


Article

Colloidal ZnCO₃ as a Powerful Depressant of Arsenopyrite in Weakly Alkaline Pulp and the Interaction Mechanism

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Abstract: The effects of ZnSO₄ on arsenopyrite depression were studied with sodium carbonate and sodium isobutyl xanthate (SIBX) as the pH regulator and collector, respectively. In both micro and real ore flotation tests, ZnSO₄ showed better depression on arsenopyrite (pH 7.5–9.0 adjusted by Na₂CO₃) compared with sodium humate. The depression mechanism of ZnSO₄ on arsenopyrite flotation was studied by electrokinetic potential, adsorbed amount measurements, scanning electron microscope (SEM) observation and energy dispersive spectra (EDS) detection. The electrokinetic potential measurement results show a potential increase for the arsenopyrite treated with ZnSO₄ in the pH range 7.5–9.0, which could be attributed to the formation of the precipitated zinc carbonate (ZnCO_{3(s)}). For arsenopyrite treated with both ZnSO₄ and SIBX, the electric surface potentials also display an increase, to approximate the values with solely ZnSO₄ treated, at pH 7.5–9.0, indicating the inhibition of ZnCO_{3(s)} upon the SIBX adsorption onto arsenopyrite. Adsorption results demonstrated that SIBX adsorption onto arsenopyrite indeed was inhibited at the pH 7.5–9.0 through the sharp decrease in SIBX adsorbed amount with ZnSO₄ as the depressant at this pH range. SEM observation and EDS detection results verify the formation of colloidal ZnCO₃ on the arsenopyrite, with ZnSO₄ as the depressant in combination with Na₂CO₃.

Keywords: colloidal zinc carbonate; depressant; flotation; adsorption; arsenopyrite

1. Introduction

As one of the most dangerous pollutants, arsenic often causes incidents of public health and pollutes the environment in several regions of the world [1]. Arsenopyrite, the most common arsenic mineral, is usually found in complex sulfide ores [2]. The separation of valuable sulfide minerals, like galena [3,4], chalcopyrite [5], sphalerite [6,7] and pyrite [8,9] from arsenopyrite is very important because arsenic is a penalty element in copper, lead and zinc metal concentrates that are prepared for smelting in the subsequent pyrometallurgical process [10]. The flotation separation of arsenopyrite from the valuable sulfide minerals is still the most relatively effective method compared with gravity and magnetic concentration, which utilizes the difference in the surface wetting properties of different minerals [11]. However, unfortunately, it is difficult to remove the arsenopyrite from the valuable concentrates due to their similar natural floatability.

Therefore, the tailoring of the surface wetting properties and thus the floatability of arsenopyrite in flotation has been extensively researched and practiced. The development of selective collectors

and depressants is an effective way to expand the difference in the floatability of minerals with similar natural surface wettability [12]. Lu et al. [7] reported a novel thiocarbamate collector in chalcopyrite/arsenopyrite separation. They argued that the selective chemisorption of the collector on chalcopyrite against arsenopyrite could be ascribed to the stronger reactivity and the high density of Cu ions on the chalcopyrite surfaces, allowing the selective flotation of chalcopyrite from arsenopyrite. Sirkeci [13] used hexyl thioethylamine as a collector in a single mineral study of pyrite/arsenopyrite separation. They found that the selectivity of the collector was distinctively better than xanthates at alkaline pH values and attributed the differential flotation of pyrite to the higher adsorption rate of hexyl thioethylamine onto pyrite in comparison to arsenopyrite. The reported new selective collectors were also proven to be highly efficient in real ore separation. However, when the economic and source aspects are taken into consideration, xanthates are still the most popular collectors. Therefore, the research about the depressants of arsenopyrite in sulfide flotation is also growing vigorously. Herkenhoff [14] demonstrated the possibility of selective flotation of pyrite using a selective depressant by floating pyrite from arsenopyrite with permanganate as a depressant for arsenopyrite. Combined triethylenetetramine and sodium sulfite also had an effective depression effect for arsenopyrite [15]. A new reagent containing cyclic propylene trithiocarbonate and oxypropylene sulfides was synthesized for arsenopyrite depression. Interestingly, the reagent was found to depress arsenopyrite while increasing the flotation of pyrite simultaneously [16].

Colloidal ZnCO_3 has been proven as the depressant of sphalerite and arsenopyrite, in particular with the flotation practice of copper/zinc [17], lead/zinc [18] and sulfur/arsenic [19] separation. However, the relevant publications scarcely mentioned the preparation method of the colloidal ZnCO_3 depressant and the depression mechanism.

