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Strengthening effect of a microwave field on sulfurization flotation of hemimorphite

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Abstract: Hemimorphite is a typical silicate zinc oxide mineral characterized by strong hydrophilicity and poor floatability. It is commonly recovered by the "sulfurization pretreatment-xanthate collector flotation" method. However, the Zn^{2+} in hemimorphite is blocked by SiO_4^{2-}, making Zn-O bonds difficult to break and preventing the reaction between Zn^{2+} and S^{2-} in solution. Therefore, enhancing sulfurization is essential for the flotation of hemimorphite. In this study, a microwave field was used for the first time to increase the surface sulfurization of hemimorphite, and the interactions between the minerals and collectors were increased by forming a sulfurization layer on the mineral surface to improve hemimorphite flotation. Compared with the conventional sulfurization pretreatment, microwave field sulfurization pretreatment exhibited better floatability under the same conditions, and the recovery reached 29.82%, which was much higher than that without microwave treatment. The mechanism of hemimorphite sulfurization in the microwave field was investigated with infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy. These results indicated that the microwave field enhanced the surface sulfurization of hemimorphite, and increased the proportions of newly generated sulfides, thus boosting sulfurization flotation of hemimorphite.

Keywords: hemimorphite, microwave, sulfurization, activation, flotation

1. Introduction

Zinc (Zn), as an important nonferrous metal, is widely used in automobiles, biomedicine, construction, shipbuilding, catalysis, and sensor components due to its ductility and corrosion resistance (Ejtemaei et al., 2014, Liu et al., 2012, Sethurajan et al., 2017, Wu et al., 2015, Zhang et al., 2013b). Sulfide ore is the main source of Zn (Irannajad et al., 2009). With continuous mining of zinc sulfide, it is gradually being depleted. Given the important role of zinc in industrial production, the development and utilization of zinc oxide ore have attracted much attention (Feng et al., 2022, Feng et al., 2018, Li et al., 2012, Zhao et al., 2022, Zuo et al., 2020).

Zinc oxide ores exist as silicates or carbonates. Common zinc oxide minerals include smithsonite, hemimorphite, hydrozincite, and zincite (Kashani and Rashchi, 2008, Medas et al., 2017, Mehdilo et al., 2014, Safari et al., 2009, Zhang et al., 2022). At present, the zinc oxide ore being developed is mainly high-grade rich ore. Generally, these ores are enriched through simple beneficiation or direct smelting of rich ore, while lower grades of zinc oxide ore are less commonly used. Flotation is recognized as one of the most promising methods for the enrichment of hemimorphite(Ben Said et al., 2019). The flotation

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methods for zinc oxide ore include the sulfurization-amine collector flotation method, sulfurization-xanthate collector flotation, direct flotation with fatty acid collectors, and other flotation methods. Among them, the sulfurization-xanthate collector flotation method is effective for enriching zinc oxide ore, which improves the reactivity between the minerals and collectors by sulfurizing the surfaces of zinc oxide minerals (Alguacil and Cobo, 1998, Liu et al., 2019, Marabini et al., 1984, Salum et al., 1992). The surface of hemimorphite is extremely hydrophilic, and the zinc atoms are blocked by the surrounding anionic groups (Chen et al., 2016). Hemimorphite is composed of Si-O double tetrahedra and Zn-O tetrahedra. There is [SiO_4] on the surface of the broken mineral, resulting in hydrophilicity of the mineral surface, low activity of the zinc atoms, a complex environment of zinc atoms, and large steric effects caused by the surrounding anionic groups (Ejtemaei et al., 2011). Therefore, due to the strong Zn-O chemical bonds and the shielding effect of SiO_4^{2-}, S^{2-} and HS^- do not react readily with Zn, and the efficiency of conventional surface sulfurization (the minerals are conditioned in sulfurization agent) is low, and the collectors do not readily provide adsorption on the surface of hemimorphite. Therefore, the activity of the zinc is low, and S^{2-} and HS^- do not bind with Zn due to shielding by SiO_4^{2-}, resulting in a lower direct sulfurization efficiency (Jia et al., 2017). Based on the characteristics of hemimorphite, flotation recovery of hemimorphite with the sulfurization-xanthate collector flotation method is not very effective. Therefore, improving the reactivity of zinc in hemimorphite, achieving effective sulfurization, and forming stable zinc sulfur compounds on the surface of hemimorphite are crucial for flotation using sulfurization -xanthate collector technology.

Microwaves are electromagnetic waves with wavelengths short enough to enable the use of waveguide and resonator technology in the transmission and reception process, the wavelength range is 1–100 mm, and the corresponding frequency range is 3×10^5–300 MHz. Microwave heating is an important heating method (Anklekar et al., 2001, He et al., 1995, Inoue, 1998). A microwave field generates or rearranges the polar molecular dielectric and nonpolar molecular dielectric in dipoles. The intermolecular interactions lead to interference and hindrance during molecular vibrations within the microwave field, resulting in friction and molecular "stirring". This process generates a significant amount of heat (Fakhri et al., 2023, Mou and Li, 2004, Norambuena-Contreras et al., 2018). Unlike traditional heating methods, microwave heating is a thermal effect generated by dielectric heating caused by the medium in the electromagnetic field, and the heating is rapid and uniform (Buchelnikov et al., 2008, Kitchen et al., 2014, Song et al., 2016). Additionally, microwave heating does not have temperature gradients, cold centers, and hysteresis effects, and it is easy and efficient to apply (Haque, 1999, Menéndez et al., 2010, Sun et al.). Microwave irradiation may facilitate the sulfurization of hemimorphite.

Based on the advantages of microwave radiation heating, this paper studied the effect of microwave pretreatment on the "sulfurization-xanthate collector" flotation process of hemimorphite. To overcome the difficult sulfurization of hemimorphite, a microwave field was used for the first time to enhance sulfurization of the hemimorphite surface, and the interactions between minerals and collectors were increased by the sulfurization layer on the hemimorphite surface, which improved the flotation recovery of hemimorphite.

2. Materials and methods

2.1. Materials

The mineral samples used in this study were from Lanping, Yunnan. Prior to the experiments, the samples were crushed, sieved, and ground. Then, mineral particles of -75 μm +38 μm were obtained by grinding and screening for the flotation test, and the -38 μm mineral sample was ground for the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and other tests. Each diffraction peak of the mineral sample matched the standard card for hemimorphite, and there were no other crystal diffraction peaks (Fig. 1). X-ray Fluorescence Spectrometer (XRF, EDX-7000, SHIMADZU) results further confirmed that the mineral samples used owned high purity for use in this study (Table 1).

Analytical grade $Na_2S\cdot9H_2O$ was obtained from Shanghai Rhawn Reagent Company, China. Analytically pure $Pb(NO_3)_2$ was purchased from Tianjin ShengAo Reagent Company, China. The collector was sodium butyl xanthate (chemical grade, >85%) purchased from Shanghai Rhawn Reagent

Company, China. The analytical grade foaming agent MIBC was obtained from Shanghai Macklin Reagent Company, China.

