyzed via infrared spectroscopy. Figure 10 presents the spectra obtained, as well as the % w/w recovery obtained in 0.5 min. The depression of arsenopyrite using the ASSS ratios of 0.05, 0.1, 0.2, 0.4, and 0.6 g*ton⁻¹ was attributed to the presence of an intense adsorption band around 1109 cm⁻¹ adjudicated to the free sulfate ion on the mineral surface [30–34].

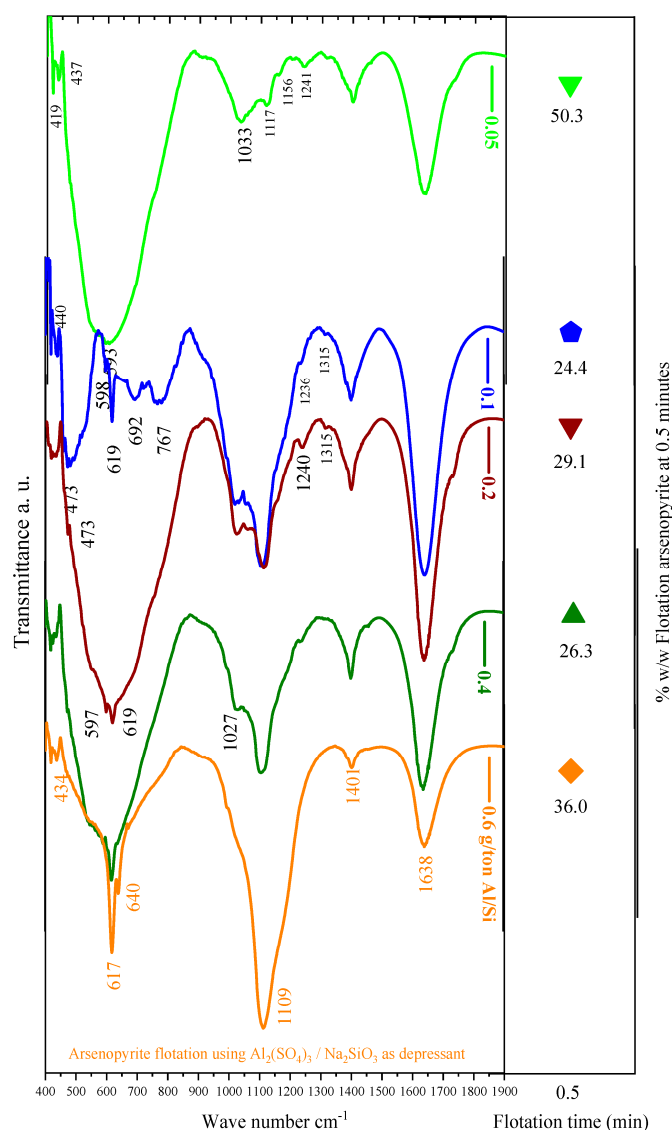


Figure 10. Infrared spectra of concentrated arsenopyrite at a flotation time of 0.5 min in the presence of 0.05, 0.1, 0.2, 0.4, and 0.6 g*ton⁻¹ of the Al₂(SO₄)₃/Na₂SiO₃ ratio.

Whereas when the flotation of arsenopyrite was higher (using 0.05 g*ton⁻¹) four adsorption bands were present at 1033, 1117, 1156, and 1241 cm⁻¹, indicating the presence

of coordination bonds of the sulfate ions with iron forming bidentate compounds [30] that promote flotation.

In addition, the formation of As–O bonds was identified with the signals at 434 cm^{-1} , 1401 cm^{-1} , and 1027 cm^{-1} ; this last band is not present when the arsenopyrite flotation was around 50.3 % *w/w*; that is, the lower degree of oxidation of the particle allowed a greater flotation of the mineral.

