

Article

Coupled Transformation Processes of Cr-Adsorbed Schwertmannite and Chromium Redistribution Controlled by Ca(II) Speciation

Guiping Liao¹, Hongmei Tang¹, Jiayan Wu¹, Quanyun Ye² , Yihao Li², Zhongbo Shang³, Leiye Sun^{1,*} and Pingxiao Wu^{1,4,*} 

¹ School of Environment and Energy, South China University of Technology, Guangzhou 510006, China; luckybottle0806@163.com (G.L.); ttthongmei@163.com (H.T.); wwujy@foxmail.com (J.W.)

² South China Institute of Environmental Science, Ministry of Ecology and Environment (MEE), Guangzhou 510655, China; quanyunye@scies.org (Q.Y.); yihao806@163.com (Y.L.)

³ School of Plant Protection and Environment, Henan Institute of Science and Technology, Xinxiang 453003, China; shangzhongbo@126.com

⁴ The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, China

* Correspondence: sunly131415@scut.edu.cn (L.S.); pppxwu@scut.edu.cn (P.W.)

Abstract

Schwertmannite (Sch) is a widespread iron oxyhydroxysulfate mineral in acid mine drainage (AMD) systems, and its transformation strongly influences the environmental fate of chromium (Cr). However, the role of Ca(II), which is commonly introduced during alkaline neutralization of AMD, in regulating the transformation of Cr(VI)-adsorbed schwertmannite (Cr-Sch) and subsequent Cr redistribution remains insufficiently understood. In this study, transformation experiments were conducted under various pH conditions (3.0, 7.0, and 10.0) to investigate the effects of Ca(II) speciation on mineral transformation and Cr behavior. The results demonstrated that the transformation of Cr-Sch was predominantly pH-dependent. Under acidic conditions, Cr-Sch transformed into goethite via dissolution–recrystallization, resulting in transient Cr release followed by partial refixation. The presence of Ca(II) exerted only a minor influence due to weak interactions between Ca²⁺ and positively charged mineral surfaces. Under alkaline conditions, Cr-Sch preferentially transformed into hematite through dehydroxylation and cation rearrangement, leading to the sustained release of adsorbed Cr(VI). In contrast, Ca(II) predominantly precipitated as CaCO₃ precipitate (calcite, aragonite, and vaterite) under alkaline conditions, which coated mineral surfaces and inhibited phase transformation and Cr release. These findings reveal that Ca(II) regulates Cr redistribution primarily through pH-dependent speciation and mineral–surface interactions, highlighting coupled geochemical processes governing iron mineral transformation and contaminant mobility in AMD environments. This study provides mechanistic insights for predicting Cr behavior and optimizing alkaline remediation strategies in mining-impacted systems.

Keywords: schwertmannite; transformation; adsorbed chromium; calcium; redistribution



Academic Editor: Juan García Rodríguez

Received: 1 March 2026

Revised: 10 April 2026

Accepted: 13 April 2026

Published: 15 April 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Chromium (Cr) is a prevalent environmental contaminant derived from natural weathering of Cr-bearing minerals and mineral resource exploitation [1]. High Cr concentrations are frequently detected in water, soil and sediment surrounding mining areas [2,3], particularly in AMD systems and associated sediment, where concentrations often exceed safety

thresholds. For example, Cr concentrations as high as 343 mg/kg have been reported in riverbed sediments near the Iberian pyrite belt [4], while values up to 812 mg/kg have been observed in AMD sediments from German silver mines [5]. In natural environments, Cr commonly exists in two stable oxidation states: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) [6]. Among them, Cr(VI) is of particular concern because of its high toxicity, carcinogenicity, and strong mobility and solubility, and it has been designated as a priority pollutant by the U.S. Environmental Protection Agency [7]. The environmental and health risks of Cr(VI) are strongly influenced by interactions with coexisting environmental matrices, particularly natural minerals [8]. During geochemical processes, minerals can react with Cr through adsorption–desorption, precipitation–dissolution and oxidation–reduction [9,10]. Hence, understanding the transformation and distribution of Cr(VI) at the solid–liquid interface of minerals is critical for accurate risk assessment and remediation strategy development.

Schwertmannite (Sch) is a characteristic iron oxyhydroxysulfate mineral commonly found in environments with high sulfate (SO_4^{2-}) concentrations. Its general chemical formula is $\text{Fe}_8\text{O}_8(\text{OH})_x\text{SO}_y \cdot n\text{H}_2\text{O}$ ($8 - x = y$, $1.0 \leq y \leq 1.75$) [11,12]. In AMD systems, SO_4^{2-} is prone to complexing with Fe species and competes with hydroxyl groups, thereby inhibiting the crystallization of Fe hydroxides, promoting Sch formation [13]. Due to its large specific surface area, positive surface charge, and tunnel-like structure, Sch serves as an efficient adsorbent for heavy metals [14,15]. In particular, SO_4^{2-} in Sch has a similar ionic radius to CrO_4^{2-} ($r(\text{SO}_4^{2-}) = 0.23 \text{ nm}$ and $r(\text{CrO}_4^{2-}) = 0.24 \text{ nm}$, making it easy to be replaced by CrO_4^{2-} through ion exchange reactions [16]. Previous studies have shown that the ion exchange capacity between CrO_4^{2-} and SO_4^{2-} in Sch can reach up to 15.3% without altering the mineral structure and phase [5]. Hence, Sch serves as an important carrier of Cr, and Sch-bound-state Cr is often the dominant form in AMD systems. However, Sch is poorly crystalline and thermodynamically unstable, and it readily transforms into secondary minerals such as goethite, hematite, and jarosite [17,18]. Given that these secondary minerals exhibit different affinities for Cr, Sch transformation inevitably leads to changes in Cr speciation and redistribution between solid and aqueous phases. Despite this, the underlying mechanisms remain insufficiently understood.

Alkaline reagents such as limestone are commonly used to neutralize AMD, which results in elevated concentrations of Ca(II) in the wastewater [19]. In fact, this kind of environmental disturbance is easily overlooked, particularly regarding the influence of Ca(II) on the transformation of iron minerals. Previous studies have shown that Ca(II) can form complexes with mineral surfaces and influence processes such as electric double-layer compression, adsorption, charge neutralization, and cation bridging [20]. For example, Kanematsu et al. reported that Ca(II) can enhance arsenic adsorption by minerals [21]. Due to its poor crystalline and chemical instability, the transformation of Sch is highly sensitive to coexisting ions such as Ca(II) [22]. Moreover, Ca(II) exhibits different speciation under various environmental conditions [23,24], which further complicates its influence on Sch transformation. Since Sch transformation directly governs Cr redistribution, the presence of Ca(II) is expected to play an important regulatory role. There have been many previous studies about the influence of metal ions on Sch transformation, such as the influence of Cr(VI) in the study of Fan et al. [25], and the influence of Mn(II) in our previous study [26]. These studies focused on the effect of redox properties of metal ions, and the Sch transformation was inhibited by the oxidizing Cr(VI) and promoted by the reductive Mn(II). In contrast, our study focused on the influence of Ca(II) speciation on Sch transformation, and indicated that different speciation of Ca(II) (including free Ca^{2+} and Ca(II) precipitates) at various pHs might represent a newly discovered influence on the Cr–Sch transformation and Cr redistribution; however, the effect mechanism of different Ca(II) speciation is still

unknown. Hence, the mechanism of this interaction process between Ca(II) and Cr-Sch during the transformation, as well as the redistribution behavior of adsorbed Cr, needs to be further studied.