Here, the chalcopyrite/arsenopyrite separation and the beneficiation of an As-bearing Cu ore using the ZnSO_4 were conducted with xanthate as the collector in Na_2CO_3 solution, and particularly, corresponding depression mechanism was in-depth investigated through micro flotation, zeta potential measurements, adsorption tests, scanning electron microscopy (SEM) observations, and energy dispersive X-ray Spectroscopy (EDS) detection.

2. Materials and Methods

2.1. Minerals and Reagents

Pure minerals of arsenopyrite and chalcopyrite were obtained from Beijing Shuiyuan Shanchang mineral specimen Co. LTD (Beijing, China). They were dry-ground [20] using a jar mill equipped with porcelain balls. The products were classified using screens with 0.074 and 0.038 mm sieve pores, respectively. The $-0.074+0.038$ mm fractions [21] were used for the micro flotation, adsorption and SEM tests, and -0.038 mm fractions were used for the zeta potential measurements. The $-0.074+0.038$ mm fractions of pure arsenopyrite/chalcopyrite were analyzed using X-ray diffractometer (X Pert pro, PANalytical B.V., Almelo, The Netherlands) to obtain the corresponding XRD spectra. The XRD results of pure arsenopyrite/chalcopyrite and corresponding PDF data are shown in Figure 1, and the purities are all shown to be more than 96% by comparing with the corresponding PDF cards in Jade 6.0. The specific surface areas of arsenopyrite samples (-0.074 and $+0.038$ mm) were measured $0.78 \text{ m}^2/\text{g}$ by the method of N_2 adsorption [22].

Analytically pure hydrochloric acid and sodium carbonate Na_2CO_3 were used as the pH regulators. Zinc sulfate (ZS, ZnSO_4), sodium humate (SH, $\text{C}_9\text{H}_8\text{Na}_2\text{O}_4$), sodium hexametaphosphate (SHMP, $\text{Na}_6\text{O}_{18}\text{P}_6$), and terpinol ($\text{C}_{10}\text{H}_{18}\text{O}$) were also analytical reagent grade. The analytically pure reagents were purchased from Sinopharm Group. Sodium isobutyl xanthate (SIBX) was industrial grade, which was bought from Tieling Flotation Reagents, Co., Ltd, Liaoning province, China.

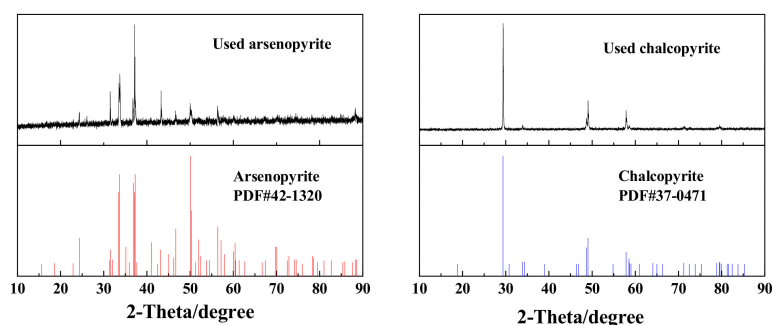


Figure 1. XRD patterns of arsenopyrite and chalcopyrite, and the corresponding PDF data.

2.2. Flotation Tests

2.2.1. Micro Flotation

Floatability tests upon pure minerals were conducted in a 40 mL micro flotation cell. Pure mineral particles (2.0 g) were placed in micro flotation cell filled with 35 mL distilled water and stirred (1680 r/min) for 2 min, and subsequently, pH regulators, i.e., HCl or Na₂CO₃, were added for adjustment to the desired pH [23,24]. Under this pH, ZnSO₄ or SH was added as depressant, followed by isobutyl xanthate (SIBX) collector, with 3 min of stirring after each addition. After the terpinol frother was added and stirred for 2 min, the flotation process was performed for 4 min. The froth fractions, together with the tailings, were separately filtered, dried and weighed. Then, the recovery was calculated in accordance with the dry weight of products. The researchers established three flotation tests in the same conditions, and the average values were reported. The difference in the three tests was insured within 3%. For the mixed minerals flotation, 1 g chalcopyrite and 1 g arsenopyrite were intensively mixed together.