Arsenopyrite flotation responded to a greater degree when an intense and broad adsorption band was formed on the surface because of the formation of the Fe–O bonds of the akaganeite $\beta\text{-FeOOH}$ located at 593 cm^{-1} . The dissolution of the Fe–O bonds of the akaganeite and the formation of a goethite band located at around 619 cm^{-1} further promoted the depression of the arsenopyrite, as can be seen in Figure 10.

The values represented in Figure 9 are the result of the cumulative flotation of arsenopyrite after 10 min; it is observed that there is no linear or uniform behavior in the flotation results with respect to the increase in the concentration of the depressants $\text{Al}_2(\text{SO}_4)_3$ and Na_2SiO_3 ; this is attributed to the chemical (pH) and electrochemical (Eh) nature of the pulp together with the superficial changes that occur in the last atomic layer of the mineral.

For example, when a low concentration ($0.05\text{ grs}\cdot\text{ton}^{-1}$) of the depressant reagents is used: $\text{Al}_2(\text{SO}_4)_3$ and Na_2SiO_3 , the arsenopyrite surface is activated and the cumulative flotation is greater even than the test without depressants.

This is attributed to the generation of strong oxidizing conditions +0.4 V and a flotation pH around 5.75, these properties generate a surface with an intense adsorption band corresponding to the Fe–O bonds of akaganeite at 593 cm^{-1} , as well as the presence of an intense band of the As–O bond at 1401 cm^{-1} .

Weak adsorption bands of the presence of metal sulfates between 1000 and 1200 cm^{-1} forming bidentate compounds evidenced by the formation of four adsorption bands. These conditions provide greater hydrophobicity to the mineral, and it floats indiscriminately.

Higher concentrations (0.1 , 0.2 , and $0.4\text{ g}\cdot\text{ton}^{-1}$) of these reagents depress the surface of the mineral, decreasing its cumulative flotation due to the reduction of the oxidizing potential of the pulp. This chemical variation in the pulp affects the surface of the arsenopyrite by the presence of more intense adsorption bands of the As–O bonds located at 1401 cm^{-1} .

As well as the presence in the sulfur zone of a single and intense sulfate ion band at 1109 cm^{-1} , the presence of strong hydroxyl ion adsorption bands at 1638 cm^{-1} , and the conversion of the akaganeite phase at 593 cm^{-1} , the goethite described with the 617 cm^{-1} band led to the surface of the mineral having a hydrophilic character, therefore decreasing its flotation.

While the arsenopyrite surface is activated again by the effect of the increase in the oxidizing pulp potential resulting from the increase in the concentration of $\text{Al}_3(\text{SO}_4)_3$ and Na_2SiO_3 , the sulfate ion signal continues to present a single adsorption band at 1109 cm^{-1} , while the band that represents the As–O bond at 1401 cm^{-1} decreases notoriously, so that the species formed on the surface when high concentrations of $\text{Al}_2(\text{SO}_4)_3$ and Na_2SiO_3 are used improve their hydrophobic properties, activate and float, in greater proportion.

3.4. Collectorless Flotation and Depression of FeAsS Using Mixture of Chlorides

Figure 11 shows the effect of the proportion in $\text{g}\cdot\text{ton}^{-1}$ of the chloride mixture in the flotation without the collector and depression of arsenopyrite. The use of $0.1\text{ g}\cdot\text{ton}^{-1}$ depressed the mineral in a greater proportion, obtaining only 57.48 % *w/w*, this could be attributed to the chemical conditions and pulp potential (Eh) (V).

The addition of this proportion to the flotation pulp gave it a slightly acidic character with a pH of 6.1, and an Eh of +0.3 V favorable conditions for the depression of arsenopyrite using the mixture of chlorides.

Nevertheless, the important depressant action of the chloride mixture, going from a flotation efficiency without a collector and without a depressant of 77.5% *w/w* to 57.48% *w/w* in the presence of the chloride mixture, reducing arsenopyrite flotation by 20 %, and the

use of an optimum proportion of $0.4 \text{ g}\cdot\text{ton}^{-1}$ of ASSS, the flotation of FeAsS was reduced by 28%.

