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Trans. Nonferrous Met. Soc. China 34(2024) 629−642

Transactions of Nonferrous Metals Society of China
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Sulfidization performance of hemimorphite surface in sodium sulfide system and identification of sulfidization products

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Received 22 June 2022; accepted 24 November 2022

Abstract: The sulfidization performance and mechanism of hemimorphite surface in a sodium sulfide (Na_2S) system were revealed, and surface sulfidization products were identified through various analytical methods. The results showed that Na_2S concentration had a significant effect on the sulfidization of the hemimorphite surface. An increase in Na_2S concentration could promote the interaction between S species in the pulp and mineral surfaces, thereby increasing the content of sulfidization products and hydrophobicity of hemimorphite surface. XPS and ToF-SIMS analyses showed that the sulfidization product was not the sole monosulfide on hemimorphite surfaces and it was composed of monosulfide (S^{2-}) and polysulfide (S_n^{2-}). The content of polysulfide on mineral surface increased with an increase in the Na_2S concentration, which improves the activity of sulfidization products on hemimorphite surface.

Key words: sulfidization performance; hemimorphite; Na_2S concentration; zinc sulfide species; polysulfide

1 Introduction

Zinc is an important non-ferrous metal that is widely used in zinc plating, biomedical applications, catalysis, and sensor components; in non-ferrous metal consumption, only copper and aluminum are ranked more highly than zinc [1−4]. Zinc is refined mainly from zinc sulfide ore, but some zinc is refined from zinc oxide ore [5]. However, with the exploitation of easily enriched zinc sulfide ores, these resources are gradually being depleted [6,7]. Developing and utilizing refractory zinc oxide minerals is important to reduce the discrepancy between the supply and the demand for zinc resources. Naturally occurring zinc oxide minerals with industrial value include hemimorphite ($Zn_4Si_2O_7(OH)_2H_2O$), willemite (Zn_2SiO_4), smithsonite ($ZnCO_3$), and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) [8−10]. Generally, zinc oxide ores contain a large amount of mud and iron-bearing minerals [11]. The strong hydrophilicity of zinc oxide minerals causes these minerals to be more difficult to recover than zinc sulfide minerals.

Hemimorphite is an important zinc oxide mineral. In the process of grinding and flotation, some zinc ions on the mineral surface are dissolved in the pulp solution [12]. At the same time, a hydroxylation reaction occurs on the surface of hemimorphite, resulting in the hemimorphite being strongly hydrophilic and having poor floatability. Thus, the direct flotation recovery of hemimorphite is poor. Therefore, it is necessary to add a sulfidization reagent to sulfidize the surface

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DOI: 10.1016/S1003-6326(23)66423-4

of hemimorphite and then use a collector for collection [13−15]. In the process of crushing and grinding hemimorphite, the Zn—O bonds are broken preferentially because the bond strength between the Si—O bonds is greater than that between the Zn—O bonds in hemimorphite. After the Zn—O bonds are broken, SiO_4^{2-} and Zn^{2+} are often exposed on the surface of hemimorphite [16]. However, Zn^{2+} can be shielded by SiO_4^{2-}, which has a larger volume and is more active, so the surface of the mineral shows similar surface properties to those of quartz. Thus, it is difficult for sulfide ions to interact with zinc sites on the surface of hemimorphite, resulting in slow sulfidization rate and low sulfidization efficiency. These factors make it difficult for the surface of hemimorphite to be sufficiently sulfidized; the lack of sulfidization is one of the reasons for the unsatisfactory flotation performance of hemimorphite.

Surface activation and enhanced sulfidization have been investigated to improve the flotation behavior of hemimorphite. ZHANG et al [17] found that the addition of metal ions (e.g., copper, lead, or zinc ions) before sulfidization increased the optimal pH range for hemimorphite flotation and improved the floatability. ZHAO et al [18] demonstrated that when Pb^{2+} was used to pretreat the surface of hemimorphite, and Zn−O−Pb and Si−O−Pb complexes were formed on its surface. Salicylic hydroxamic acid showed a strong interaction with these newly formed Pb complexes, which improved the hydrophobicity of the mineral surface. XING et al [16] showed that more zinc sites were exposed on the mineral surface after the interaction of fluorine ions with hemimorphite, which effectively increased the number of active sites on the mineral surface and created favorable conditions for the subsequent adsorption of the collector. The flotation properties, surface structure, and surface strengthening of hemimorphite have been widely studied. However, there have been few reports regarding the surface sulfidization process and analysis of the sulfidization products of hemimorphite. Therefore, an in-depth study on the potential mechanism of the formation of sulfidization products on the surface of hemimorphite would be useful to provide a theoretical basis for enhancing the sulfidization of hemimorphite.

Sulfidization flotation is the main method for the enrichment of hemimorphite [19], and sulfidization is critical for this process. However, the surface sulfidization mechanism and surface sulfidization products of hemimorphite have not been analyzed in-depth, and better knowledge of these aspects may improve the recovery of hemimorphite. In the present study, the generation and type of sulfidization products on hemimorphite were investigated using surface adsorption, contact angle, zeta potential measurements, and X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) analyses. The sulfidization characteristics of the hemimorphite surface and the evolution of the hydrophobicity of the hemimorphite surface after sulfidization were investigated.

2 Experimental

2.1 Materials and reagents

The hemimorphite samples used in this study were from Yunnan Province, China. The hemimorphite was crushed and purified by hand, and the surface of the hemimorphite was repeatedly washed with deionized water and dried. Then, the preliminarily crushed ore was ground by a three-head agate grinder, and the ground hemimorphite samples were screened by a standard sieve. Different sizes of mineral particles were obtained: particles <38 μm were used for surface adsorption and XPS analysis, and particles <5 μm were used for zeta potential measurements. The purity of the hemimorphite sample was determined by elemental analysis. The Zn content of the hemimorphite sample was 53.09 wt.%, which met the requirements for the measurements of a single mineral. X-ray diffraction (XRD) was used to analyze the mineral composition of the hemimorphite samples to determine the purity. As shown in Fig. 1, the XRD peaks of the hemimorphite samples were consistent with the standard peaks of the mineral provided in the JCPDS (Joint Committee on Powder Diffraction Standards) card (No. 85-1387), and no obvious impurity peaks were observed. These results indicate the purity of the samples used in the study. Deionized water (18.25 MΩ·cm) was used in all experiments.

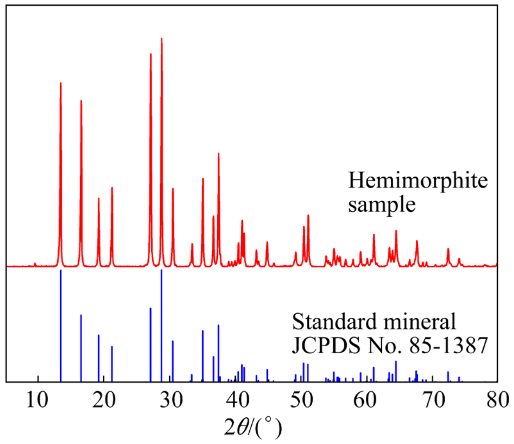

Fig. 1 XRD patterns of hemimorphite sample and standard mineral

2.2 X-ray photoelectron spectroscopy (XPS)

The XPS analysis was carried out using a PHI 5000 Versa Probe II X-ray photoelectron spectrometer produced by the ULVAC−PHI Company in Japan. The samples (1 g) were put into 50 mL of deionized water in a beaker, and then solutions of different concentrations of Na_2S were added to obtain the mixed solutions. The mixed solutions were stirred by magnetic stirring at 600 r/min for 30 min. After stirring, the samples were filtered and washed three times with deionized water. The samples were collected and dried in ambient conditions. The full and partial spectra of the surface elements of the samples were fitted and calculated using MultiPak spectral analysis software. The energy range of the full-spectrum scanning was 0−1400 eV. Using the surface contaminant C 1s (284.80 eV) as the standard, the spectral data were corrected and then fitted.