2.2.2. Bench Scale Flotation

The raw ore for flotation tests was obtained from Qinghai Province, China. The element composition and mineral composition are shown in Tables 1 and 2, respectively. The main Cu and As minerals were chalcopyrite and arsenopyrite, respectively. The open circuit flow sheet with one roughing and one scavenging is shown in Figure 2. Three hundred grams of raw ore was ground to $-74\ \mu\text{m}$ particles accounting for 66% and placed into the 1.0 L flotation cell (XFD-type flotation apparatus) [25], and the flotation cell was filled with water to prepare a pulp with the solid concentration of approximately 40 wt %. The pH value of slurry was regulated at approximately 8–8.5 using Na₂CO₃ solution; SHMP was used as the dispersant to make the pulp fully dispersed; ZnSO₄ or SH was employed as the depressant; SIBX and terpinol were used as the collector and frother, respectively. The condition time for each step and the reagent dosage are shown in Figure 2. After finishing the roughing operation, the scavenging was conducted with lower reagent dosage. The floated fractions of both operations were mixed together as the concentrate for assay. The product that remained in flotation cell was the tailings. The final concentrate (C) and tailings (T) were filtered, dried, weighed and analyzed for As and Cu.

Table 1. Analysis results of the chemical composition of raw ore.

Elements	Cu	As	S	WO ₃	Pb	Zn	CaO	Al ₂ O ₃	MgO	SiO ₂
Content (%)	0.36	0.02	2.58	0.039	0.0053	0.031	18.146	5.721	4.682	61.410

Table 2. Results of mineral quantitative analysis.

Minerals	Chalcopyrite	Covellite	Malachite	Arsenopyrite	Pyrite	Quartz	Feldspar	Biotite
Content (%)	1.165	0.064	0.015	0.042	0.0064	42.343	28.650	6.214

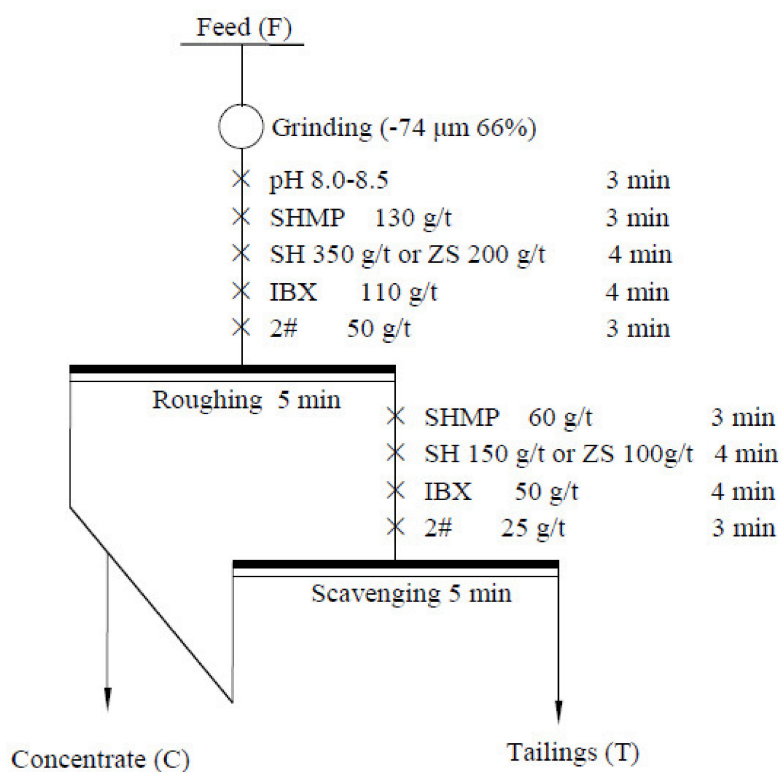


Figure 2. Flow chart of open circuit flotation test.

2.3. Electrokinetic Potential Tests

Using a zeta potential analyzer (ZetaPlus, Bruker, Berlin, Germany), the electrokinetic potential values were measured at 20 ± 0.5 °C. Then, at a given pH and reagent concentration, the preparation of mineral ($-5 \mu\text{m}$, by grinding -0.038 mm fractions using agate mortar) pulp containing solids (0.02 g) and KCl (40 mL, 1 mM) background electrolyte was carried out in a beaker [26]. After standing the solutions for 5 min, the supernate was taken to measure the electrokinetic surface potential. For the mineral/depressant/collector system, the sample was successively conditioned with depressant and collector solution. The interval between each operation is the same as that in micro flotation.