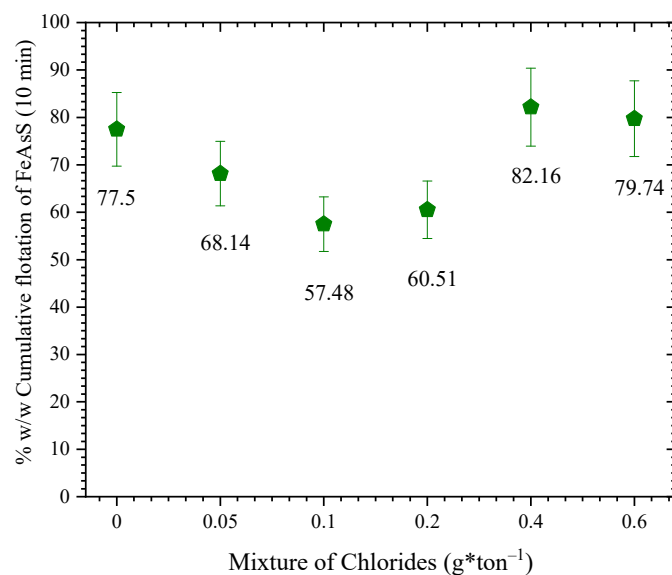


Figure 11. Cumulative flotation of arsenopyrite as a function of the concentration of a mixture of chlorides.

The behavior of arsenopyrite flotation as a function of time (min) in the presence of different concentrations of the chloride mixture is shown in Figure 12. It can be observed that the flotation gradually increased with time: with $0.2 \text{ g}\cdot\text{ton}^{-1}$, after 0.5 min of flotation, a concentrate containing 18.2 % w/w of arsenopyrite was obtained. It was also observed that in 4 min the greatest amount of arsenopyrite separation was achieved.

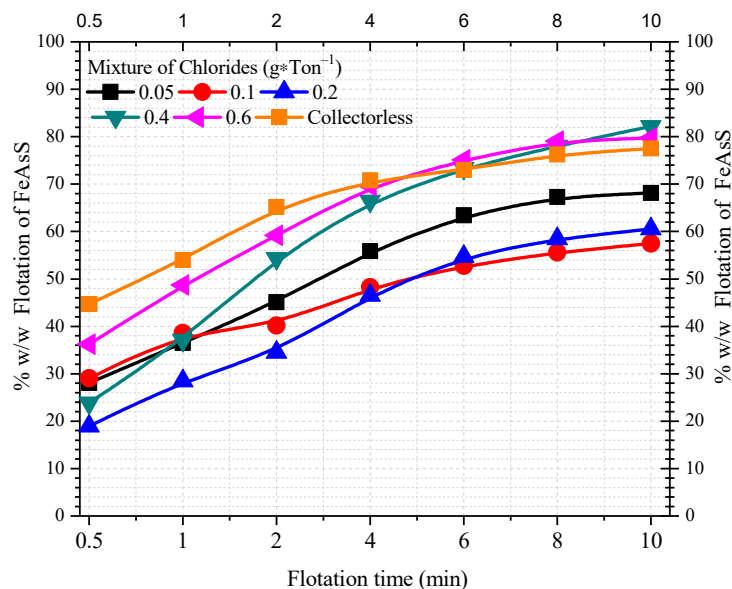


Figure 12. % w/w cumulative flotation of arsenopyrite depending on the time, in the presence of a variety of concentrations of the mixture of chlorides.

This mixture of chlorides was also applied to the enargite depression. The authors highlighted a good selectivity to achieve the proposed objective, hypothesizing the modification of the hydrophobic surface to a hydrophilic one because of the adsorption effect

of the compounds in the chloride mixture, indicating the formation of arsenic ammonium magnesium hexahydrate $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ [25].

