Article

Enhanced Monovalent Cation Biomineralization Ability by Quartz Sand for Effective Removal of Soluble Iron in Simulated Acid Mine Drainage

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Abstract: Acid mine drainage (AMD) is characterized by low pH, high soluble Fe, and heavy metal concentrations. Conventional lime neutralization produces large amounts of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, which complicate subsequent disposal. Secondary iron minerals synthesized by biomineralization can reduce the concentration of soluble Fe in addition to adsorbing and removing heavy metals in AMD. Therefore, an appropriate method for improving the precipitation efficiency of Fe is urgently needed for AMD treatment. Using simulated AMD, this work analyzes the influence of quartz sand (40 g/L) on the Fe^{2+} oxidation and total Fe deposition efficiencies, as well as the phases of secondary iron minerals in an *Acidithiobacillus ferrooxidans* system including K^+ , Na^+ , or NH_4^+ (53.3 mmol/L). Quartz sand had no significant effect on Fe^{2+} oxidation and 160 mmol/L Fe^{2+} was completely oxidized by *A. ferrooxidans* in 168 h, but contributed to the oxidized product (Fe^{3+}) mineralization, improving the total Fe removal efficiency in simulated AMD. Compared with treatments involving K^+ or Na^+ alone, quartz sand improved the total Fe precipitation efficiency by 26.6% or 30.2%, respectively. X-ray diffraction showed that quartz sand can promote the transformation of the biomineralization pathway from schwertmannite to jarosite with higher yields, which is important for improving the removal efficiency of heavy metals in AMD.

Keywords: acid mine drainage; *Acidithiobacillus ferrooxidans*; biomineralization; monovalent cations; quartz sand

1. Introduction

Acid mine drainage (AMD), which results from the combined action of air, water, microorganisms, and sulfide minerals during mining, beneficiation, and runoff from the waste ore and tailing heap after mining [1]. AMD is highly acidic and contains soluble Fe (Fe^{2+} , Fe^{3+}), SO_4^{2-} , and heavy metals (e.g., Cr, Cu, Cd, Ni), thus posing a threat to the environment and human health [2,3]. Currently, lime neutralization is a common method to raise the pH and remove Fe, SO_4^{2-} , and other toxic metals from AMD [4,5]. However, when AMD passes through the lime ditch, Fe in the AMD preferentially forms $\text{Fe}(\text{OH})_3$, which coats the limestone surfaces, preventing further neutralization reactions between the limestone and AMD and resulting in a large increase in lime consumption or low heavy-metal removal efficiencies. In addition, a great amount of toxic waste residue, consisting of CaSO_4 , $\text{Fe}(\text{OH})_3$, and toxic metal oxides, are produced in this method, which increases the burden of post-disposal [6–8]. Therefore, it was urgently to explore environment-friendly and high-efficient ways to recover the valuable Fe and remove part of the SO_4^{2-} in AMD in order to reduce the disposal burden of subsequent lime neutralization.

Soluble Fe in AMD exists partly as Fe^{2+} , and the pH required for complete precipitation of Fe^{2+} (pH >8.5) is much higher than that of Fe^{3+} (pH = 3.5). Accordingly, the rapid conversion of Fe^{2+} to Fe^{3+} and inhibition of $\text{Fe}(\text{OH})_3$ formation are crucial for the treatment of AMD. Previous studies have shown that under extremely acidic conditions and high concentrations of SO_4^{2-} , S will combine with Fe to preferentially form secondary iron minerals over $\text{Fe}(\text{OH})_3$ [9,10]. Nevertheless, when the pH of the solution is <3.5, the atmospheric oxidation efficiency constant of Fe^{2+} is extremely low (only $10^{-3.5}/\text{d}$), greatly limiting the transformation of Fe^{2+} to secondary iron minerals [11]. Numerous studies have shown that the oxidation efficiency of Fe^{2+} can be increased 10^5 to 10^6 times by *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*, an acidophilic chemoautotrophic Fe^{2+} -oxidizing bacterium) in acidic sulfate environments [12]. In addition, Fe^{2+} oxidation by *A. ferrooxidans* is often accompanied by the mineralization of Fe^{3+} , producing secondary iron minerals such as schwertmannite and jarosite [13–15]. The specific reaction can be described as follows [14]:

M^+ represents K^+ , Na^+ , or NH_4^+ . Schwertmannite and jarosite have been proven to exert a large adsorption or coprecipitation effect on heavy metals, which makes them ideal adsorbent materials [16–18]. A preliminary trial indicated that in an Fe^{2+} -rich system, schwertmannite was very easily obtained after Fe^{2+} was biologically oxidized by *A. ferrooxidans*. However, only a small amount of the resultant Fe^{3+} in the solutions was converted to schwertmannite. Correspondingly, in the presence of monovalent cations (such as K^+ , Na^+ , and NH_4^+) of a certain concentration in acidic sulfate environments, Fe^{3+} will participate during the synthesis of jarosite, which was much higher than the formation of schwertmannite. In this case, the yield of pure jarosite is approximately 1.5 times greater than that of pure schwertmannite when the same amount of Fe^{3+} is consumed (Equations (2) and (3)). Therefore, inducing the formation of jarosite instead of schwertmannite is beneficial, as jarosite can reduce the Fe content in AMD and remove heavy metals.

In general, the formation of secondary iron minerals can be roughly divided into three steps: Fe^{2+} is oxidized to Fe^{3+} ; Fe^{3+} is hydrolyzed and forms mineral crystal nucleus, and the nucleus gradually agglomerates and expands [19]. The synthesis of secondary iron minerals involves new phase formation, so the existence of an induction period can lower the initial precipitation efficiency of Fe^{3+} [20]. Numerous studies have confirmed that the existence of crystal seeds provide nucleation sites for mineral formation, eliminating the induction period and accelerating initial precipitation efficiency [20–22]. For example, Dutrizac found that the addition of crystal seeds (sodium, ammonium, and potassium jarosites) can accelerate the hydrolysis and mineralization of Fe^{3+} and raise the mineral output [20]. However, these results were based on chemical methods, mainly investigating the effect of crystal seeds on the synthesis of jarosite at high temperatures (60–100 °C). Few reports regarding the application of crystal seeds in the biosynthesis of jarosite by *A. ferrooxidans* have been published, except for that of Wang et al. [23] who used quartz sand as a crystal seed to form K-jarosite in a $\text{FeSO}_4\text{--K}_2\text{SO}_4\text{--}A. \text{ferrooxidans}$ system. In addition, members of our team have investigated the influence of quartz sand on secondary iron mineral formation by biomineralization in municipal sludge filtrate mixture systems (including K^+ , Na^+ , and NH_4^+), the results showed that 10 g/L quartz sand can induce and promote K-jarosite formation when the concentration of Fe^{2+} is 4–8 g/L, but Na-jarosite and NH_4 -jarosite were not detected in the collected minerals [24]. Previous studies have shown that quartz sand can promote the transformation of soluble Fe to jarosite in acid sulfate environment. Nevertheless, it is still unclear how quartz sand impacts the efficiency of Fe^{2+} oxidation and total Fe precipitation in *A. ferrooxidans* culture solutions, including K^+ , Na^+ , or NH_4^+ . In previous studies, only the influence of K^+ concentration has been taken into account [23], and the relative mineralizing ability of K^+ , NH_4^+ , or Na^+ , the differences in mineral phases between the secondary iron minerals in the presence of

quartz sand, have not yet been reported. The study on the influence of quartz sand on the ability of monovalent cation biomineralization has certain reference significance for the biological treatment of AMD.

Therefore, based on the biosynthesis of secondary iron minerals using *A. ferrooxidans*, the objective of the present work is to analyze the influence of quartz sand on the *A. ferrooxidans*-mediated biomineralization in simulated AMD. The addition of quartz sand (40 g/L) and concentration of monovalent cation ($K^+ = 53.3$ mmol/L) were adjusted in reference to the study by Wang et al. [23]. The biomineralization capability of three monovalent cations (K^+ , NH_4^+ , and Na^+) in the presence of quartz sand in an acidic sulfate system was investigated and compared by determining Fe^{2+} oxidation efficiency, total Fe precipitation efficiency, and synthetic mineral phases. We believe that the afforded results may provide an essential theoretical basis to promote the transformation of Fe to secondary iron minerals from AMD.

2. Materials and Methods

2.1. Preparation of *A. Ferrooxidans* Cell Suspensions and Quartz Sand

A. ferrooxidans LX5 (CGMCC No. 0727), obtained from the China General Microbiological Culture Collection Center, was grown in a 9 K medium, which contained the following analytical grade salts: 3.00 g $(NH_4)_2SO_4$, 0.10 g KCl, 0.50 g K_2HPO_4 , 0.50 g $MgSO_4 \cdot 7H_2O$, 0.01 g $Ca(NO_3)_2$, and 44.48 g $FeSO_4 \cdot 7H_2O$ in 1 L of deionized water [25]. Preparation of the *A. ferrooxidans* cell suspensions was performed as described by Song et al. [26]. The concentration of *A. ferrooxidans* was determined to be 6×10^7 CFU/mL by the double-layer plate method [27].