2.4. Adsorption Measurements

By measuring absorbance at the wavelength (301 nm) for xanthate utilizing an ultraviolet (UV-3100) spectrometer [27], respectively, the amounts of SIBX adsorbed onto arsenopyrite were determined in the pH range of 6.5–11.0. After pulping a 2.0 g sample ($-0.074+0.038$ mm fractions) with 40 mL of distilled water with the addition of given amounts of desired reagents, the researchers stirred the solution for 15 min and then used a high-speed refrigerated centrifuge (S-1-150s, HONGHUAYIQI Co., Ltd, Chengdu, China) to centrifuge the solution for 10 min at 4500 rpm. Then, the absorbance of the supernate was measured using the UV spectrometer. By contrast with the standard curve (Figure 3), the concentration of the supernate was obtained. The quantities of the xanthate adsorbed on the minerals were computed according to the difference in the initial and residual concentrations of the SIBX [28].

2.5. SEM Observation and EDS Detection

2.0 g arsenopyrite particles were placed in plexiglass cell for 2 min to be conditioned; then, Na_2CO_3 was used to adjust the pulp pH to 8.1 for another 3 min. For another 2.0 g arsenopyrite particles, under the pH 8.1 adjusted by Na_2CO_3 , ZnSO_4 was added into the pulp and conditioned for 3 min. These particles were filtered and vacuum-dried at room temperature and then used

for tests. Microtopographies and local energy-dispersive spectra of the samples were determined using scanning electron microscopy (SEM) (Zeiss-Sigma 300, Zeiss, Berlin, German) equipped with an energy-dispersive X-ray Spectroscopy (EDS) detector (EDAX Inc, (Washington, DC, USA) [29]. The main operating parameters were 10 kV EHT (acceleration voltage), 8.1 mm WD (working distance) and 5.0 KX Mag (magnification times).

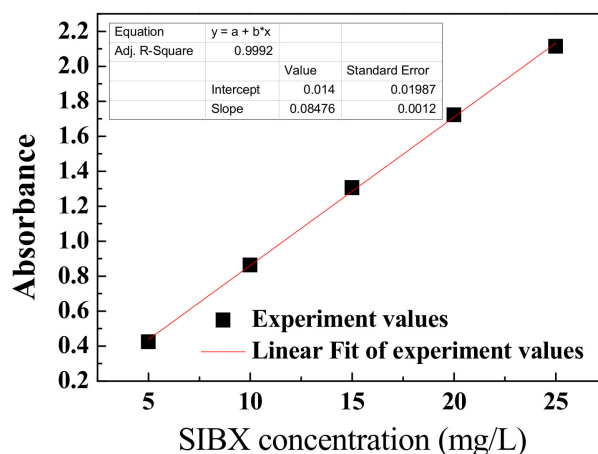


Figure 3. The standard curve of sodium isobutyl xanthate (SIBX).

3. Results and Discussion

3.1. Flotation

3.1.1. Micro Flotation

Flotation tests of single minerals were performed to investigate the effects of depressant's type and dosage and pulp pH upon the recovery of arsenopyrite (AP) and chalcopyrite (CP). The results are shown in Figure 4. Without depressant, chalcopyrite had good floatability in the test pH range of 4–11 when SIBX was used as the collector, while arsenopyrite's floatability was slightly worse than chalcopyrite in the pH range 4–8. When the pulp pH > 8, the floatability of arsenopyrite apparently decreased. The separation of chalcopyrite and arsenopyrite only can be achieved in the strong alkali pulp (pH > 10.5) without depressant in SIBX solution, which is consistent with the results reported before [11,19].

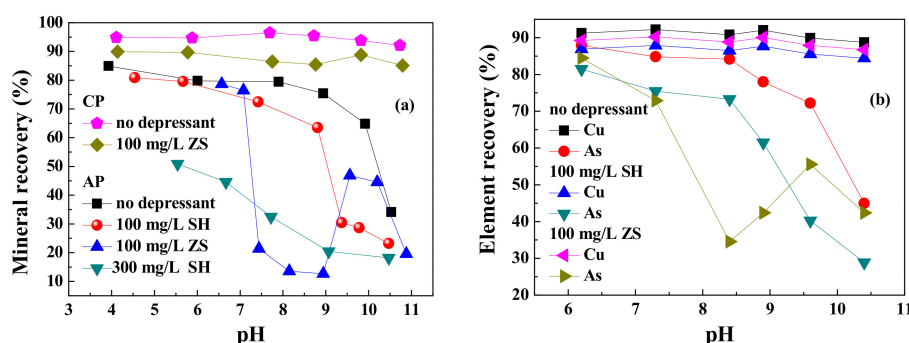


Figure 4. Effects of pH on the recovery of arsenopyrite and chalcopyrite for (a) single mineral system and (b) mixed minerals system. (The concentration of collector SIBX was 8×10^{-4} M.)