2.3 Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

ToF-SIMS analysis was carried out using a ToF-SIMS V spectrometer produced by ION-ToF. Hemimorphite samples with smooth surfaces were obtained by manual slicing and polishing. Deionized water (50 mL) was added to a 100 mL beaker, different concentrations of Na_2S were added, and block hemimorphite samples were put into the solutions for 10 min; the samples were then removed. The samples were rinsed with deionized water three times and dried at room temperature, after which they were subjected to vacuum pumping. After the vacuum value was increased to the test range, the samples were used for ToF-SIMS analysis.

2.4 Adsorption experiment

The sulfide ion adsorption test on the surface of hemimorphite was carried out as follows. 1 g of pure hemimorphite was placed into 25 mL of deionized water and the pulp was stirred at 600 r/min and room temperature. A freshly prepared solution of $Na_2S\cdot 9H_2O$ was added to act on the mineral surface under ambient conditions. After stirring for 10 min, 15 mL of the mixed solution was extracted and passed through a centrifuge for solid−liquid separation. The separated liquid was collected and tested for residual S by inductively coupled plasma optical emission spectroscopy (ICP-OES; Thermo ICAP PRO, Germany).

2.5 Zeta potential tests

Zeta potential measurements were carried out using a Zetasizer−3000HS surface potential meter from Malvern, UK. 0.05 g hemimorphite sample was added to a beaker containing KCl solution, followed by the addition of the required reagent; the pulp was then stirred magnetically for 5 min. The suspension was extracted using a plastic siphon (2 mL) and transferred to the measurement vessel. The zeta potential was measured at 20 °C, and the measurements were repeated three times under different concentrations of Na_2S. The final reported value was the average value of the samples.

2.6 Contact angle measurements

Hemimorphite slices (10 mm × 10 mm × 2 mm) were ground, polished, washed, and placed into solutions of different concentrations of Na_2S. After soaking for 5 min, the slices were washed with deionized water and dried under ambient conditions. Then, the contact angle was measured by a JY−82B video contact angle goniometer (Chengde Dingsheng Testing Machine Co., Ltd., China).

3 Results and discussion

3.1 Distribution of S species

The distribution coefficients of various S species in the Na_2S solution as a function of pH are shown in Fig. 2. Na_2S in solution is firstly ionized to form S^{2-}, and then hydrolyzed to form HS^- and H_2S. At the solution pH<7.0, Na_2S mainly exists in the form of H_2S; at pH>4.0, HS^- species begins to appear, and its content increased with the increase of solution pH; at 7.0<pH<13.9, HS^- becomes the dominant component in the solution; at pH>13.9, the sulfide species in Na_2S mainly exists in the form of S^{2-} in solution. In this study, the pulp pH is within the range of 10.3−12.0 after different concentrations of Na_2S solutions are added to the hemimorphite pulp, so HS^- is the dominant species interacted with the mineral surface.

3.2 XPS spectra

The XPS spectra of the hemimorphite after reaction with different concentrations of Na_2S solutions are shown in Fig. 3. As shown in Fig. 3(a), the characteristic peaks of Zn 2p, Si 2p, O 1s, and C 1s can be observed. However, there was no characteristic peak for the S species in the spectra of the pure minerals; the absence of this element indicates the purity of the minerals. After treatment with a solution of 3×10^{-4} mol/L Na_2S (Fig. 3(b)), the S species were adsorbed on the mineral surface; thus, S 2s and S 2p peaks were evident in the spectra of the sulfidized hemimorphite. As the concentration of Na_2S concentration increased (Figs. 3(c) and (d)), the S 2s and S 2p peaks in the hemimorphite spectra became more obvious. This phenomenon indicates that with increasing concentrations of the Na_2S solutions, the probability of contact between the S species and the mineral surface increased. Therefore, larger amounts of S species were adsorbed onto the mineral surface at higher concentrations.

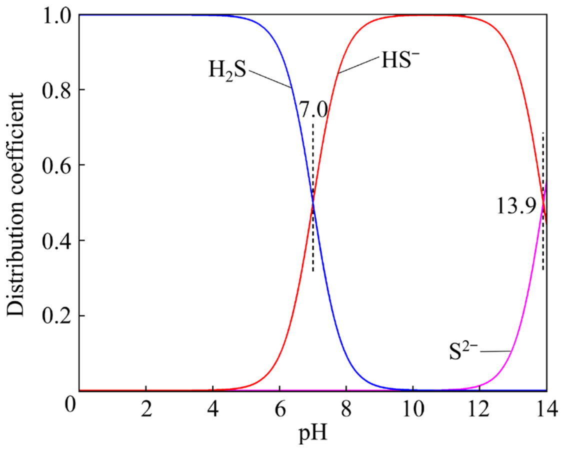

Fig. 2 Distribution coefficients of various S species in Na_2S solutions as function of pH

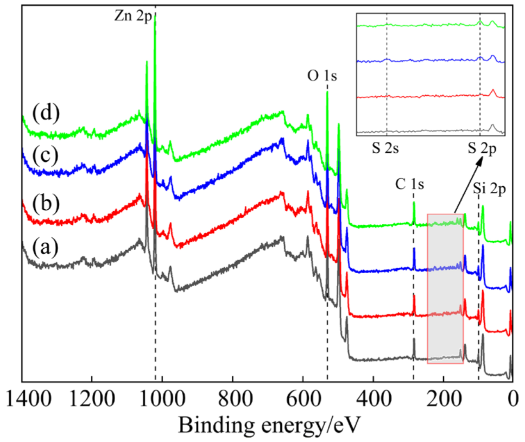

Fig. 3 XPS survey spectra of hemimorphite sulfidized with different Na_2S concentrations: (a) 0 mol/L; (b) 3×10^{-4} mol/L; (c) 7.5×10^{-4} mol/L; (d) 3×10^{-3} mol/L

The molar fractions for the main elements on the surface of hemimorphite after treatment with different concentrations of Na_2S are shown in Table 1. As the concentration of Na_2S increased, the S 2p molar fraction on the surface of hemimorphite increased (1.52%, 2.53%, and 3.69%, respectively), which was consistent with the results for XPS. The molar fraction of O 1s decreased from 57.52% (Sample a) to 53.57% (Sample d). This result indicated that with an increase in the S species formation, the hydroxylation of the mineral surface decreased, which may lead to a decrease in the —OH species. As the adsorption of S 2p increased, the content of the Zn 2p and Si 2p species on the mineral surface changed slightly.