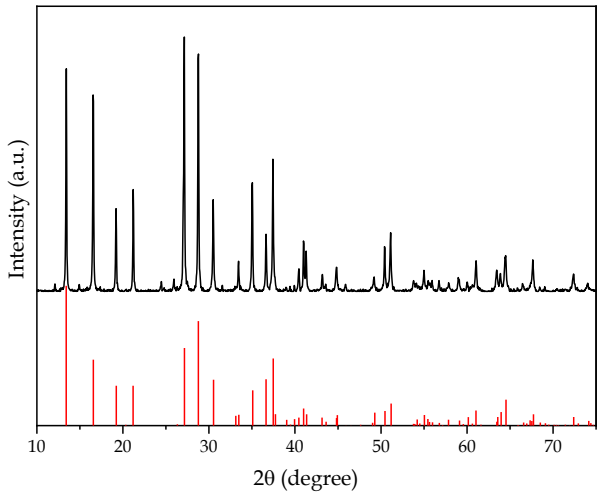

Fig. 1. XRD pattern for hemimorphite

Table 1. Chemical compositions of the hemimorphite sample

Element	Si	S	Fe	Cu	Zn	Pb
Content (%)	10.497	0.163	0.015	0.167	88.349	0.809

2.2. Methods

2.2.1. Microwave sulfurization experiments

The typical microwave sulfurization (sulfurization of hemimorphite in sulfurization agent with microwave radiation) experiment was carried out in a beaker in an M1-L213B microwave oven. 2 g of the mineral sample with particle sizes of −75 μm + 38 μm was used for sulfurization, and these mineral samples were sulfurized in a 2 ×10^{-3} mol/L $Na_2S·9H_2O$ solution in the microwave oven for 1 min. The sulfurization product was immediately transferred to the flotation cell for the flotation experiments.

2.2.2. Micro-flotation experiments

The micro-flotation experiments were conducted in an XFGC flotation machine with a flotation cell volume of 50 mL. First, 2 g of the mineral sample (−75 μm + 38 μm) was placed in the flotation cell and conditioned for 2 min. Subsequently, $Na_2S·9H_2O$ and then $Pb(NO_3)_2$ were added to the cell and conditioned for 3 min, and then sodium butyl xanthate (SBX) was introduced to the pulp and conditioned for 3 min. MIBC was added to the flotation cell and conditioned for another 1 min. The flotation was conducted for 6 min. The entire flotation process is shown in Fig. 2. The concentrates and tailings were filtered, dried, and weighed, and the flotation recovery was calculated from the solid mass distributions of the two products. The flotation tests of the presulfurized minerals in a microwave field followed the same flotation process.

2.2.3. XRD analysis

An X-ray diffractometer (D8 Advance, Bruker, Germany) was used to characterize the samples. The X-ray source provided Cu-Kα1 radiation (λ = 0.154 nm) with a voltage of 40 kV and a current of 40 mA. The scanning range was 10–85° with a step size of 0.02°, and the tests were carried out in air at room temperature. The diffraction pattern was compared with the standard crystallographic data cards to identify the crystalline phases.

2.2.4. XPS analysis

XPS was performed with a Thermo ESCALAB 250, (Thermo Fisher Scientific, USA) system equipped

with an Al Kα source (hv=1486.6 eV). The vacuum pressure of the analytical chamber was 8×10^{-10} Pa. The survey spectrum and the narrow spectra were obtained with pass energies of 50 eV and 20 eV. The peak for the C 1s binding energy of 284.8 eV was used for calibration. The samples were subjected to microwave/surface sulfurization in a Na_2S solution (0.02 mol/L), and the sulfurization products were freeze-dried.

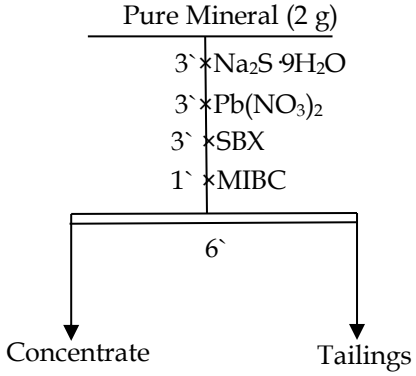

Fig. 2. Flotation flowsheet for hemimorphite

2.2.5. SEM analysis

The samples were glued to the conductive adhesive, and gold was sprayed with a Quorum SC7620 sputtering coater with a current of 10 mA. Scanning electron microscopy and dispersive X-ray spectroscopy (SEM-EDS) (SEM-EDS, ZEISS GeminiSEM 300, Germany) were used to photograph the morphologies and determine the major elements of the samples. The acceleration voltages used for the topographical determinations and the energy spectrum maps were 3 kV and 15 kV, respectively(Shen et al., 2024).

2.2.6. Attenuated total reflection Fourier transform infrared spectrum (ATR-FTIR) and Raman spectra analysis

The sulfide agent, activator, and collector were added to the mineral sample in sequence while stirring. After freeze-drying, the ATR-FTIR spectra of the sulfurization product were obtained with an Invenio R spectrometer (Bruker, GER). All tests were performed in the mid-infrared region (wavenumber range of 400–4000 cm^{-1})(Kazak and Tor, 2022). The obtained samples were probed with Raman spectroscopy and a 532 nm laser in the DXR 3Xi instrument (Thermo Scientific, United States). Raman spectroscopy detects vibrations through inelastic scattering. The sample preparation method was the same as that for ATR-FTIR.

3. Results and discussion

3.1. Sulfide flotation of minerals in a microwave field

3.1.1. Effect of Pb^{2+} on flotation recovery

The flotation of hemimorphite with the "sulfurization pretreatment (in the presence or absence of microwave field) - xanthate collector" process was studied, with Na_2S and Pb^{2+} as sulfurizing and activating agents. The flotation results for hemimorphite with different concentrations of the activator Pb^{2+} are shown in Fig. 3, with 2×10^{-3} mol/L Na_2S and 2×10^{-3} mol/L SBX. The flotation recovery was 8.48% when the concentration of Pb^{2+} was 2×10^{-3} mol/L using the surface sulfurization technology (sulfurization in the absence of microwave field). The recovery initially increased with increasing Pb^{2+} concentration, and when the concentration of Pb^{2+} reached 3.5×10^{-3} mol/L, the flotation recovery reached 97.66% and remained stable as the Pb^{2+} concentration was increased further. When the sulfurization process was enhanced by microwave radiation (microwave sulfurization technology), the flotation recovery was 92.22% at a Pb^{2+} concentration of 2×10^{-3} mol/L, and when the concentration of Pb^{2+} exceeded 3×10^{-3} mol/L, the flotation recovery for hemimorphite surpassed 95% as the Pb^{2+}

concentration was increased. Compared to the process without a microwave field, the flotation recovery of hemimorphite was increased by strengthening the sulfurization process with microwave radiation.