The addition of the mixture in proportions of 0.2, 0.4, and $0.6 \text{ g} \cdot \text{ton}^{-1}$ did not contribute to improving the depression. In fact, it activated the arsenopyrite surface, achieving flotation efficiencies of around 82.16% *w/w*. Under these conditions, in general, the pulp acquires an alkaline pH of around 8.8 with an Eh of + 0.174 V; that is, the oxidizing potential of the pulp decreased and the arsenopyrite floated indiscriminately.

Regarding surface speciation, Figure 13 shows the IR spectra of the arsenopyrite particles present in the 0.5 min concentrate. It can be observed that the surface of the arsenopyrite particles concentrated in the presence of 0.2 and $0.4 \text{ g} \cdot \text{ton}^{-1}$ of the chloride mixture had two adsorption bands corresponding to the As–O bonds at around 1033 cm^{-1} and 1401 cm^{-1} with the % *w/w* flotation being 18.9 and 23.8% *w/w*, respectively, while when the separation was greater than 28 % *w/w*, there was, in addition to the signals described, a band around 436 cm^{-1} of the bond As–O.

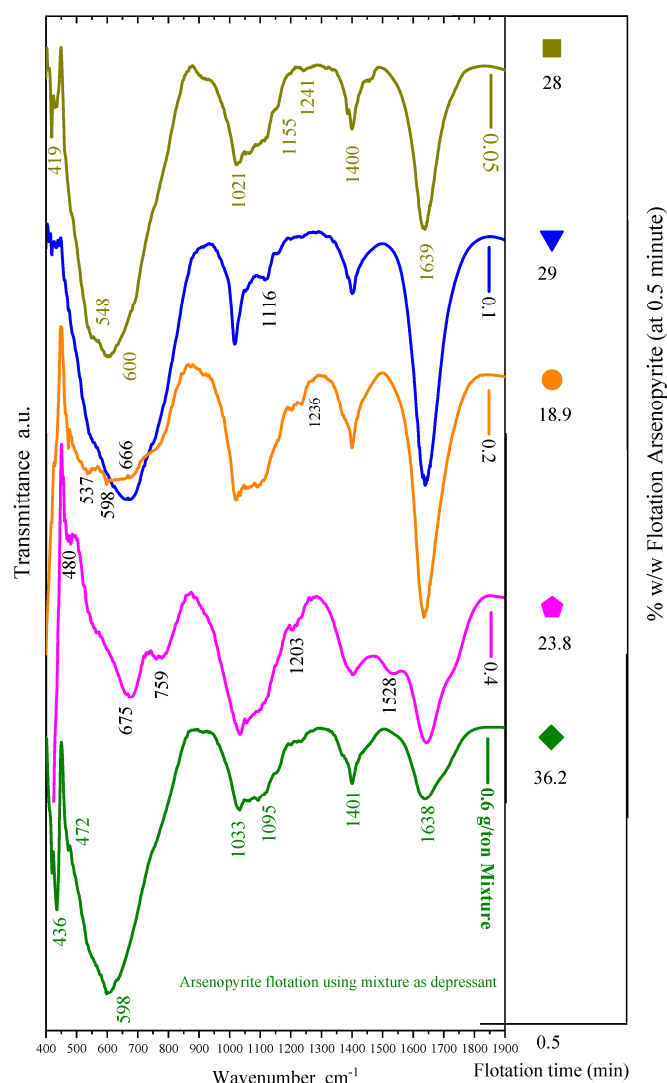


Figure 13. FTIR spectra of concentrated arsenopyrite at a 0.5 min flotation time in the presence of 0.05, 0.1, 0.2, 0.4, and $0.6 \text{ g} \cdot \text{ton}^{-1}$ of the chloride mixture.