Table 1 Element contents of hemimorphite samples sulfidized with different Na_2S concentrations

Na_2S concentration/	Element content/at.%			
($mol\cdot L^{-1}$)	Si 2p	O 1s	Zn 2p	S 2p
0 (Sample a)	11.22	57.52	31.26	0.00
3×10^{-4} (Sample b)	11.70	54.94	31.84	1.52
7.5×10^{-4} (Sample c)	12.01	53.73	31.73	2.53
3×10^{-3} (Sample d)	11.91	53.57	30.83	3.69

To gain more insight into the sulfidization mechanism of hemimorphite, we fitted the O 1s, S 2p, Si 2p, and Zn 2p spectral peaks on the hemimorphite surface after treatment with different concentrations of Na_2S. In Fig. 4(a), the O 1s XPS spectra can be fitted to three peaks with different binding energies. The spectral peaks with binding energies at 531.36, 532.00, and 533.39 eV can be attributed to —Zn—O, —Si—O, and —OH species, respectively, on the surface of hemimorphite [13,14]. As shown in Fig. 4(b) and

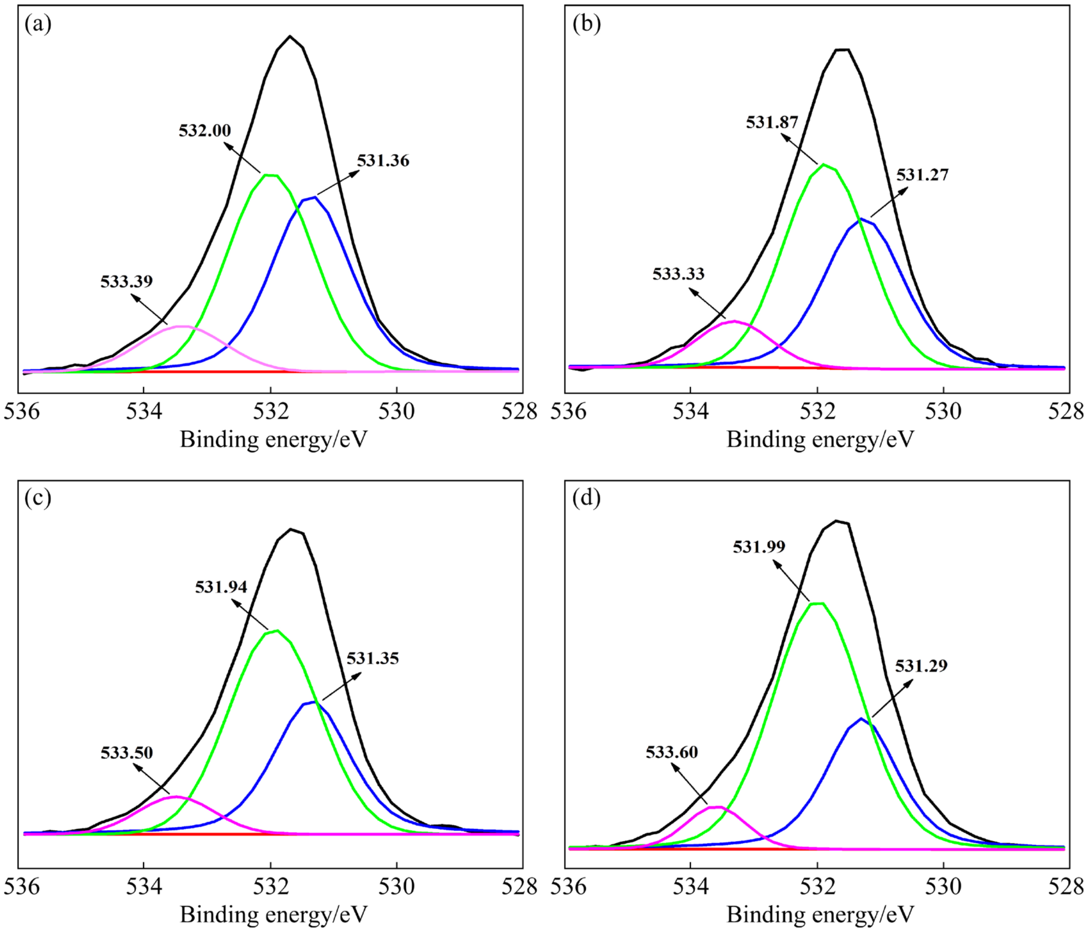

Fig. 4 O 1s XPS spectra of hemimorphite sulfidized with different Na_2S concentrations: (a) 0 mol/L; (b) 3×10^{-4} mol/L; (c) 7.5×10^{-4} mol/L; (d) 3×10^{-3} mol/L

Table 2, compared with the unsulfidized hemimorphite, the binding energies of the O species changed slightly after treatment with 3×10^{-4} mol/L Na_2S. The content of O in hydroxyl compounds decreased from 10.67% to 9.85%, making the hemimorphite less hydrophilic. At a Na_2S concentration of 7.5×10^{-4} mol/L (Fig. 4(c)), the binding energy of the —OH species shifted to 533.50 eV, and the binding energy of the —Zn—O and —Si—O species changed slightly. As can be seen in Table 2, the —OH species decreased to 8.45% at this higher concentration. This phenomenon indicates that the changes in the chemical environment on the mineral surface were more obvious for the —OH component than for the other species. The hydroxylation of the mineral surface decreased and the activity was improved at the higher concentration of Na_2S. After treatment with 3×10^{-3} mol/L Na_2S, the binding energy of the O present in the hydroxyl compounds on the surface of the mineral was 533.60 eV, and the

Table 2 O 1s quantification of hemimorphite samples sulfidized with Na_2S concentrations of 0, 3×10^{-4}, 7.5×10^{-4}, and 3×10^{-3} mol/L

Sample	Species	Binding energy/eV	Species proportion/%
a	—Zn—O	531.36	43.00
	—Si—O	532.00	46.33
	—OH	533.39	10.67
b	—Zn—O	531.27	39.57
	—Si—O	531.87	50.58
	—OH	533.33	9.85
c	—Zn—O	531.35	36.11
	—Si—O	531.94	55.44
	—OH	533.50	8.45
d	—Zn—O	531.29	30.00
	—Si—O	531.99	63.10
	—OH	533.60	6.90

content of O in the hydroxyl compounds decreased from 10.67% to 6.90% (Fig. 4(d)). These results indicate that high concentrations of Na_2S affected the chemical state of O atoms on the surface of hemimorphite to decrease the content of the total O present in hydroxyl groups. In summary, with increasing the Na_2S concentration, more sulfidization products were formed, and the content of O in hydroxyl compounds showed a decreasing trend.

Figure 5 shows the S 2p spectra of sulfidized hemimorphite samples after treatment with different concentrations of Na_2S. No obvious peak of S 2p was detected in the spectrum of unsulfidized hemimorphite (Fig. 5(a)). As shown in Fig. 5(b), the peak at 161.43 eV in the S 2p spectrum of the sulfidized hemimorphite surface was attributed to S^{2-}, and the peak at 163.28 eV was attributed to S_n^{2-} [7,20−22]. These generated S^{2-} and S_n^{2-} components suggest that a large amount of S components were adsorbed on the surface of the hemimorphite after sulfidization. As shown in Figs. 5(c) and (d), with increasing concentration of Na_2S, the binding energy changed only slightly, which indicates that the sulfidization products were still S^{2-} and S_n^{2-} species at high concentrations. However, the formed characteristic peak intensity increased with an increase in the Na_2S concentration in the solution, which may be caused by the adsorption of more S species on the hemimorphite surface. In addition, the sulfidization products on the surface of hemimorphite consist of monosulfide and polysulfide; polysulfide is important for enhancing the floatability of the mineral [6]. Therefore, we explored the content of different S species formed under different conditions. The results are shown in Fig. 6.