3.1.2 Effect of SBX dosage on flotation recovery

The effects of sulfurization on the flotation recovery for hemimorphite with or without a microwave field and at different SBX dosages are shown in Fig. 4. When the concentration of SBX was 1×10^{-4} mol/L, the flotation recovery for hemimorphite conditioned with microwave sulfurization was 61.73% and that conditioned with surface sulfurization was 45.63%. When the concentration of SBX was 3×10^{-4} mol/L, the flotation recovery of hemimorphite conditioned with microwave sulfurization was 85.02%, and the recovery of the surface sulfurization was 75.76%. These results indicated that the flotation recovery for hemimorphite samples conditioned with microwave sulfurization or surface sulfurization increased with increasing SBX dosage. With the same dosage of SBX, the flotation recovery for sulfurized hemimorphite with microwave radiation was higher, which indicated that the microwave field facilitated sulfurization of the minerals, and the microwave sulfurized hemimorphite had more active sites and a higher hydrophobicity. In summary, microwaves strengthened the sulfurization process of hemimorphite, resulting in a decrease in the dosage of xanthate needed and an increase in the flotation recovery, which improved hemimorphite flotation.

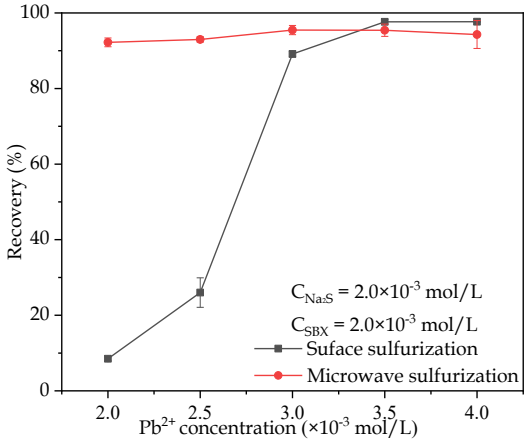

Fig. 3. Flotation recovery of hemimorphite as a function of the Pb^{2+} concentration with 2.0×10^{-3} mol/L Na_2S used as the sulfurizing reagent with and without microwave radiation

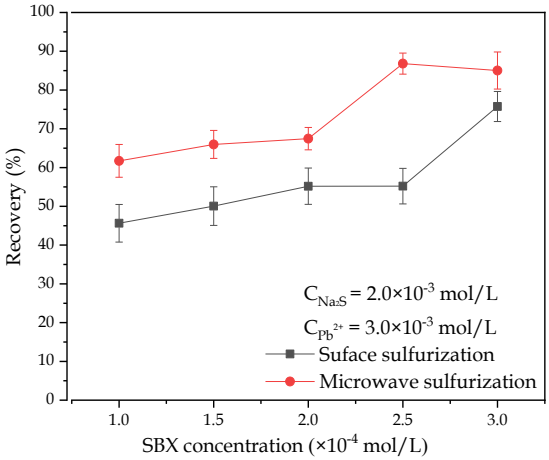

Fig. 4. Effect of the SBX dosage on flotation recovery of hemimorphite conditioned in a Na_2S solution with and without microwave radiation

3.2. X-ray photoelectron spectroscopy

Hemimorphite is different from smithsonite; it is a zinc silicate mineral, and it is very difficult to sulfurize hemimorphite. Microwave radiation was used to enhance the sulfurization of zinc oxide

minerals. The sulfurization of hemimorphite in the presence or absence of a microwave field was studied. The XPS spectra of the minerals treated with different sulfurization methods are shown in Fig. 5. As shown in Fig. 5a, Zn 2p, O 1s, and Si 2p peaks were observed, while no peak corresponding to S was found in the XPS spectrum of native hemimorphite. As shown in Figs. 5b and c, following surface sulfurization and microwave sulfurization, an S 2p peak emerged, and the element concentrations of S are higher after microwave radiation. These results demonstrated that microwave pretreatment enhanced the sulfurization process, promoted the reactions of Na_2S with hemimorphite, and led to the formation of sulfide compounds.

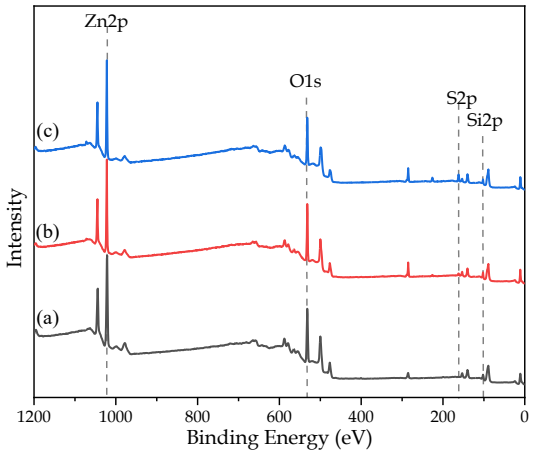

Fig. 5. XPS spectra of hemimorphite with and without sulfurization; (a) hemimorphite, (b) surface sulfurization in the Na_2S solution, and (c) microwave sulfurization in the Na_2S solution

The atom concentrations (XPS semi-quantification) on the surfaces of hemimorphite treated by different sulfurization methods are shown in Table 2. The concentration of S atoms on the surface of the mineral increased from 4.74% to 12.39% after microwave sulfurization. After surface sulfurization, the concentration of O on the surface of hemimorphite was decreased by 0.36%, while the concentration of O on the surface of hemimorphite sulfurized in a microwave field was decreased by 8.47%. These results showed that microwave sulfurization pretreatment strengthened the sulfurization process of hemimorphite and formed a sulfurization layer on its surface. The Zn content on the surface of the mineral rarely changed after both microwave sulfurization and surface sulfurization.

Table 2. Elemental concentrations in hemimorphite conditioned with different sulfurization methods: (a) hemimorphite, (b) surface sulfurization in Na_2S solution, and (c) microwave sulfurization in Na_2S solution

Sample	Element Concentrations (%)			
	Zn	Si	O	S
a	45.15	10.31	44.54	-
b	41.99	9.09	44.18	4.74
c	44.54	7.00	36.07	12.39

The O 1s, S 2p, Si 2p, and Zn 2p peaks for the surface of hemimorphite after sulfurization with and without microwave irradiation were fitted to probe the mechanism for hemimorphite sulfurization. Figs. 6-9 show the spectral analysis of the key elements O, S, Si, and Zn, respectively. A comparison of the peak intensities is shown in the figures below, which indicate that the main change arose from the addition of sulfur.

In Fig. 6(a), the O 1s XPS peak was deconvoluted to give three peaks with different binding energies. The peaks with binding energies of 531.11, 531.77, and 532.96 eV were attributed to -Zn-O, -Si-O, and -OH on the surface of hemimorphite, respectively (Zhao et al., 2019). As shown in Fig. 6b and Table 3, the O 1s binding energies changed slightly after surface sulfurization with Na_2S. The O content in -Zn-O decreased from 34.80% to 30.11%, which may indicate a decrease in the hydrophilicity of hemimorphite. As shown in Fig. 6c, after sulfurization with Na_2S under microwave irradiation, the -Zn-

O content decreased to 20.60%. This indicated that the change in surface -Zn-O content of minerals after microwave sulfurization was more significant than that of surface sulfurization. The semiquantitative XPS results showed that the microwave-enhanced sulfurization process may have reduced surface Zn-O species and increased the hydrophobicity.

