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# Innovative scheme for hemimorphite flotation: Synergistic activation performance and mechanism

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**Abstract:** Hemimorphite exhibits poor floatability during sulfidization flotation. $Cu^{2+}$ and $Pb^{2+}$ addition enhances the reactivity of the hemimorphite surface and subsequently improves its flotation behavior. In this study, the mechanisms of $Cu^{2+}$ + $Pb^{2+}$ adsorption onto a hemimorphite surface were investigated. We examined the interaction mechanism of xanthate with the hemimorphite surface and observed the changes in the mineral surface hydrophobicity after the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$. Microflotation tests indicated that individual activation with $Cu^{2+}$ or $Pb^{2+}$ increased the flotation recovery of hemimorphite, with $Pb^{2+}$ showing greater effectiveness than $Cu^{2+}$. Meanwhile, synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ considerably boosted the flotation recovery of hemimorphite. $Cu^{2+}$ and $Pb^{2+}$ were both adsorbed onto the hemimorphite surface, forming an adsorption layer containing Cu or Pb. Following the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the activated layer on the hemimorphite surface consisted of Cu and Pb and a larger amount of the active product compared with the surface activated by $Cu^{2+}$ or $Pb^{2+}$ alone. In addition, xanthate adsorption on the hemimorphite surface increased noticeably after synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, suggesting a vigorous reaction between xanthate and the activated minerals. Therefore, synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ effectively increased the content of active products on the hemimorphite surface, thereby enhancing mineral surface reactivity, promoting collector adsorption, and improving surface hydrophobicity.

**Keywords:** hemimorphite flotation; synergistic activation; $Cu^{2+}$; $Pb^{2+}$

## 1. Introduction

Zn is an essential industrial material that ranks behind Cu and Al in terms of nonferrous metal consumption [1]. In nature, zinc metal is primarily found in sulfide and oxide ores. Zinc sulfide ores are easily enriched through mineral processing; however, continuous extraction has led to the gradual depletion of these resources. The development and utilization of refractory zinc oxide minerals are of great importance in meeting the growing demand for Zn resources. Zinc oxide minerals result from the prolonged weathering of zinc sulfide minerals in nature. Smithsonite ($ZnCO_3$) is typically formed when sphalerite is oxidized by reacting with carbonate minerals. Hemimorphite ($Zn_4(Si_2O_7)(OH)_2$) is formed when smithsonite interacts with $SiO_2$ and $CO_2$. The mineral processing industry primarily uses flotation to enrich zinc oxide minerals. However, conventional flotation methods for treating zinc oxide ores often fail to achieve the ideal flotation index [2–3]. The floatability of gangue minerals in zinc oxide ores is similar to that of target minerals [4–6]. Therefore, effectively separating the target minerals from gangue minerals during flotation becomes challenging. In addition, zinc oxide ores contain considerable amounts of soluble salt minerals. Dissolving these salt minerals results in a high concentration of unavoidable ions in the pulp that deteriorate the flotation environment and reduce the selectivity of the flotation reagents [7–9].

Anionic collectors are commonly used for zinc oxide minerals and exhibit effective flotation capabilities for zinc oxide minerals containing siliceous gangue [10–11]. Shi *et al.* [12] discovered that sodium oleate could be adsorbed onto the smithsonite surface, leading to hydrophobic flotation. Liu *et al.* [13] employed lauryl phosphate as a collector and successfully achieved flotation separation between smithsonite and calcite within a pH range of 5–9. Tan *et al.* [14] found that 1-hydroxydodecylidene-1,1-diphosphonic acid exhibits stronger selectivity for hemimorphite than lauric acid, enabling the flotation separation of hemimorphite and quartz within the pH range of 7–11. However, the flotation of zinc oxide ores containing carbonates using fatty acid collectors is challenging, especially for those with high iron content. Fatty acids are highly sensitive to temperature. Chelating collect-

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ors can interact with the metal ions on the mineral surface and form complex cyclic chelate compounds, which are then adsorbed onto the mineral surface [15]. Zuo *et al*. [16] found that sodium sulfosalicylate interacts with the hemimorphite surface, destroying its surface structure and promoting the formation of hydrophobic films and the hydrophobicity of hemimorphite. Wang *et al*. [17] combined benzohydroxamic acid with sodium oleate as a mixed collector for the flotation separation of smithsonite and calcite and achieved 90% recovery for smithsonite and 5% recovery for calcite. 8-hydroxyquinoline is a common metal chelating agent that forms a five-membered ring chelate through its N and O atoms and the Zn atoms on the smithsonite surface, enhancing its surface hydrophobicity and significantly improving its floatability under neutral conditions [18]. However, chelating collectors have specific functional group requirements, leading to challenges in their synthesis, high costs, and immature industrial applications.

The sulfidization flotation of zinc oxide minerals involves the surface sulfidization of minerals using sulfidizing agents, followed by the collection of xanthate or amine collectors [19–20]. Sulfidization promotes the generation of ZnS on the surface of zinc oxide minerals, thereby enhancing the surface reactivity. Therefore, sulfidization flotation can be used for the flotation of zinc oxide minerals at ambient temperatures, the flotation indices are often not ideal. Although heating can promote sulfidization on the mineral surface, it increases operational costs. Cai *et al*. [21] observed that increasing the sulfidization temperature from 20 to 60°C enhanced the recovery of smithsonite from 47.24% to 76.17% and facilitated the migration of sulfur ions from the pulp to the mineral surface, diminishing the depressive effect of excessive sodium sulfide on smithsonite flotation. Metal-ion activation has become an important means of reducing production costs while ensuring the efficient flotation recovery of zinc oxide minerals. Jiang *et al*. [22] found that $Cu^{2+}$, $Pb^{2+}$, and $Zn^{2+}$ could promote the sulfidization of the xanthate flotation of smithsonite, with $Cu^{2+}$ and $Pb^{2+}$ exhibiting superior activation effects than $Zn^{2+}$. Similarly, G.F. Zhang and F.Y. Zhang [23] discovered that adding $Cu^{2+}$, $Pb^{2+}$, and $Zn^{2+}$ enhances the floatability of hemimorphite, with $Pb^{2+}$ showing the best promoting effect on the sulfidization of hemimorphite. Hemimorphite is the most common zinc oxide mineral after smithsonite and is a refractory silicate zinc oxide mineral with weaker surface reactivity than smithsonite. The zinc sites on the hemimorphite surface are often shielded by silicate, making the surface structure similar to that of quartz; in addition, the reaction sites on the hemimorphite surface are fewer than those on the smithsonite surface, preventing sulfidizing reagents and xanthate from interacting with the zinc sites on the hemimorphite surface [2]. Huang *et al*. [24] suggested that adding an appropriate amount of $Pb^{2+}$ could increase the floatability of hemimorphite, reduce the dosage of sodium sulfide, and increase the number of active sites on the mineral surface. $Pb^{2+}$ can be adsorbed on the hemimorphite surface, increasing the number of active sites and promoting the formation of highly active PbS on the surface, thereby enhancing xanthate adsorption. Therefore, adding specific metal ions before sulfidization can effectively enhance the reactivity of the zinc oxide mineral surface, facilitating the subsequent adsorption of sulfur ions and collectors. However, previous studies have predominantly used individual metal ions to activate zinc oxide minerals. Research on the synergistic activation of zinc oxide minerals using combined metal ions is limited. Metal ions, especially $Cu^{2+}$ and $Pb^{2+}$, are widely used in industrial flotation production [25–27]. Hence, the present study selected $Cu^{2+}$ and $Pb^{2+}$ as activation ions for the sulfidization flotation of hemimorphite, systematically investigated the synergistic activation mechanism of $Cu^{2+}$ + $Pb^{2+}$ on the flotation of hemimorphite, and provided new insights into the efficient flotation of zinc oxide minerals. In this work, $Cu^{2+}$ and $Pb^{2+}$ are mainly adsorbed on the hemimorphite surface, and the amount of $Cu^{2+}$ and $Pb^{2+}$ in the solution is small. The $Cu^{2+}$ and $Pb^{2+}$ remaining in the pulp react with $Na_2S$ to form CuS and PbS precipitates, leading to the post-flotation solution is almost free of $Cu^{2+}$ and $Pb^{2+}$. The beneficiation wastewater has minimal impact on the environment.