Figure 6 shows the contents of S species on hemimorphite sample sulfidized with different concentrations of Na_2S. When the Na_2S concentration was 3×10^{-4} mol/L, the contents of monosulfide and polysulfide species accounted for 1.33% and 0.19% of the total S content, respectively. It may be inferred that Zn—S and Zn — S_n species were present on the sample's surface, and that monosulfide was not the only sulfidization product on the surface of hemimorphite; polysulfide species were also present. After treatment

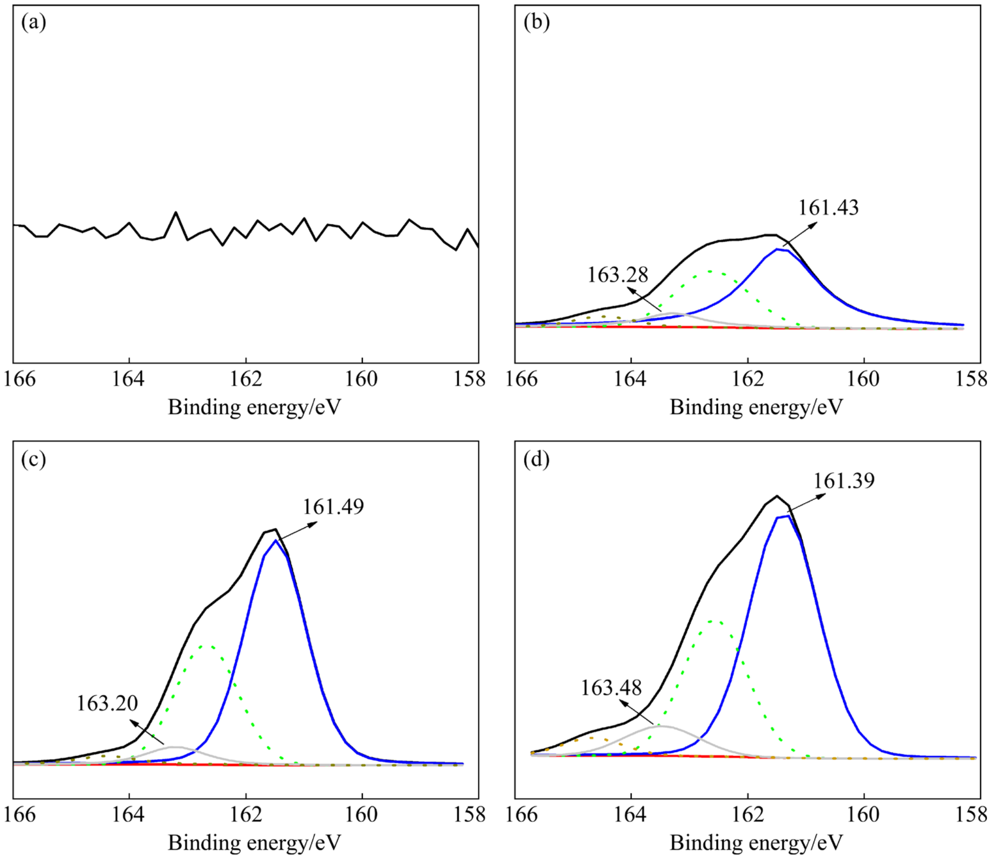

Fig. 5 S 2p XPS spectra of hemimorphite sulfidized with different Na_2S concentrations: (a) 0 mol/L; (b) 3×10^{-4} mol/L; (c) 7.5×10^{-4} mol/L; (d) 3×10^{-3} mol/L

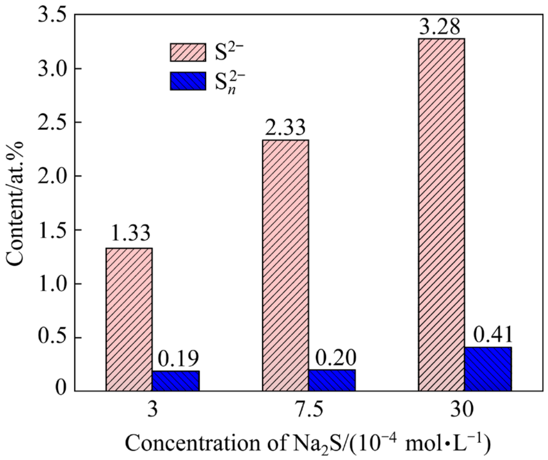

Fig. 6 Contents of S species on hemimorphite samples sulfidized with different Na_2S concentrations

with a solution of 7.5×10^{-4} mol/L Na_2S, the contents of monosulfide and polysulfide species increased to 2.33% and 0.20%, respectively. When the Na_2S concentration increased to 3×10^{-3} mol/L, the content of monosulfide on the mineral surface increased to 3.28%, and the content of polysulfide was 0.41%. These results show that with increasing Na_2S concentration, the content of S species on the surface of hemimorphite increased significantly. FENG et al [6] have shown that at a Na_2S concentration of 7.5×10^{-4} mol/L, the content of S atoms accounted for 13.96% of the total S content, and monosulfide and polysulfide species accounted for 9.01% and 4.95% of the total S content, respectively, in smithsonite. These values were much higher than those observed for hemimorphite, i.e., hemimorphite is more difficult to sulfidize than smithsonite, which may be one of the reasons for the lower selectivity of hemimorphite compared with smithsonite.

Figure 7 shows the XPS spectra of Si 2p on the surface of hemimorphite after treatment with different concentrations of Na_2S. The binding energy of Si 2p on the mineral surface was not significantly changed, which indicated that the adsorption of S component had no noticeable effect on the chemical state of Si in the mineral. Figure 8 shows the XPS spectra of Zn 2p on the hemimorphite surface after treatment with different concentrations of Na_2S. The binding energy of the

