Treatment Of Copper-Containing Acid Mine Drainage By Combined Use Of Multiple Technologies

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Abstract

This work provided a promising methodology for removing iron ions and recovering copper ions from copper-containing AMD by incorporating the copper ions sulfide precipitation, iron ions biomineralization, and lime neutralization. The experimental results indicated that nearly all copper ions were removed in the sulfide precipitation process and 82.2% of iron ions were removed after biomineralization treatment. Additionally, the consumption of lime slurry was reduced compared to the conventional direct neutralization method. By integrating various techniques, it is possible to improve the removal efficiency of iron ions, reduce the consumption of lime, and recover the copper and sulfur from the AMD.

Keywords: Acid mine drainage, copper ions, sulfidation, biomineralization

Introduction

The management of acidic mine drainage (AMD) is a global challenge faced by numerous countries due to its serious threat to the environment (Kefeni *et al.* 2017). A variety of active and passive methodologies have been developed and used for AMD treatment. Neutralization by adding alkaline materials, particularly lime slurry, is the most widely used AMD treatment technology, especially for the emergency management of AMD with high concentrations of metal ions and low pH (Chen *et al.* 2021; Johnson and Hallberg 2005). However, the neutralization process consumes a substantial amount of lime and generates large volumes of sludge containing hazardous metals. Theoretically, the consumption of alkaline materials is usually several times of the theoretical value for the neutralization of H^+ ions and the precipitation of the metal ions, especially for the AMD with high iron ions concentration (Cheong *et al.* 2022). Therefore, iron ions in AMD are critical to the consumption of the alkaline materials in the application of neutralization technology, as well as the cost of subsequent disposal of the residual sludge (Djedidi *et al.* 2009). Consequently, integrating multiple treatment technologies represents an essential strategy for effective AMD management (Mosai *et al.* 2024).

Biomineralization has been identified as a promising method for the removal of iron ions, to reduce the consumption of lime in the neutralization process, but still limited by the low removal efficiency (Jiang *et al.* 2024). It has been reported that the required doses of lime to neutralize AMD can be reduced by nearly 80% after biomineralization treatment (Song *et al.* 2022). To improve the biomineralization efficiency, many measures have been explored, including cyclic biomineralization and pH-controlled biomineralization (Jiang *et al.* 2024; Jin *et al.* 2020). A constant pH of 2.5 could lead to a greater fraction of iron precipitating during the biooxidation of Fe^{2+} (Liu *et al.* 2024). However, the pH-controlled biomineralization treatment still cannot completely remove iron ions from AMD. Consequently, subsequent neutralization with lime slurry is still required, generating neutralization residues containing hazardous metal ions.

The sulfide precipitation method has increased interest for a long time due to its ability to selectively separate dissolved metals from AMD, producing metal sulfide residues with a high concentration of the element recovered (Li *et al.* 2024b). These advantages have promoted the study of sulfide precipitation for removing and recovering several metals, such as copper, zinc and iron from AMD (Li *et al.* 2024a). Theoretically, Cu^{2+} and Fe^{2+} can react with sulfide to form precipitates, while Fe^{3+} can be reduced by sulfide to Fe^{2+}. According to the differences in reaction conditions, copper ions can be preferentially precipitated and removed from copper-containing AMD (Choi *et al.* 2006), but the influences of iron ions were unclear.

In this work, we propose a comprehensive treatment scheme that combines sulfide precipitation, biomineralization, and lime neutralization for the effective treatment of copper-containing AMD. Specifically, sodium sulfide is added to precipitate copper ions. Subsequently, *Acidithiobacillus ferrooxidans* is inoculated for biomineralization. During the biomineralization process, the pH is maintained at 2.5±0.1 by adding lime slurry. Following the completion of the biomineralization reaction, lime slurry is continuously added until the pH is elevated to 9.0. The combined use of these multiple technologies demonstrates significant advantages in improving the removal efficiency of iron ions, reducing the consumption of lime, and facilitating the recovery of copper and sulfur from the copper-containing AMD.

Materials and methods

Simulated copper-containing AMD

The initial iron concentration of the simulated AMD was 1000 mg/L with a Fe^{2+} to Fe^{3+} ratio of 7:3, and the Cu^{2+} concentration was 15 mg/L, in consistent with the AMD sample collected from a pyrite mine in Anhui Province, China. The stock solution of 3000 mg/L Fe^{3+} was prepared from the biogenic Fe^{3+}, which was derived from the cell-free supernatant of *Acidithiobacillus ferrooxidans* cultures after bacterial harvesting via centrifugation, and the stock solution of 150 mg/L Cu^{2+}, 7000 mg/L Fe^{2+} was prepared by analytical grade $CuSO_4·5H_2O$ and $FeSO_4·H_2O$ using deionized water. 0.01 mol/L H2SO4 solution and 1.0 g/L lime slurry were used for pH control.