This study focused on the influence of synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ on the flotation behavior of hemimorphite through microflotation experiments. Surface analysis techniques were employed to investigate the adsorption characteristics and revealed the synergistic activation mechanism of $Cu^{2+}$ + $Pb^{2+}$ on the hemimorphite surface. Finally, the impact of synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ on the adsorption behavior of xanthate on the hemimorphite surface was determined.

## 2. Experimental

### 2.1. Materials

Hemimorphite samples were obtained from Yunnan Province, China. Chemical analysis indicated that the hemimorphite sample contained approximately 53wt% Zn with a purity exceeding 95%. The X-ray diffraction pattern (XRD) of the hemimorphite sample is shown in Fig. 1. The diffraction peaks were highly coincident with the standard diffraction peaks, and no other impurity peaks were evident. The reagents used in the experiment included sodium hydroxide

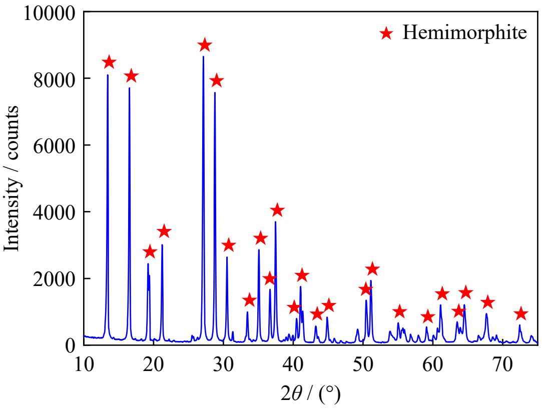

**Fig. 1. XRD pattern of hemimorphite.**

(NaOH), hydrochloric acid (HCl), copper nitrate ($Cu(NO_3)_2$), lead nitrate ($Pb(NO_3)_2$), sodium sulfide ($Na_2S\cdot9H_2O$), sodium isoamyl xanthate (NaIX, $C_5H_{11}OCSSNa$), and potassium chloride (KCl), all of which were of analytical grade.

### 2.2. Microflotation process

Microflotation experiments were conducted using XFG-II flotation machine. Initially, the hemimorphite sample and deionized water were added to the flotation cell. The pulp was conditioned for 1 min at natural pH. The reagent addition sequence was as follows: the required concentrations of $Cu^{2+}$ and $Pb^{2+}$ were added and allowed to react for 5 min. Sodium sulfide was then added, and the mixture was allowed to react for 5 min. Finally, the collector and frother were introduced and allowed to react for 3 and 1 min, respectively. The concentrate and tailings were collected 5 min after scraping the froth. Each flotation test was performed three times, and the results were averaged.

### 2.3. Surface analysis

Zeta potential was measured using Zetasizer-3000HS instrument (Malvern Instruments). First, the hemimorphite sample was added to KCl solution. The necessary reagents were then added following the same sequence in the flotation test and stirred for 5 min. The pH was adjusted using HCl and NaOH according to the requirements. After stirring, the resulting suspension was allowed to stand for 5 min and then transferred to an electrophoretic cell for analysis. Each sample was repeatedly tested three times, and the results were averaged, in which the theoretical maximum error was no more than 2.0 mV.

The amount of adsorbed xanthate was determined using UV-visible spectrophotometer (UV-2700, Shimadzu). Initially, the hemimorphite sample was placed into a beaker containing deionized water. The necessary reagents were added following the same sequence in the flotation test. After the reaction was completed, the sample was left to stand for 10 min. The supernatant obtained after centrifugation was transferred to a quartz cuvette to measure the amount of adsorbed xanthate.

Fourier transform infrared (FTIR) spectroscopy was performed using Nicolet iS50 infrared spectrometer (Thermo Fisher Scientific). Initially, the hemimorphite sample was placed into a beaker containing deionized water. Following the flotation test, the necessary reagents were added sequentially. After the reaction was completed, the sample was thoroughly rinsed with deionized water, filtered, and naturally dried for subsequent analyses.

The surface morphology and roughness of hemimorphite were measured by atomic force microscopy (AFM, Dimension Icon, Bruker Company, Germany) and NanoScope analysis. Sheet-like hemimorphite was selected as the test sample. Prior to the test, the prepared hemimorphite sample was cleaned with an ultrasonic wave, placed in a beaker, added with the reagent solution required for the test, and soaked for 20 min. The samples were allowed to dry naturally before being examined.

A time-of-flight secondary ion mass spectrometer (ToF-SIMS 5, IONTOF) was used for testing the ionic fragments on the mineral surface. Initially, the sheet-like hemimorphite sample was placed into a beaker containing deionized water. The reagents necessary for the ToF-SIMS test were added following the sequence in the flotation test. Each reagent was allowed to interact with the mineral for 10 min after its addition. Once the reagents' actions were completed, the sample was removed from the beaker and left to air-dry.

X-ray photoelectron spectroscopy (XPS) was conducted using PHI 5000 X-ray photoelectron spectrometer from ULVAC-PHI. Initially, the hemimorphite sample was added to a beaker containing deionized water. The necessary reagents were added to the sample following the same sequence in the flotation test. After the reagents' actions were completed, the sample was filtered to obtain a specimen for testing. The test results were analyzed and fitted with MultiPak spectral analysis software.

## 3. Results and discussion

### 3.1. Microflotation results

Fig. 2 demonstrates the impact of different activation conditions on the flotation recovery of hemimorphite as a function of $Cu^{2+}$ and $Pb^{2+}$ concentrations. As shown in Fig. 2(a), the flotation recovery increased with the $Cu^{2+}$ concentration from 0 to $2 \times 10^{-4}$ mol/L when using $Cu^{2+}$ or $Cu^{2+}$ and $Pb^{2+}$ for hemimorphite activation. Once the $Cu^{2+}$ concentration surpassed $2 \times 10^{-4}$ mol/L, the flotation recovery of hemimorphite began to decline. As shown in Fig. 2(b), the hemimorphite recovery increased with the $Pb^{2+}$ concentration from 0 to $5 \times 10^{-4}$ mol/L when activating hemimorphite with $Pb^{2+}$. Upon synergistic activation with $Cu^{2+} + Pb^{2+}$, the hemimorphite recovery showed an increasing trend with the $Pb^{2+}$ concentration from 0 to $3 \times 10^{-4}$ mol/L. When the $Pb^{2+}$ concentration surpassed $3 \times 10^{-4}$ mol/L, the hemimorphite recovery started to decrease. Therefore, appropriate concentrations of $Cu^{2+}$ and $Pb^{2+}$ can activate hemimorphite for sulfidization flotation, and excessive $Cu^{2+}$ and $Pb^{2+}$ in the pulp depress the sulfidization flotation of hemimorphite. The excess $Cu^{2+}$ and $Pb^{2+}$ in the pulp consumed the subsequently added sodium sulfide, thus hindering the adsorption of xanthate on the hemimorphite surface. Furthermore, the excess $Cu^{2+}$ and $Pb^{2+}$ in the pulp promoted the generation of a large number of metal hydroxides, thereby enhancing the hydrophilicity of the hemimorphite surface. According to the microflotation test results, the increase in hemimorphite floatability in different activation systems was in the following order: individual $Cu^{2+}$ activation, individual $Pb^{2+}$ activation, and synergistic activation with $Cu^{2+} + Pb^{2+}$. This phenomenon can be attributed to the adsorption of $Cu^{2+}$ and $Pb^{2+}$ onto the hemimorphite surface, causing the mineral surface to produce highly active Cu or Pb. Synergistic activation with $Cu^{2+} + Pb^{2+}$ resulted in the simultaneous presence of Cu and Pb on the hemimorphite surface, further enhancing its surface reactivity and floatability.