Therefore, this study aims to investigate the transformation behavior of Cr-Sch and the associated redistribution of Cr as regulated by Ca(II). The specific objectives are (1) to reveal the combined effects of Ca(II) and pH on the formation of secondary mineral phases, (2) to clarify the redistribution behavior of Cr during the transformation process, and (3) to propose the mechanism by which Ca(II) regulates Cr-Sch transformation. The results are expected to provide new insights into Sch transformation mechanisms and Cr behavior in AMD environments, and to support the development of effective remediation strategies.

2. Materials and Methods

2.1. Chemicals

Iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99.0\%$) and potassium chromate (K_2CrO_4 , $>99.5\%$) were purchased from Aladdin Reagent Company, Shanghai, China. Sodium hydroxide (NaOH, 96%), hydrochloric acid (HCl, 36~38%), and hydrogen peroxide (H_2O_2 , 30%) were all of analytical grades and purchased from the Guangzhou Chemical Reagent Factory, Guangzhou, China. All chemicals were used without further purification. Deionized water ($18.25 \text{ M}\Omega \cdot \text{cm}$) was used throughout the experiments.

2.2. Preparation of Sch

Sch was prepared by a rapid chemical method [26]. In brief, 790.4 mL of deionized water and 17.79 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were added to a polypropylene bottle, and continuously stirred to ensure complete dissolution. Subsequently, 9.6 mL of 30% H_2O_2 was slowly added to the above solution, and the mixture was shaken for 24 h at 25 °C. Then, the generated suspension was collected and washed with acidic (pH 2.0) and neutral (pH 6.8) deionized water 3~5 times until the pH of the washing solution remained stable. Finally, the obtained solid was freeze-dried, passed through a 200-mesh sieve, and then stored in a dark and dry container.

2.3. Transformation Experiment

All the transformation experiments were carried out in 500 mL polypropylene bottles. First, 0.6 g of Sch was added to each bottle, which contained 30 mg/L Cr(VI). The final reaction volume was set at 300 mL. The pH value of the suspension was adjusted to 3.0, 7.0 and 10.0 using 0.5 M HCl or NaOH, and then stirred and pre-equilibrated at 25 °C for 48 h to obtain the Cr-Sch suspension. After 48 h of stirring, the Cr(VI) concentration was measured by atomic absorption spectroscopy (AAS) (SHIMADZU AA-6880, Kyoto, Japan), and the Cr(VI) loading was obtained by calculating the adsorption capacity.

Subsequently, 1 mM Ca(II) was added to the Sch or Cr-Sch suspension. The mixture was then shaken at a speed of 80 rpm at 70 °C to accelerate the reaction. Although the experimental temperature exceeds typical AMD conditions, it serves as a kinetic acceleration approach to elucidate transformation mechanisms, which has been widely applied in previous studies [27]. During the transformation process, 0.5 M HCl or NaOH was used to ensure that the pH value of the reaction system remains unchanged. The experimental period was set as 30 days. Our previous results showed that the mineral phase tended to stabilize and was no longer changed after 30 days of reaction [26].

At specific sampling points (1, 3, 5, 7, 10, 15, 20, 30 days), 3 mL samples were taken from the bottle and filtered through 0.45 μm filter membrane for further analysis. After 30 days of reaction, the remaining minerals were collected by centrifugation and freeze-dried for characterization. The experimental groups were set as follows: (1) Sch; (2) Cr-Sch;

(3) Sch + 1 mM Ca(II); and (4) Cr-Sch + 1 mM Ca(II). All experiments were performed in triplicate.

2.4. Characterization

In this study, mineral species and compositions were determined by X-ray diffraction (XRD, Rigaku, D/MAX-III A, Tokyo, Japan) analysis. The morphological characteristics were analyzed using scanning electron microscopy (SEM, Zeiss, Merlin, Germany). The functional groups were analyzed by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, PerkinElmer 1725X, Waltham, MA, USA). The elemental composition and chemical states of the surface elements were determined by X-ray photoelectron spectroscopy (XPS, Anelva, AES430S, Kawasaki, Japan).

2.5. Determination of Ca and Cr Concentrations

At specific sampling points, the suspension was collected and filtered through a 0.45 µm filter membrane to collect the supernatant. The concentration of Cr and Ca in the filtered samples was determined by atomic absorption spectroscopy (AAS).

3. Results and Discussion

3.1. The Transformation of Sch and Cr-Sch in the Absence and Presence of Ca(II)

3.1.1. XRD

As shown in the XRD patterns (Figure 1), both Sch and Cr-Sch underwent phase transformation after 30 days of aging reaction, although significant differences in transformation products and degrees were observed under various pH conditions. At pH 3.0, sharp diffraction peaks appeared at around 21.22, 33.24, 34.70, 36.64, 39.98, 40.18, 47.30, 53.24, 59.12, 61.38 and 63.97°, which were attributed to the characteristic peak of goethite [25]. This indicated that both Sch and Cr-Sch tended to transform into goethite under acidic conditions. According to previous study, goethite may form through dissolution and reprecipitation, and this process is more likely to occur under acidic conditions [25]. At pH 7.0, broader and weaker diffraction peaks were observed at 21.22, 33.24, 34.70 and 36.64°, suggesting that goethite remained the dominant product, but with a lower degree of transformation compared to acidic conditions. In contrast, at pH 10.0, characteristic diffraction peaks of hematite appeared at around 24.14, 33.15, 35.61, 40.85, 49.48, 54.09, 62.44 and 63.99°, indicating that Sch tended to transform into hematite under alkaline conditions [28]. A previous study pointed out that hematite may be associated with dehydration and cation rearrangement processes, which are more favorable in alkaline environments [27]. The formation path of goethite through dissolution and reprecipitation, and that of hematite through dehydration and cation rearrangement, were concluded according to previous studies [25,27]. Future research will be conducted to directly verify these pathways using more advanced methods and equipment.

Compared with Sch, Cr-Sch exhibited weaker diffraction peaks (Figure 1), indicating that adsorbed Cr(VI) inhibited mineral transformation and reduced crystallinity. This may be attributed to the fact that CrO_4^{2-} has a similar molecular radius to SO_4^{2-} in the structure of Sch ($r(\text{SO}_4^{2-}) = 0.23 \text{ nm}$ and $r(\text{CrO}_4^{2-}) = 0.24 \text{ nm}$) [16], and ion exchange usually occurs between these two anions during the adsorption process [2]. Previous studies showed that the Cr-Fe skeleton had stronger stability than the SO_4^{2-} -Fe skeleton [5,29]. Hence, adsorbed Cr(VI) could hinder the dissolution of Fe and stabilize the mineral structure of Sch. Moreover, no obvious new phase was observed for Cr-Sch after the aging reaction at pH 7.0, and the inhibition effect of adsorbed Cr on Sch transformation was more outstanding under neutral conditions. This could be attributed to the adsorption capacity of Cr(VI) on Sch, as more adsorbed Cr had a stronger inhibitory effect on Sch transformation. Compared

with slightly acidic and alkaline conditions, Sch has a better adsorption capacity for Cr under slightly neutral conditions, which will be discussed in the following section.