Reaction between sulfide and metal ions

The sulfidation experiments were performed in 50 mL centrifuge tubes. In the stoichiometrically matched experiments, Na_2S at molar ratios of 0, 0.25, 0.5, 0.75, and 1 to the Cu^{2+} and Fe^{3+} were added. The stock solution of 7.8 g/L Na2S was prepared by analytical grade Na2S·9H2O. The metal ions solution at pH 2.5 and the Na_2S solution were well mixed with a total volume of 50 mL, and then placed in a rotator mixer at 170 rpm and 30°C.

Biomineralization

The biooxidation experiments were conducted in a 250 mL conical flask containing 100 mL of simulated AMD. *Acidithiobacillus ferrooxidans* ATCC23270 provided by the Key Lab of Biometallurgy of the Ministry of Education of China was used. The inoculated cell density was approximately 1.0×10^8 cells/mL. The pH was adjusted by lime slurry every 8 hours. The flask was placed in a rotating shaker at 170 rpm and 30 °C to initiate the biooxidation process. After biomineralization, the AMD was filtered to collect precipitates and filtrate.

Neutralization

The simulated AMD and the filtrate obtained after the biooxidation treatment was subsequently neutralized by lime. $Ca(OH)_2$ slurry (10.0 g/L) was quantitively added to the filtrate until the solution pH was maintained at about 9.0. The sludge was filtered by 0.45 μm MCE filter paper (Jinteng, China), washed, dried at 70°C, and then weighed.

Analytical methods

The pH was measured using a pH meter (Beier 620, China). The Fe^{2+} concentration was determined using the 1,10-phenanthroline method (Pham *et al.* 2009). The morphology and elemental composition of the precipitates were identified by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS, SU8010, Japan).

Results and discussion

Interaction between iron and copper ions with sulfide ions

To identify the interaction between Fe^{3+} and S^{2-}, Na_2S was added to synthetic AMD without copper ions. The Fe^{2+} concentration was monitored to give a measure of the Fe^{2+} ions as a function of the S^{2-} ions. Theoretically, a ratio of $n(S):n(Fe^{3+})$ = 0.5 serves as a threshold point (Wei and Osseo-Asare 1996).

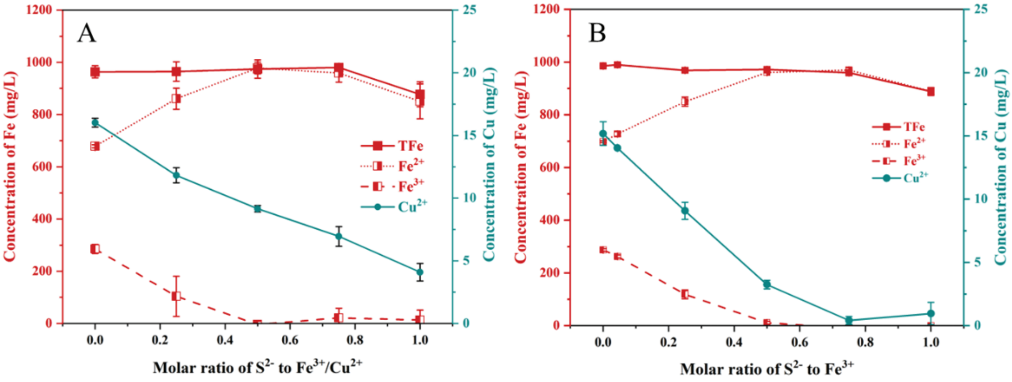

Figure 1 *Variation of copper and iron ions concentration under different sodium sulfide concentrations.*

The results suggested that each S^{2-} ion reduced two Fe^{3+} ions, which was inconsistent with the theoretical value (Fig. 1A). The sludge generated during the Fe^{3+} reduction process was sulfur. No FeS precipitates were formed during the reduction process due to the relatively high solubility of FeS under acidic conditions (Rickard 2006).

For the sulfide precipitation reaction of Cu^{2+}, Na_2S was added to the iron-free simulated AMD. It has been reported that the copper precipitate produced by reacting with sulfide ions is considered to be a form of CuS (Choi *et al.* 2006). In this work, Cu^{2+} was not completely removed when the ratio of n(S): n(Cu^{2+}) was 1:1, with a residual concentration of 4 mg/L (Fig. 1A). When the pH is within the range of 2 to 5, the precipitation rate of Cu^{2+} decreases as the pH drops (Choi *et al.* 2006). Specifically, at a pH of 2, the precipitation rate of Cu^{2+} only reached about 82%. Therefore, we speculated that some S^{2-} may have combined with H^+ to form H_2S or HS^-.