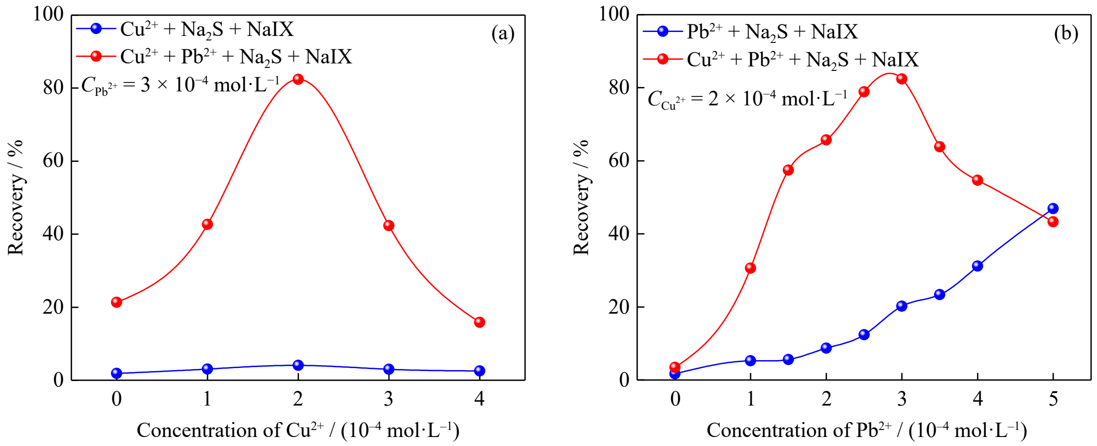

**Fig. 2. Flotation recovery of hemimorphite as a function of (a) $Cu^{2+}$ and (b) $Pb^{2+}$ concentrations in the synergistic activation system (*C* denotes the concentration).**

### 3.2. Zeta potential tests

During flotation, the preferential adsorption of ions in the pulp onto the mineral surface results in the generation of a certain amount of charge on the mineral surface. The addition of flotation reagents typically influences the surface electrochemistry of minerals, thereby altering their physicochemical properties [28–29]. Therefore, this study investigated the interactions between $Cu^{2+}$/$Pb^{2+}$ and the hemimorphite surface using zeta potential tests. Fig. 3 illustrates the relationship between the zeta potential of the hemimorphite surface and the pH under different conditions. As shown in Fig. 3, the surface potentials of hemimorphite were consistently negative when the pulp pH ranged between 6 and 12. With an increase in pulp pH, the mineral surface potential decreased. Upon the addition of $Cu^{2+}$, $Pb^{2+}$, or $Cu^{2+}$ + $Pb^{2+}$, the zeta potentials of the hemimorphite surface exhibited significant increase across the entire tested pH range compared to that of untreated hemimorphite surface. This finding indicated that after activation by $Cu^{2+}$, $Pb^{2+}$, or $Cu^{2+}$ + $Pb^{2+}$, positively charged metal ions were adsorbed on the hemimorphite surface, causing a positive shift in the mineral surface's potential. Compared with that after the addition of $Cu^{2+}$ or $Pb^{2+}$ alone, the zeta potential of the hemimorphite surface exhibited the greatest positive shift after the addition of $Cu^{2+}$ + $Pb^{2+}$. This result suggested that the hemimorphite surface adsorbed a high amount of active metal ions, providing favorable conditions for the subsequent interaction of sodium sulfide and xanthate with the hemimorphite surface.

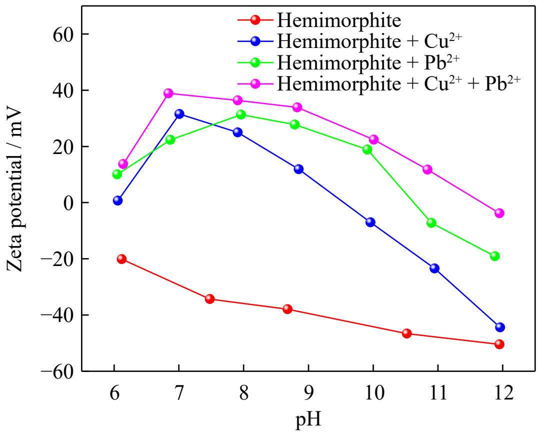

**Fig. 3. Zeta potential of hemimorphite as a function of pH.**

### 3.3. Adsorption amount analysis

The microflotation tests showed that synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ could effectively enhance the flotation behavior of hemimorphite. The adsorption behavior of xanthate on the hemimorphite surface in different activation systems was examined via adsorption experiments to investigate the influence of synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ on the hemimorphite floatability. As shown in Fig. 4, the amount of xanthate adsorbed on the hemimorphite surface in the different activation systems increased with the concentration of the metal ions. The number of active adsorption sites on the hemimorphite surface increased with the initial concentration of metal ions in the pulp, facilitating the interaction of the collector reagent with the surface. Furthermore, the amount of xanthate adsorbed onto the hemimorphite surface was higher following the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ compared with that when the mineral surface was activated solely by $Cu^{2+}$ or $Pb^{2+}$. In the synergistic activation system with $Cu^{2+}$ + $Pb^{2+}$, the increase in the type and quantity of active sites on the hemimorphite surface is conducive to the adsorption of sulfidizing agents and xanthate on the mineral surface, thereby enhancing the hemimorphite floatability.

### 3.4. FTIR analysis

The adsorption experiments demonstrated that synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ enabled the great adsorption of xanthate on the hemimorphite surface, thereby enhancing the surface hydrophobicity of hemimorphite. The FTIR spectra of hemimorphite in different activation systems were analyzed to further clarify the effect of synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ on the adsorption behavior of xanthate on the hemimorphite surface. Fig. 5 shows the FTIR spectra of hemimorphite in various activation systems. Following activation with $Cu^{2+}$, the distinct characteristic peaks of xanthate appeared at 2924 and 2853 cm$^{-1}$. Similar to that in the $Cu^{2+}$

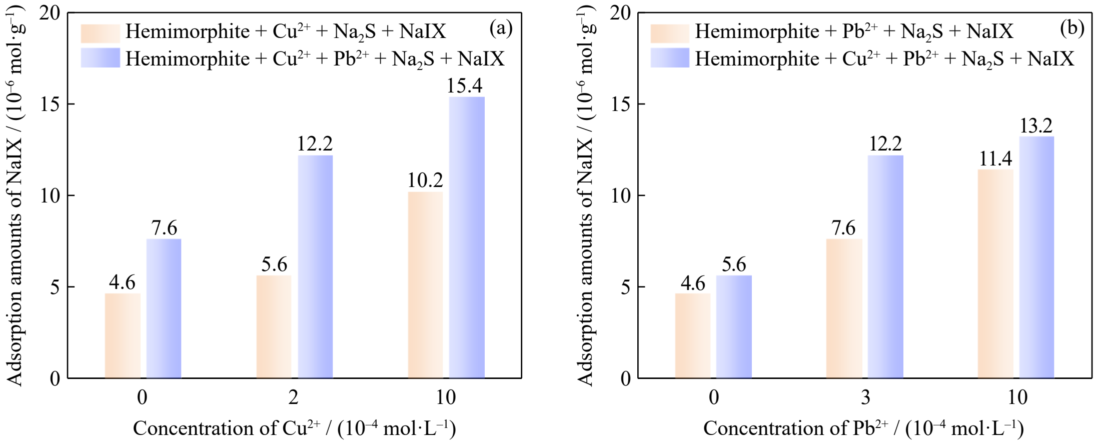

**Fig. 4. Adsorption amounts of the collector on the hemimorphite surface as a function of (a) $Cu^{2+}$ and (b) $Pb^{2+}$ concentrations.**

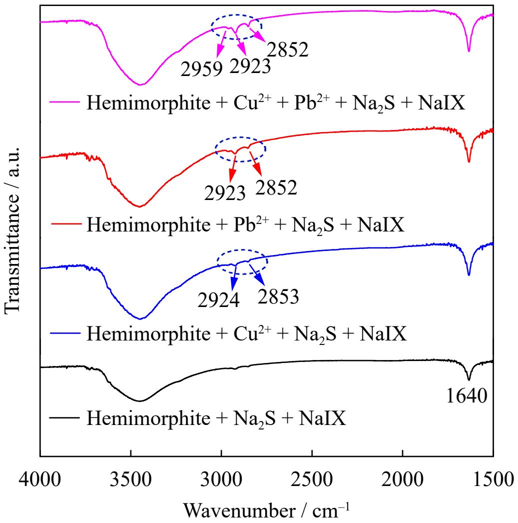

**Fig. 5. FTIR spectra of hemimorphite under different conditions.**

activation system, clear xanthate characteristic peaks were observed at 2923 and 2852 $cm^{-1}$ in the $Pb^{2+}$ activation system. This finding indicated that $Cu^{2+}$ or $Pb^{2+}$ activation promoted xanthate adsorption on the hemimorphite surface. Following synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the characteristic peaks of xanthate at 2923 and 2852 $cm^{-1}$ became highly pronounced. In addition, new peak appeared in the infrared spectra of hemimorphite at 2959 $cm^{-1}$, which was attributed to the asymmetric stretching vibration peak of C–H in xanthate. Therefore, the FTIR spectra results further corroborated that synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ significantly enhanced xanthate adsorption on the hemimorphite surface, thereby augmenting the surface hydrophobicity.