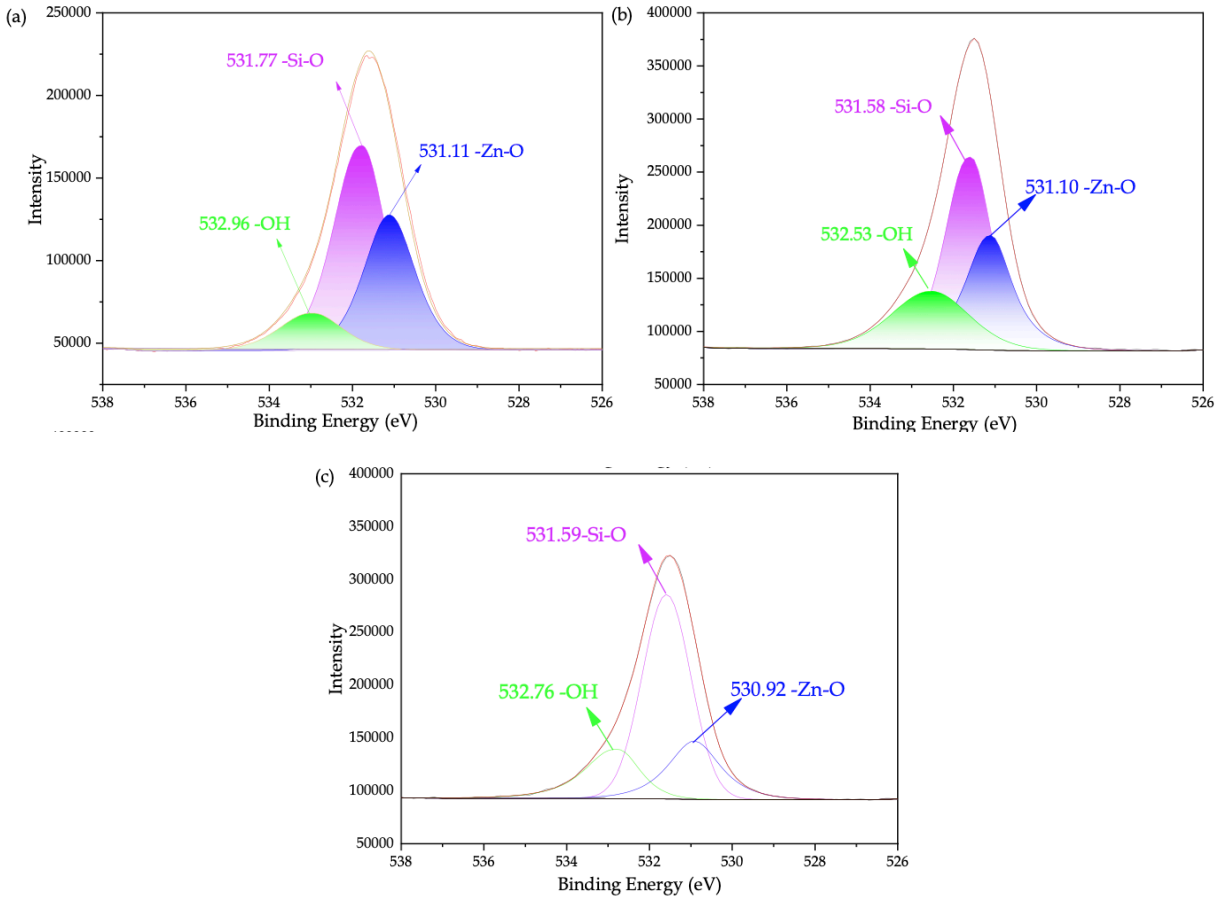

Fig. 6. O 1 s XPS data for products obtained by different sulfurization methods; (a) hemimorphite, (b) surface sulfurization in a Na_2S solution, and (c) microwave sulfurization in a Na_2S solution

Table 3. Oxygen atom contents in the vulcanized products obtained by different sulfurization methods; (a) hemimorphite, (b) surface sulfurization in a Na_2S solution, and (c) microwave sulfurization in a Na_2S solution

Samples	Species	Binding Energy (eV)	Species distribution (%)
a	−Zn−O	531.11	34.80
	−Si−O	531.77	53.60
	−OH	532.96	11.61
b	−Zn−O	531.10	30.11
	−Si−O	531.58	46.22
	−OH	532.53	23.68
c	−Zn−O	530.92	20.60
	−Si−O	531.59	61.24
	−OH	532.76	18.16

Fig. 7 shows the S 2P spectra of the samples treated with different sulfurization methods. No obvious S 2p peaks were detected in the spectrum for native hemimorphite (Fig. 7a). As shown in Fig. 7b and c, the peaks at 161.44 eV in the S $2p_{3/2}$ spectrum of sulfurized hemimorphite were attributed to ZnS (Dake et al., 1989, Langer and Vesely, 1970, Yu et al., 1990). The S components from ZnS constituted 4.74% and 12.39% of the overall composition on the surface of hemimorphite conditioned with surface sulfurization and microwave sulfurization, respectively. The findings suggest that the microwave field

enhanced the sulfurization process through radiation-induced heating, leading to increased adsorption of the sulfur components on the mineral surface and subsequent formation of additional ZnS on the hemimorphite surface. The formation of ZnS on the mineral surface enhanced the hydrophobicity of the sample and its reactivity with xanthate, which improved the flotation performance of hemimorphite.