The signal corresponding to the sulfate ion at around 1000 to 1200 cm^{-1} very low intensity, and in some cases, it was not possible to detect it. This situation occurred for all of the concentrations of the chloride mixture studied. Regarding the Fe–O bonds on the surface of the arsenopyrite particles, it presented a variety of species: the band at 598 cm^{-1}

could be assigned to the Fe–O bonds of an iron oxide type (Fe_3O_4), and the signals at around 675 cm^{-1} and 666 cm^{-1} indicated the presence of an oxy hydroxide sulfate.

When a concentration of $0.2\text{ g}\cdot\text{ton}^{-1}$ of the chloride mixture was used in the collectorless flotation of arsenopyrite, the adsorption bands corresponding to the Fe–O bonds almost dissolved; forming a broad and low-intensity signal centered at 598 cm^{-1} of Fe_3O_4 , the particles floated in the presence of $0.4\text{ g}\cdot\text{ton}^{-1}$ presented a band at 759 cm^{-1} assigned to the Fe–O bonds in the green rust complexes.

Previous studies have reported that this species is a precursor of the magnetic phase [42]. Precisely when a concentration of the chloride mixture of $0.6\text{ g}\cdot\text{ton}^{-1}$ was used, the band assigned to the Fe–O bonds of the Fe_3O_4 species presented at 598 cm^{-1} , as previously described [34]. In all of the cases, the arsenopyrite adsorbed the water molecules detected with the stretching vibration band of the OH^{-1} group at around 1639 cm^{-1} .

The activation of the arsenopyrite by the effect of the concentrations of the chloride mixture at 0.4 and $0.6\text{ g}\cdot\text{ton}^{-1}$ is due to the chemical change of the pulp, generating an alkaline pH of around 8.5 and a pulp potential Eh of 0.200 V in both for proportions of 0.05 and $0.1\text{ g}\cdot\text{ton}^{-1}$, where the pH is slightly acid at 6.5 with a pulp potential of 0.280 V , the pH and the concentration are critical variables in the depression or activation of arsenopyrite in the presence of mixtures of chlorides, the increase in pH decomposes the ammonium ion to ammonia [43]. This behavior begins at pH 7.0 , and at pH 9 , $50\%\text{ w/w}$ analysis is given; this causes the arsenopyrite to activate with the increase in the concentration of the chloride mixture.

3.5. Collectorless Flotation and Depression of FeAsS Using Ordinary Portland Cement (OPC)

The effect of OPC on the depression of arsenopyrite is presented in Figure 14 by using concentrations of 0.05 , 0.1 , 0.2 , and $0.4\text{ g}\cdot\text{ton}^{-1}$. It was evident that the increase in OPC in the flotation pulp depressed the FeAsS mineral to a greater degree; the greatest depression was achieved with $0.4\text{ g}\cdot\text{ton}^{-1}$ of OPC, obtaining a $46.42\%\text{ w/w}$ of cumulative flotation (for 10 min), as compared to the test collectorless flotation and without a depressor, $31\%\text{ w/w}$ less flotation.

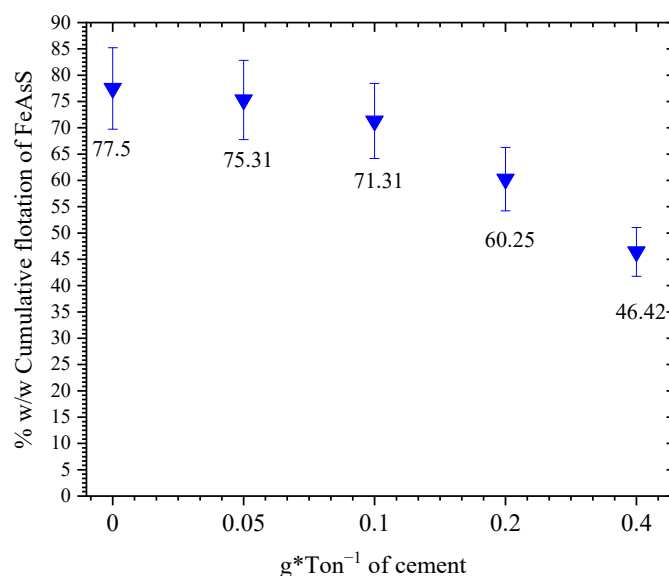


Figure 14. Cumulative flotation of arsenopyrite as a function of OPC ordinary Portland cement concentration.

