Lead species formation on pure hemimorphite surface and its performance for subsequent sulfidization

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Abstract: Hemimorphite is important-supplementary resource for the commercial zinc production, but it easy loses into tailings due to extreme difficulty for its surface sulfidization. Adding active metal ions after sulfidization have been widely proposed for enhancing hemimorphite floatability, but its desired efficiency in flotation practice has not yet been completely achieved caused by the instability of sulfide layer. Whereas pre-adsorption of active metal ions to modify the hemimorphite surface has strong potential to make up for this shortcoming. Herein, the feasibility and appropriate environment of free Pb^{2+} for modifying the pure hemimorphite surface was evaluated. Subsequently, the performance of Pb^{2+} adsorption for enhancing sulfidization stability and floatability of hemimorphite were investigated. The X-ray photoelectron spectroscopy results indicated that the Pb^{2+} adsorption on hemimorphite surface was achieved through the Pb ions displacement for Zn ions, and it was bond to oxygen-containing groups on hemimorphite surface. Such adsorption was strengthened with the increasing of solution pH, owing to the abundant Pb hydroxyl species precipitated on mineral under alkaline conditions, in term of the results of visual MINTEQ modeling and time-of-flight secondary-ion mass spectrometry. In addition, the X-ray photoelectron spectroscopy results showed dominant Pb hydroxyl species further reacted with sulfur during subsequent sulfidization to generate much more S species than that of without Pb^{2+} pre-modification. Meanwhile, such sulfide layer composed by Pb^{2+} on the mineral surface presented much higher stability than Zn-S species, which was verified via adsorption and desorption tests. As a result, the sulfidization and flotation recovery of hemimorphite increased after Pb^{2+} pre-adsorption.

Keywords: hemimorphite, lead ions adsorption, hydroxy lead, sulfidization, xanthate flotation

1. Introduction

Zinc oxide minerals are often found in the weathering region of most large-scale Pb-Zn deposits at significant proportion, and they are an important-supplementary resource for the commercial zinc production with the steadily consumption of easy-handle zinc sulfides (Boni et al., 2009; Reichert and Borg, 2008; Zhang et al., 2019a). In the Pb-Zn industrial concentrating, the lead sulfide, zinc sulfide, and often lead oxide minerals can be effectively enriched by traditional mineral processing techniques, while the processing of zinc oxide has been a complex challenging, especially when the hemimorphite $(Zn_4(Si_2O_7)(OH)_2)$ at high content was found in the ores (Frenay, 1985), which results in the low recovery of total zinc in concentrating plants. Although sulfidization xanthate flotation is one of the most proposed technologies for economicly and selectively enriching zinc oxide minerals, the flotation is still low efficient for recovering hemimorphite in the most mining enterprises (Jia et al., 2017; Liu et al., 2016; Liu et al., 2012; Navidi Kashani and Rashchi, 2008; Önal et al., 2005; Shiel et al., 2010).

The crystal structure of hemimorphite cell is composed of Zn-O and Si-O tetrahedra combination at the vertex in a threedimensional spatial framework. The volume of SiO_4 group is significantly larger than that of Zn in a Zn-O-Si unit, and it commonly shields the active Zn sites in the hemimorphite, and thus limits the Zn ions exposing on hemimorphite surface (Xing et al., 2021). These result in a strong

hydrophilicity on hemimorphite surface by mass SiO_4 groups, and that very few active Zn ions participates in sulphidizing reaction, leading to limited sulfidization adsorption and sulfidization layer instability. Salum et al. (Salum et al., 1992) verified that hemimorphite requires a sulfidizing time in solution with two times longer than that for willemite, in order that the similar sulfidization effect was reached. Therefore, active metal ions such as copper and lead ions, was proposed to use for further activating flotation of zinc oxide minerals after sulfidization, which was achieved via formations of copper or lead sulfides that has extremely affinity to xanthate collector on the mineral surface (Jia et al., 2018; Jia et al., 2017). Although these investigations provides very valuable research background for enhancing the flotation of zinc oxide minerals, this flotation method is still low efficiency for hemimorphite in practice as the amount of sulfidization products are very limited on hemimorphite surface in front sulfidization treatment (Jia et al., 2017).

Our team has proposed a technical route that the Pb pre-modification was used to tend the smithsonite surface to the surface of lead oxide mineral, and then sulfurized with Na_2S. The results indicated that Pb carbonates formed by substituting Pb ions in the place of Zn ions on the smithsonite surface and the Pb carbonate transformed into essential Pb-S species via S ion adsorption upon further sulfidization, which potentially and effectively enhanced the stability of the sulfide layer (Zhang et al., 2021; Zhang et al., 2019b). Unlike the octahedral structure of smithsonite, the zinc ion sites of hemimorphite are shielded by mass SiO_4 groups, making difficult for its adsorption of flotation agents. Furthermore, the silicates such as mica and quartz, contains analogous SiO_4 groups as in hemimorphite crystal. Several studies suggested that the metal ions adsorption on silicates surface are much more complex than simply ionic minerals, and it is commonly achieved via hydrogen bonding interaction. This is mainly because there are no satisfied heavy metal ion sites on silicates surface for exchanging adsorption of active metal ion (Dash et al., 2022; Yang et al., 2023; Zhang et al., 2021). Currently, there are few reports for the pre-adsorption of metal ions on the hemimorphite surface, which are very important for the subsequently stable sulfurization and xanthate adsorption of hemimorphite surface. Therefore, it is worth exploring whether Pb ions can adsorb on the surface of hemimorphite and how about the tendentious adsorption conditions.

In this study, the feasibility and appropriate environment of free lead ion for modifying the pure hemimorphite surface, following the effects of Pb^{2+} pre-adsorption on subsequent sulfidization for hemimorphite were systematically investigated. These results may provide a significant theoretical basis for the application of adsorption of metal ions on the silicate zinc minerals surface.