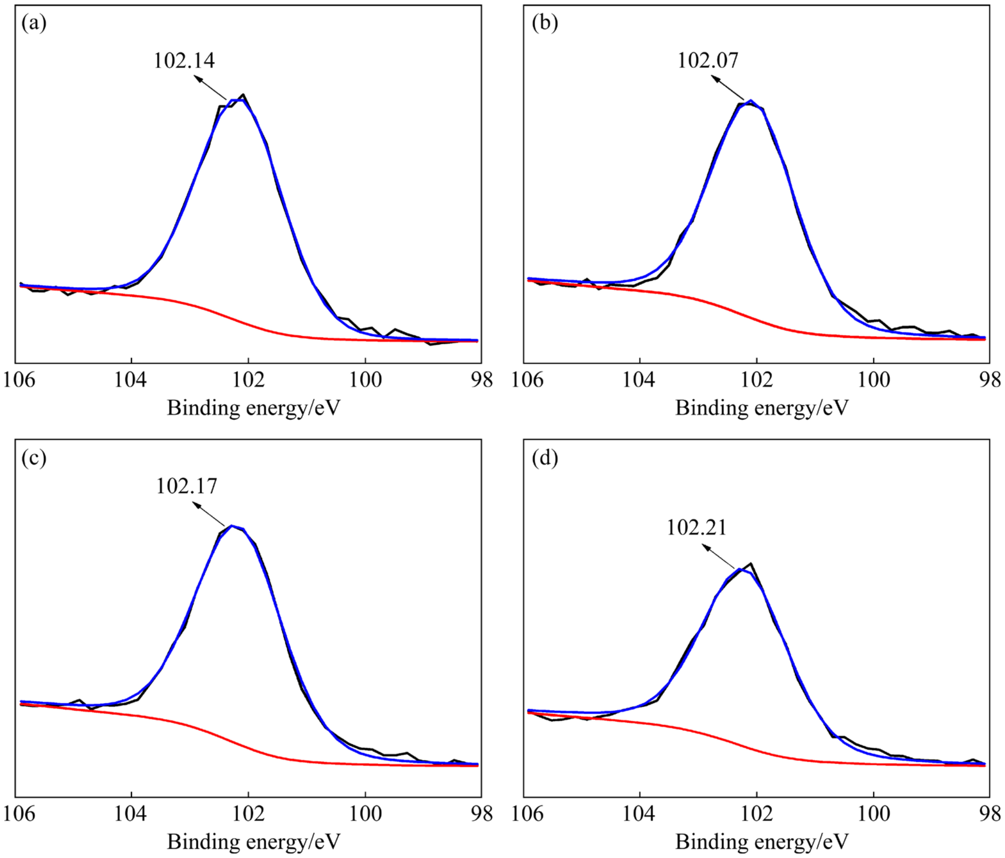

Fig. 7 Si 2p XPS spectra of hemimorphite sulfidized with different Na_2S concentrations: (a) 0 mol/L; (b) 3×10^{-4} mol/L; (c) 7.5×10^{-4} mol/L; (d) 3×10^{-3} mol/L

Zn species was shifted after sulfidization. These results show that the reaction between the zinc component and the sulfur component in Na_2S led to the formation of sulfidization products (Zn−S and Zn−S_n species) on the mineral surface.

3.3 ToF-SIMS results

ToF-SIMS is a means of analyzing the chemical composition of a mineral surface. ToF-SIMS analysis (two-dimensional distribution, semi-quantitative analysis, three-dimensional distribution, or negative-ion depth profiling) has been used to characterize the S species on the surface of different grades of minerals treated with different concentrations of Na_2S [23−25].

First, we analyzed the 2D distribution of sulfur species (S^- and S_2^-) signals on the mineral surface at different concentrations of Na_2S. Figure 9(a) shows the 2D distribution of S^- and S_2^- signals of the unsulfidized hemimorphite; only a small number of fragment peaks for S species were detected. Figures 9(b), (c), and (d) show the 2D distribution of S^- and S_2^- signals after treatment with different concentrations of Na_2S. S^- and S_2^- signals were detected on the surface of the sulfidized hemimorphite; these signals were more obvious with increasing Na_2S concentrations. These results are consistent with those obtained from XPS. In addition, with increasing the Na_2S concentration, the signal intensity of the component decreased, which may be due to the increased adsorption of S species shielding the ionic signal of the samples.

The normalized negative ion strength of the hemimorphite surface is shown in Fig. 10. A large number of SiO_3^- signals and a small number of S^- signals were detected on the surface of unsulfidized hemimorphite. SiO_3^- signals correspond to SiO_4^{2-} ions in hemimorphite. S^- signals may have been sputtered by a monosulfide, and S_2^- may have been sputtered by a polysulfide. Compared with the unsulfidized hemimorphite, the SiO_3^- signal on the surface of the sulfidized hemimorphite was reduced; the S^- and S_2^- signals were increased, indicating that S species were transferred to the surface of the samples; and zinc sulfide species were formed, resulting in the observed decrease in the relative

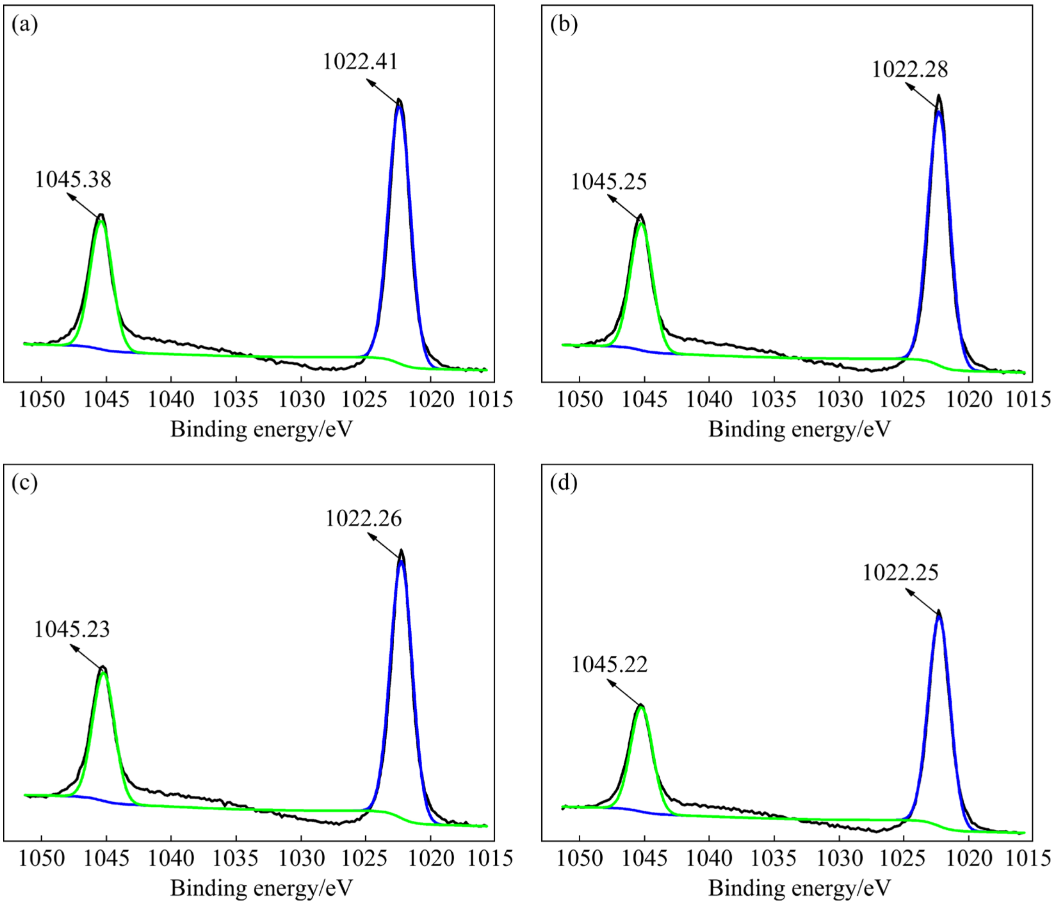

Fig. 8 Zn 2p XPS spectra of hemimorphite sulfidized with different Na_2S concentrations: (a) 0 mol/L; (b) 3×10^{-4} mol/L; (c) 7.5×10^{-4} mol/L; (d) 3×10^{-3} mol/L