### 3.5. AFM analysis

The interaction of the mineral surface with flotation agents changes the morphology of its microscopic regions. AFM was used to detect the hemimorphite surface under various activation conditions to investigate the effect of synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ on the surface properties of hemimorphite (Fig. 6). As shown in Fig. 6(a), the surface roughness of the untreated hemimorphite was low, and its root mean square deviation ($R_q$) was 9.87 nm. As shown in Fig. 6(b) and (c), the surface morphology of the hemimorphite treated with $Cu^{2+}$ or $Pb^{2+}$ changed significantly. New particle products were generated on the hemimorphite surface, and the $R_q$ increased to 13.4 and 28.9 nm. This phenomenon can be attributed to the adsorption of active metal ions, which contributed to the formation of Cu- and Pb-containing components on the mineral surface, thus increasing the surface roughness. Compared with that after the individual addition of $Cu^{2+}$ or $Pb^{2+}$, the surface morphology of hemimorphite was greatly changed, and many particle products were observed after the addition of $Cu^{2+}$ + $Pb^{2+}$ (Fig. 6(d)). The $R_q$ of the hemimorphite surface further increased to 45.5 nm, indicating that synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ generated a large number of active components on the mineral surface and enhanced its reactivity.

### 3.6. ToF-SIMS analysis

ToF-SIMS was used to detect the chemical composition of the mineral surface for the subsequent elemental analysis, semi-quantitative analysis, and secondary ion imaging. Deep profiling enabled the 3D imaging of the substances formed on the mineral surface, providing a spatial distribution map of the target components. Initially, we investigated the 2D distribution of $Cu^+$ and $Pb^+$ ion fragments and the normalized intensity of secondary ions on the hemimorphite surface in the absence and presence of $Cu^{2+}$ and $Pb^{2+}$, as shown in Fig. 7. Sparse $Cu^+$ and $Pb^+$ signals were detected on the untreated hemimorphite surface, potentially due to the sensitivity of the instrument. Distinct $Cu^+$ and $Pb^+$ signals appeared on the hemimorphite surface after activation with $Cu^{2+}$ and $Pb^{2+}$, respectively. Upon the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, $Cu^+$ and $Pb^+$ signals were observed simultaneously on the hemimorphite surface. Moreover, the $Pb^+$ signals were more intense than those recorded after the activation with $Pb^{2+}$ alone. This finding indicated that the $Cu^{2+}$ and $Pb^{2+}$ ions from the pulp could be adsorbed onto the hemimorphite surface, generating Cu and Pb. Compared with the Zn on the hemimorphite surface, the newly generated Cu and Pb possessed greater reactivity and were more prone to react with the subsequently added sulfidizing agents. Hence, the addition of $Cu^{2+}$ and $Pb^{2+}$ before the sulfidization of hemimorphite en-

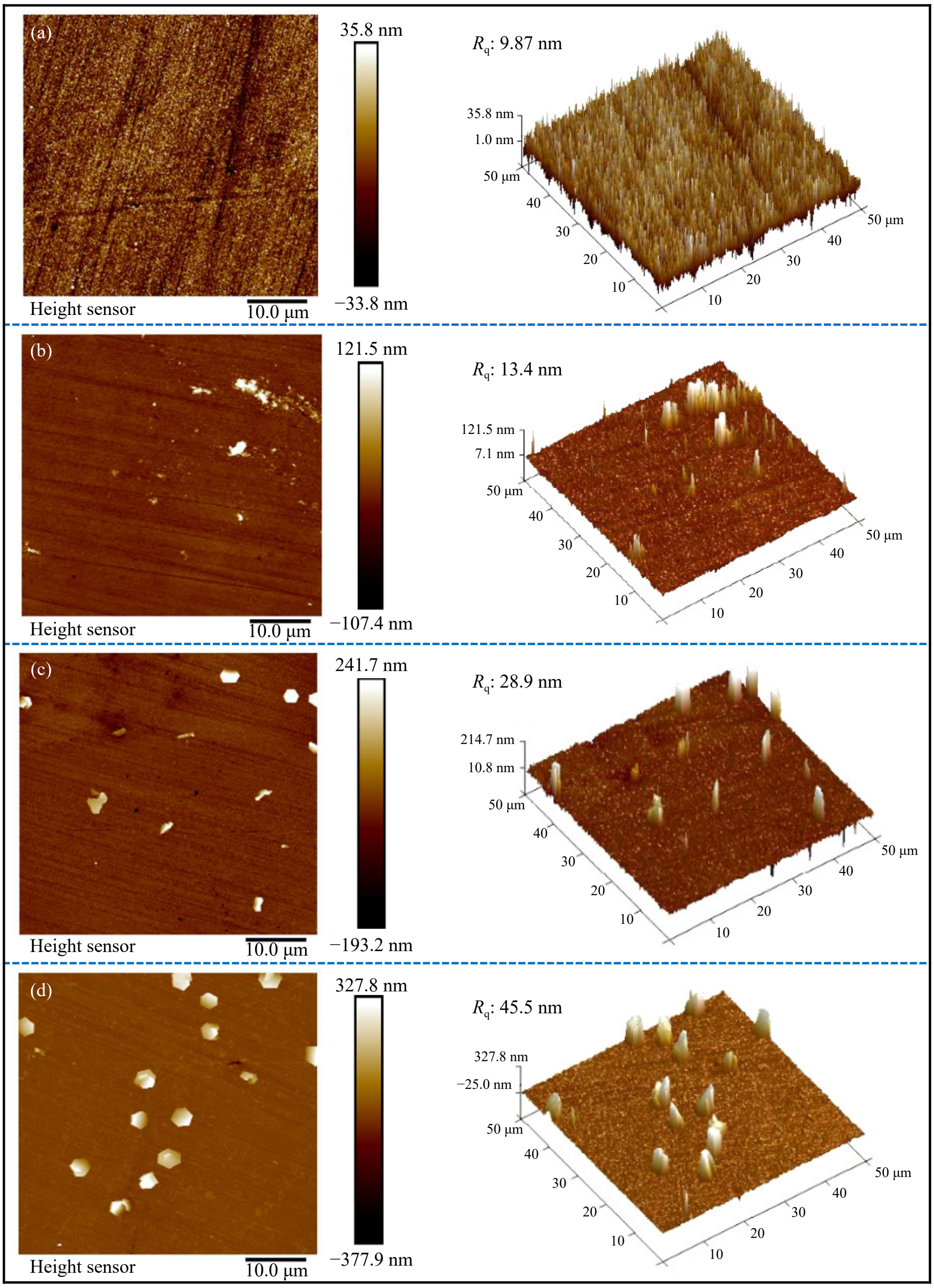

**Fig. 6. AFM images of hemimorphite surfaces treated with (a) ultrapure water, (b) $Cu^{2+}$, (c) $Pb^{2+}$, and (d) $Cu^{2+}$ + $Pb^{2+}$.**

hanced the reactivity of the mineral. The normalized intensity of the secondary ions on the hemimorphite surface is shown in Fig. 7. Abundant $SiO_3^-$, $Zn^+$ signals, and trace amounts of $Cu^+$ and $Pb^+$ signals were detected on the hemimorphite surface without metal-ion activation. The $SiO_3^-$ and $Zn^+$ signals correspond to the $ZnSiO_4$ substance within hemimorphite, and the minimal $Cu^+$ and $Pb^+$ signals may arise from instrumental measurement errors. Compared with those in the untreated hemimorphite, the $SiO_3^-$ and $Zn^+$ signals decreased, and the $Cu^+$ or $Pb^+$ signals increased on the hemimorphite surface when activated with $Cu^{2+}$ or $Pb^{2+}$, respectively. After the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the $SiO_3^-$ and $Zn^+$ signals on the hemimorphite surface further decreased, and the $Cu^+$ and $Pb^+$ signals intensified. This finding suggested that many Cu and Pb components from the pulp were transferred to the hemimorphite surface, significantly reducing the relative content of $SiO_3^-$ and $Zn^+$ on the mineral surface. After the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the $Pb^+$ signal on the hemimorphite surface became stronger.