With 100 mg/L SH as the depressant, the recovery of arsenopyrite shows a few drops compared with that of no depressant. When 100 mg/L ZnSO₄ was introduced into the pulp, the arsenopyrite's recovery displays a sharp decrease around pH 7 from 74% to 21%, and when the pH > 9, the recovery shows a sharp increase to the value close to that without depressant. It is an interesting phenomenon

and will be discussed with the detection results. One hundred milligrams per liter of ZnSO_4 shows almost no effect on chalcopyrite flotation. Although 300 mg/L SH can distinctly inhibit the flotation of arsenopyrite in the test pH range, considering the dosage of the SH far more than ZnSO_4 , ZnSO_4 was thought as the better depressant for arsenopyrite in SIBX solution [7]. The most difference in the recovery of arsenopyrite and chalcopyrite was in the pH range 7.5–9, with 100 mg/L ZnSO_4 as depressant in Na_2CO_3 and SIBX solution.

When chalcopyrite and arsenopyrite were mixed together, the performance of the depressants was similar to that in single mineral flotation, and the difference in As recoveries and Cu recoveries was smaller for mixed minerals, which may be ascribed to the activation of Cu ions released from chalcopyrite on arsenopyrite flotation. ZnSO_4 showed a better depression performance on arsenopyrite than SH, for single mineral system or mixed minerals system.

3.1.2. Bench Scale Flotation

The depression performance of ZnSO_4 and SH on arsenopyrite was also comparatively studied by bench scale flotation on a real ore with Na_2CO_3 as the pH regulator. Table 3 shows the results of the open circuit bench flotation. With SH as the depressant, the optimal Cu grade of the concentrate is 7.3%, with a Cu recovery of 82.7%, while with the ZnSO_4 as the depressant, the Cu grade is 8.5%, with a Cu recovery of 84.1%. The As grade, and particularly As recovery (58% to 39%), in the concentrate distinctly decreased after replacing SH with ZS, indicating that more arsenopyrite was depressed in the tailings [30].

Table 3. Effects of different depressants on the Cu/As grades and recoveries in rougher concentrate.

Depressant Type*	Products	Ratio/wt. %	Cu Grade/%	Cu Recovery/%	As Grade/%	As Recovery/%
SH, 350/150 g/t (Roughing/Scavenging)	C	4.08	7.301	82.74	0.284	57.89
	T	95.92	0.0651	17.26	0.0088	42.11
	F	100.00	0.36	100.00	0.02	100.00
ZS, 200/100 g/t (Roughing/Scavenging)	C	3.58	8.467	84.19	0.218	38.79
	T	96.42	0.059	15.81	0.0127	61.21
	F	100.00	0.36	100.00	0.02	100.00

* The optimized dosages of different depressants. C represents Concentrate; T represents Tailings; F represents Feed.

From both the results of the micro flotation of pure minerals and the bench scale flotation of real ore, ZnSO_4 showed a high-efficiency depression on arsenopyrite flotation and indeed could promote the separation of chalcopyrite from arsenopyrite in SIBX solution at a suitable pulp pH adjusted by Na_2CO_3 . Therefore, hereafter, the depression of ZnSO_4 on arsenopyrite in Na_2CO_3 and SIBX solution was focused on.

3.2. Electrokinetic Potential

To understand the depression mechanism of ZnSO_4 on arsenopyrite, electrokinetic potentials of the mineral were measured. The results are shown in Figure 5. The particles show negatively charge at any reagent conditions in the tested pH range. After interaction with SIBX (8×10^{-4} M), the electrokinetic potentials of arsenopyrite display a dramatic decrease, indicating the adsorption of SIBX anions onto arsenopyrite surface [31]. Moreover, the variation of the electrokinetic surface potentials of arsenopyrite is great at lower pH values and minor at higher solution pH, which may be due to the different adsorbed amount of SIBX at different pH and is consistent with the good and poor recovery at lower and higher pH range (Figure 4a), respectively.