2. Materials and methods

2.1. Materials and reagents

The hemimorphite ore sample was obtained from Yunnan Province, China. The sample was crushed by a rock hammer, and gangue minerals were removed via handpicking to obtain a pure hemimorphite sample. Then, the hemimorphite sample with particle size below 74 µm was cleaned in 50% ethanol solution for hours and cleaned repeatedly with deionized water, and finally dried at room temperature. The 38-74 µm size fraction was obtained from the sample for micro-flotation tests and adsorption experiments. And, the -38 µm size fraction was used for the X-ray photoelectron spectroscopy (XPS), the time-of-flight secondary-ion mass spectrometry (ToF-SIMS), the X-ray diffraction (XRD) and chemical element analysis.

The XRD and chemical element analysis results of the hemimorphite ore sample are shown in Fig. 1 and Table 1, respectively. These results indicated that the sample was high-purity hemimorphite with no obvious impurities. The reagents used in this study included lead nitrate ($Pb(NO_3)_2$, analytical grade, Xilong Chemical Co., Ltd), methyl isobutyl carbinol (MIBC, commercial grade, Yunnan Tiefeng Mining & Chemical New Technology Co., Ltd.) and sodium sulfide (Na_2S, commercial grade, Yunnan Tiefeng Mining & Chemical New Technology Co., Ltd.). Potassium isoamyl xanthate (KIAX, commercial grade, Yunnan Tiefeng Mining & Chemical New Technology Co., Ltd.) was used as collector in this study as its long carbon chain, which was beneficial to the collection for hemimorphite (Ejtemaei et al., 2014). Deionized water with a resistivity of 18.25 MΩ obtained from an Exceed-Ac-16 water purifier was used throughout the study.

Table 1. Chemical compositions of pure hemimorphite used for experiments.

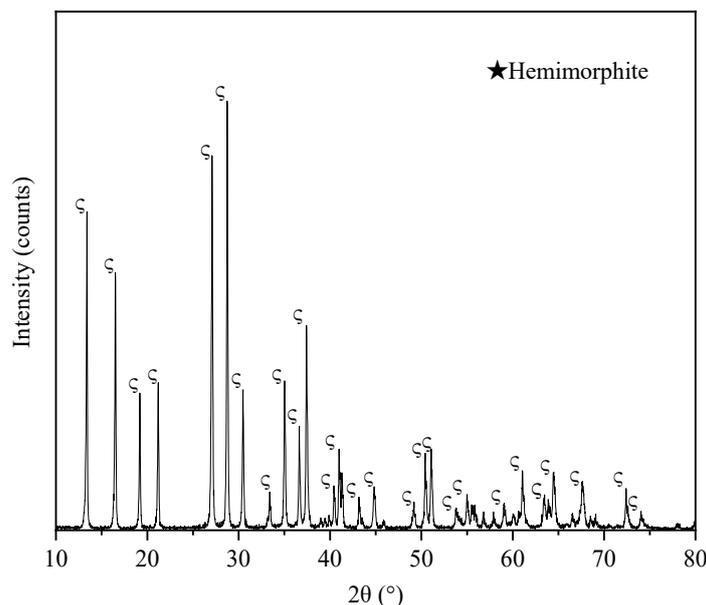| Compositions	Zn	SiO$_2$	CaO	Pb	Fe	Al$_2$O$_3$	MgO	S
Content (%)	51.10	23.27	0.042	0.056	0.059	0.019	0.020	0.059

Fig. 1. XRD pattern of pure hemimorphite sample

2.2. Methods

2.2.1. Micro-flotation experiments

The micro-flotation experiments were performed using an XFG laboratory scale flotation machine with a 50 mL cell at room temperature. The flotation was conducted at an agitation rate of 1600 rpm and a constant air flow rate of 15 cm^{3}min^{-1}. For each micro-flotation test, 2.0 g hemimorphite ore sample and 35 mL deionized water were mixed in the flotation cell and stirred for 5 min. When needed, the Pb(NO$_3$)$_2$ solution and Na$_2$S solution were poured to the pulp, and reacted for 3 min respectively. Then, the collector (KIAX) and frother (MIBC; concentration of 40 mg/L in pulp) were added and conditioned for 2 and 1 min, respectively. After aeration, the concentrate was collected for 3 min using a manual froth scraper. The concentrate mass (m$_1$) and the tailings mass (m$_2$) were weighed after they were dried in air at room temperature, and the flotation recovery ε was calculated according to formula (1).

Each experiment was performed in triplicate, and the average flotation recovery was calculated.

$$\varepsilon = \frac{m_1}{m_1 + m_2} \times 100\% \tag{1}$$

2.2.2. X-ray photoelectron spectroscopy

1.0 g hemimorphite ore sample was mixed with 35 mL deionized water in a beaker. When needed, the fresh Pb(NO$_3$)$_2$ solution and Na$_2$S solution were added to the pulp individually or together, and stirred according to the time of micro-flotation experiments. In order to avoid the interference of residual lead ions on sulfur adsorption, the sample treated with Pb(NO$_3$)$_2$ was filtered and cleaned with 35 ml deionized water before the adding of Na$_2$S. The sample without adding reagents was cleaned by ultrasonic wave. All samples were filtered and transferred to a vacuum oven. After dried, the samples were employed for XPS tests.

XPS detection of samples was conducted using a PHI 5000 Versa Probe II (ULVAC-PHI, Japan) equipped with a monochromatic Al Kα X-ray source. During detecting, the voltage, power and passing energy of the system were 15 kV, 50 W, and 46.95 eV, respectively. All spectra obtained were fitted and

analyzed using MultiPak (ver. 9.0), the spectra were calibrated according to the standard C1s binding energy (284.8 eV), and further fitted using Gauss-Lorentz method.

2.2.3. Visual MINTEQ model

The chemical equilibrium software Visual MINTEQ (ver. 3.1) was used to calculate the saturation index (SI) of the sediment formed when the Na_2S was poured to the pulp with or without Pb^{2+} modified at natural pH and temperature. SI was obtained according to formula (2). IAP and K_S were defined as the ion activity quotient and the equilibrium constant for the mineral dissolution reaction, respectively. The concentration of Zn^{2+} was 1.77×10^{-4} mol/L, which from the dissolution of hemimorphite when dissolution was in equilibrium. During calculation, the concentrations of Pb^{2+} and S^{2-} were fixed at 5×10^{-4} mol/L and 1×10^{-3} mol/L, respectively.

$$\mathrm{SI} = \log \frac{\mathrm{IAP}}{K_s} \tag{2}$$

2.2.4. ToF-SIMS analysis

1.0 g hemimorphite ore sample was mixed with 35 mL deionized water in a beaker. When needed, the fresh $Pb(NO_3)_2$ was added to the pulp to maintain the Pb ion concentration at 5×10^{-4} mol/L. After 3 min, the fresh Na_2S was added to the pulp until a concentration of 1×10^{-3} mol/L reached. After 6 min of conditioning, the sample was filtered and dried at room temperature, and then employed for ToF-SIMS tests.