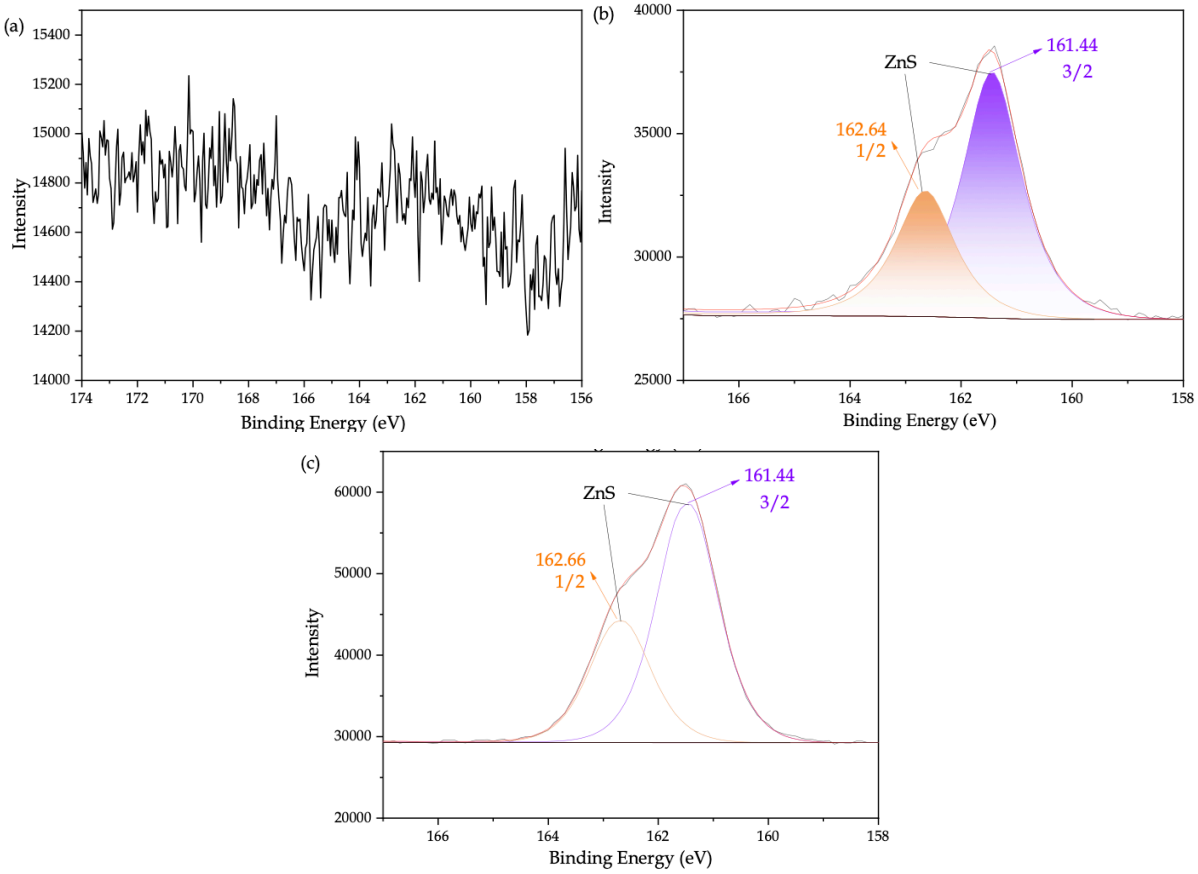

Fig. 7. S 2p XPS spectra of the products obtained by different sulfurization methods; (a) hemimorphite, (b) surface sulfurization in a Na_2S solution, and (c) microwave sulfurization in a Na_2S solution

Fig. 8 shows the Si 2p XPS data for hemimorphite treated with different sulfurization methods. There was no obvious change in the Si 2p binding energies for the mineral surface, indicating that the sulfurization method and the adsorption of the S component had no obvious effect on the chemical state of the Si in hemimorphite.

Fig. 9 shows the Zn 2p high-resolution spectra. The peak at 1021.36 eV for native hemimorphite was attributed to -Zn-O groups (in Fig. 9a). As presented in Figs. 9b and c, the Zn 2p peaks for the surface of sulfurized hemimorphite and the microwave sulfurized hemimorphite were fitted into two pairs of Zn $2p_{3/2}$ and$2p_{1/2}$ doublets, and the Zn $2p_{3/2}$ peaks at 1021.95 eV and 1021.78eV were derived from -Zn-O, and the peaks at 1022.20 eV and 1022.30 eV were due to ZnS species (Strohmeier and Hercules, 1984). These results indicated that the sulfide species on the surface primarily existed in the form of ZnS; however, it is difficult to distinguish the peaks of the two components due to their proximity.

In conclusion, sulfurization products on the surface of minerals are present in the form of ZnS, while the percentage of O from -Zn-O decreased, thus enhancing the hydrophobicity, and reactivity and improving the floatability. These findings were consistent with the results of the flotation experiment.

3.3. SEM analysis

Surface sulfurization changes the composition and properties of the mineral surface. SEM was used to analyze the surface components before and after sulfurization. The surface morphologies of hemimorphite treated with different sulfurization methods were determined and analyzed in detail, and the results are shown in Fig. 10.

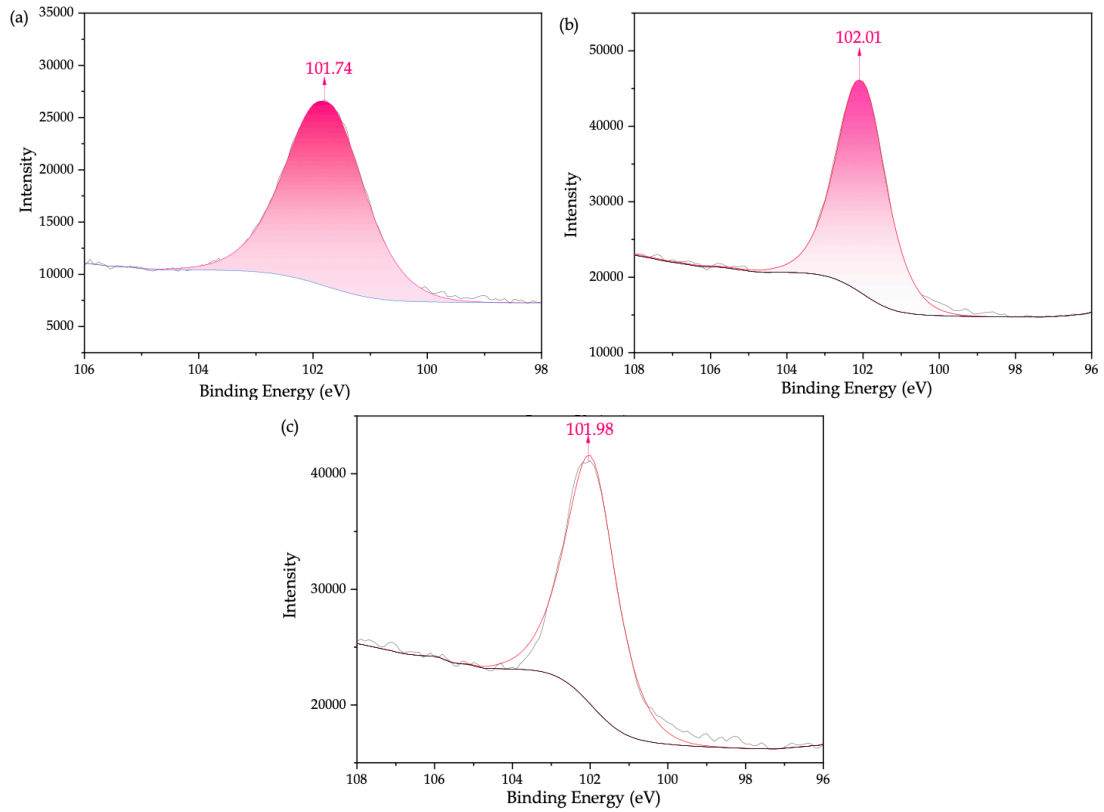

Fig. 8. Si 2p XPS spectra of products obtained by different sulfurization methods; (a) hemimorphite, (b) surface sulfurization in a Na_2S solution, and (c) microwave sulfurization in a Na_2S solution