The particle size of quartz sand used in this study was 30~40 mesh; it was firstly soaked in 1 mol/L H_2SO_4 for 24 h and then dried for further use.

2.2. Biomineralization of Simulated AMD

Preparation of simulated AMD: approximately 135 mL of deionized water, 15 mL of *A. ferrooxidans* cell suspension, and 6.63 g of $FeSO_4 \cdot 7H_2O$ were added to a series of 250 mL Erlenmeyer flasks. Subsequently, two experimental groups were prepared, one with quartz sand addition and a control group without the sand. The first group contained no quartz sand and four treatments were used: $K^+ = 53.3$ mmol/L, $Na^+ = 53.3$ mmol/L, $NH_4^+ = 53.3$ mmol/L (K^+ , NH_4^+ , or Na^+ , added as K_2SO_4 , $(NH_4)_2SO_4$, or Na_2SO_4 , respectively), and the control check (CK) without any monovalent cations. The four treatments of the first group were used for the second group containing 40 g/L of quartz sand [23]. The effective volume of each Erlenmeyer flask was 150 mL. Simultaneously, the initial pH of each solution was adjusted to 2.50, with 5 mol/L H_2SO_4 . The density of *A. ferrooxidans* in each treatment was approximately 6×10^6 CFU/mL, as determined by the bilayer flat band method. All Erlenmeyer flasks were subjected to 180 rev/min shaking cultivation in a rotary shaker and were inoculated for 168 h at 28 °C. All experiments were performed in triplicate. The pH was measured every 24 h, and 1 mL of the supernatant was sampled with a pipette through a 0.22 μm filter membrane to determine the concentrations of Fe^{2+} and total Fe (TFe) in simulated AMD. According to the variation in the concentration of TFe, the TFe precipitation efficiencies at different time nodes were calculated using the following formulas:

$$\text{TFe precipitation efficiencies at different time nodes (\%)} = (C_0 - C_t)/C_0 \times 100\%$$

Where C_0 is the TFe concentration (g/L) at 0 h, C_t is the TFe concentration (g/L) at t h.

At the end of the culturing, the secondary iron minerals were collected with qualitative filter paper and washed twice with deionized water to remove impurities. After drying at 55 °C, the minerals were ground into powder using an agate mortar and identified via X-ray diffraction (XRD).

2.3. Analytical Procedures

The solution pH was measured using a PHS-3C model digital pH-meter with a resolution of 0.01 pH unit. Fe^{2+} and TFe concentrations were determined using the 1,10-phenanthroline method by a spectrophotometer (721, XTZ Optical Instrument Factory, Shanghai, China) with detection wavelength at 530 nm [28]. The mineral phase of the sample was determined via X-ray diffraction (XRD, Bruker D8A25, Bruker Corporation, Karlsruhe, Germany) using $\text{CuK}\alpha$ radiation (40 kV, 40 mA); the samples were scanned from 10 to $80^\circ 2\theta$ with a step increment of $0.01^\circ 2\theta$ and $6^\circ/\text{min}$ scanning speed. The data shown in the figures are presented as mean values with standard deviations to indicate the reproducibility and reliability of the results.