For the surface analysis measurement conditions, a primary ion beam of 30 kV Bi_3^+ was operated in a static mode with an analysis current of 0.95 pA, an area of 500×500 μm^2 for each spectral acquisition, and an analysis time of 52 s. The Negative secondary ion mass spectra were calibrated using CH^-, Cl^-, SiO_2^-. And the Positive secondary ion mass spectra were calibrated using CH_3^+, Zn^+, Si^+.

2.2.5. Adsorption and desorption tests

First, 1.0 g hemimorphite ore sample and 20 mL deionized water were mixed in a beaker inserted in a 25°C thermostatic magnetic stirrer. The $Pb(NO_3)_2$ solution was added to maintain the Pb ion concentration of 5×10^{-4} mol/L in the pulp. After stirring for a certain time, the pulp was filtered and the filtrate was stored. All filtrate was used as the samples for Pb species adsorption tests.

To avoid the interference of the free Pb^{2+} in the pulp on subsequent test sections, 20 mL deionized water was used to rinse the filter residue on the filter paper after filtering, and the filter residue was transferred to another reactor and mixed with 20 mL deionized water. And, the Na_2S solution was added to the pulp to keep S ions at constant. After stirring for 3 min, the pulp was filtered and the filtrate was stored as the sample for S species adsorption tests.

20 mL deionized water was used to rinse the filter residue on the filter paper, and the filter residue was transfered to another reactor and mixed with 20 mL deionized water. The filter residues after sulfurized were filtered and rinsed for three times, and all the filtrate was used as the sample of Pb and S species adsorption tests.

The concentrations of Pb (C_{Pbx}) and S (C_{Sx}) in all prepared samples including the original reagents and filtrate were measured by Inductively Coupled Plasma Optical Emission Spectrometer(ICP-OES, PQ9000，Jena，Germany). Then, the adsorption capacities of Pb (Γ_{Pbx}) and S (Γ_{Sx}) were calculated using formulas (3) and (4), respectively. The desorption rates of Pb (D_{Pb}) and S (D_S) after filterring and rinsing for three times were calculated using formulas (5) and (6), respectively.

$$\Gamma_{Pbx} = \frac{V \times (C_{Pbo} - \sum_0^{x+0} C_{Pbx})}{m} \tag{3}$$

$$\Gamma_{Sx} = \frac{V \times (C_{So} - \sum_0^{x+0} C_{Sx})}{m} \tag{4}$$

$$D_{Pb} = \frac{\Gamma_{Pbo} - \Gamma_{Pb3}}{\Gamma_{PbO}} \times 100\% \tag{5}$$

$$D_S = \frac{\Gamma_{So} - \Gamma_{S3}}{\Gamma_{SO}} \times 100\% \tag{6}$$

where, C_{Pbo} and C_{So} represent original concentrations; x= 0, 1, 2, or 3, represents the rinsing times; V represents the volume of deionized water; m represents the mass of hemimorphite sample.

3.   Results and discussion

3.1. Flotation performance of hemimorphite

The recovery of hemimorphite with respect to the pH in presence and absence of Pb ions is shown in Fig. 2(a). As can be seen, the sulfidization flotation for hemimorphite without Pb ions pre-modification was low efficient with a maximal recovery of only approximately 15%. The poor floatability is resulted from that the inhomogeneity of the hemimorphite surface structure leads to the shielding of Zn by SiO_4 groups, which makes it difficult for zinc sites to interact with sulfur and xanthate ions (Yi et al., 2022). With addition of 5×10^{-4} mol/L Pb ions for pre-modifying hemimorphite surface, its recovery has been significantly improved, especially increased from 6% without Pb ions to 96% at pH 11.

The flotation performance of hemimorphite as a function of KIAX is presented in Fig. 2(b). The recovery showed an overall upward trend with and without Pb ions. When the concentration of Pb ions was 5×10^{-4} mol/L, the flotation recovery increased from 23.05% to 96.51% with the increasing of xanthate concentration, while the increase is small without lead ions.

The flotation results clearly reveal that Pb ions pre-treatment significantly increases in floatability of hemimorphite. Such increasing is enhanced under alkaline conditions. These imply that the Pb ions pre-treatment participated in the sulfidization on hemimorphite surface, which may achieve via Pb ions adsorption for providing mass metal active sites to facilitate the subsequent sulfidization adsorption. While the number of metal active sites would be increased with increasing pH. In addition, the sulfidization layer formed with Pb ions pre-treatment may have much higher stability and intensity for xanthate adsorption. But these speculations require further investigating.
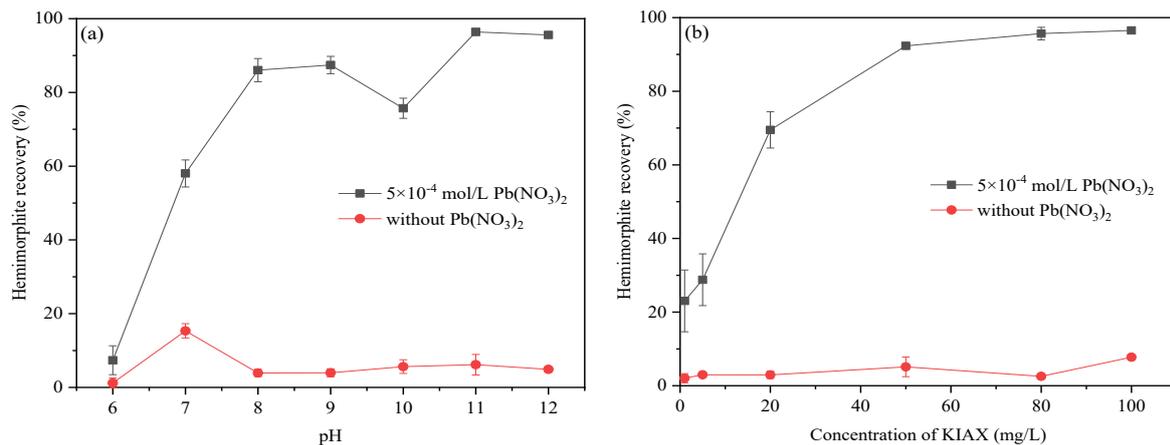