The experiment of the interaction between iron and copper ions with sulfide ions was conducted by introducing Na_2S into the copper-containing AMD. Compared to the Fe^{3+} reduction and the Cu^{2+} precipitation experiment, it can be found that the precipitation of Cu^{2+} from the AMD occurred synchronously with the reduction of Fe^{3+} (Fig. 1B). However, Cu^{2+} is not completely precipitated when Fe^{3+} is reduced. Instead, complete precipitation of Cu^{2+} occurs at the molar ratio of n(S): n(Fe^{3+}) higher than 0.5. The result at this point exhibited consistency with prior experiments, hypothesizing that partial S^{2-} ions may undergo protonation to form H_2S or HS^- species, thereby influencing the precipitation reactions.

Biomineralization of the AMD at pH 2.5

The metal ions removal efficiency by the direct biomineralization and sequential sulfidation treatment followed by biomineralization was investigated. It has been reported that a constant pH of 2.5 could lead to a greater fraction of iron precipitating during the

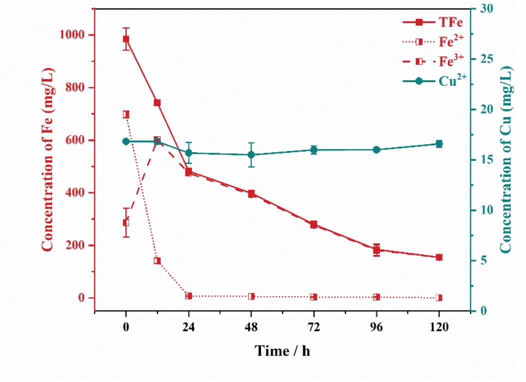

Figure 2 Variation of the metal ions concentration in AMD during the biomineralization process.

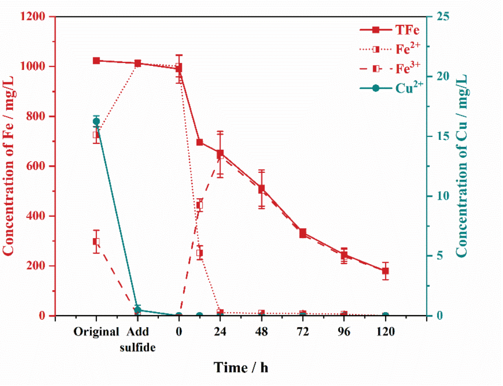

Figure 3 Variation of the metal ions concentration in AMD during the sulfidation and biomineralization process.

biooxidation of Fe2+ (Liu *et al.* 2024), therefore, the pH was maintained at 2.5 during the biomineralization process.

In the direct biomineralization group (Fig. 2), the Fe^{2+} was oxidized to Fe^{3+} within 24 hours. The total iron concentration decreased fastest in the first 24 hours, and then slowly decreased to the final concentration of about 150 mg/L, at which point the mineralization efficiency was 84.3%. Additionally, it could be found that the Cu^{2+} was not removed during the biomineralization process, indicating that the formed secondary minerals did not contain Cu and did not adsorb Cu^{2+} at the experimental condition.

The results of the sulfidation-biomineralization group indicated that the Fe^{3+} was reduced to Fe^{2+}, and Cu^{2+} no longer existed in the solution after sulfidation treatment (Fig. 3). After inoculation, the Fe^{2+} was oxidized to Fe^{3+} within 24 hours, and the final mineralization efficiency was 82.4%. Compared to the direct biomineralization experiment, the total iron removal rate is essentially the same. However, the rate of decrease in total iron was reduced, indicating that the biomineralization rate was decreased. This could be due to an increase in ferrous ion concentration after sulfide reduction, thereby delaying the mineralization reaction. The sulfidation treatment did not improve the efficiency of iron ions removal but could completely remove copper ions. After biomineralization treatment, the concentration of Fe^{3+} was about 150 mg/L, lower than the initial concentration of Fe^{3+} in the simulated AMD (300 mg/L). Combining the results of these two experiments, it can be inferred that for the simulated AMD used in this work, biomineralization for iron removal followed by sulfidation precipitation for copper removal can reduce the amount of sodium sulfide used.