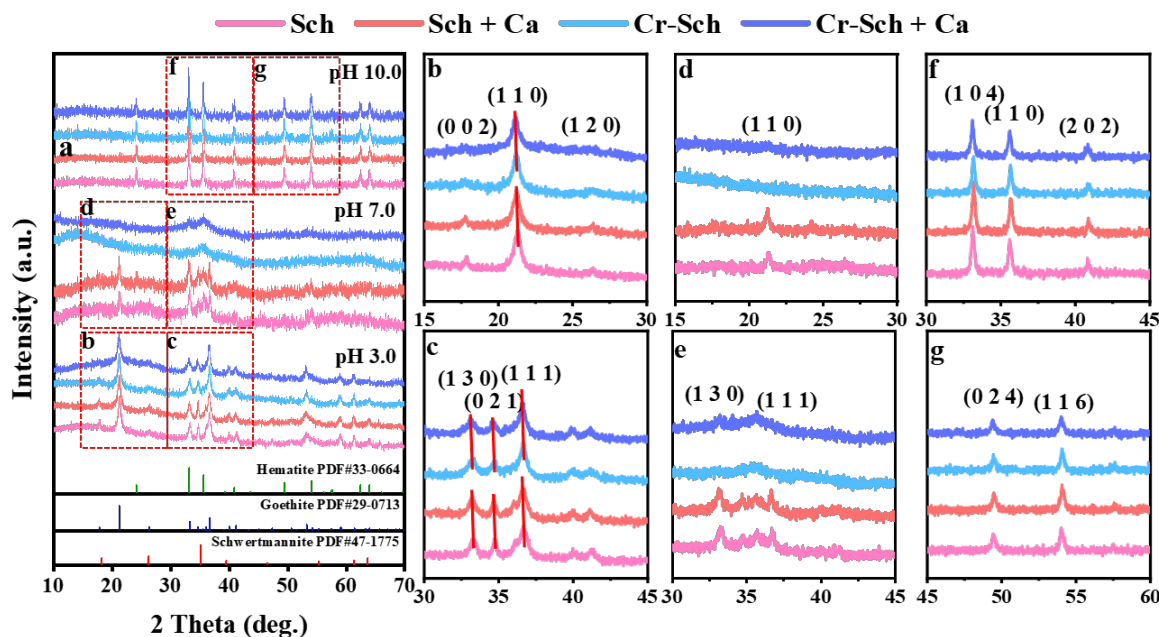


Figure 1. XRD patterns of transformation products of Sch and Cr-Sch (a) and partial enlarged detail of XRD patterns (b–g).

XRD results showed similar patterns in the presence or absence of Ca(II); the presence of Ca(II) had no obvious impact on the secondary minerals of Sch and Cr-Sch. However, the partial enlarged detail of XRD patterns showed that at pH 3.0, Ca(II) caused several diffraction peaks of the transformation product to slightly shift towards a smaller 2θ degree compared with the absence of Ca(II) (Figure 1b,c). In general, the atomic radius of Ca was much larger than that of Fe, making it difficult for Ca to enter the lattice structure of Fe minerals through ion exchange [30]. The shift in XRD peaks indicated that the presence of Ca(II) might have an impact on the recrystallization of mineral transformation under acidic conditions. At pH 7.0, Ca(II) showed a slight promoting effect on the transformation of Sch and Cr-Sch (Figure 1d,e). This might be because positively charged Ca(II) was conducive to the release of SO_4^{2-} , further accelerating the structural collapse of Cr-Sch [31]. In addition, Figure 1f,g showed that Ca(II) led to a slight weakening and broadening of the XRD peaks, indicating a decrease in the crystallization of the transformation product. Hence, at pH 10.0, the presence of Ca(II) slightly inhibited the transformation of Sch and Cr-Sch. Under alkaline conditions, Ca(II) ions may tend to hydrolyze and form CaCO_3 minerals such as calcite and aragonite. These CaCO_3 minerals deposited on the surface of iron minerals might play a protective role, thereby inhibiting the dehydration and transformation process of Sch and Cr-Sch.

3.1.2. SEM

As shown in Figure 2, the SEM results revealed distinct morphological changes during transformation. The original Sch exhibited an irregular spherical morphology. After transformation at pH 3.0, rod-like structures formed uniformly on Sch and Cr-Sch particle surfaces, resulting in a sea-urchin-like morphology (Figure 2a–d). Similar results have also been found in previous studies, indicating that this is connected to a distinctive morphology change in the transformation of Sch into goethite [26,32].

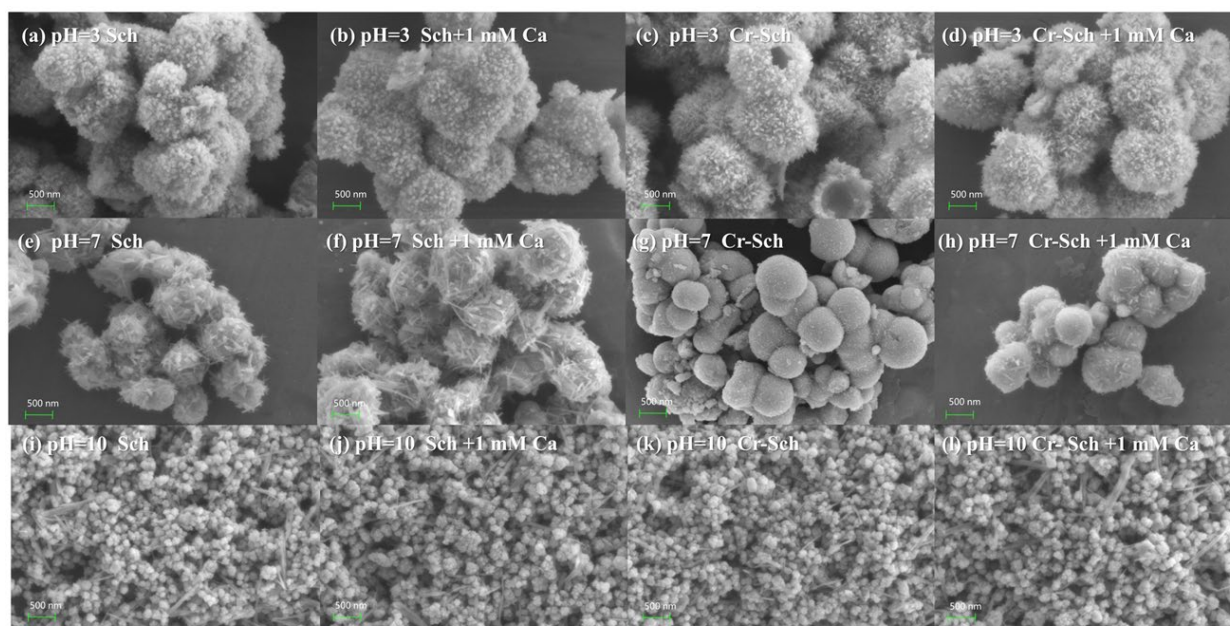


Figure 2. SEM micrographs of transformation products of Sch and Cr-Sch.

At pH 7.0, only a small quantity of rod-shaped products adhered to the surface of spherical Sch, even though there were no rod-shaped products in the Cr-Sch system. These phenomena indicated that neutral conditions were not conducive to the transformation of Sch into goethite, and Cr-Sch was even less likely to transform. Compared to Figure 2e,f, the presence of Ca(II) in the system made the rod-like coating on the surface of particles longer and more abundant, suggesting a slight promoting effect of Ca(II) on the Sch transformation.