Fig. 2. Flotation recovery of hemimorphite with respect to (a) pH, and (b) KIAX concentration in absence and presence of 5×10^{-4} mol/L Pb(NO₃)₂. (a: Na₂S= 5×10^{-4} mol/L, KIAX= 100 mg/L; b: pH=11, Na₂S= 5×10^{-4} mol/L)

3.2. Formation of lead and sulfur species

To investigate the formation of lead species during the adsorption of lead ions on the hemimorphite surface and its effect on the formation of sulfur species during subsequent sulfidation, XPS tests of hemimorphite under different conditions were performed. The element composition and chemical state on the surface of the hemimorphite can be determined by XPS (Fang et al., 2018; Liu et al., 2019). The relating survey spectra and elements amounts on smithsonite surface over a binding energy range of 0 - 1100 eV was displayed in Fig. 3 and Table 2, respectively. Compared with the original sample (Fig. 3a), the Pb4f peak of Fig. 3b after Pb ions treatment at the binding energy of about 140 eV was significantly larger, and the content of Pb4f was 0.92%, while the relative content of zinc was lower than original sample. This may be due to the partial substitution of zinc on the mineral surface by some Pb ions. An obvious S peak appeared in the energy spectrum of the hemimorphite surface in presence of Pb^{2+} and Na₂S (Fig. 3d), and the content of S 2p was 1.63%, which was 0.39% higher than direct sulfidization (Fig. 3c). This showed that the sulfidization of hemimorphite was indeed promoted by Pb ions pre-adsorption.

Fig. 4 shows the high-resolution XPS spectra of Pb4f on the surface of hemimorphite samples. It can be seen from Fig. 4a that in the spectrum of the sample without Na₂S treatment, there was still an

obvious peak at the binding energy of about 140 eV, which was the peak of Zn3s in hemimorphite. The peak overlapped with the peaks of Pb4f after $Pb(NO_3)_2$ treatment (Liu et al., 2020; Wang et al., 2020). The binding energy of main peak $Pb4f_{7/2}$ in the first set was 138.90 eV, corresponding to the lead nitrate adhered in the mineral surface (Bertrand et al., 1980; Zhang et al., 2019b). In the second set of the split peak, the binding energy of $Pb4f_{7/2}$ was 137.30 eV, which may belonged to the Pb species of Pb-O/OH (Kim et al., 1973), which is mainly caused by Pb ion of $Pb(NO_3)_2$ exchanged with Zn ions and interacted with O atoms on the hemimorphite surface. Fig. 4b shows the curve fitting results of the samples treated by $Pb(NO_3)_2$ and Na_2S successively. The peak at the binding energy of 140.24 eV was the reference of Zn3s in hemimorphite, which was 0.15 eV higher than that in raw ore, which may be related to the addition of S ions. The binding energy of the third set was 136.96 eV, which may be the Pb species of sulfides of lead similar to Pb-S phase of galena (Xie et al., 2021). This indicates that the lead species adsorbed on the hemimorphite surface provided lead sites that could react with sulfides to form stable lead sulfides.
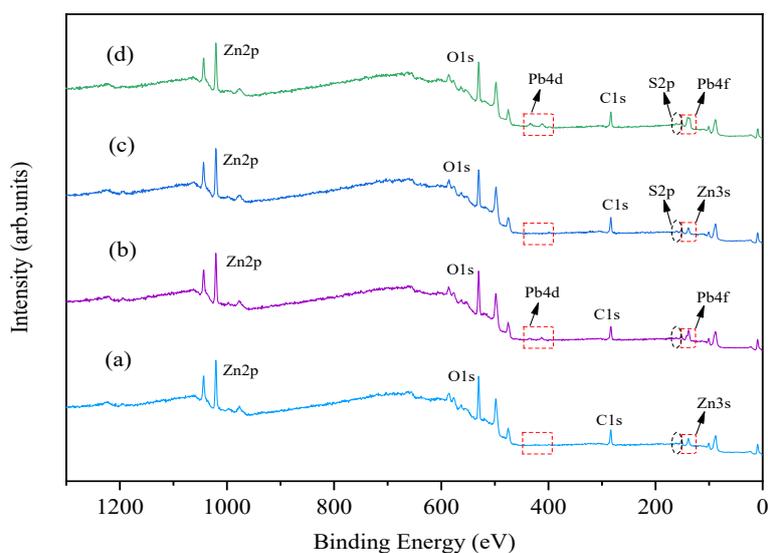

Fig. 3. XPS spectra of hemimorphite surface treated with (a) deionized water, (b) $5×10^{-4}$ mol/L $Pb(NO_3)_2$, (c) $1×10^{-3}$ mol/L Na_2S, and (d) $5×10^{-4}$ mol/L $Pb(NO_3)_2$ and $1×10^{-3}$ mol/L Na_2S

Table 2. Relative amounts of elements on the hemimorphite surface treated with (a) deionized water, (b) $5×10^{-4}$ mol/L $Pb(NO_3)_2$, (c) $1×10^{-3}$ mol/L Na_2S, and (d) $5×10^{-4}$ mol/L $Pb(NO_3)_2$ and $1×10^{-3}$ mol/L Na_2S

Samples	Relative amounts (%)						
	C1s	O1s	Zn2p3	Si2p	Pb4f	Pb4d5	S2p
a	34.17	38.45	15.75	11.63			
b	30.97	39.93	15.79	10.90	0.92	1.45	
c	34.14	35.84	15.87	12.91			1.24
d	30.74	35.40	14.75	12.58	1.36	3.55	1.63