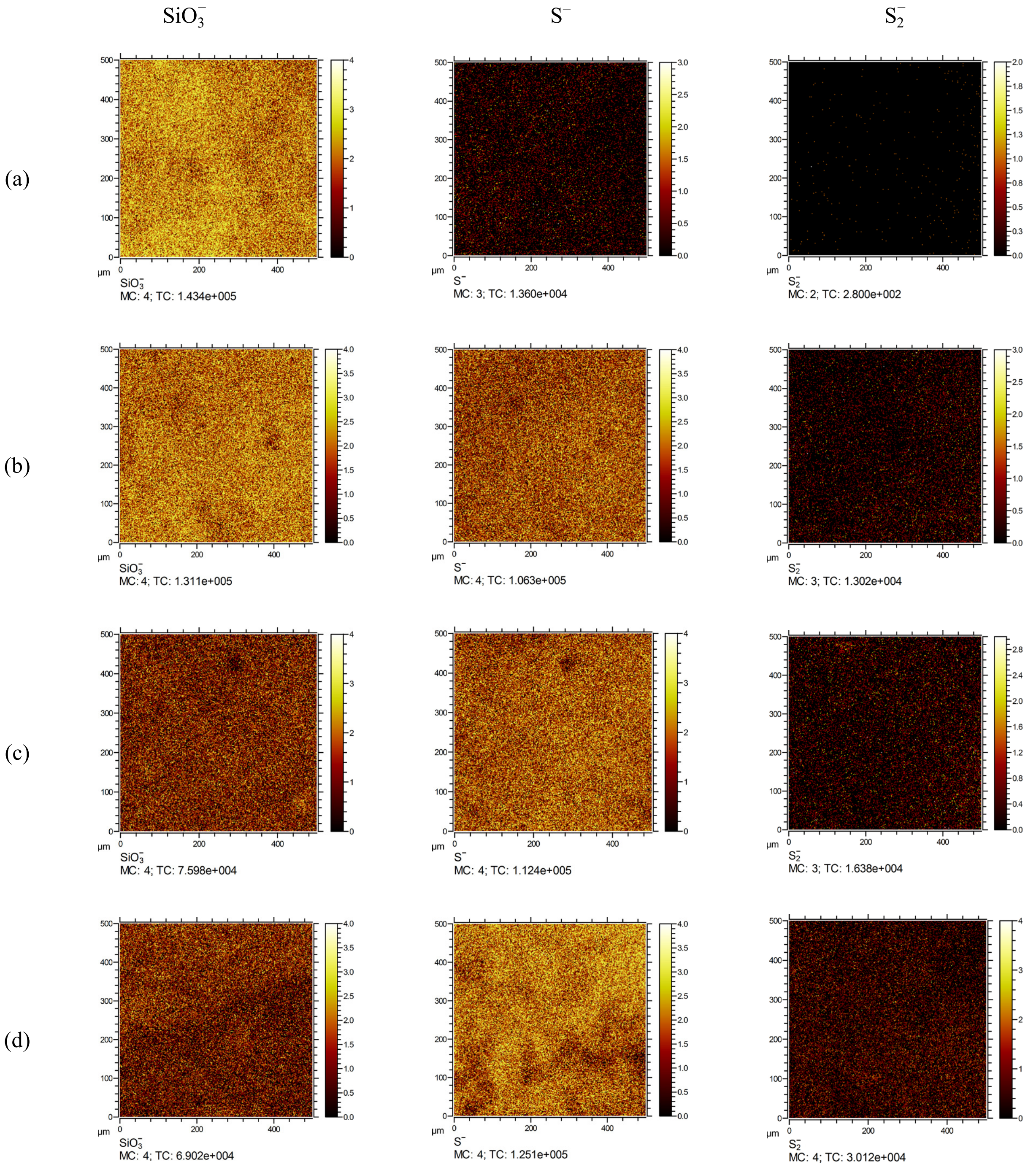

Fig. 9 ToF-SIMS 2D ion fragment distribution of SiO_3^-, S^-, and S_2^- on hemimorphite surface after treatment with different Na_2S concentrations: (a) 0 mol/L; (b) 3×10^{-4} mol/L; (c) 7.5×10^{-4} mol/L; (d) 3×10^{-3} mol/L

content of SiO_3^-. With increasing the Na_2S concentration, S^- and S_2^- signals were further increased. This result implies that increasing the concentration of Na_2S can increase the sulfide concentration on the surface of the sample, resulting in the formation of more zinc sulfide species. This observation is consistent with the XPS results.

To further analyze the adsorption layer of the S species (S^- and S_2^-) on the surface of hemimorphite, we performed ToF-SIMS depth profiling of the S^- and S_2^- signals to obtain the 3D distribution of samples. In Fig. 11(a), the S^- and S_2^- signals are almost absent on the surface of the sample, indicating that there are no S species in pure minerals. After treatment with Na_2S, obvious S^- and S_2^- species (Figs. 11(b), (c), and (d)) coating layers were observed on the surface of the mineral. With increasing the Na_2S concentration, the coating of S^-

and S_2^- components became denser. The S species in the solution migrated to the hemimorphite surface during the sulfidization process, and the generated sulfidization products had a certain spatial depth.

To further investigate the 3D distribution of S species on the surface of the sample, we plotted the deep profile curves of the SiO_3^-, S^-, and S_2^- ions, before and after the sulfidization of hemimorphite. In Fig. 12(a), the SiO_3^-, S^-, and S_2^- signals leveled off with an extension of etching time, which was caused by the extremely weak intensity of the S^- and S_2^- signals because only mineral ion signal was present on the surface layer of hemimorphite before the reaction with Na_2S. The deep profile curve was

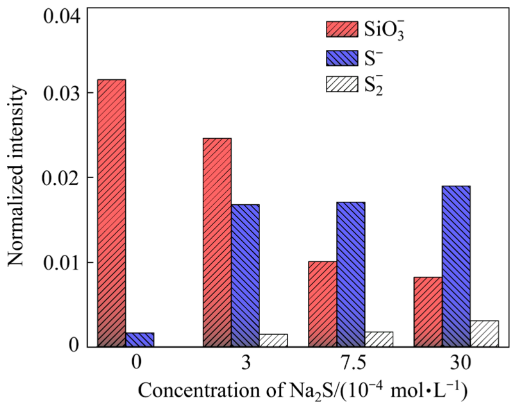

Fig. 10 Normalized peak intensities of negative ion ToF-SIMS of hemimorphite samples sulfidized with different Na_2S concentrations