3. Results and Discussion

3.1. Changes in Fe^{2+} Concentration During Biomineralization of Simulated AMD

Figure 1 shows the changes in the Fe^{2+} concentration during *A. ferrooxidans* mediated biomineralization with and without quartz sand addition. Overall, the combined application of quartz sand and monovalent cations had no significant effect on the biooxidation activity of *A. ferrooxidans*, and Fe^{2+} was completely oxidized after 168 h. During the initial inoculation stage of *A. ferrooxidans*, the oxidation of Fe^{2+} was slow, with an average oxidation efficiency of only 10.3% after 24 h. The poor oxidation of Fe^{2+} during the initial stage of the reaction can be attributed to the adaptive phase of *A. ferrooxidans*. Fe^{2+} was then rapidly oxidized between 24 and 168 h, which agrees with the results of Wang et al. [23]. The addition of quartz sand and K^+ had no significant influence on the biooxidation efficiency of Fe^{2+} under the same experimental conditions. In addition, Wang et al. [29] confirmed that at concentrations of Na^+ ranging from 81.6 to 326.5 mmol/L, the growth curves of *A. ferrooxidans* were nearly unchanged. When the Na^+ concentration increased to 653 mmol/L, the *A. ferrooxidans* growth was inhibited. Song et al. [30] confirmed that the NH_4^+ tolerance of *A. ferrooxidans* ranged from 80 to 160 mmol/L and that the critical concentration where *A. ferrooxidans* growth was completely suppressed was between 160 and 320 mmol/L. Csonka [31] reported that the ability of organisms to respond to fluctuations in their environments is an important physiological process that determines their growth in various habitats. High salt concentrations may cause changes in the osmotic pressure of *A. ferrooxidans* and the biooxidation efficiency of Fe^{2+} , therefore confirming that the variety and concentration of monovalent cations exhibit considerable influence on the biological oxidation of Fe^{2+} in AMD. Specifically, a high concentration of monovalent cations inhibits the oxidizing ability of *A. ferrooxidans*. This will help us to choose the appropriate concentration of monovalent cations for the bio-mineralization treatment of AMD. However, the concentration of monovalent cations selected in this study was 53.3 mmol/L and was within the tolerance range of *A. ferrooxidans*.

Figure 1. Change of Fe^{2+} concentration (a) without and (b) with quartz sand in simulated acid mine drainage (AMD) system.

3.2. Changes in Solution pH During Biomineralization of Simulated AMD

According to Equations (1)–(3), the oxidation of Fe^{2+} consumes acid (Equation (1)), while the hydrolysis of Fe^{3+} is accompanied by the production of acid (Equations (2) and (3)) [14]. Figure 1 confirms that, regardless of the presence of quartz sand (40 g/L) or monovalent cations (53.3 mmol/L), *A. ferrooxidans* exhibited no significant effect on the oxidation efficiency of Fe^{2+} . Hence, the hydrolytic ability of Fe^{3+} under different treatment conditions can be preliminarily judged from changes in pH.

When the quartz sand was not added to the reaction system (Figure 2a), the pH variations were similar for the systems containing Na^+ , NH_4^+ , and CK, where the pH values rose from 2.50 to 2.64, 2.63, and 2.61 at 24 h, then gradually decreased to 2.31, 2.32, and 2.34, respectively, after 168 h. Thus, it can be inferred that 53.3 mmol/L Na^+ or NH_4^+ added individually exerted no effect on the biological mineralization process. In contrast, when 53.3 mmol/L K^+ was added individually, the solution pH exhibited a downward trend, decreasing from 2.50 to 2.17. According to the biochemical reactions (Equations (1)–(3)) for secondary iron mineral formation, a lower pH promotes Fe^{3+} hydrolysis on the minerals. Bai et al. [32] also showed that, compared with Na^+ or NH_4^+ , K^+ exhibited a stronger ability to induce mineralization in a 160 mmol/L Fe^{2+} solution containing *A. ferrooxidans*.

Figure 2. Change of pH (a) without and (b) with quartz sand in simulated acid mine drainage (AMD) system.

After the addition of 40 g/L quartz sand to the reaction system (Figure 2b), the pH of the treatments with only quartz sand, and those with quartz sand and Na^+ or NH_4^+ , showed a decreasing trend. This indicates that the introduction of quartz sand promoted Fe^{3+} hydrolysis and that, even in the absence of monovalent cations, the process with only quartz sand accelerated Fe^{3+} hydrolysis. The pH variation curves of the solutions with only quartz sand and quartz sand with Na^+ were comparable. Thus, it could be concluded that even upon the introduction of quartz sand, 53.3 mmol/L Na^+ had no significant effect on Fe^{3+} hydrolysis, and its ability to induce Fe^{3+} biological mineralization remained poor. Here, the decreasing pH can be solely attributed to the quartz sand rather than Na^+ . Interestingly, at the same concentration of NH_4^+ , after the addition of quartz sand to the system, the pH showed a more obvious decline compared to the treatments involving the separate addition of NH_4^+ or quartz sand. This decline indicated that when NH_4^+ and quartz sand interact, a synergistic effect promoted the formation of secondary iron minerals. This is the first report of such a phenomenon. Although the mineralization ability of NH_4^+ was weaker and its effect on Fe^{3+} hydrolysis was smaller, the introduction of quartz sand likely aids in the synthesis of secondary iron minerals, which subsequently promoted the effective removal of soluble Fe in simulated AMD.