In general, the use of OPC in depression of arsenopyrite caused the pH to increase until values of around 12.0 pH and a pulp potential of $+0.078\text{ V}$ were reached; the electrical conductivity (k) also increased with the OPC concentration, having a maximum value of $235\text{ }\mu\text{S}\cdot\text{cm}^{-1}$. This indicates that the addition of OPC to the pulp released ions or

anions that increased k . At the end of the test, the pH, Eh (V), and $k \mu\text{S}\cdot\text{cm}^{-1}$ remained without changes.

The ordinary Portland cement used for this study was a commercial one from the Mineral de la Reforma Hidalgo area, Mexico. It was characterized using the X-ray diffraction technique and Fourier transform infrared spectroscopy. Figure 15 shows the XRD spectrum. It can be used to observe that the characteristic phases of cement such as alite, belite, and celite were present.

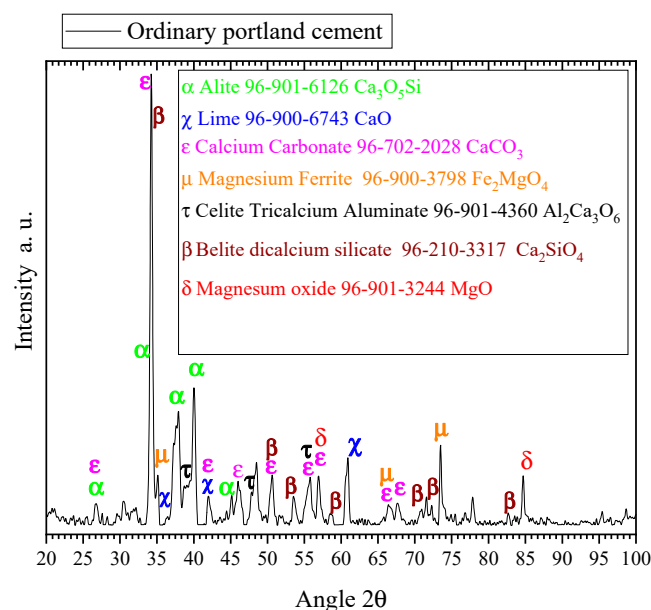


Figure 15. Diffractogram of ordinary Portland cement.

Together with species such as lime, calcium carbonate, and magnesium oxide and ferrite. Figure 15 shows the PDF numbers. The main species responsible for the increase in the pH were lime and magnesium oxide, also influencing the pulp potential.

Figure 16 shows the infrared spectrum of the cement particles. It was observed that it was made up of multiple characteristic adsorption bands of the Si–O, Al–O, Ca–O, and Mg–O bonds; the carbonate ion; and the Fe–O characteristic species of the OPC.

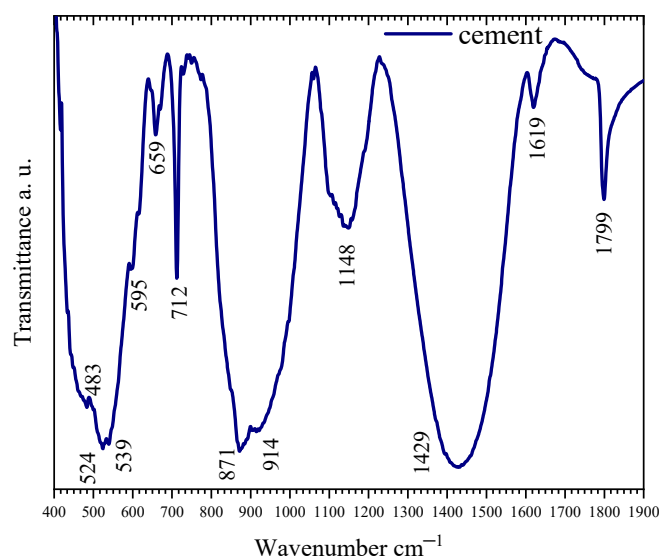


Figure 16. FT-IR spectra of ordinary Portland cement.