The ToF-SIMS depth analysis of $Cu^+$ and $Pb^+$ on the hemimorphite surface under different activation conditions was

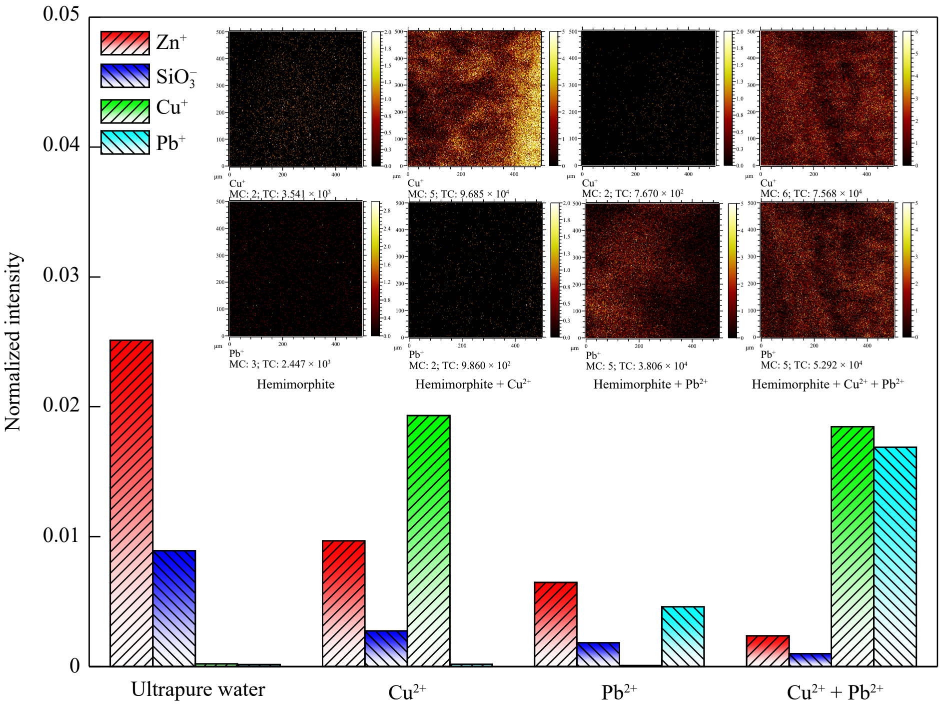

**Fig. 7.** **2D distribution of $Cu^+$ and $Pb^+$ ion fragments and normalized intensity of secondary ions on hemimorphite surfaces treated with ultrapure water, $Cu^{2+}$, $Pb^{2+}$, and $Cu^{2+}$ + $Pb^{2+}$.**

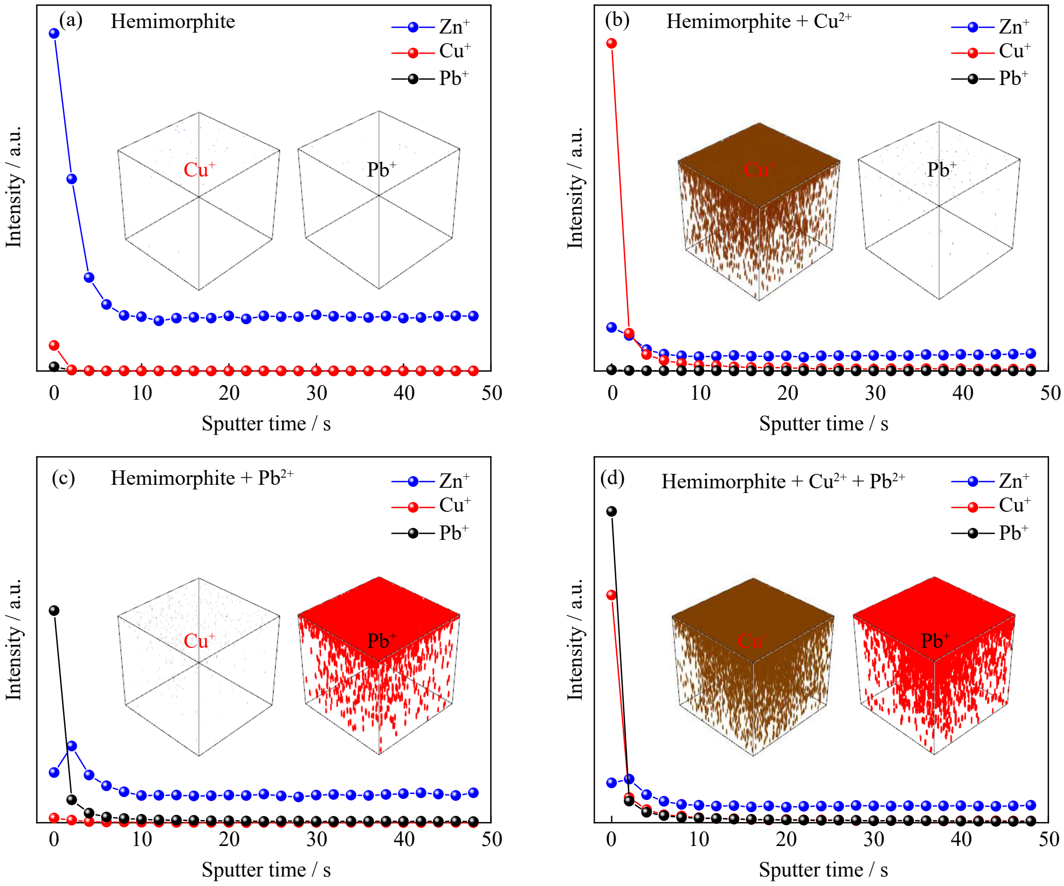

**Fig. 8.** **3D distribution and ToF-SIMS depth profile of secondary ions on the hemimorphite surface treated with (a) ultrapure water, (b) $Cu^{2+}$, (c) $Pb^{2+}$, and (d) $Cu^{2+}$ + $Pb^{2+}$.**

performed to determine their spatial distribution on the mineral surface. As shown in Fig. 8(a), no longitudinal distribution of $Cu^+$ and $Pb^+$ was found on the untreated hemimorphite surface. After activation with either $Cu^{2+}$ or $Pb^{2+}$, distinct covering layers of $Cu^+$ or $Pb^+$ appeared on the hemimorphite surface, respectively (Fig. 8(b) and (c)). After the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the hemimorphite surface exhibited simultaneous covering layers of $Cu^+$ or $Pb^+$ (Fig. 8(d)). Compared with the individual $Cu^{2+}$ or $Pb^{2+}$ activation, the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ led to a denser distribution of $Cu^+$ and $Pb^+$ on the hemimorphite surface. With the formation of certain thicknesses of Cu and Pb absorption layers, the generation of a denser activated layer on the mineral surface is promoted. Fig. 8 shows the deep profiling curves of the positive ions on the hemimorphite surface under different activation conditions. Among these ions, $Zn^+$ is a characteristic ion of hemimorphite. According to the deep profiling curves of the untreated hemimorphite, the signal intensity of $Zn^+$ stabilized with the increase in sputtering time (Fig. 8(a)). This finding indicated that the selected characteristic ions were present in the mineral. After the hemimorphite surface was activated with $Cu^{2+}$ or $Pb^{2+}$, $Cu^+$ or $Pb^+$ signals appeared on the mineral surface in Fig. 8(b) and (c), respectively. The initial intensities of these signals were significantly higher than those of $Zn^+$ present in hemimorphite. With the increasing sputtering time, the $Cu^+$ and $Pb^+$ signals in the $Cu^{2+}$ and $Pb^{2+}$ activation systems gradually decreased and eventually stabilized. After the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the $Cu^+$ and $Pb^+$ signals appeared simultaneously on the hemimorphite surface, with the signal intensity of $Pb^+$ being higher than that of $Cu^+$. With the increasing sputtering time, the $Cu^+$ and $Pb^+$ signals in the different activation systems gradually decreased and eventually stabilized, ultimately falling below the signal intensity of $Zn^+$, as shown in Fig. 8(d). Therefore, these curves further prove that $Cu^{2+}$ and $Pb^{2+}$ were adsorbed on the hemimorphite surface, generating certain thicknesses of Cu and Pb adsorption layers.

### 3.7. XPS analysis

Fig. 9 shows the XPS spectra of hemimorphite and the atomic concentrations of elements on the hemimorphite surface under different activation conditions. As shown in Fig. 9, the natural hemimorphite sample surface exhibited no Cu or Pb peaks. After activation with $Cu^{2+}$, a distinct Cu 2p peak appeared on the mineral surface. Similarly, $Pb^{2+}$ addition resulted in a noticeable Pb 4d peak on the hemimorphite surface. Upon the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, distinct Cu 2p and Pb 4d peaks were observed on the mineral surface. This finding indicated that the $Cu^{2+}$ and $Pb^{2+}$ in the pulp can be transferred to the hemimorphite surface, generating Cu- or Pb-containing components on the mineral surface. Compared with individual $Pb^{2+}$ activation, the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ increased the Pb content on the hemimorphite surface from 1.90% to 2.75%. This increment indicated a further increase in the Pb-containing components on the hemimorphite surface in the synergistic activation system, thereby enhancing the reactivity of the mineral surface.