3.3. Changes in TFe Precipitation Efficiency During Biomineralization of Simulated AMD

With the participation of various monovalent cations, changes in the TFe precipitation efficiency for systems with or without quartz sand are shown in Figure 3. For the separate additions of Na^+ ,

NH_4^+ , and CK (Figure 3a), the TFe precipitation efficiencies were essentially identical. At 168 h, the TFe precipitation efficiencies were only 9.5%, 12.1%, and 12.6% after the mineralization reaction for the Na^+ , NH_4^+ , and CK treatments, respectively. Separate additions of 53.3 mmol/L Na^+ or NH_4^+ could not induce the mass removal of soluble Fe in simulated AMD. For the treatment involving K^+ alone, the TFe precipitation efficiency was much higher than that of the CK treatment. This was beneficial for the mass synthesis of minerals, and the TFe precipitation efficiency increased from 12.6% to 31.5% after mineralization. The results of this study are consistent with those reported by Wang et al. [23], who reported that at K^+ concentrations of 7.14, 16, 32, 53.3, and 80 mmol/L, the TFe precipitation efficiencies for biomineralization mediated by *A. ferrooxidans* were approximately 36%, 42%, 46%, 50%, and 52%, respectively. Since the addition of K^+ did not accelerate the oxidation efficiency of Fe^{2+} (Figure 1), the increased TFe precipitation efficiency can be mainly attributed to the Fe^{3+} hydrolysis induced by K^+ .

Figure 3. Change of TFe concentration (a) without and (b) with quartz sand in simulated acid mine drainage (AMD) system.

By comparison, the TFe precipitation efficiency of the treatment with quartz sand was higher than that obtained without quartz sand (Figure 3b). In other words, the addition of quartz sand contributed to Fe^{3+} hydrolysis, improving the TFe removal efficiency in the simulated AMD. As stated earlier, the addition of quartz sand showed no significant effect on the oxidation efficiency of Fe^{2+} , indicating that quartz sand can induce additional syntheses of secondary iron minerals at the same Fe^{3+} supply rate. Crystal seeds provide nucleation sites for the generation of solid phase materials, accelerating the initial precipitation efficiencies of the secondary minerals and promoting TFe precipitation [20–22]. In addition, quartz sand and monovalent cations (K^+ or NH_4^+) showed a synergistic effect, promoting the generation of secondary iron minerals, and increasing the TFe precipitation rate to 26.6% or 30.2% compared to those of the single monovalent cation, respectively. Therefore, the combination of the induced mineralization of K^+ or NH_4^+ and crystal seed stimulation of quartz sand promotes Fe^{3+} hydrolysis, achieving improved Fe removal. However, the TFe precipitation efficiencies for both treatments, quartz sand with or without Na^+ , were similar, which is analogous to the trends of solution pH shown in Figure 2. This indicates that the synergistic effect of 53.3 mmol/L Na^+ and quartz sand on TFe mineralization precipitation was not significant. In conclusion, at monovalent cation concentrations of 53.3 mmol/L and under the synergistic action of 40 g/L quartz sand, the order of the mineralization ability is $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+$. This result indicates a difference in the abilities of these three ion species to catalyze the transformation of Fe into secondary iron minerals. Gramp et al. [33] reported that the mineralization capacity of K^+ is 75 and 200 times higher than those of NH_4^+ and Na^+ , respectively.

The effect of the Fe^{3+} concentration on biomineralization was investigated by Deveci et al. [34], who suggested that regardless of the material added, mineralization ability is limited at low Fe^{3+} concentrations. In the early stages, the Fe^{2+} oxidation efficiency was low, owing to the adaptation

period required for *A. ferrooxidans*. Therefore, only a small amount of Fe^{3+} was produced and the low concentration of Fe^{3+} was not conducive to hydrolysis. This resulted in a low TFe precipitation efficiency at the beginning of the reaction, and the increased TFe precipitation efficiency in all treatments was the slowest between 0 and 24 h (Figure 3a). In addition, the low TFe precipitation efficiency indicates that only small amounts of secondary iron minerals were generated during this period. The TFe precipitation efficiency in the presence of Na^+ , NH_4^+ , and CK alone did not show significant improvements in any reaction period. Although K^+ exhibited the strongest mineralization ability, its ability remained limited during the initial stages of the reaction, with a TFe precipitation rate of only 4.3% in the 0–24 h period. However, in the late stages of the reaction (120–168 h), the induced mineralization of K^+ was apparent due to the sufficient supply of Fe^{3+} , indicating that the TFe precipitation efficiency increased sharply.