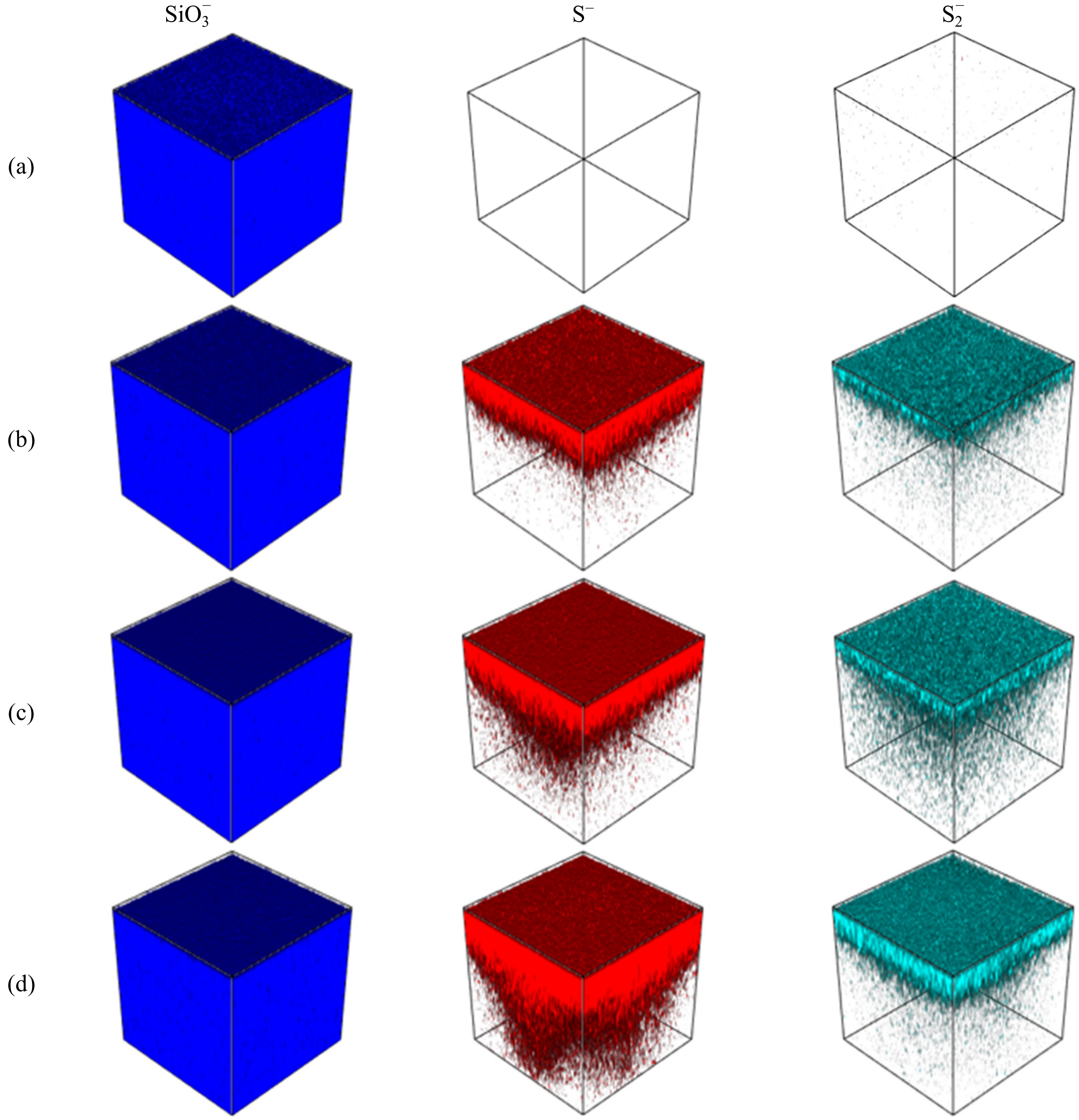

Fig. 11 ToF-SIMS 3D ion fragment distribution of negative ions on hemimorphite surface after treatment with different Na_2S concentrations: (a) 0 mol/L; (b) 3×10^{-4} mol/L; (c) 7.5×10^{-4} mol/L; (d) 3×10^{-3} mol/L

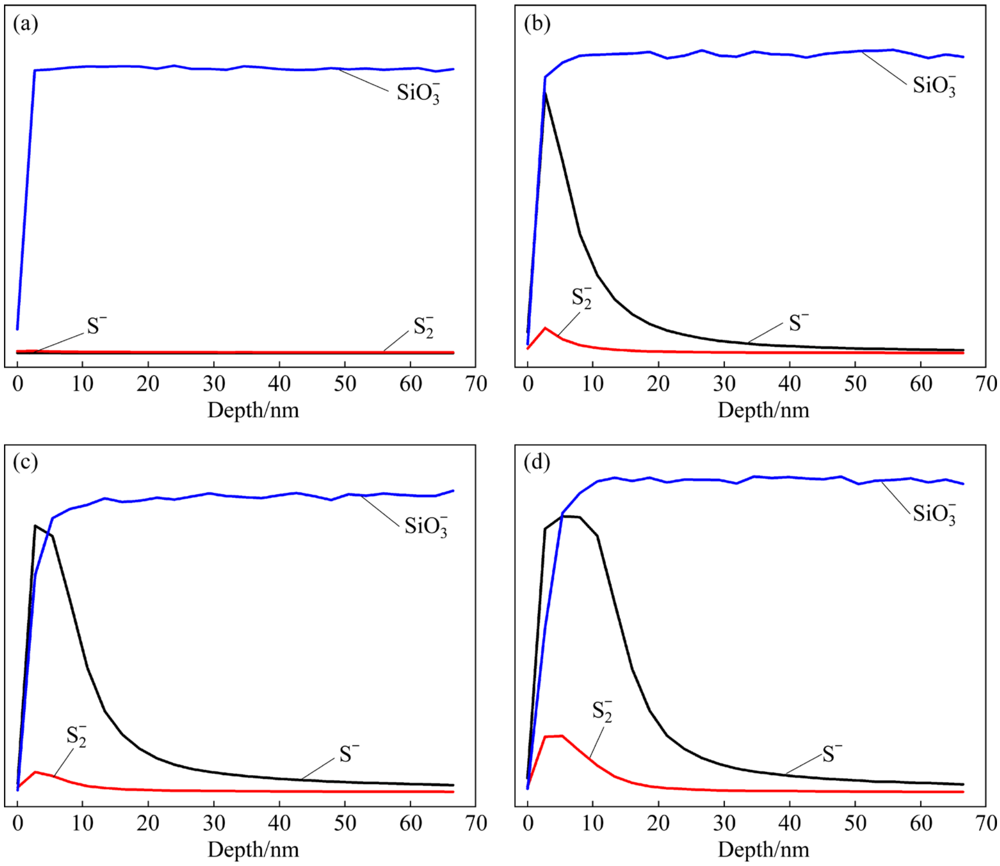

Fig. 12 ToF-SIMS negative ion depth distribution on hemimorphite surface after treatment with different Na_2S concentrations: (a) 0 mol/L; (b) 3×10^{-4} mol/L; (c) 7.5×10^{-4} mol/L; (d) 3×10^{-3} mol/L

obtained by the gradual etching of the negative ions from the sulfidization products at the top layer of the mineral surface to the lower layer of the hemimorphite. Therefore, when hemimorphite was sulfidized (Figs. 12(b), (c), and (d)), the intensity of the signals of the S^- and S_2^- decreased with the extension of etching time. The higher the concentration of Na_2S was, the more slowly the intensity of the S^- and S_2^- signals decreased. The intensity of the S_2^- signal was weaker than that of the S^- signal, i.e., the content of monosulfide on the mineral surface was higher than that of polysulfide. The results showed that the sulfidization products were generated on the mineral. With increasing the concentration of Na_2S, the thickness of the sulfide layer on the mineral surface increased, and the sulfidization product on the mineral surface was mainly monosulfide.

3.4 Adsorption characteristics

In the sulfidization of hemimorphite, the S in the solution transfers to the mineral surface. The adsorption amount of sulfide ions on the surface of hemimorphite was determined by the concentration difference (initial S concentration minus residual S concentration).

Figure 13 shows the amount of S adsorbed onto hemimorphite after treatment with different concentrations of Na_2S. As shown in Fig. 13, with increasing the concentration of Na_2S, the probability of the S species contacting the sample surface was increased, resulting in more S components being adsorbed on the mineral surface. This result is consistent with the results of the XPS and ToF-SIMS analyses. Some of the S species added to the pulp were transferred to the mineral surface and combined with Zn on the mineral surface to generate Zn−S and Zn−S_n compounds. With increasing Na_2S concentration, the amount of Zn−S and Zn−S_n substances increased, and the surface activity of hemimorphite increased. However, when too much Na_2S is added to the pulp, a large number of sulfide ions will remain in the pulp. These residual ions will affect the adsorption of subsequent collectors, thereby affecting the floatability of the mineral.