After treatment with 100 mg/L ZnSO_4 , the electrokinetic potentials of arsenopyrite slightly decreased, followed by a increase from -28 mV (pH 6.5) to -15 mV (pH 7.8), and then fell to the values approximating to that in water at higher pH values. According to the results of solution chemical speciation calculations conducted by Jiao et al. using Visual MINTEQ package [22], when ZnSO_4 concentration surpassed 5×10^{-4} M, solid-state $\text{ZnCO}_3(\text{s})$ would be formed in the pH range of 7.5–9.0, which is the possible reason for the potential increase.

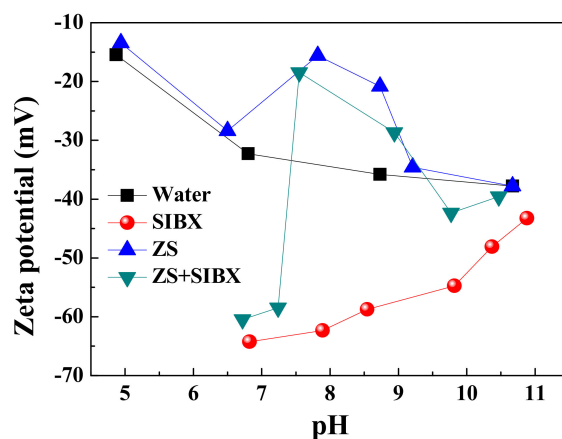


Figure 5. Zeta potential values shown as a function of pH for arsenopyrite before and after interaction with reagents (8×10^{-4} M SIBX, 100 mg/L ZnSO_4).

When the arsenopyrite particles were treated with SIBX after ZnSO_4 treatment, the electrokinetic potentials show a similar value to that directly treated with SIBX at $\text{pH} < 7.5$ and > 9.0 . However, in the pH range 7.5–9.0, the electrokinetic potentials approximate the values treated with ZnSO_4 . These indicate that ZnSO_4 displays almost no effect on SIBX adsorption onto arsenopyrite beyond the pH range 7.5–9.0 but strong depression on SIBX adsorption in this range [32]. Obviously, the formed ZnCO_3 precipitate inhibited the mass adsorption of SIBX anions onto arsenopyrite surface. So far, two assumptions, i.e., the formation of ZnCO_3 precipitate and the change in SIBX adsorbed amount, should be verified to support the deduction.

3.3. Adsorption Amounts of SIBX

To quantitatively determine the adsorption of SIBX on arsenopyrite under different reagent conditions and pulp pH , adsorption tests were carried out and the amounts of SIBX adsorbed onto the surfaces of arsenopyrite were taken as functions of pH (Figure 6) [33]. With increasing pH , the adsorbed amount of SIBX showed a gradual decrease when there was no depressant, being consistent with the declined flotation recovery as shown in Figure 4. For arsenopyrite particles treated with SIBX after treatment with ZnSO_4 , the adsorbed amount sharply decreased from 1.98×10^{-5} mol/m² at pH 7.4 to 3.2×10^{-8} at pH 8 adjusted using Na_2CO_3 , and then increase to the values approximating that without depressant at higher pH range. The pH range (7.5–9.5) where SIBX showed lower adsorbed amount displays good agreement with the corresponding micro flotation and zeta potential results.

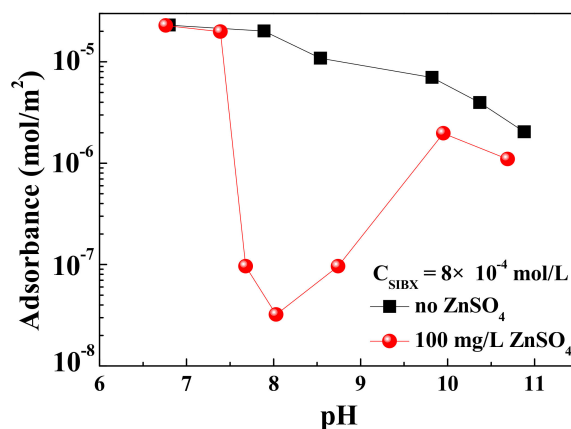


Figure 6. Adsorbed amount of SIBX onto arsenopyrite as a function of pH .

3.4. SEM and EDS Results

SEM observation and EDS measurement were used to verify the formation of solid-state $\text{ZnCO}_3(\text{s})$ precipitate on arsenopyrite surface when 100 mg/L ZS was introduced into pH 8.1 Na_2CO_3 solution. The results are shown in Figure 7. The arsenopyrite surface treated with only pH 8.1 Na_2CO_3 solution (Figure 7a) was relatively clean and had some nicks formed in the grinding process [34]. In comparison, a lot of granular substances, with tens to hundreds of nm in diameter, were generated on arsenopyrite surface treated with both pH 8.1 Na_2CO_3 and 100 mg/L ZnSO_4 solutions (Figure 7b). The particle size of the granular substances was in colloid size.