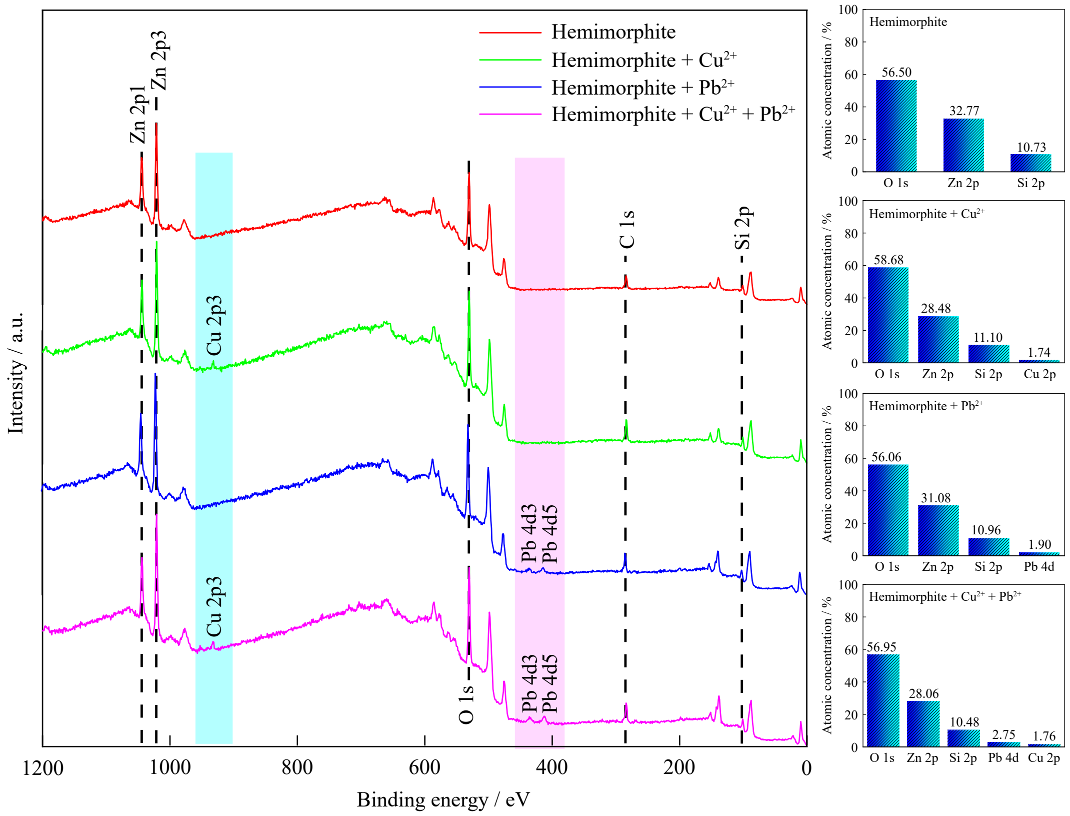

**Fig. 9. XPS spectra and atomic concentration in hemimorphite surfaces.**

Fig. 10 shows the O 1s XPS spectra of hemimorphite under different activation conditions. As shown in Fig. 10(a), the O 1s XPS peaks at binding energies of 531.24, 531.93, and 533.33 eV correspond to the O in the ZnO, Si–O, and –OH found on the hemimorphite surface, respectively [16]. After $Cu^{2+}$ activation, the proportion of O in the ZnO on the hemimorphite surface increased by 1.78%, whereas that in the –OH decreased by 1.56% (Fig. 10(b)). Following $Pb^{2+}$ addition, the proportion of O in the ZnO on the hemimorphite surface increased by 3.01%, and that in the –OH decreased by 2.98% (Fig. 10(c)). Compared with that under individual $Cu^{2+}$ or $Pb^{2+}$ activation, the proportion of O in the –OH on the hemimorphite surface further decreased to 3.32% after synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, as shown in Fig. 10(d). This phenomenon occurred because the metal ions in the pulp underwent hydrolysis to form the corresponding metal-ion –OH complexes. These newly formed metal hydroxide complexes can undergo dehydration and condensation reactions with the –OH groups on the hemimorphite surface [30], leading to the adsorption of metal ions on the mineral surface and a reduction in the content of –OH. The interactions of $Cu^{2+}$ + $Pb^{2+}$ with the hemimorphite surface can increase the number of active sites for the subsequent interactions with the sulfidizing agents and collectors. In addition, the interaction between the metal hydroxide complexes and –OH groups reduces the hydrophilic components on the mineral surface, thus enhancing the floatability of hemimorphite. Therefore, according to the results of zeta potential, AFM, and ToF-SIMS, $Cu^{2+}$ + $Pb^{2+}$ can interact with the hemimorphite surface either through direct adsorption as metal ions or indirect adsorption as metal hydroxide complexes.

Fig. 11 shows the Cu 2p and Pb 4d XPS spectra of hemimorphite under different activation conditions. As shown in Fig. 11(a), no significant Pb 4d peak was observed on the hemimorphite surface after activation with $Cu^{2+}$. However, a Cu 2p peak was detected at a binding energy of 932.96 eV [31–32]. Following $Pb^{2+}$ activation, the Pb 4d peak was detected at a binding energy of 413.67 eV on the hemimorphite (Fig. 11(b)) [2]. Upon the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, Cu 2p and Pb 4d peaks were detected at binding energies of 932.88 and 413.88 eV, respectively. This finding indicated that $Cu^{2+}$ and $Pb^{2+}$ can be adsorbed onto the hemimorphite surface. Furthermore, under the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the mineral surface can simultaneously generate Cu and Pb components. In the full spectra, the types and quantities of active components on the hemimorphite surface increased after the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, thereby effectively enhancing the reactivity of the min-