Fig. 5a shows the high-resolution XPS spectra of S2p on the surface of hemimorphite sample treated with Na_2S. The binding energy of the first set of the split peak was 163.49 eV, the S species may be contributed by polysulfide (S_n^{2-}) (Smart et al., 1999). In the second set of the split peak, the binding energy of $S2p_{3/2}$ was 161.29 eV, which belonged to the monosulfide (S^{2-}) (Asahi et al., 1999). Fig. 5b shows the curve fitting results of S2p in the sample treated by $Pb(NO_3)_2$ and Na_2S successively, in which the binding energy of the first set of split peak was 162.73 eV, corresponding to the polysulfide (S_n^{2-}) (Feng and Wen, 2017; Herron et al., 2015; Smart et al., 1999). In the second set of the split peak, the binding energy of $S2p_{3/2}$ was 161.24eV, which should be the monosulfide (S^{2-}) (Li et al., 2018). The binding energy of the third set was 160.41 eV, which may be lead sulfides (Brion, 2002). It can be inferred from the above results that the sulfidization of hemimorphite achieved through reaction of S and Pb on

the surface of the mineral to form metal sulfides. In addition, the area of S2p on the surface of Pb ions pre-treatment sample was obviously larger than that of Pb-free sample, which indicated that the Pb ion pre-adsorption increased the content of active sites that were easy for reaction with sodium sulfides.
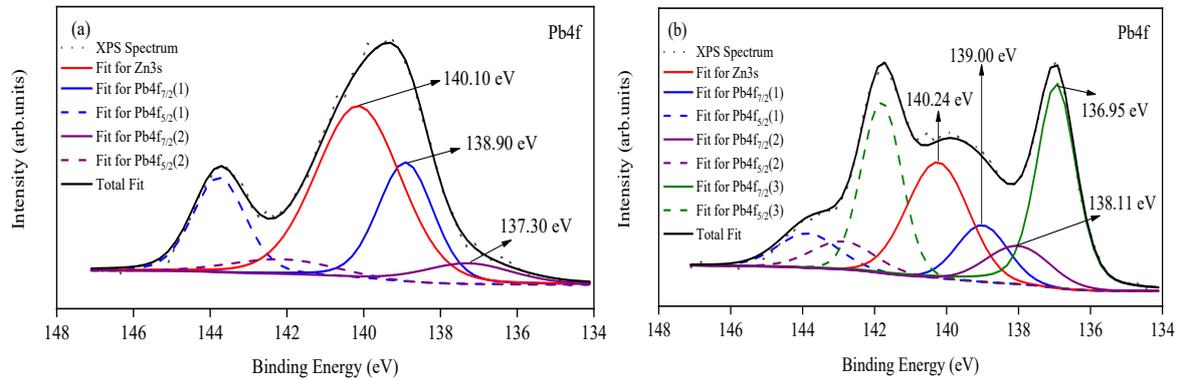

Fig. 4. Pb4f XPS spectra on the hemimorphite surface treated with (a) 5×10^{-4} mol/L Pb(NO$_3$)$_2$, (b) 5×10^{-4} mol/L Pb(NO$_3$)$_2$ and 1×10^{-3} mol/L Na$_2$S
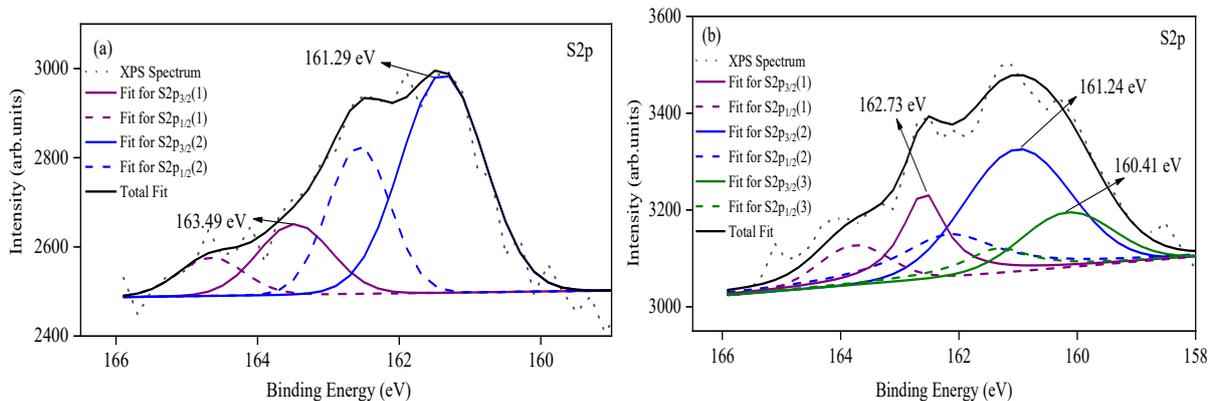
Fig. 5. S2p XPS spectra on the hemimorphite surface treated with (a) 1×10^{-3} mol/L Na$_2$S, and (b) 5×10^{-4} mol/L Pb(NO$_3$)$_2$ and 1×10^{-3} mol/L Na$_2$S

Fig. 6 shows the high-resolution XPS spectra of Zn2p on the surface of hemimorphite samples under various treatment conditions. The curve fitting result of Zn2p in the hemimorphite surface treated by deionized water was shown in Fig. 6a. The binding energy of the main spin-orbit split peak of Zn2p$_{3/2}$ was 1022.19 eV, which should correspond to the Zn(Ⅱ) in hemimorphite (Yifu et al., 2018; Zhao et al., 2020). Under the other three treatments, the binding energies of Zn2p varied within 0.05 eV, as seen from Fig. 6b, Fig. 6c and Fig. 6d. That may be due to the slight effect of Pb ions modification and Na$_2$S sulfidization on Zn atoms, which meant there were no Zn species new formed.

3.3. Mechanisms of lead species adsorption and sulfidization

3.3.1. Visual MINTEQ model

To further investigate the lead species formed in the adsorption of lead ions on the hemimorphite surface and the subsequent sulfidization products, the flotation solution chemistry study and the ToF-SIMS study were conducted.