Neutralization of the AMD and pretreated AMD by lime

The lime slurry was used to neutralize the simulated AMD and the pretreated AMD. The results showed that at a final pH of approximately 9, the remaining total Fe concentration was 9.29 mg/L and 0.86 mg/L for the simulated AMD group and the pretreated AMD group. Notably, Cu2+ was completely removed in all groups. The lime consumption was 12.4 mL and 4.5 mL, respectively. When taking the lime slurry used to maintain the pH into consideration, the total lime slurry consumption was 12.4 mL and 9.4 mL. Therefore, the sulfide precipitation and biomineralization treatment can reduce the amount of alkali required for neutralization (Song *et al.* 2022). In terms of the sludge, including the sulfide precipitation, the biomineralization and the neutralization sludge, the total weight of the sludge generated after pretreatment was higher than that without pretreatment. This is primarily due to the greater quantity of biomineralization slag, which consists mainly of schwertmannite containing sulfate ions

(Schoepfer and Burton 2021). In summary, the pretreated AMD drastically reduced the required lime slurry in the subsequent lime neutralization process and improved the removal efficiency of iron ions.

Identification of the sludges

The morphology and elemental composition of the sludges generated at each stage were analyzed by SEM-EDS, including the sulfidation sludge, the biomineralization sludge and the neutralization sludge.

The results revealed that the primary components of the sulfide precipitation residue were copper sulfide and elemental sulfur (Fig. 4A). The elemental sulfur existed in a granular form with particle sizes exceeding 10.0 µm, while the copper sulfide was found in a loose aggregated state. The biomineralization sludge exhibited a morphology highly consistent with schwertmannite, namely, they were comprised of spherical aggregates resembling pincushions with diameters of approximately 3.0 µm (Fig. 4B). The neutralization residue exhibited distinct calcium sulfate crystals, while the iron oxides formed during neutralization did not show visible crystalline structures. This is also the primary reason why the neutralization residue is difficult to settle and filter (Fig. 4C).

Conclusion

The sulfidation treatment facilitated the complete precipitation of copper ions from AMD, and resulted in the reduction of Fe^{3+} to Fe^{2+}, which can facilitate the recovery of copper as CuS. No FeS precipitates were generated during the sulfidation process. The stoichiometric ratio of Fe^{3+} to S^{2-} was approximately 0.5, whereas the ratio of Cu^{2+} to S^{2-} exceeded 1.0. After biomineralization treatment, 88.2% of iron ions were removed. The usage of lime slurry was also reduced compared to the conventional direct neutralization method, with the residual iron ions concentration decreased to 0.86 mg/L. SEM-EDS analysis confirmed that the main phase of the sulfidation sludge was CuS and elemental sulfur, the biomineralization sludge was schwertmannite and the neutralization sludge was calcium sulfate and iron oxide. This work provided a promising integrated approach for the efficient removal of iron ions and recovery of copper ions from AMD by incorporating the copper ions sulfide precipitation, iron ions biomineralization, and lime neutralization.

Acknowledgments

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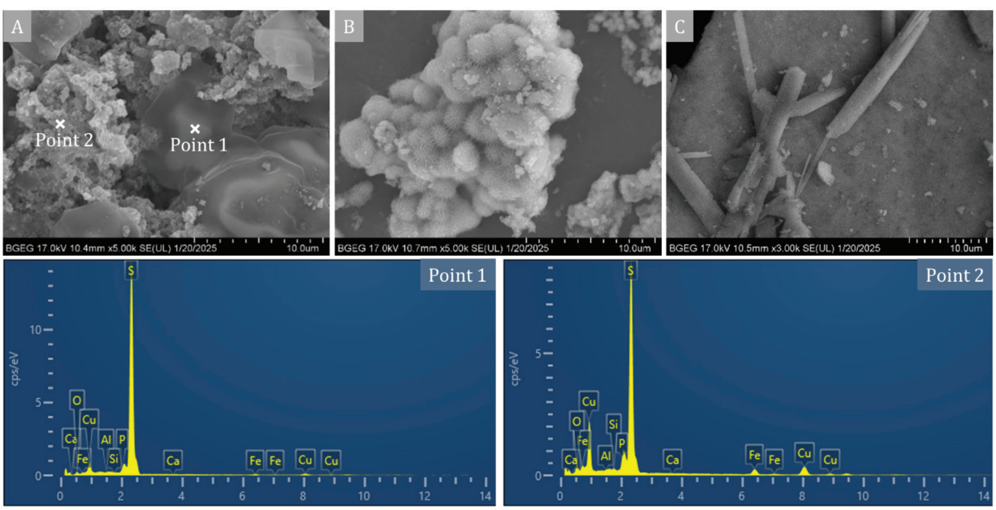

Figure 4 *SEM-EDS of the sludge generated at the sulfidation stage (A), the biomineralization stage (B) and the neutralization stage (C).*

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