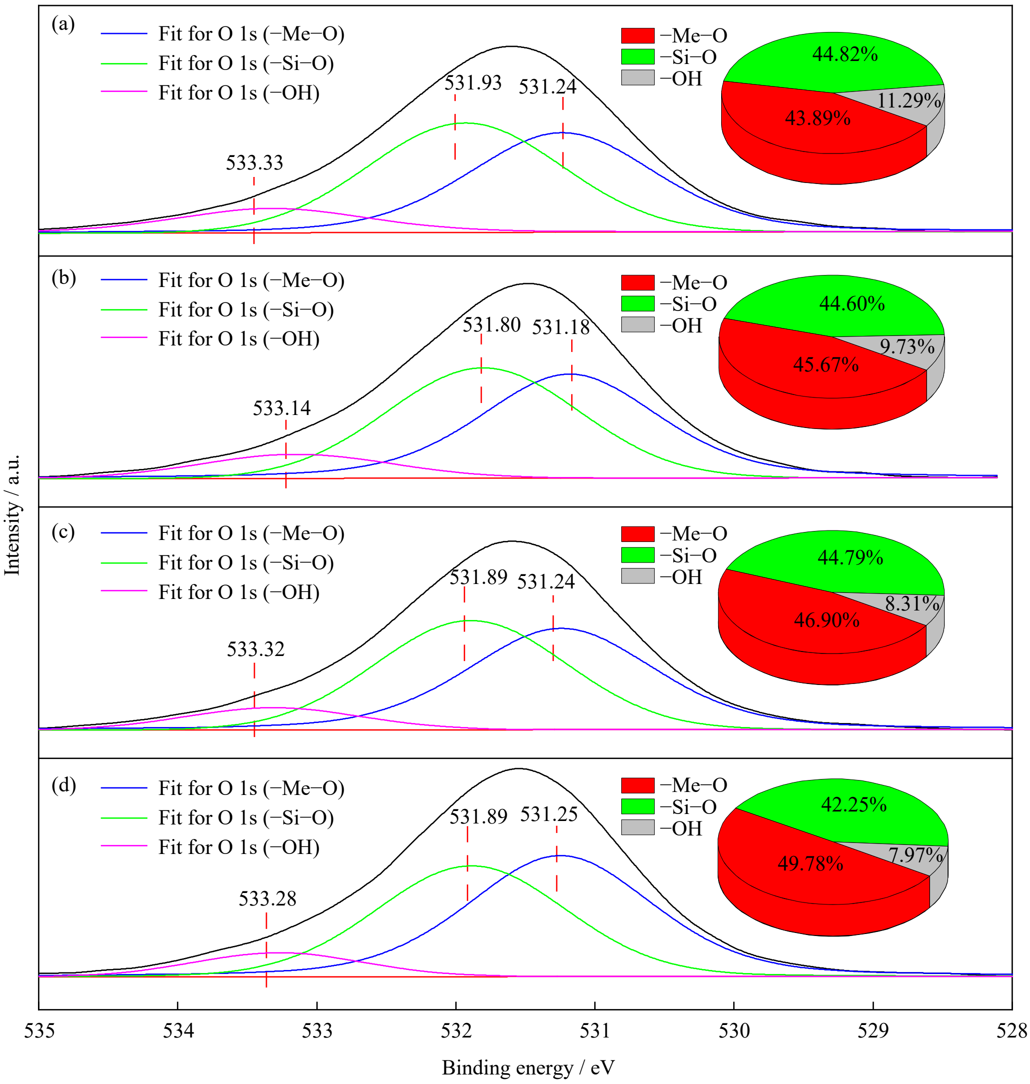

**Fig. 10. O 1s XPS spectra of hemimorphite surfaces treated with (a) ultrapure water, (b) $Cu^{2+}$, (c) $Pb^{2+}$, and (d) $Cu^{2+}$ + $Pb^{2+}$ (Me denotes the metal).**

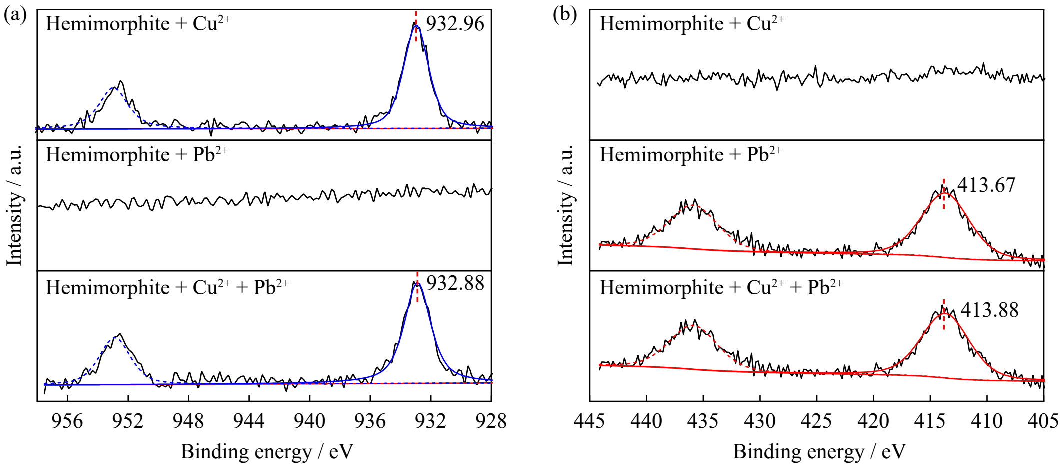

**Fig. 11. XPS spectra for hemimorphite surfaces: (a) Cu 2p; (b) Pb 4d .**

eral surface.

The results suggested that after the synergistic activation of hemimorphite by $Cu^{2+}$ + $Pb^{2+}$, metal ions were adsorbed onto the mineral surface, causing a positive shift in the surface potential of the mineral. Moreover, the zeta potential was higher than that of the mineral surface activated solely by $Cu^{2+}$ or $Pb^{2+}$. This finding indicated that synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ favors the adsorption of $Cu^{2+}$ and $Pb^{2+}$ onto the mineral surface. Following the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the content of –OH, which is indicative of hydrophilicity, notably decreased on the hemimorphite. Meanwhile, the content of highly reactive Pb significantly increased. ToF-SIMS results demonstrated that the hemimorphite surface formed Cu and Pb layers of certain thicknesses after the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$. This phenomenon led to an increase in the number of active metal sites on the hemimorphite surface that facilitated subsequent interactions with flotation reagents.

On the basis of the aforementioned results, a schematic illustrating the mechanism of synergistic activation of hemimorphite surfaces with $Cu^{2+}$ + $Pb^{2+}$ for hemimorphite flotation was generated, as shown in Fig. 12. In individual $Cu^{2+}$ or $Pb^{2+}$ activation systems, $Cu^{2+}$ and $Pb^{2+}$ can interact with the hemimorphite surface through direct metal-ion adsorption or indirect adsorption as metal hydroxide complexes. This interaction leads to the formation of highly active Cu or Pb components on the hemimorphite surface, thereby facilitating the subsequent adsorption of sulfidizing agents and the collector. Following the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the number and type of active components on the hemimorphite surface increase. Compared with those under individual $Cu^{2+}$ or $Pb^{2+}$ activation, the active components on the hemimorphite surface under the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ are composed of Cu- and Pb-containing species. Furthermore, the content of these active components increases. In the synergistic activation system with $Cu^{2+}$ + $Pb^{2+}$, the adsorption of sulfidizing agents and xanthate on the hemimorphite surface is significantly enhanced, providing favor-

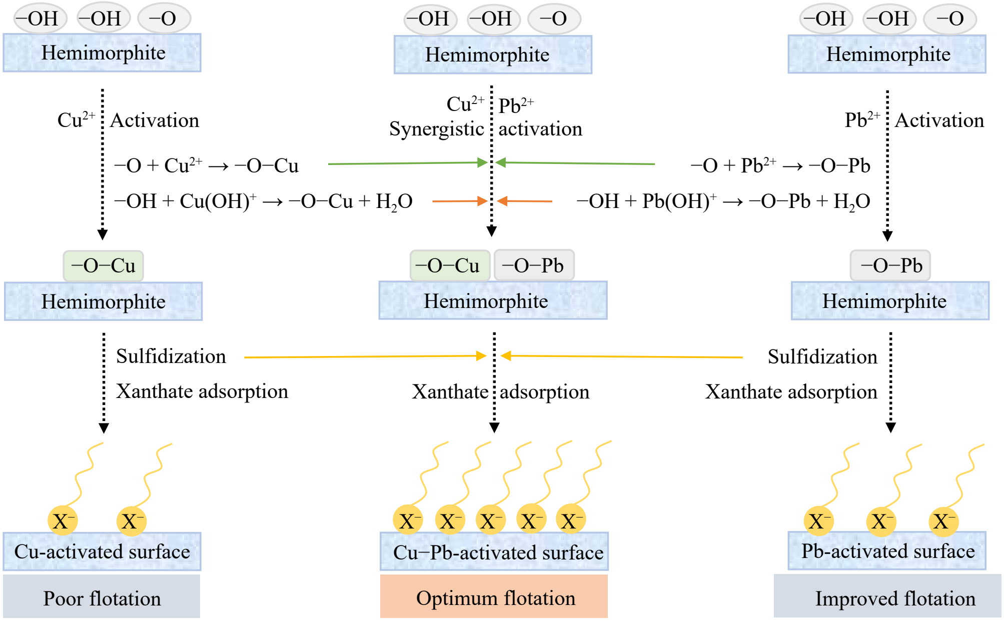

**Fig. 12. Schematic of the synergistic activation of hemimorphite surfaces with $Cu^{2+}$ + $Pb^{2+}$ and its response to xanthate adsorption and flotation.**

able conditions for achieving the desired flotation performance. The research approach in this study provides a new pathway for floating hemimorphite, offering insights into the efficient recovery of refractory zinc oxide minerals.

## 4. Conclusions

This study clarified the adsorption characteristics and mechanism of synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ for the hemimorphite surface and elucidated its impact on the adsorption behavior of xanthate on the hemimorphite surface. The conclusions are as follows:

(1) Synergistic activation with $Cu^{2+}$ + $Pb^{2+}$ significantly enhanced the flotation behavior of hemimorphite. Compared with that in the individual $Cu^{2+}$ or $Pb^{2+}$ activation system, the hemimorphite recovery in the synergistic system further increased.

(2) After the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$, the adsorption of $Pb^{2+}$ on the hemimorphite surface notably increased. The Pb adsorption layer on the hemimorphite surface became thicker, providing abundant active sites for the subsequent interaction between the flotation reagents and the hemimorphite surface.

(3) The reactivity between the hemimorphite surface and xanthate intensified after the synergistic activation with $Cu^{2+}$ + $Pb^{2+}$. The amount of xanthate adsorbed on the hemimorphite surface increased, thereby enhancing the surface hydrophobicity and floatability of hemimorphite.