The visual MINTEQ is a free chemical equilibrium model which is widely used to calculate the speciation, solubility equilibrium and adsorption of metals in aqueous phase (Zhang et al., 2019b). The dominant solution components of Pb and S species in the solution under different pH conditions were calculated as shown in Fig. 7. At pH 11, the dominant components of Pb species were Pb(OH)$_{2(aq)}$ and

$Pb(OH)_3^-$, followed by $Pb(OH)^+$ and Pb^{2+}; and the dominant component of S species was HS^-, followed by $H_2S_{(aq)}$ and S^{2-}. It was noted that the lead hydroxide is dominant component under alkaline conditions, precipitating of which on the mineral surface is other source of lead sites for subsequent sulfidization flotation.

The results of Visual MINTEQ can reveal the saturation index (SI) of the precipitation products of Zn^{2+} and S^{2-} in presence or absence of Pb^{2+} under different pH conditions. Generally, it can be noted that the precipitation can form when the SI value of the chemical reaction exceeds 0. The calculated results
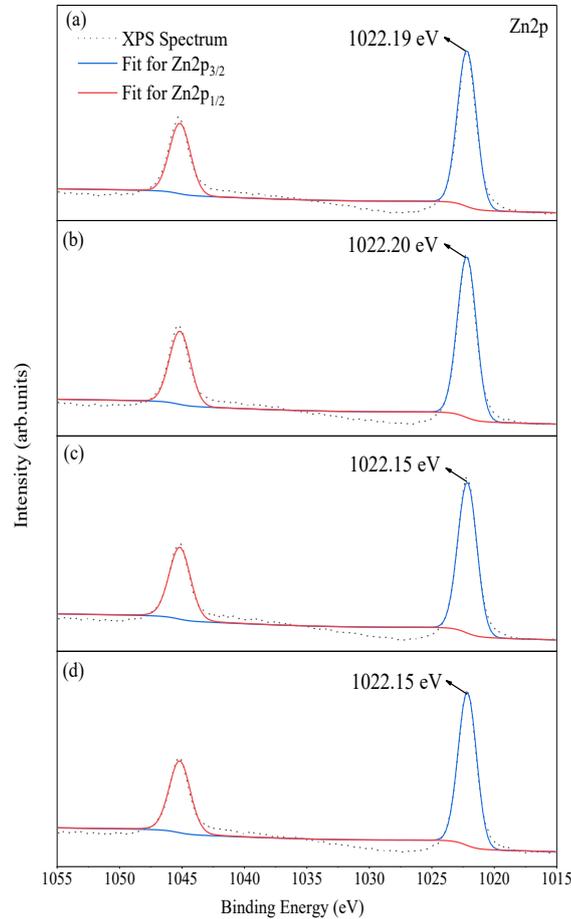

Fig. 6. Zn2p XPS spectra on the hemimorphite surface treated with (a) deionized water, (b) 5×10^{-4} mol/L $Pb(NO_3)_2$, (c) 1×10^{-3} mol/L Na_2S, and (d) 5×10^{-4} mol/L $Pb(NO_3)_2$ and 1×10^{-3} mol/L Na_2S

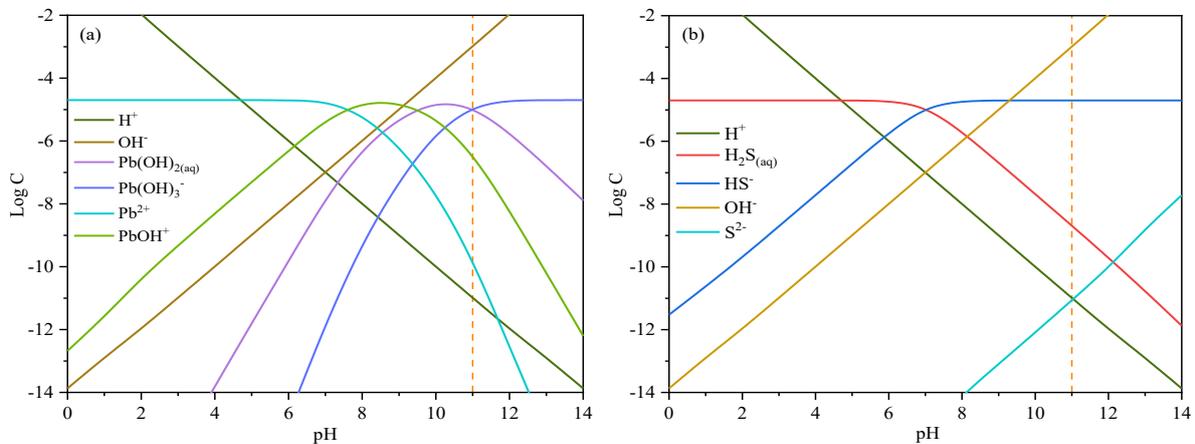Fig. 7. Solution chemistry component distribution of (a) $Pb(NO_3)_2$ and (b) Na_2S as a function of pH (Conditions: $C_{Pb^{2+}} = 5\times10^{-4}$ mol/L, $C_{S^{2-}} = 1\times10^{-3}$ mol/L)