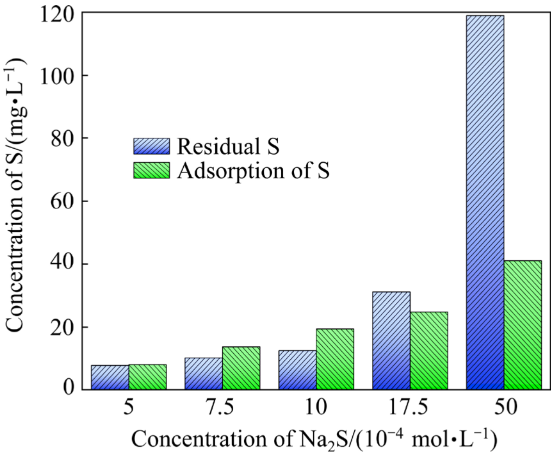

Fig. 13 Residual and adsorption concentrations of S from hemimorphite after treatment with different concentrations of Na_2S

3.5 Zeta potential

The XPS, ToF-SIMS, and adsorption measurement results show that with increasing the Na_2S concentration, more S species were adsorbed on the hemimorphite surface, resulting in the formation of more zinc sulfide components. Therefore, we analyzed the effect of sulfidization on the surface of hemimorphite by measuring the changes in the zeta potential of hemimorphite after treatment with different concentrations of Na_2S.

Figure 14 shows the zeta potential values of hemimorphite after treatment with different concentrations of Na_2S. In the absence of Na_2S, the zeta potential of hemimorphite was −30.9 mV. When Na_2S was added, the zeta potential of hemimorphite decreased with increasing the Na_2S concentration because the negatively charged S species can interact with zinc sites on the surface, resulting in a large number of sulfide ions adsorbed on the surface of hemimorphite. The zeta potential measurements show that increasing the Na_2S concentration resulted in the adsorption of more sulfide ions on the mineral surface. The adsorption of the negatively charged S species resulted in the observed decrease in the zeta potential of the mineral surface.

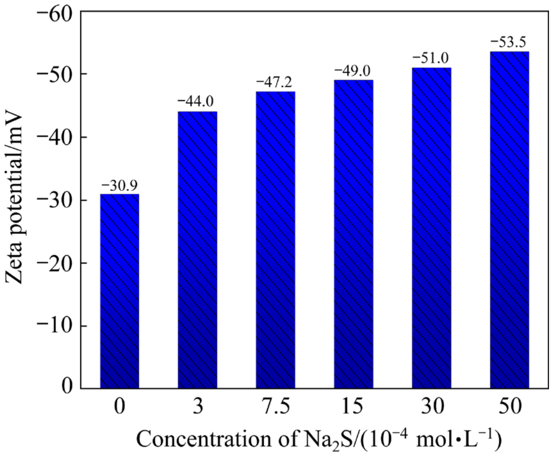

Fig. 14 Zeta potential of hemimorphite after treatment with different concentrations of Na_2S

3.6 Contact angle

The contact angle is the most intuitive means to reflect the hydrophobicity of a mineral surface [26−28]. Figure 15 shows the contact angle of hemimorphite after treatment with different concentrations of Na_2S. As shown in Fig. 15(a), the contact angle of untreated hemimorphite was 45.24°, indicating that the untreated mineral surface has strong hydrophilicity, which is consistent with previous results [29]. With increasing Na_2S concentrations to 3×10^{-4}, 7.5×10^{-4}, and 1.5×10^{-3} mol/L, the contact angles were respectively increased by approximately 7°, 10°, and 15° compared with those of pure hemimorphite, and the contact angle and the surface hydrophobicity of the hemimorphite increased. Combined with the XPS and ToF-SIMS results, these results indicated that with increasing the Na_2S concentration, more sulfide ions were adsorbed

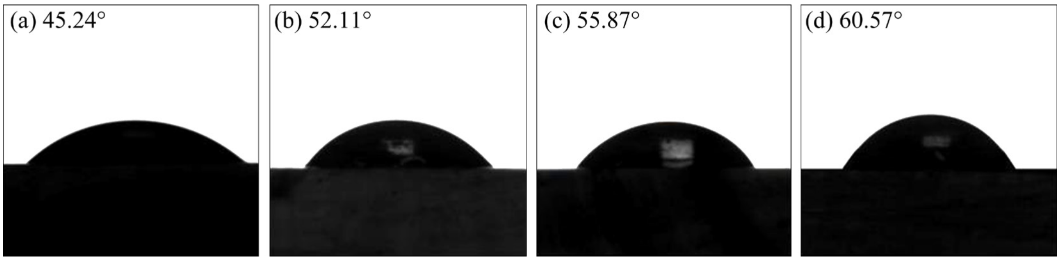

Fig. 15 Contact angles of hemimorphite after treatment with different concentrations of Na_2S: (a) 0 mol/L; (b) 3×10^{-4} mol/L; (c) 7.5×10^{-4} mol/L; (d) 1.5×10^{-3} mol/L

from the pulp solution and highly active sulfidization products were formed on the mineral surface, which resulted in increased hydrophobicity of the mineral surface. The amount of zinc sulfide components was increased significantly, increasing the surface hydrophobicity, which will be beneficial to the flotation recovery of hemimorphite.

4 Conclusions

(1) In the sulfidization process, HS^- species is the dominant component in the solution. S species in solution can be adsorbed on the hemimorphite surface, and it interacted with Zn sites on the mineral surface to produce Zn−S species. The sulfidization product of mineral surfaces was composed of monosulfide and polysulfide, and the surface polysulfide positively contributed to the activity of sulfidization products of hemimorphite.

(2) Increasing the Na_2S concentration was beneficial to the generation of sulfidization products and enhancement of surface reactivity. And the surface hydrophobicity of hemimorphite increased with an increase in the Na_2S concentration, which was conductive to the improvement of hemimorphite floatability. These results provide a theoretical basis for the sulfidization flotation recovery of hemimorphite, which will support the efficient recovery of zinc oxide minerals.

CRediT authorship contribution statement

Ga ZHANG: Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing − Original draft preparation; **Mei-li WANG:** Investigation, Resources, Supervision, Writing – Review & editing; **Yong-xin HE:** Resources, Supervision, Writing – review & editing; **Han WANG:** Data curation, Formal analysis, Investigation, Methodology, Software, Writing – Review & editing; **Qi-cheng FENG:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Writing – Review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 52264026), and the Ten Thousand Talent Plans for Young Top-notch Talents of Yunnan Province, China (No. YNWR-QNBJ-2018-051).

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硫化钠体系中异极矿表面的硫化特性及硫化产物解析

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摘　要：通过多种分析检测方法揭示硫化钠体系中异极矿表面的硫化特性和机理，并对异极矿表面硫化产物进行分析测试。研究结果表明，硫化钠浓度对异极矿表面的硫化效果具有显著影响，即提高硫化钠浓度能促进矿浆溶液中硫组分与矿物表面反应，从而提高异极矿表面硫化产物的含量及矿物表面的疏水性。XPS 和 ToF-SIMS 分析表明，异极矿表面的硫化产物并非单一的硫化物，而是由硫化物(S^{2-})和多硫化物(S_n^{2-})组成，且矿物表面多硫化物含量随硫化钠浓度的增加而增加，从而增强异极矿表面硫化产物的活性。

关键词：硫化特性；异极矿；硫化钠浓度；硫化锌组分；多硫化物

(Edited by Wei-ping CHEN)