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## Conflict of Interest

Qicheng Feng is an editorial board member for this journal and not involved in the editorial review or the decision to publish this article. The authors declare that there is no conflict of interest regarding the publication of this paper.

## References

[1] E. Abkhoshk, E. Jorjani, M.S. Al-Harahsheh, F. Rashchi, and M. Naazeri, Review of the hydrometallurgical processing of non-sulfide zinc ores, *Hydrometallurgy*, 149(2014), p. 153.

[2] Y.H. Yi, P.X. Li, G. Zhang, Q.C. Feng, and G. Han, Stepwise activation of hemimorphite surfaces with lead ions and its contribution to sulfidization flotation, *Sep. Purif. Technol.*, 299(2022), art. No. 121679.

[3] X. Zhang, Y. Wang, J.S. Deng, *et al.*, Effect of ammonium sulfate on the formation of zinc sulfide species on hemimorphite surface and its role in sulfidation flotation, *Int. J. Miner. Metall. Mater.*, 30(2023), No. 11, p. 2147.

[4] Q.B. Cao, H. Zou, D.W. Liu, S.M. Wen, and X.M. Chen, Flotation separation of smithsonite from calcite using an amino-acid collector, *Sep. Purif. Technol.*, 281(2022), art. No. 119980.

[5] Y.J. Luo, G.F. Zhang, C.B. Li, *et al.*, Flotation separation of smithsonite from calcite using a new depressant fenugreek gum, *Colloids Surf. A*, 582(2019), art. No. 123794.

[6] R.D. Deng, Y. Hu, J.G. Ku, Y.Q. Ma, and Z.G. Yang, Ion migration law in flotation pulp and its influence on the separation of smithsonite and quartz, *Sep. Sci. Technol.*, 53(2018), No. 5, p. 833.

[7] M. Ejtemaei, M. Irannajad, and M. Gharabaghi, Role of dissolved mineral species in selective flotation of smithsonite from quartz using oleate as collector, *Int. J. Miner. Process.*, 114(2012), p. 40.

[8] Q.C. Feng, W.H. Yang, M.H. Chang, S.M. Wen, D.W. Liu, and G. Han, Advances in depressants for flotation separation of Cu–Fe sulfide minerals at low alkalinity: A critical review, *Int. J. Miner. Metall. Mater.*, 31(2024), No. 1, p. 1.

[9] J. Yao, X.Q. Ban, Y. Xie, W.Z. Yin, Y.L. Wang, and F.J. Xue, Research advancement of efficient flotation separation technologies for magnesium-containing minerals, *Green Smart Min. Eng.*, 1(2024), No. 2, p. 140.

[10] H.P. Zhou, Z.Z. Yang, Y.B. Zhang, F.X. Xie, and X.P. Luo, Flotation separation of smithsonite from calcite by using flaxseed gum as depressant, *Miner. Eng.*, 167(2021), art. No. 106904.

[11] M. Ejtemaei, M. Gharabaghi, and M. Irannajad, A review of zinc oxide mineral beneficiation using flotation method, *Adv. Colloid Interface Sci.*, 206(2014), p. 68.

[12] Q. Shi, Q.M. Feng, G.F. Zhang, and H. Deng, Electrokinetic properties of smithsonite and its floatability with anionic collector, *Colloids Surf. A*, 410(2012), p. 178.

[13] W.P. Liu, Z.X. Wang, X.M. Wang, and J.D. Miller, Smithsonite flotation with lauryl phosphate, *Miner. Eng.*, 147(2020), art. No. 106155.

[14] W. Tan, G.Y. Liu, J.Q. Qin, and H.L. Fan, Hemimorphite flotation with 1-hydroxydodecylidene-1, 1-diphosphonic acid and its mechanism, *Minerals*, 8(2018), No. 2, art. No. 38.

[15] Q.C. Feng, W.H. Yang, S.M. Wen, H. Wang, W.J. Zhao, and G. Han, Flotation of copper oxide minerals: A review, *Int. J. Min. Sci. Technol.*, 32(2022), No. 6, p. 1351.

[16] Q. Zuo, J. Yang, Y.F. Shi, and D.D. Wu, Activating hemimorphite using a sulfidation-flotation process with sodium sulfosalicylate as the complexing agent, *J. Mater. Res. Technol.*, 9(2020), No. 5, p. 10110.

[17] L. Wang, G.Y. Hu, W. Sun, S.A. Khoso, R.Q. Liu, and X.F. Zhang, Selective flotation of smithsonite from dolomite by using novel mixed collector system, *Trans. Nonferrous Met. Soc. China*, 29(2019), No. 5, p. 1082.

[18] Z.Y. Song, S.M. Wen, G. Han, and Q.C. Feng, Recent progress on chelating reagents in flotation of zinc oxide ores: A review, *Minerals*, 13(2023), No. 10, art. No. 1278.

[19] Q.C. Feng, G. Zhang, Q. Zhang, and W.J. Zhao, Synergistic activation of sulfidized hemimorphite with copper–lead species for improving surface hydrophobicity and floatability, *Sep. Purif. Technol.*, 332(2024), art. No. 125854.

[20] Y.G. Chen, Y.S. Sun, and Y.X. Han, Efficient flotation separation of lead–zinc oxide ores using mineral sulfidation reconstruction technology: A review, *Green Smart Min. Eng.*, 1(2024), No. 2, p. 175.

[21] J.P. Cai, D.W. Liu, P.L. Shen, *et al.*, Effects of heating-sulfidation on the formation of zinc sulfide species on smithsonite surfaces and its response to flotation, *Miner. Eng.*, 169(2021), art. No. 106956.

[22] S.P. Jiang, G.F. Zhang, Y.Q. Chang, Q.M. Feng, and B.F. Zhang, Effect of metal ions on sulfiding flotation of smithsonite, *Nonferrous Met. Miner. Process*, 2(2016), p. 23.

[23] G.F. Zhang and F.Y. Zhang, Effect of metal ions on sulfiding flotation of hemimorphite, *J. Cent. South Univ. Sci. Technol.*, 48(2017), No. 7, p. 1689.

[24] Y.Q. Huang, W.Z. Yin, R.D. Deng, D.Q. Xing, and F. Rao, Strengthening sulfidation flotation of hemimorphite *via* pretreatment with $Pb^{2+}$, *Minerals*, 9(2019), No. 8, art. No. 463.

[25] N. Sehlotho, Z. Sindane, M. Bryson, and L. Lindvelt, Flowsheet development for selective Cu–Pb–Zn recovery at Rosh Pinah concentrator, *Miner. Eng.*, 122(2018), p. 10.

[26] H.S. Han, Y.H. Hu, W. Sun, *et al.*, Fatty acid flotation versus BHA flotation of tungsten minerals and their performance in flotation practice, *Int. J. Miner. Process.*, 159(2017), p. 22.

[27] X. Fan and N.A. Rowson, The effect of $Pb(NO_3)_2$ on ilmenite flotation, *Miner. Eng.*, 13(2000), No. 2, p. 205.

[28] Z.H. Wang, G. Han, and Q.C. Feng, Selective flotation of galena and sphalerite using N-(phosphonomethyl) iminodiacetic acid as an eco-friendly depressant, *Green Smart Min. Eng.*, 1(2024), No. 1, p. 96.

[29] X.K. Li, Y. Zhang, H.Y. He, Y. Wu, D.Y. Wu, and Z.H. Guan, Flotation separation of scheelite from calcite using luteolin as a novel depressant, *Int. J. Miner. Metall. Mater.*, 31(2024), No. 3, p. 462.

[30] Z.H. Shen, S.M. Wen, H. Wang, *et al.*, Effect of dissolved components of malachite and calcite on surface properties and flotation behavior, *Int. J. Miner. Metall. Mater.*, 30(2023), No. 7, p. 1297.

[31] J. Liu, Z.G. Liu, J. Tan, and F. Hu, Flotation separation of pyrite from chalcopyrite by tetrazinan-thione collectors, *J. Cent. South Univ.*, 30(2023), No. 8, p. 2587.

[32] Y.C. Zhang, W.J. Zhao, G. Han, and Q.C. Feng, A novel activation method for regulating surface characteristics and flotation performance of smithsonite: XPS, SEM-EDS, AFM, ToF-SIMS and FT-IR studies, *Sep. Purif. Technol.*, 352(2025), art. No. 128276.

## 2024 Innovative Young Scientist

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