The microscopic morphology of the transformation products at pH 10.0 was significantly different from that under neutral and acidic conditions (Figure 2i–l). The spherical morphology completely disappeared, generating a large number of agglomerated particles, and it also contained a few rod-shaped products. Moreover, SEM results intuitively displayed that the aggregate particle size of the transformation products at pH 10.0 was much smaller than that at pH 3.0 and 7.0. SEM results did not obviously reveal the influence of Ca(II) on the transformation of Sch and Cr-Sch.

3.1.3. FTIR

FTIR results showed the changes in functional group after the transformation of Sch and Cr-Sch (Figure 3). The characteristic absorption peak at 1131 cm^{-1} and two shoulder peaks at 1211 and 1048 cm^{-1} were attributed to the triple-degenerate antisymmetric stretching vibration of the SO_4^{2-} [33]. The absorption peak at 979 cm^{-1} was assigned to the intramolecular symmetric stretching vibration of SO_4^{2-} ($\nu_1(\text{SO}_4^{2-})$), which represents the outer-sphere complexation of SO_4^{2-} with Sch [32,34]. The absorption peak at 610 cm^{-1} was caused by the triple-degenerate out-of-plane bending vibration ($\nu_4(\text{SO}_4^{2-})$), which represents SO_4^{2-} in tunnel structure of Sch [34]. SO_4^{2-} can exist in Sch both as surface-complexed species and as structural components supporting the tunnel framework. After the transformation of Sch and Cr-Sch, the absorption intensity of $\nu_1(\text{SO}_4^{2-})$, $\nu_3(\text{SO}_4^{2-})$ and $\nu_4(\text{SO}_4^{2-})$ were all significantly weakened, and some peaks even disappeared completely in the FTIR of the transformation product at pH 10.0. These results indicate that the complexed state and the tunnel structural state of SO_4^{2-} in Sch were lost to varying degrees during the transformation process. Many previous studies on Sch transformation have also shown the phenomenon of SO_4^{2-} release during the transformation process [26,32].

The release of SO_4^{2-} led to the collapse of the Sch structure, and formed other weakly crystalline Fe hydroxides (as shown in Equation (1)), which was the vital step leading to the subsequent transformation of Sch. The complete disappearance of SO_4^{2-} in the transformation products at pH 10.0 further indicates that alkaline conditions are more favorable for Sch transformation and correspond to a higher transformation degree.

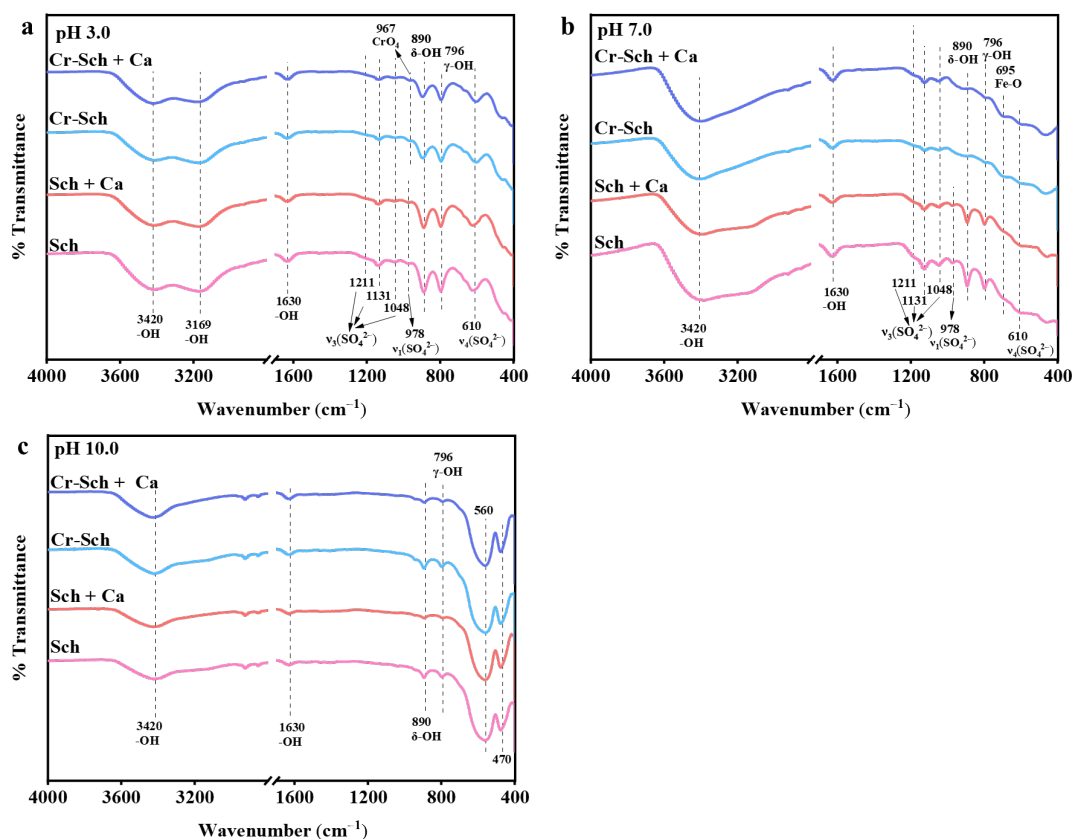


Figure 3. FTIR spectra of transformation products of Sch and Cr-Sch at pH 3.0 (a), 7.0 (b) and 10.0 (c).

The FTIR of transformation products showed obvious peaks in the hydroxyl group (-OH) near the wavenumbers of 796, 890, 1630, 3169 and 3420 cm^{-1} (Figure 3). Among them, 1630 cm^{-1} represented adsorbed H_2O . The bands at 3169 and 3420 cm^{-1} were assigned to the stretching vibrations of structural -OH in Fe oxyhydroxides [35]. The absorption bands at 796 and 890 cm^{-1} were attributed to the bending vibrations of $\delta\text{-OH}$ and $\gamma\text{-OH}$, respectively, which are characteristic of goethite [36]. In contrast, the secondary minerals formed under alkaline conditions (pH 10.0) showed weaker -OH absorption bands than those formed under acidic (pH 3.0) and neutral conditions (pH 7.0), suggesting differences in mineral phase composition and indicating that goethite was not the dominant phase at pH 10.0. Specifically, the FTIR spectra of the secondary minerals formed at pH 10.0 showed strong absorption bands at 470 and 560 cm^{-1} . Hematite typically exhibits its most characteristic absorption bands in the low-frequency region ($<600\text{ cm}^{-1}$) [36]. Moreover, the intensities of these hematite-related bands were slightly weaker in the presence of Ca(II) , indicating that coexisting Ca(II) slightly inhibited the transformation of Sch and Cr-Sch under alkaline conditions, consistent with the XRD results.