The infrared analysis results of the arsenopyrite particles floated in the presence of OPC and the % *w/w* of flotation in 0.5 min are presented in Figure 17. Under these above-mentioned conditions, it was generally found that the characteristic bands of the sulfate ion formed compounds coordinated with iron with three adsorption bands (monodentate) and four bands (bidentate); these compounds were almost entirely dissolved, presenting weak adsorption shoulders around 1053 cm^{-1} , 1110 cm^{-1} , 1161 cm^{-1} , and 1240 cm^{-1} .

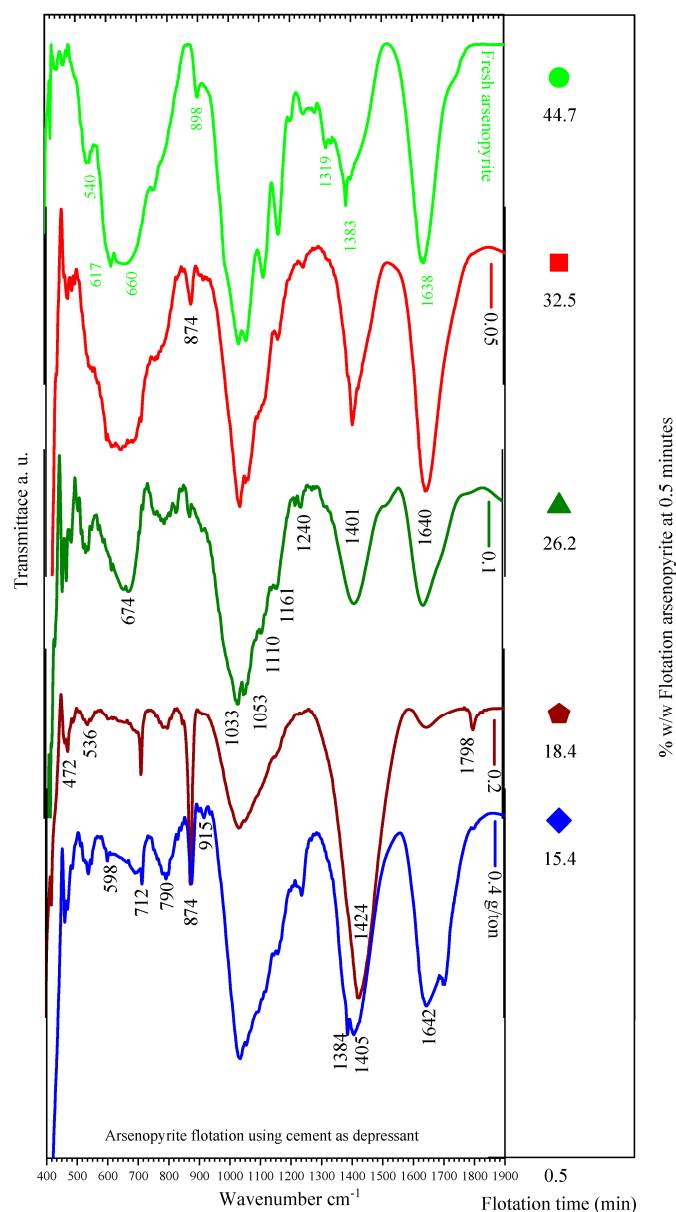


Figure 17. FTIR spectra of concentrated arsenopyrite at a 0.5 min float time in the presence of 0.05, 0.1, 0.2, 0.4, and 0.6 $\text{g}\cdot\text{ton}^{-1}$ of OPC ordinary Portland cement.