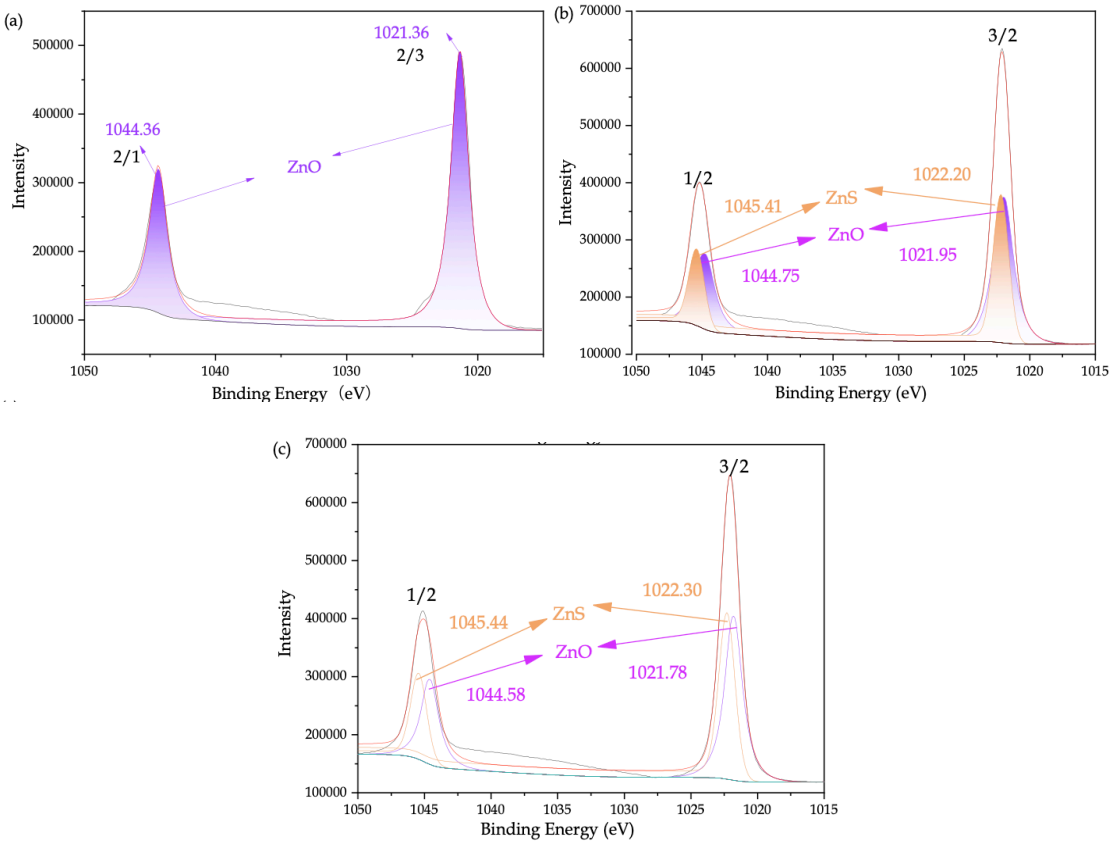

Fig. 9. Zn 2p XPS data for products obtained with different sulfurization methods: (a) hemimorphite, (b) surface sulfurization in a Na_2S solution, and (c) microwave sulfurization in a Na_2S solution

Fig. 10a shows the SEM image of native hemimorphite. EDS scans detected the presence of Zn, O, and Si, with elemental compositions detailed in Table 4, confirming the purity of the sample. Fig. 10b shows the SEM image of hemimorphite conditioned with surface sulfurization. The EDS scans showed that the S content was 0.36% and the O content was 60.25% for the sulfurized surface of hemimorphite. Fig. 10c shows the SEM image of hemimorphite conditioned with the microwave sulfurization. There were many granular substances on the surface, and the S content was 0.57% higher than that shown for surface sulfurization. Pb^{2+} acts as an activator in sulfurization flotation. Fig. 10d shows the SEM image of hemimorphite activated by Pb^{2+} after sulfurization. Surface scanning showed that the contents of Pb and S on the surface were 0.35% and 0.15%, respectively. Fig. 10 shows the SEM image of the Pb^{2+} activated hemimorphite after microwave sulfurization. The EDS maps showed that the contents of Pb and S on the surface were 0.74% and 0.65% higher than those on the surface sulfurization product, respectively. Therefore, the increase in Pb content of hemimorphite sulfurized in the microwave field was caused by the increased S content on the surface of hemimorphite; this increased the number of active sites for binding of SBX on the hemimorphite surface, thereby facilitating its flotation. In summary, microwave treatment strengthened the sulfurization process of hemimorphite, promoted the formation of zinc sulfide compounds, formed a sulfide layer on the surface of hemimorphite, and increased the hydrophobicity and reactivity of the mineral.

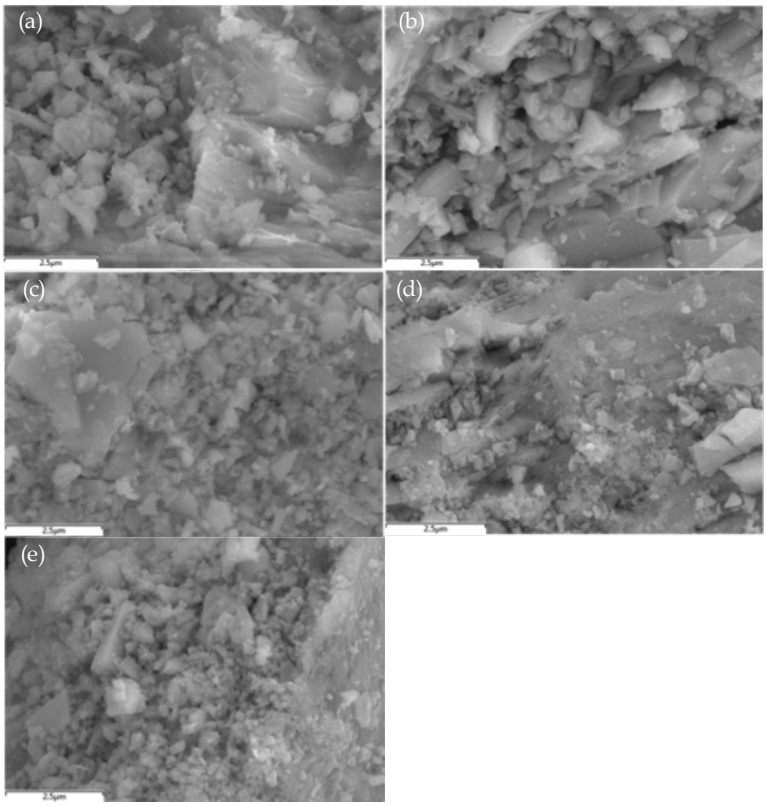

Fig. 10. SEM images of products obtained with different sulfurization methods; (a) hemimorphite, (b) surface sulfurization (hemimorphite + Na_2S), (c) microwave sulfurization (hemimorphite + Na_2S), (d) surface sulfurization (hemimorphite + Na_2S+ Pb^{2+}) and (e) microwave sulfurization (hemimorphite + Na_2S + Pb^{2+})