3.1.4. XPS

In this study, XPS analysis was conducted on the secondary minerals of Cr-Sch in the presence and absence of Ca(II). As shown in Figure 4a, the high-resolution Fe 2p_{3/2} peak appeared at a binding energy higher than 710.0 eV, indicating that Fe in the transformation products was mainly present in the trivalent state [37]. For transformation products at pH 3.0 and 7.0, the peak position of Fe 2p_{3/2} was located near 711.2 eV. Relatively, the Fe 2p_{3/2} peak of transformation products at pH 10.0 shifted slightly toward lower binding energy and showed a shoulder peak at 710.4 eV. Previous studies have reported that Fe ions in iron oxyhydroxides are usually coordinated with O^{2−} ligands, and their peak position of Fe 2p_{3/2} mostly ranges between 710.6 and 711.2 eV [36]. The binding energy peak at 711.2 eV corresponded to α-FeOOH species, and the binding energy peak at 710.8 eV corresponded to α-Fe₂O₃ species [36]. These results further confirm that the main transformation product of Cr-Sch was goethite under acidic and neutral conditions, but hematite under alkaline conditions.

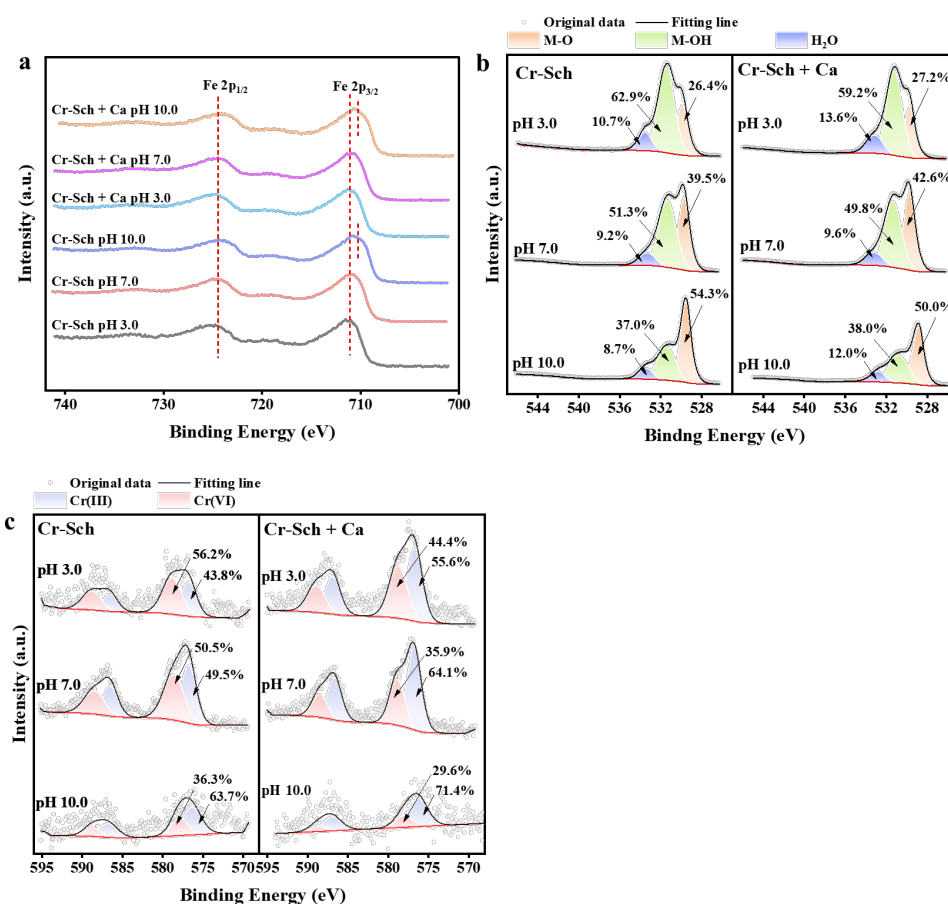


Figure 4. XPS spectra (a), high-resolution O 1s spectra (b), and high-resolution Cr 2p spectra (c) of transformation products of Cr-Sch in the presence and absence of Ca(II).

The high-resolution O 1s spectra of the secondary minerals could be deconvoluted into three subpeaks (Figure 4b). Therein, the peaks centered at approximately 529.7, 531.5 and 533.4 eV were attributed to metal oxides (M-O), hydroxyl groups bound to metals (M-OH), and adsorption-type H₂O, respectively [38]. For transformation products at pH 3.0 and 7.0, no obvious difference was observed in the O 1s peak pattern and sub-peak proportion, whether Ca(II) was present or not. However, under alkaline conditions, the presence of Ca(II) reduced the proportion of Fe-coordinated −OH in the transformation products. This result indirectly indicates that Ca(II) had little effect on the transformation

of Cr-Sch under acidic and neutral conditions, but slightly inhibited its transformation into hematite under alkaline conditions.

3.2. Fate of Cr and Ca During Phase Transformation of Cr-Sch

The transformation process of Cr-Sch was accompanied by changes in Cr species. First, we analyzed the Cr distribution in the system before the transformation experiment. The adsorption of Cr(VI) by Sch under different initial pH conditions is shown in Figure 5a. Results showed that initial Cr(VI) loading was respectively 6.2–13.8 mg/g, which conformed to the range of Cr loading of Sch in actual AMD sediments. Regenspurg et al. found that the concentrations of Cr in AMD sediments was up to 0.812 mg/g, and they also pointed out that the maximum loading amount of Cr in Sch could reach 15.3 wt% [5]. Sch exhibited the most outstanding adsorption capacity for Cr(VI) at pH 7.0. This result was consistent with previous studies, indicating that the adsorption capacity of Sch for Cr(VI) first increased and then decreased with the increasing pH [25]. The ion exchange between Cr(VI) and sulfate is the dominant adsorption mechanism [39]. Increasing pH could cause sulfate in Sch to shift from an inner-sphere to outer-sphere coordination, and the latter is more likely to undergo ion exchange with Cr(VI) [40]. In addition, sulfates in Sch could also be replaced by OH^- ions; therefore, a large amount of OH^- could compete with Cr for adsorption sites in alkaline conditions. On the other hand, at pH 10.0, CrO_4^{2-} was the dominant species (Figure 5b), which exhibited stronger electrostatic repulsion with negative Sch (the zero point is 7.0). This was an important reason for the low adsorption capacity of Sch for Cr(VI) at pH 10.0.