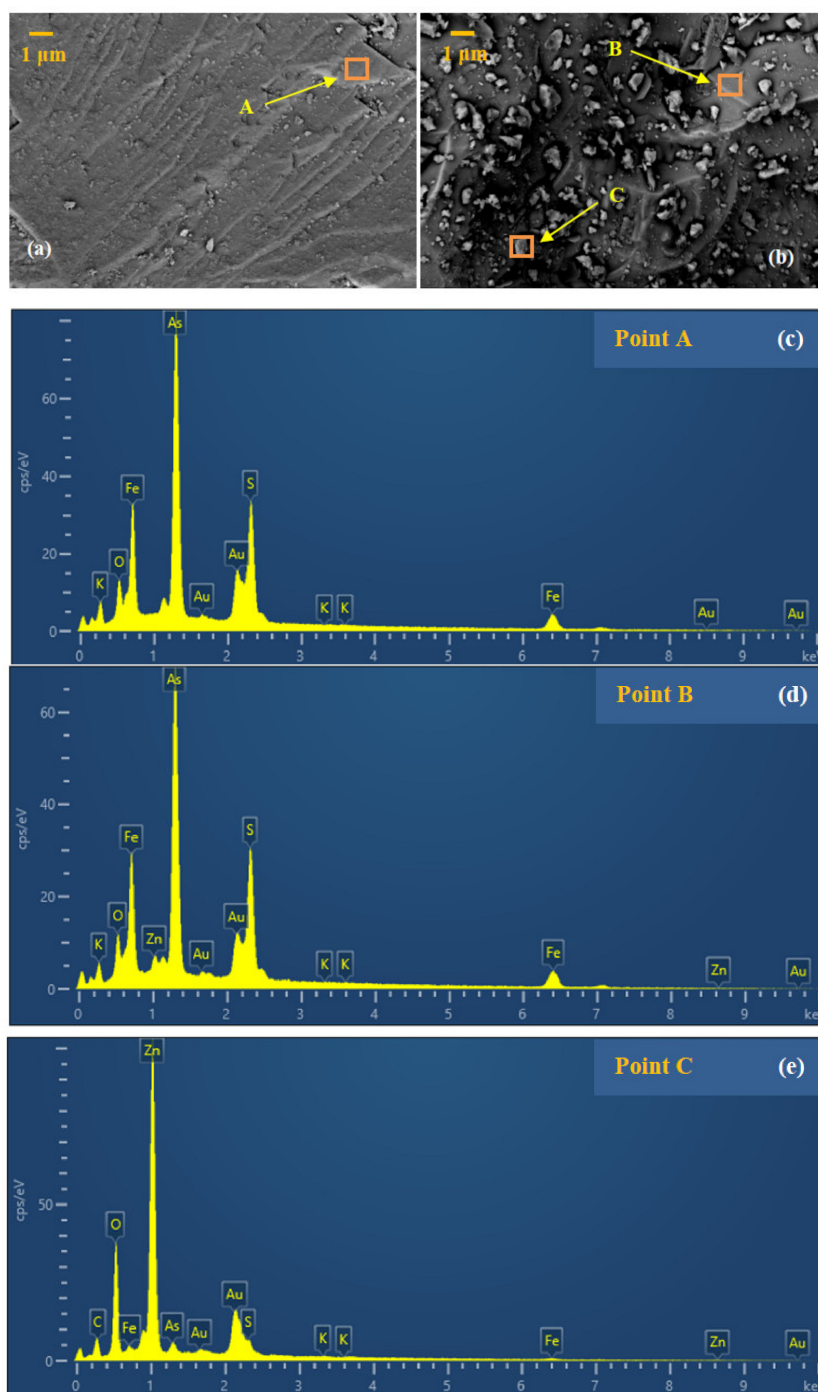


Figure 7. SEM images of (a) sample treated with Na_2CO_3 and (b) sample treated with $\text{Na}_2\text{CO}_3 + \text{ZS}$; EDS spectrum of (c) point A, (d) point B and (e) point C.