Table 4. SEM-EDS analysis on the surface of hemimorphite

Area	Mole fraction/ %				
	O	Si	Zn	S	Pb
a	66.03	9.92	24.05	-	-
b	60.25	12.60	26.79	0.36	-
c	61.91	11.16	26.00	0.93	-
d	65.55	9.98	23.98	0.15	0.35
e	64.59	9.74	23.78	0.80	1.09

3.4. XRD analysis

Fig. 11 shows the XRD pattern for a hemimorphite sample sulfurized in a Na_2S solution (2×10^{-3} mol/L) with and without microwave irradiation after Pb^{2+} activation. The results indicate that the XRD pattern for the hemimorphite samples after surface sulfurization and then activated by Pb^{2+} had only a few changes compared with the pattern for native hemimorphite (Figs. 11a and b). However, when microwave sulfurization conditioned hemimorphite was subsequently activated by Pb^{2+}, more pronounced PbS peaks appeared. The results showed that microwave sulfurization facilitated sulfurization relative to surface sulfurization. These results showed that Pb^{2+} reacted with the newly formed sulfide layer on the surface of hemimorphite to generate PbS, which may have similar properties to galena and strong binding with SBX, increasing the adsorption of SBX on the surface of hemimorphite.

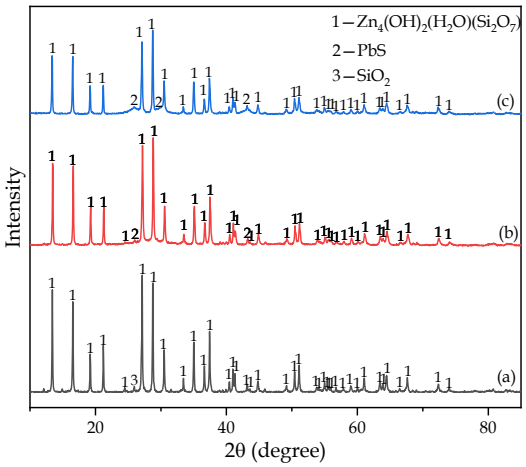

Fig. 11. XRD analysis of the sulfurization products obtained from different sulfurization methods; (a) hemimorphite, (b) surface sulfurization (hemimorphite + Na_2S+ Pb^{2+}), and (c) microwave sulfurization (hemimorphite + Na_2S + Pb^{2+})

3.5. Raman spectroscopy

Fig. 12 demonstrates the Raman spectra of the hemimorphite samples (sulfurization in different ways and activation by Pb^{2+}) conditioned with SBX. As seen from Fig. 12 (b and c), a new peak appeared at 195.76 cm^{-1}, which was caused by Zn-S, indicating that the sulfurization process was enhanced by the microwave field, which generated a sulfide layer on the surface of hemimorphite (Xu et al., 1997, Yu et al., 2003). The peaks at 384.75 cm^{-1} and 434.89 cm^{-1} were caused by Si-O-Si bending vibrations, and the peak strength decreased significantly after microwave sulfurization (Jian et al., 2009). The peaks at 689.46 cm^{-1} were caused by C-O-C bending vibrations. The peaks at 847.58 cm^{-1} were caused by C-C-O-C bending vibrations, and the peak strength was increased after microwave sulfurization (Gao et al., 2007). The Si-O symmetric stretching vibration generated a peak at 917.01 cm^{-1}, and the Si-O peak strength was decreased after sulfurization. The C-O-C peak at 689.46 cm^{-1} and C-C-O-C at 847.58 indicated that SBX was adsorbed on the surface of the microwave-sulfurized hemimorphite. In summary, the microwave field strengthened the sulfurization process of hemimorphite, advanced the formation of the sulfide layer on the surface of hemimorphite, and thus increased the reaction sites for hemimorphite and SBX, which facilitated the flotation of hemimorphite.

3.6. FTIR analysis

Fig. 13 shows the ATR-FTIR spectrum of SBX. In the infrared absorption spectrum, the spectral peak at 2964.05 cm^{-1} is an asymmetric stretching vibration of $-CH_3$. The symmetric vibration of $-CH_2$ appeared at 2871.49 cm^{-1} (Rath et al., 2000). The C-H bending modes for methylenes ($-CH_2$) generated a band at 1461.78 cm^{-1}. The peak at 1033.66 cm^{-1} is associated with C=S asymmetric stretching. The spectral peak with wavenumbers of 1187.94 cm^{-1} is assigned to the stretching vibration of C-O-C (Zhang et al., 2013a). Finally, the band at approximately 813.81 cm^{-1} for SBX was assigned to the C-S stretching vibration.

Fig. 14 shows the ATR-FTIR spectra of the hemimorphite samples treated with conventional surface

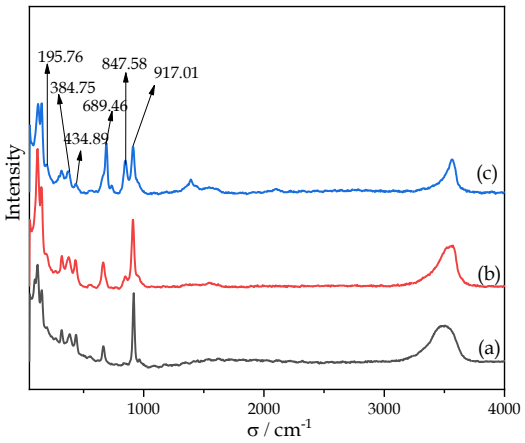

Fig. 12. Raman spectra showing the interactions between hemimorphite and SBX after different sulfurization methods; (a) hemimorphite, (b) surface sulfurization with SBX (hemimorphite + Na_2S + Pb^{2+} + SBX), and (c) microwave sulfurization with SBX (hemimorphite + Na_2S + Pb^{2+} + SBX)

sulfurization and microwave sulfurization, followed by SBX treatment. The infrared spectrum in Fig. 14a showed peaks at 676.94 cm^{-1} and 1087.74 cm^{-1} that were caused by symmetric and antisymmetric stretching vibrations of Si-O-Si groups. The peaks at 862.09 cm^{-1} and 921.88 cm^{-1} were due to Si-O antisymmetric stretching bending vibrations, respectively. The bending vibration of crystalline water gives a peak at 1633.53 cm^{-1}. The strong absorption band at approximately 3456.07 cm^{-1} was attributed to the stretching mode of the crystalline water in hemimorphite. The Zn-O and the Si-O bending vibrations gave peaks at 594.01 cm^{-1}, 541.94 cm^{-1} and 547.73 cm^{-1}(Jia et al., 2017). Fig. 14b shows the ATR-FTIR spectra of sulfurized hemimorphite conditioned with surface sulfurization (hemimorphite + Na_2S + Pb^{2+} + SBX). These bands were the same as those in Fig. 14a. Compared to the spectrum for the product of surface sulfurization in Fig. 14b, the spectra intensities of the Zn-O and the Si-O bands of hemimorphite conditioned with microwave sulfurization (Fig. 14c, hemimorphite + Na_2S (microwave sulfurization) + Pb^{2+} + SBX) were weaker. The C-O-C stretching vibrational peak appeared at 1203.45 cm^{-1} and the peak strength increased after microwave sulfurization. These data indicated that more SBX was adsorbed on the hemimorphite surface after microwave sulfurization. These results show that hemimorphite treated with microwave sulfurization more readily combines with xanthate, enabling the flotation of hemimorphite.