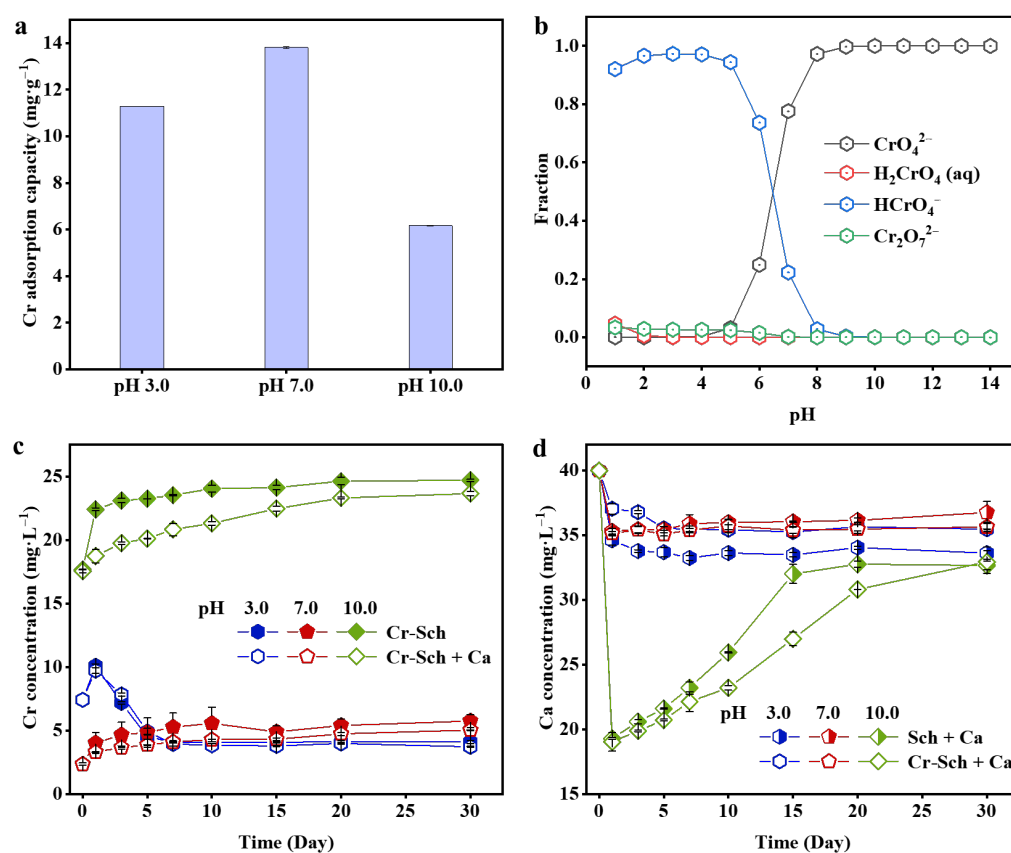


Figure 5. Adsorption capacity of Cr(VI) on Sch at various pH (a), Cr(VI) species distribution (b), Cr concentration changes during transformation (c), and Ca concentration changes during transformation (d).

The change in Cr(VI) concentration in the reaction system tended to stabilize at 30 days' reaction, which could also indirectly prove that mineral transformation approached a stable stage during 30 days' reaction. Cr concentration changes indicated that the transformation process of Cr-Sch was accompanied by the redistribution of Cr. As shown in Figure 4c, Cr in the transformation products exists in both trivalent and hexavalent states simultaneously, indicating that the transformation process of Cr-Sch was accompanied by the reduction in partial Cr(VI). As shown in Figure 5c, the initial stage of the Cr-Sch transformation was accompanied by the release of Cr, which might be caused by the collapse of the mineral structure. Previous studies have shown that hematite and goethite exhibit lower Cr(VI) adsorption capacities than Sch [41]. Adsorption experiments for goethite and hematite for Cr(VI) were conducted, showing that the adsorption capacity of goethite for Cr(VI) was 2.8, 1.8 and 1.3 mg/g, and that of hematite was 2.4, 2.1 and 1.5 mg/g at pH 3.0, 7.0 and 10.0, respectively. Sch (11.3, 13.8 and 6.2 mg/g at pH 3.0, 7.0 and 10.0, respectively) exhibited a significantly higher adsorption capacity than goethite and hematite at experimental pH. This difference suggests that the increase in aqueous Cr during Sch transformation may be attributed not only to Cr release associated with mineral transformation, but also to surface desorption resulting from the lower Cr retention capacity of the newly formed hematite and goethite [42]. At pH 3.0, Cr showed a redistribution pattern of initial release followed by refixation (Figure 5c). The dissolution and recrystallization process during Cr-Sch transformation under acidic conditions was inferred to be the key of such a Cr redistribution phenomenon [32]. At the initial stage of the reaction, the massive dissolution of Cr-Sch was accompanied by the release of adsorbed Cr. As the reaction proceeds, the recrystallization process may have led to the refixation of part of the released Cr through coprecipitation. Moreover, at pH 3.0, Cr redistribution was not significantly affected by coexisting Ca(II), which might be because the minimal influence of Ca(II) on the Cr-Sch transformation. Dissimilarly, at pH 7.0 and 10.0, adsorbed Cr was gradually released as the transformation proceeded, and the Cr concentration in the system increased. This may be related to the relatively weak adsorption capacity of secondary minerals (goethite and hematite) [43,44]. Moreover, Ca(II) had an obvious inhibitory effect on the release of Cr during the transformation process at pH 7.0 and 10.0. This might be because the fixation of Ca(II) brought more positive charge to the mineral surface, which was conducive to the adsorption of Cr. On the other hand, Ca(II) could inhibit the transformation of Cr-Sch and weaken the crystallization of secondary minerals under alkaline conditions, which may be an important reason for the lower Cr release in the presence of Ca(II).

The changes in Ca concentration in each reaction system were determined (Figure 5d). At pH 3.0 and 7.0, Ca concentration in the system only decreased slightly (<10%). Under acidic and neutral conditions, positively charged Sch exhibited strong electrostatic repulsion with positive ion Ca(II). Therefore, the adsorption of Ca on the Sch surface was weak, which has also been proven in previous studies [30]. Interestingly, at pH 3.0, the transformation of Sch exhibited a stronger immobilization ability of Ca than that of Cr-Sch. At pH 10.0, Ca concentration in the system dropped rapidly and then gradually increased. Ca is unstable and prone to hydrolysis to form precipitates under alkaline conditions. A large amount of SO_4^{2-} was released along with a decrease in pH during the transformation of Sch, which might lead to the dissolution of Ca precipitates and an increase in Ca concentration. Moreover, Cr-Sch showed a relatively slower dissolution rate than that of Sch, which might be because of the inhibiting effect of Cr on the Sch transformation.

3.3. Mechanism Illumination: The Regulatory Effect on Cr-Sch Transformation by Ca(II) Species Differences at Various pHs

The influence of Ca(II) on transformation of Cr-Sch at various pHs showed distinguishing results. This phenomenon may be attributed to the species differences in Ca

at various pHs. To verify this hypothesis, we calculated the Ca(II) species distribution and saturation index by Visual MINTEQ. The Visual MINTEQ calculation was carried out using representative experimental conditions, including 1 mM Ca(II), 70 °C, and a standard atmosphere (0.00041 atm CO₂ pressure). Figure 6a shows that Ca(II) mainly existed in the form of free ions (Ca²⁺) at pH < 8.0. As the pH increased to 8.0, Ca²⁺ gradually shifted to CaHCO₃[−] and CaCO₃(aq), while CaCO₃(aq) was the only species in the system at pH > 10.0. As shown in Figure 6b, when the pH exceeded 8.0, the saturation indices of aragonite, calcite, and vaterite gradually became positive. This indicated that three types of CaCO₃ precipitates, including aragonite, calcite and vaterite, might appear in the reaction system under alkaline conditions. XPS spectra provided additional evidence for the presence of Ca-containing carbonate phases in the transformed products at pH 10.0 (Figure 6c). The high-resolution Ca 2p spectrum showed a distinct Ca signal that could be deconvoluted into sub-peaks assigned to calcite, vaterite, and aragonite, suggesting that CaCO₃ formation may contribute to surface passivation and thereby inhibit mineral transformation under alkaline conditions [45]. This inference was concluded from XPS data only, and there was no direct microscopic imaging.