In alkaline environments, the sulfates formed on the surface of the mineral decomposed by the action of the OH^{-1} hydroxyl ion formed by the dissolution of the lime contained in the cement. This decomposition of the sulfate has been described in jarosite-type compounds, which contain high percentages of sulfates [44].

The surface arsenic of the arsenopyrite form As–O bonds assigned to the adsorption bands at around 1424 cm^{-1} , at 1033 cm^{-1} , and at 472 cm^{-1} , as described previously [33]; there are also the bonds of Fe–O akaganeite $\beta\text{-FeOOH}$ at 536 cm^{-1} , of the magnetite Fe_3O_4

at 598 cm^{-1} , of the oxyhydroxide sulfate at 674 cm^{-1} , and of the goethite $\alpha\text{-FeOOH}$ at 790 cm^{-1} and 874 cm^{-1} signals, as mentioned previously [30–34].

The band at 712 cm^{-1} showed the adsorption of the cement phases to the surface; in addition, the arsenopyrite adsorbed the water molecules assigned to the vibration adsorption band at 1642 cm^{-1} , corresponding to the OH^- ion.

The lowest flotation of arsenopyrite or depression was achieved with the dissolution of both iron-coordinated sulfates with three and four adsorption bands on the mineral surface. As well as the dissolution of oxyhydroxide sulfate, the greatest depression of arsenopyrite in 0.5 min with 15.4 % *w/w* was achieved.

To achieve the greatest depression of arsenopyrite, the addition of OPC was needed in a concentration of $0.4\text{ g}\cdot\text{ton}^{-1}$; this led to the dissolution of metal sulfates and oxyhydroxide sulfate from the mineral surface, as well as the presence of goethite $\alpha\text{-FeOOH}$, akaganeite $\beta\text{-FeOOH}$, iron oxides such as magnetite Fe_3O_4 , the oxidation of arsenic, and its subsequent formation of As–O, as well as the adsorption of the OPC to the Al–O bonds.

For successful collectorless flotation of arsenopyrite, it is necessary for the surface to form Fe–O bonds of the oxyhydroxide species, as well as to form coordinated sulfate compounds with iron in a monodentate manner with the of three absorption bands or sulfates coordinated with iron in a bidentate manner with four adsorption bands, in addition to the presence of $\alpha\text{-FeOOH}$ goethite, akaganeite $\beta\text{-FeOOH}$, As–O bonds, and hydroxyl ion adsorption.

4. Conclusions

The presence of arsenopyrite in concentrates has both environmental and economic effects, which is why the depression of FeAsS continues to be under investigation.

- In this work, it was found that aqueous metal ions such as Cu^{2+} or Fe^{2+} in concentrations of $75\text{ g}\cdot\text{ton}^{-1}$ activate the FeAsS surface.
- The presence of Zn^{2+} and Cu^{2+} in a concentration of $5\text{ g}\cdot\text{ton}^{-1}$ depressed it.
- The FTIR revealed the speciation of the particles obtained during the arsenopyrite flotation. It was found that the depression of the mineral surface was due to the dissolution of the oxyhydroxide sulfate, 674 cm^{-1} , and the sulfate iron coordinated in either a monodentate or bidentate with three and four adsorption bands, respectively.
- The presence of multiple Fe–O bonding bands of $\alpha\text{-FeOOH}$ goethite with adsorption bands at around 790 cm^{-1} and 874 cm^{-1} and $\beta\text{-akaganeite}$ at 536 cm^{-1} as well as the presence of As–O bonds at 1401 cm^{-1} , 1033 cm^{-1} , and 434 cm^{-1} was identified.
- This surface state was favored by the addition of ordinary Portland cement, achieving the greatest depression of FeAsS with $0.4\text{ g}\cdot\text{ton}^{-1}$ at pH 12 and a pulp potential of + 0.068 V.

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