When quartz sand was introduced into the system (Figure 3b), the TFe precipitation efficiency for the treatment containing K^+ and NH_4^+ significantly increased in the 0–24 h period. This increased efficiency suggested that the introduction of quartz sand overcame the limitations associated with low Fe^{3+} concentration during the initial stage of the reaction. Because quartz sand had no significant effect on the oxidation of Fe^{2+} , the increased TFe precipitation efficiency occurred because the quartz sand shortened the induction period and accelerated the synthesis of the secondary iron minerals [20–22]. The trends of the TFe precipitation efficiency for the treatment containing Na^+ and quartz sand and that with only quartz sand were similar in each period. This result further confirmed that the synergistic effect of 53.3 mmol/L Na^+ and quartz sand on the mineralization of soluble Fe was insignificant. However, Dutrizac [20] reported that the TFe precipitation efficiency increased with increasing Na^+ concentration from 20 to 60 mmol/L when the system contained 50 g/L of crystal seeds. This result is inconsistent with our study, likely because the reaction involved the chemical synthesis of minerals and temperature of 98 °C, which increases the rate and efficiency of Fe^{3+} mineralization at low Na^+ concentrations. Therefore, over a suitable monovalent cations concentration range, the induction of crystal seeds can promote the precipitation efficiency of TFe in simulated AMD, and secondary iron mineral production can be increased.

3.4. X-ray Diffraction Analysis of the Biomineralization Products

Photographs and XRD patterns of the secondary iron minerals collected for each biomineralization treatment are shown in Figures 4 and 5, respectively. With reference to the standard (JCPDS) [35], XRD patterns of crystalline jarosite and amorphous schwertmannite, the data suggested that at 53.3 mmol/L monovalent cation concentration, treatments with K^+ , Na^+ , and NH_4^+ mediated by *A. ferrooxidans* produced K-jarosite, schwertmannite, and schwertmannite, respectively. This indicates that Na^+ and NH_4^+ were not involved in the synthesis of Na-jarosite or NH_4 -jarosite, which is consistent with the results of Bai et al. [32]. However, after adding 40 g/L quartz sand to the NH_4^+ system, the secondary iron minerals exhibited diffraction peaks characteristics of schwertmannite and NH_4 -jarosite. Thus, 40 g/L quartz sand induced and promoted changes in the synthesis process of the secondary iron minerals, forming NH_4 -jarosite more easily than schwertmannite. However, the dominant mineral obtained from the Na^+ and quartz sand process remained schwertmannite, which further confirmed that Na^+ was not involved in the biosynthesis reaction of Na-jarosite. The same trends of the solution pH and TFe precipitation efficiency were observed for the treatments of Na^+ and CK, whether quartz sand was added or not (Figures 2 and 3). According to Equations (2) and (3), if the secondary iron minerals were produced by a single pathway, the yield of jarosite produced by the same amount of Fe^{3+} should be 1.5 times that of schwertmannite. The addition of quartz sand may lead to increased production of biogenerated secondary iron minerals. This process effectively removes soluble Fe in AMD, which is of great significance for the optimization of the bio-mineralization treatment of AMD.

Figure 4. Photographs of the secondary iron minerals for different biomineralization treatments.

Figure 5. X-ray diffraction patterns of the secondary iron minerals for different biomineralization treatments.

4. Conclusions

To remove soluble Fe from simulated AMD, biomineralization of each system, with and without the addition of 40 g/L quartz sand, was investigated with an initial Fe^{2+} concentration of 160 mmol/L and monovalent cations (K^+ , Na^+ , and NH_4^+) concentration of 53.3 mmol/L. The addition of quartz sand contributed to Fe^{3+} hydrolysis (the oxidation product of Fe^{2+}), improving TFe removal efficiency in the simulated AMD. For example, the TFe removal efficiencies of the K^+ , Na^+ , and NH_4^+ systems rose from 31.5%, 9.5%, and 12.1% to 58.1%, 22.2%, and 42.3%, respectively, with the addition of quartz sand. The quartz sand shortened the induction period of the biomineralization reaction, improving the TFe precipitation efficiency of the simulated AMD during the initial stage. The XRD patterns showed that 40 g/L quartz sand can improve the biomineralization removal efficiency of soluble Fe in the simulated AMD and induce the Fe^{3+} biomineralization pathway from schwertmannite to jarosite. In the next step, we will continue to optimize the experimental method of this study and apply it to the treatment of real AMD to evaluate the feasibility of its practical application.

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