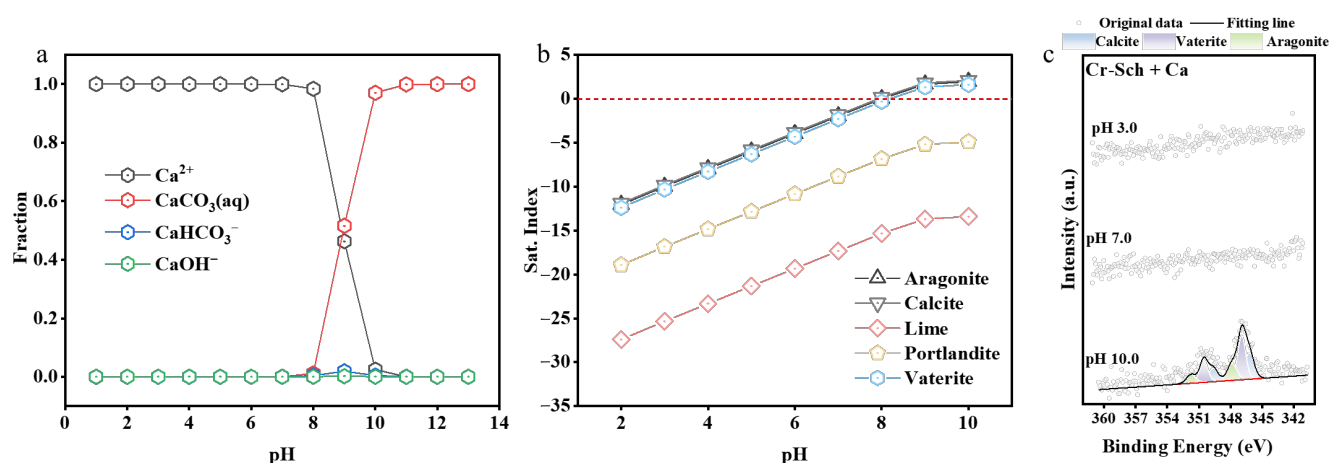


Figure 6. Ca(II) species distribution (a), saturation index (b), and high-resolution spectra of Ca 2p (c).

As discussed above, differences in Ca(II) speciation at different pH values are key to its distinct effects on Cr-Sch transformation. Based on these results, the mechanism by which Ca(II) regulates Cr-Sch transformation at different pH values is discussed below. Under acidic conditions, Cr-Sch might transform into goethite by the path of dissolution and recrystallization [26]. This process was also accompanied by the release and refixation of adsorbed Cr(VI). Positively charged Sch exhibited strong electrostatic repulsion with positive-ion Ca(II), and the interaction between the two was weak [30]. Hence, Ca(II) showed only a slight effect on the transformation of Cr-Sch. Under neutral conditions, Cr-Sch also was inferred to transform into goethite by the path of dissolution and recrystallization [26]. Under alkaline conditions, hematite was the main secondary mineral of Cr-Sch transformation. However, Ca(II) existed in the form of CaCO₃ precipitates such as calcite, aragonite and vaterite under alkaline conditions. These species deposited on the surface of Cr-Sch could inhibit the transformation of Cr-Sch and the release of Cr. Previous research explored the influence of adsorbed Ca(II) on the transformation of Sch, their results showed that adsorbed Ca(II) could inhibit the transformation of Sch due to the change in the transformation path [30]. Differently, this study found that different Ca(II) species at various pHs exhibited differences in the influence and mechanism on the transformation of Cr-Sch and redistribution of Cr. The results showed that Ca(II) existed in dissociative Ca²⁺ in a neutral environment, and dissociative Ca²⁺ could increase the surface positive charge

and enhance stability of Cr on minerals. Moreover, Ca(II) existed in dissociative CaCO_3 precipitates in a neutral environment, and its deposition on the surface of minerals could inhibit the transformation of Cr-Sch and redistribution of Cr. The Cr-Sch transformation pathways of dissolution–recrystallization under acidic conditions and dehydration–cation rearrangement under alkaline conditions were concluded according to previous research, and they were not directly verified experimentally. Future research needs to strive to achieve a deeper understanding of Cr-Sch transformation processes.

4. Conclusions

This study systematically investigated the transformation behavior of Cr-Sch under different pH conditions and elucidated the regulatory role of coexisting Ca(II) in mineral transformation and Cr redistribution. The results demonstrated that the transformation of Sch and Cr-Sch was predominantly pH-controlled, while the influence of Ca(II) depended on its species variation and precipitation behavior. Under acidic conditions (pH 3.0), Cr-Sch mainly transformed into goethite via dissolution and recrystallization. This process induced a transient release of adsorbed Cr(VI), followed by partial refixation through coprecipitation with newly formed iron oxyhydroxides. The presence of Ca(II) had only a minor effect on both mineral transformation and Cr redistribution, owing to strong electrostatic repulsion between Ca^{2+} and positively charged Sch surfaces. Under neutral conditions, the transformation products were mainly goethite, but with a lower degree of transformation compared to acidic conditions. Under alkaline conditions (pH 10.0), Cr-Sch preferentially transformed into hematite through dihydroxylation and cation rearrangement. This transformation pathway resulted in a sustained release of adsorbed Cr(VI), reflecting the relatively weaker affinity of secondary minerals (goethite and hematite) for Cr compared with Sch. In contrast, under alkaline conditions, Ca(II) predominantly precipitated mainly as CaCO_3 phases (calcite, aragonite, and vaterite). These precipitates deposited on mineral surfaces, inhibiting Sch transformation, weakening mineral crystallinity, and suppressing Cr release. Overall, this study highlights that the fate of Cr-Sch is jointly governed by mineral transformation pathways and coexisting Ca species. The findings provide new insights into the coupled geochemical cycling of iron minerals, chromium, and calcium in AMD-impacted environments, and offer important implications for predicting Cr mobility and optimizing remediation strategies involving alkaline neutralization processes.

Author Contributions: Conceptualization, G.L. and L.S.; methodology, G.L. and L.S.; software, G.L., J.W. and L.S.; validation, G.L., Q.Y. and Y.L.; formal analysis, G.L., Z.S. and L.S.; investigation, G.L., Z.S. and H.T.; resources, J.W.; data curation, H.T., Q.Y. and J.W.; writing—original draft preparation, G.L. and J.W.; writing—review and editing, G.L., J.W. and Y.L.; visualization, H.T. and G.L.; supervision, L.S. and P.W.; project administration, L.S. and P.W.; funding acquisition, Y.L. and P.W. All authors have read and agreed to the published version of the manuscript.

Funding: The authors appreciate financial support from the National Natural Science Foundation of China (42572038 and 42407349), Guangdong Science and Technology Program (2020B121201003), and Key Technologies Research and Development Program (2025YFC3909904).