3.7. Mechanism

As microwaves penetrated the medium, the polar molecular dielectric and the nonpolar molecular dielectric formed dipoles, or the existing dipoles were rearranged. Additionally, the molecules vibrated and rearranged due to the microwave field(Mou and Li, 2004). In this process, the molecules overcame

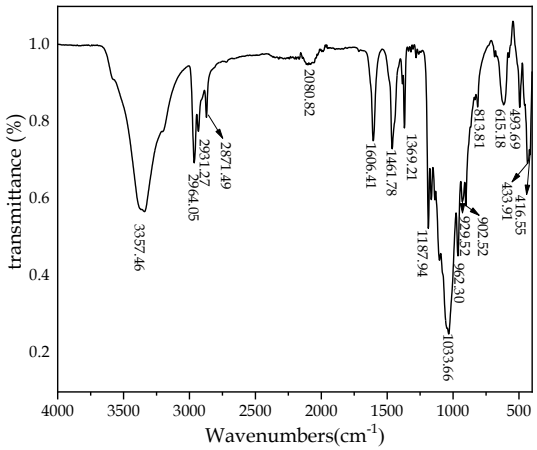

Fig. 13. Infrared spectrum of SBX

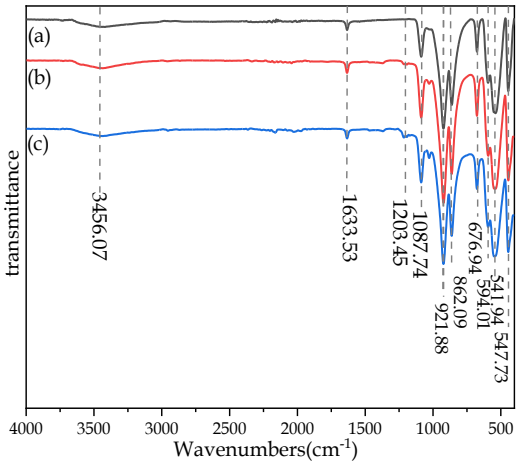

Fig. 14. Infrared spectra of (a) hemimorphite, (b) hemimorphite + Na_2S (surface sulfurization) + Pb^{2+}+ SBX, and (c) hemimorphite + Na_2S (microwave sulfurization) + Pb^{2+}+ SBX

the original thermal motions and the interactions between molecules, producing a friction-like effect, and then producing a large amount of heat(Fakhri et al., 2023, Norambuena-Contreras et al., 2018). The enhancement of the sulfurization process due to microwave irradiation may have occurred because microwaves generated molecular-level agitation and molecular rearrangements with the high-frequency electric field, which increased the probability of S^{2-} collisions with Zn on the surface of hemimorphite. Additionally, the substantial amount of heat generated by the microwaves accelerated the sulfurization reaction. The flotation phenomenon and these test results show that compared with the traditional surface sulfurization method, microwaves provide higher energy in a shorter time. Consequently, the degree of sulfurization achieved after 1 minute of microwave irradiation was significantly better than that obtained after 3 min of conventional surface sulfurization.

Based on the flotation process and the test results described above, a model was established for sulfurization hemimorphite under different sulfurization conditions (Na_2S pretreatment (in the presence or absence of microwave field) + Pb^{2+} activation) (Fig. 15). During conditioning in the Na_2S solution, zinc sulfide was generated on the surface of hemimorphite, and subsequently, PbS was also generated after adding Pb^{2+} activator. Because the molecular vibrations and rearrangements caused by microwaves generate a large amount of heat when hemimorphite sulfurization occurs in an applied microwave field. The presence of microwave fields promoted the collision of S and Zn atoms at the reaction interface, more ZnS and PbS were generated on the surface of hemimorphite, which facilitated the flotation process.

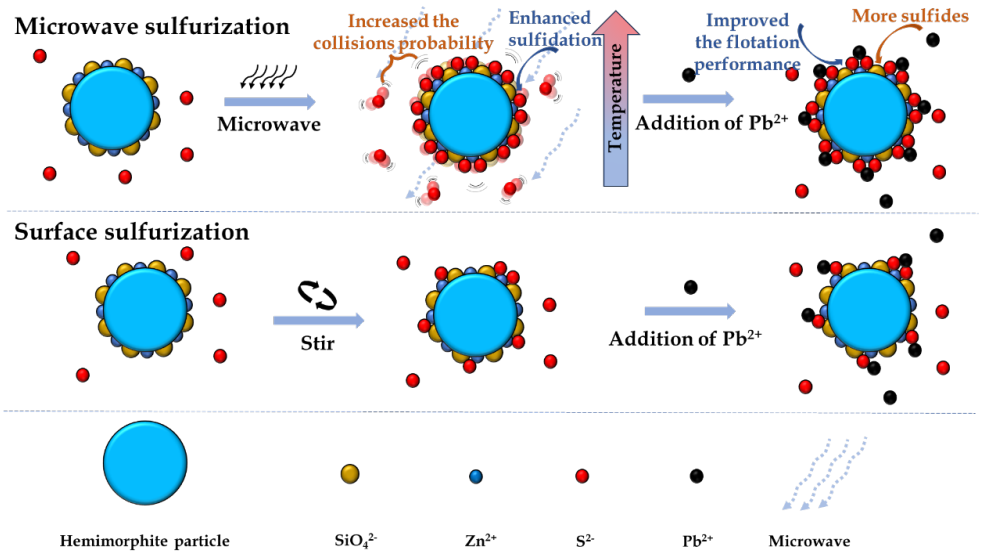

Fig. 15. Mechanism for hemimorphite sulfurization in a microwave field

4. Conclusions

(1) The flotation results showed that microwave irradiation during the sulfurization pretreatment process significantly improved the flotation of hemimorphite. When the concentration of Pb^{2+} was 2×10^{-3} mol/L, the flotation recovery of hemimorphite was 8.48%. After the sulfurization process with microwave radiation, the flotation recovery increased to 92.22%.

(2) During the sulfurization process, a sulfide layer was formed on the surface of hemimorphite. The S^{2-} in the solution reacted with Zn on the hemimorphite surface to form a sulfide layer on the mineral surface. The sulfide products on the mineral surface are mainly composed of ZnS and PbS. The sulfide layer on the mineral surface facilitated the flotation of hemimorphite.

(3) Microwave pretreatment enhanced the sulfurization of hemimorphite. The XPS and SEM results indicated that microwave sulfurization provided better sulfurization than conventional surface sulfurization, and the mineral surface adsorbed more S components. Infrared and Raman spectroscopy indicated that the collector showed stronger adsorption on the surface of hemimorphite following microwave sulfurization treatment, which improved the efficiency of SBX collection on hemimorphite. Compared with conventional surface sulfurization, the sulfurization product obtained with microwave irradiation contained a higher amount of metal sulfides on the surface, which increased the adsorption of SBX on the surface of hemimorphite and improved its floatability.

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