can describe the relationship between pH and SI of saturated species. As shown in Fig. 8(a), sphalerite (ZnS) and wurtzite (ZnS) were saturated due to the interaction of Zn^{2+} and S species in absence of Pb^{2+}, and their highest SIs reached 7.63 and 5.43 at pH=6. Then, the SIs decreased as the pH increased, which meant that it was difficult to form zinc sulfide under alkaline conditions. Therefore, it can be inferred that there was very slight zinc sulfide attached to the mineral surface in the pulp due to the low solubility of the hemimorphite (McPhail et al., 2006), which was not conducive to improve the floatability of hemimorphite. When Pb^{2+} presented, galena (PbS), sphalerite (ZnS), wurtzite (ZnS), $Pb(OH)_2$, zincite (ZnO) and litharge (PbO) would reach saturation in succession due to the interaction of Zn^{2+}, S^{2-} and Pb^{2+}. The SI value of galena (PbS) reached the maximum value 12.04 at pH 10, and it was much higher than the SIs of other species. That indicated that lead sulfides formed easier than zinc sulfides in this system under ideal condition when Pb^{2+} presented, with a great tendency to form and a wide pH range. At the same time, free lead sulfides and other lead species in the solution precipitated onto the mineral surface, which all are beneficial for the subsequent collection of hemimorphite by xanthate.
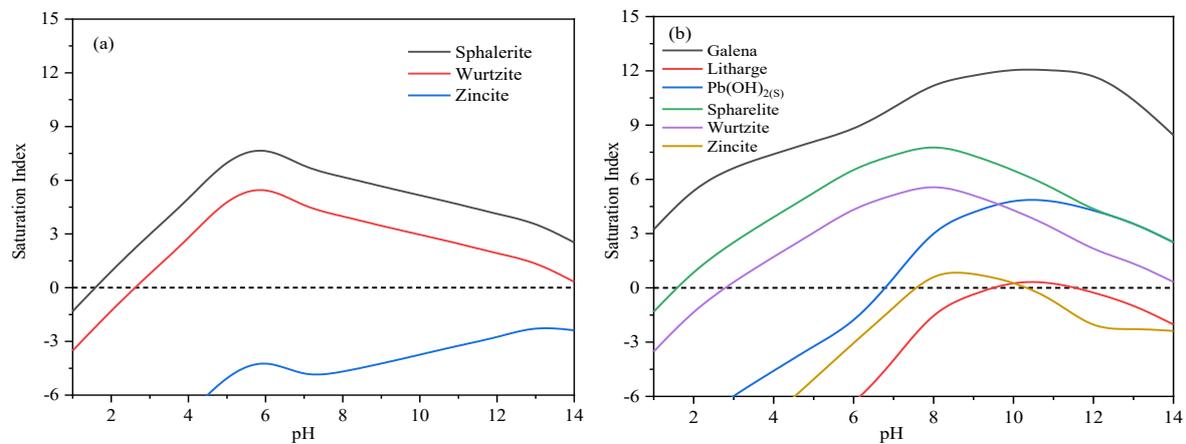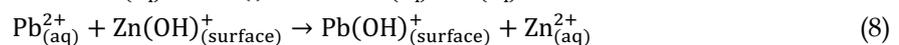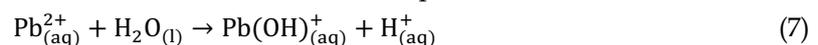

Fig. 8. Effects of the pH on SIs of the representative species in the (a) binary solution system (Zn^{2+}, S^{2-}) and (b) ternary solution system (Zn^{2+}, Pb^{2+}, S^{2-})

3.3.2. ToF-SIMS study

The ToF-SIMS is essential for the surface analysis of mineral and materials, and its peak intensities can express important information and often were applied to compare mineral surface structure treated under different conditions (Bai et al., 2020). The ToF-SIMS analysis of positive and negative ions on hemimorphite surface treated under different conditions were performed and the results are shown in Fig. 9. There are weak Pb^+ and S^- mass signals on the surface of hemimorphite sample without treatment, which may be caused by residual trace of Pb^+ and S^- fragment ions that cannot be eliminated in the detection chamber (Zhang et al., 2022). It can be seen from the Fig. 9 that the content of lead species on the hemimorphite surface significantly increased when treated with $Pb(NO_3)_2$, indicating that lead ions could adsorb on the mineral surface under alkaline conditions. Furthermore, the $Pb(OH)^+$ was the main adsorption product, which came from the hydrolysis of Pb ion in alkaline solution and displacement reaction with Zn of hemimorphite. The results were also in line with the XPS analysis and solution chemical calculation results mentioned above. And the main reaction processes are as follow:

$$Pb^{2+}_{(aq)} + H_2O_{(l)} \rightarrow Pb(OH)^+_{(aq)} + H^+_{(aq)} \tag{7}$$

$$Pb^{2+}_{(aq)} + Zn(OH)^+_{(surface)} \rightarrow Pb(OH)^+_{(surface)} + Zn^{2+}_{(aq)} \tag{8}$$

It is worth noting that the S^- intensity on hemimorphite surface was significantly enhanced after Na_2S treatment, suggesting obvious occurrence of S ions adsorption; however, the hemimorphite recovery by sulfidization-xanthate flotation was commonly low efficiency in practice, which may be due to the unstable adsorption of sulfide on the mineral surface, furthermore, the subsequent collection by xanthate was not easy. When the hemimorphite surface treated with $Pb(NO_3)_2$ and Na_2S successively, the intensities of Pb-S species on the hemimorphite surface were higher than that of hemimorphite

treated with Na_2S alone, which indicated that the pre-adsorption of Pb ions provided large number of active sites for subsequent sulfidization to generate lead sulfides. So the inferred potential reaction processes may be as follow：

$$Pb(OH)^+_{(surface)} + S^{2-}_{(aq)} \rightarrow PbS_{(surface)} + OH^-_{(aq)} \tag{9}$$

$$Pb(OH)^+_{(surface)} + HS^-_{(aq)} \rightarrow PbS_{(surface)} + H_2O_{(l)} \tag{10}$$
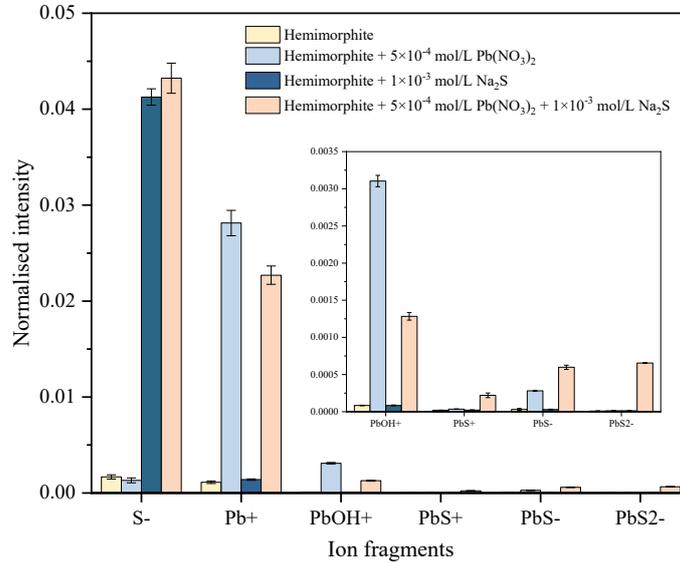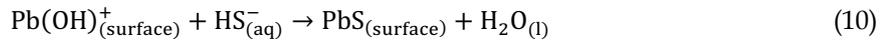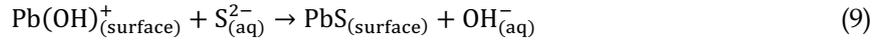