The EDS spectrum of point A (Figure 7c) shows that the main elements are As, Fe and S, corresponding to the elementary composition of arsenopyrite. For the point B on the smoother areas of the arsenopyrite surface with colloidal particles, the EDS result shows that Zn was also detected except the main elements of arsenopyrite (Figure 7d), which indicates some very fine ZnCO_3 precipitate may exist. The EDS result for the colloidal particle at point C displays that the main element of the precipitate is Zn, and C was also found, indicating that the main component of this particle is ZnCO_3 and demonstrating the solution chemical speciation calculation results obtained by Jiao et al. [22].

3.5. Suggested Adsorption Model

The schematic diagram for the depression mechanism of colloidal ZnCO_3 on the flotation of arsenopyrite is shown in Figure 8. As shown in Figure 8a, in Na_2CO_3 solution, when SIBX is added into arsenopyrite pulp, the SIBX anions are adsorbed onto mineral surface by the chemisorption of the polar head groups and the active sites on arsenopyrite surface, resulting in a hydrophobic surface [35]; hydrophobic arsenopyrite particles adhering to an air bubble, which has been stabilized by the frother molecules, then are floated [36]. However, with the addition of ZnSO_4 before introducing SIBX, hydrophilic colloidal ZnCO_3 occurred on arsenopyrite surface, resulting in most of the active sites on the surface being masked, and thus the adsorbed amount of SIBX decreased drastically; strong hydrophilic arsenopyrite particles are difficult to be adhered to an air bubble and could not be floated, i.e., the flotation of arsenopyrite is depressed.

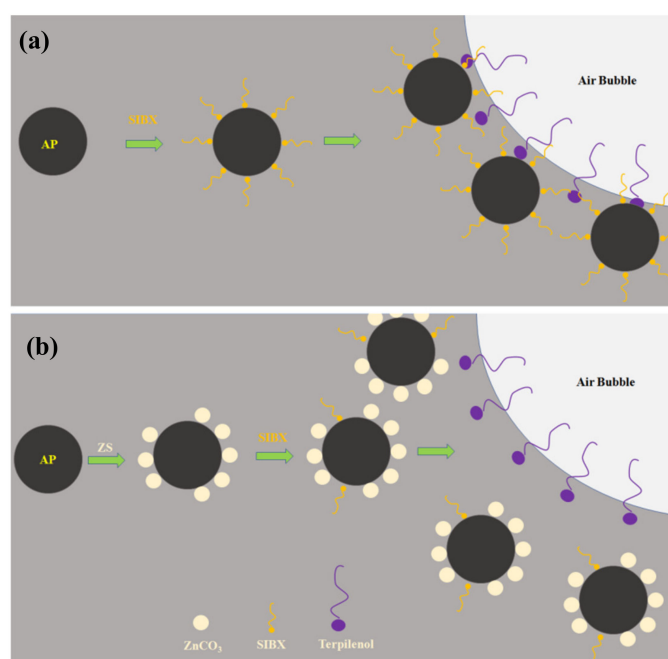


Figure 8. Schematic diagram for the depression mechanism of colloidal ZnCO_3 on the flotation of arsenopyrite. (The relative size of mineral particles, ZnCO_3 (s) precipitation, reagent molecular and bubble is not the physical truth.). (a) Arsenopyrite particle became hydrophobic due to the collector adsorption and can adhere to the bubble and floated; (b) Arsenopyrite particle became hydrophilic due to the Colloidal ZnCO_3 precipitate and cannot adhere to the bubble.

4. Conclusions

- (1) The depression effect of ZnSO_4 on arsenopyrite was superior to the traditional depressant sodium humate in Na_2CO_3 and SIBX solution. The greatest recovery difference between chalcopyrite and arsenopyrite was achieved in the weakly alkaline pH range 7.5–9.0 with ZnSO_4 as the depressant.
- (2) For real ore flotation, ZnSO_4 also exhibited better depression performance on the arsenopyrite minerals with Na_2CO_3 as the pH regulator, and Cu roughing concentrate with 8.5%/0.2% Cu/As

grades and 84%/39% Cu/As recoveries was obtained through the open circuit flow with one rougher and one scavenger. The As recovery in concentrate decreased 20 percentage points.

- (3) With the addition of ZnSO₄ into the pH 7.5–9.0 Na₂CO₃ and SIBX solution, the adsorption of SIBX onto arsenopyrite surface was inhibited, resulting in the higher electrokinetic potentials of arsenopyrite and low adsorbed amount of SIBX. This depression effect of ZnSO₄ was attributed to the formation of colloidal ZnCO₃ on the arsenopyrite surface.

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