Fig. 9. Normalized intensities of different ions on the surface of hemimorphite samples under different treatments. The inset is the corresponding enlarged intensities of Pb components

3.4. Stability of lead and sulfur species

The above research results showed that Pb ions would be adsorbed on the mineral surface, as well as the subsequent sulfidization would be promoted. However, the adsorption stability of Pb species and sulfide layer on the hemimorphite surface was not clear. Therefore, the adsorption and desorption tests were performed in this section. Fig. 10 shows the adsorption stability of Pb species on hemimorphite surface. It can be seen from the figure that there was no obvious change in the adsorption capacity of Pb species on the mineral surface with the increasing of stirring time from 3 min to 9 min. On the other hand, the adsorption capacity of Pb species did not decrease significantly at each stirring time with the increasing of rinse times. The results indicated that Pb species were adsorbed on the mineral surface with excellent stability.
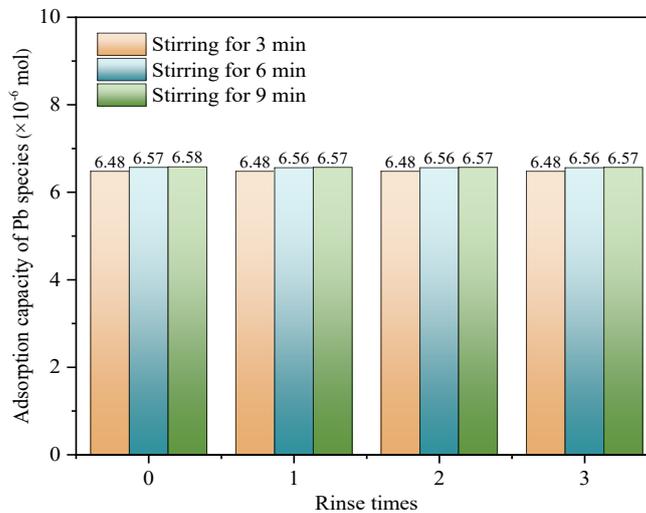

Fig. 10. Adsorption capacity of Pb species under different rinsing times and stirring time

Fig. 11 shows the adsorption capacity of S species on hemimorphite surface. The adsorption capacity of S species in presence of Pb ions was significantly higher than that in absence of Pb ions, which verified that Pb ions pre-treatment has promoted the subsequent sulfidization. On the other hand, the presence of Pb ions also affected the desorption rate of S species. After three times of rinsing, the desorption rate was 5.82% when Pb ions was present, while in absence of Pb, the desorption rate reached 11.04%, nearly twice of the former. It can be concluded that the stability of sulfide layer improved significantly under Pb ions pre-treatment.
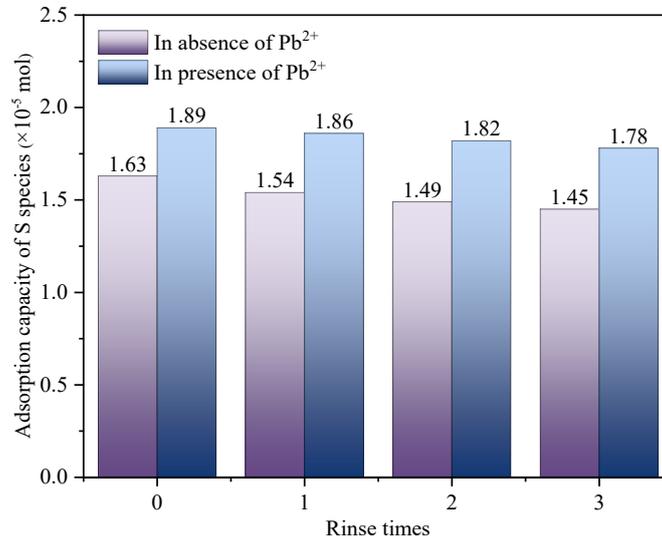

Fig. 11. Adsorption capacity of S species under different rinse times in absence and presence of $Pb(NO_3)_2$, treated with 1×10^{-3} mol/L Na_2S

4. Conclusions

In light of extensive researches, we know that adding active metal ions after sulfidization have been widely proposed for enhancing hemimorphite floatability, but its desired efficiency in flotation practice has not yet been completely achieved caused by the instability of sulfide layer. In this work, the feasibility and appropriate environment for Pb ions adsorption on the hemimorphite surface were evaluated, and then the effects of Pb ions adsorption on the sulfidization-xanthate flotation of hemimorphite were revealed from a new perspective. The conclusions can be recorded as follows:

1. The Pb ions adsorption on hemimorphite surface was achieved through the Pb ions displacement for Zn ions, and it was potentially bond to oxygen-containing groups on hemimorphite surface.
2. The Pb ions adsorption was strengthened with the increasing of solution pH, owing to the abundant Pb hydroxyl species precipitated on the mineral surface under alkaline conditions.
3. The formed Pb species on Pb ions pre-modified hemimorphite surface further reacted with S ions during subsequent sulfidization to generate Pb-S species. Meanwhile, the lead sulfides precipitate in solution would attach on the mineral surface. Accordingly, the flotation recovery of hemimorphite increased from 6% to 96% after Pb ions pre-adsorption.
4. The Pb ions could be adsorbed on the hemimorphite surface with high stability. Furthermore, the stability of the sulfide layer was enhanced by Pb ions pre-adsorption, embodying in the decrease in desorption rate of S species from 11.08% to 5.82%, which is beneficial for the subsequent xanthate collection.
5. These may provide a new perspective and significant theoretical basis for employing metal ions to enhance the floatation of hard-collected silicate zinc minerals.

Acknowledgments

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