Data Availability Statement: Data is unavailable due to privacy or ethical restrictions.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Dhal, B.; Thatoi, H.N.; Das, N.N.; Pandey, B.D. Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: A review. *J. Hazard. Mater.* **2013**, *250–251*, 272–291. [CrossRef]
2. Li, X.; Guo, C.; Jin, X.; He, C.; Yao, Q.; Lu, G.; Dang, Z. Mechanisms of Cr(VI) adsorption on schwertmannite under environmental disturbance: Changes in surface complex structures. *J. Hazard. Mater.* **2021**, *416*, 125781. [CrossRef]

3. Liang, C.; Fu, F.; Tang, B. Mn-incorporated ferrihydrite for Cr(VI) immobilization: Adsorption behavior and the fate of Cr(VI) during aging. *J. Hazard. Mater.* **2021**, *417*, 126073. [[CrossRef](#)]
4. Torres, E.; Auleda, M. A sequential extraction procedure for sediments affected by acid mine drainage. *J. Geochem. Explor.* **2013**, *128*, 35–41. [[CrossRef](#)]
5. Regenspurg, S.; Peiffer, S. Arsenate and chromate incorporation in schwertmannite. *Appl. Geochem.* **2005**, *20*, 1226–1239. [[CrossRef](#)]
6. Manceau, A.; Schlegel, M.L.; Musso, M.; Sole, V.A.; Gauthier, C.; Petit, P.E.; Trolard, F. Crystal chemistry of trace elements in natural and synthetic goethite. *Geochim. Cosmochim. Acta* **2000**, *64*, 3643–3661. [[CrossRef](#)]
7. Xie, Y.; Ye, H.; Wen, Z.; Dang, Z.; Lu, G. Sulfide-induced repartition of chromium associated with schwertmannite in acid mine drainage: Impacts and mechanisms. *Sci. Total Environ.* **2022**, *848*, 157863. [[CrossRef](#)]
8. Hausladen, D.M.; Fendorf, S. Hexavalent Chromium Generation within Naturally Structured Soils and Sediments. *Environ. Sci. Technol.* **2017**, *51*, 2058–2067. [[CrossRef](#)]
9. Hu, S.; Zhang, H.; Yang, Y.; Wang, W.; Zhou, W.; Shen, X.; Liu, C. Reductive Sequestration of Cr(VI) and Immobilization of C during the Microbially Mediated Transformation of Ferrihydrite-Cr(VI)-Fulvic Acid Coprecipitates. *Environ. Sci. Technol.* **2023**, *57*, 8323–8334. [[CrossRef](#)]
10. Zhang, H.; Lu, Y.; Ouyang, Z.; Zhou, W.; Shen, X.; Gao, K.; Chen, S.; Yang, Y.; Hu, S.; Liu, C. Mechanistic insights into the detoxification of Cr(VI) and immobilization of Cr and C during the biotransformation of ferrihydrite-polygalacturonic acid-Cr coprecipitates. *J. Hazard. Mater.* **2023**, *448*, 130726. [[CrossRef](#)] [[PubMed](#)]
11. Acero, P.; Ayora, C.; Torrentó, C.; Nieto, J.-M. The behavior of trace elements during schwertmannite precipitation and subsequent transformation into goethite and jarosite. *Geochim. Cosmochim. Acta* **2006**, *70*, 4130–4139. [[CrossRef](#)]
12. Bigham, J.M.; Carlson, L.; Murad, E. Schwertmannite, a new iron oxyhydroxysulphate from Pyhäsalmi, Finland, and other localities. *Mineral. Mag.* **2018**, *58*, 641–648. [[CrossRef](#)]
13. Bigham, J.M.; Schwertmann, U.; Traina, S.J.; Winland, R.L.; Wolf, M. Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochim. Cosmochim. Acta* **1996**, *60*, 2111–2121. [[CrossRef](#)]
14. Antelo, J.; Fiol, S.; Gondar, D.; Pérez, C.; López, R.; Arce, F. Cu(II) incorporation to schwertmannite: Effect on stability and reactivity under AMD conditions. *Geochim. Cosmochim. Acta* **2013**, *119*, 149–163. [[CrossRef](#)]
15. Burton, E.D.; Johnston, S.G. Impact of silica on the reductive transformation of schwertmannite and the mobilization of arsenic. *Geochim. Cosmochim. Acta* **2012**, *96*, 134–153. [[CrossRef](#)]
16. Choppala, G.; Karimian, N.; Burton, E.D. An X-ray absorption spectroscopic study of the Fe(II)-induced transformation of Cr(VI)-substituted schwertmannite. *J. Hazard. Mater.* **2022**, *431*, 128580. [[CrossRef](#)] [[PubMed](#)]
17. Fan, C.; Guo, C.; Zhang, J.; Ding, C.; Li, X.; Reinfelder, J.R.; Lu, G.; Shi, Z.; Dang, Z. Thiocyanate-induced labilization of schwertmannite: Impacts and mechanisms. *J. Environ. Sci.* **2019**, *80*, 218–228. [[CrossRef](#)]
18. Fan, C.; Guo, C.; Chen, M.; Huang, W.; Wan, J.; Reinfelder, J.R.; Li, X.; Zeng, Y.; Lu, G.; Dang, Z. Transformation of cadmium-associated schwertmannite and subsequent element repartitioning behaviors. *Environ. Sci. Pollut. Res.* **2019**, *26*, 617–627. [[CrossRef](#)]
19. Yokoyama, Y.; Tanaka, K.; Takahashi, Y. Differences in the immobilization of arsenite and arsenate by calcite. *Geochim. Cosmochim. Acta* **2012**, *91*, 202–219. [[CrossRef](#)]
20. Guo, H.; Zhang, D.; Ni, P.; Cao, Y.; Li, F.; Jia, Y.; Li, H.; Wan, L.; Wang, G. On the scalability of hydrogeochemical factors controlling arsenic mobility in three major inland basins of P.R. China. *Appl. Geochem.* **2017**, *77*, 15–23. [[CrossRef](#)]
21. Kanematsu, M.; Young, T.M.; Fukushi, K.; Sverjensky, D.A.; Green, P.G.; Darby, J.L. Quantification of the Effects of Organic and Carbonate Buffers on Arsenate and Phosphate Adsorption on a Goethite-Based Granular Porous Adsorbent. *Environ. Sci. Technol.* **2011**, *45*, 561–568. [[CrossRef](#)] [[PubMed](#)]
22. Wang, H.; Bigham, J.M.; Tuovinen, O.H. Formation of schwertmannite and its transformation to jarosite in the presence of acidophilic iron-oxidizing microorganisms. *Mater. Sci. Eng. C* **2006**, *26*, 588–592. [[CrossRef](#)]
23. Vital, M.; Martínez, D.E.; Babay, P.; Quiroga, S.; Clément, A.; Daval, D. Control of the mobilization of arsenic and other natural pollutants in groundwater by calcium carbonate concretions in the Pampean Aquifer, southeast of the Buenos Aires province, Argentina. *Sci. Total Environ.* **2019**, *674*, 532–543. [[CrossRef](#)]
24. Fang, L.; Zhou, A.; Li, X.; Zhou, J.; Pan, G.; He, N. Response of antimony and arsenic in karst aquifers and groundwater geochemistry to the influence of mine activities at the world's largest antimony mine, central China. *J. Hydrol.* **2021**, *603*, 127131. [[CrossRef](#)]
25. Fan, C.; Guo, C.; Zeng, Y.; Tu, Z.; Ji, Y.; Reinfelder, J.R.; Chen, M.; Huang, W.; Lu, G.; Yi, X.; et al. The behavior of chromium and arsenic associated with redox transformation of schwertmannite in AMD environment. *Chemosphere* **2019**, *222*, 945–953. [[CrossRef](#)]
26. Tang, H.; Chen, M.; Wu, P.; Li, Y.; Wang, T.; Wu, J.; Sun, L.; Shang, Z. The influence of Mn(II) on transformation of Cr-absorbed Schwertmannite: Mineral phase transition and elemental fate. *Water Res.* **2024**, *257*, 121656. [[CrossRef](#)] [[PubMed](#)]

27. Hu, S.; Lu, Y.; Peng, L.; Wang, P.; Zhu, M.; Dohnalkova, A.C.; Chen, H.; Lin, Z.; Dang, Z.; Shi, Z. Coupled Kinetics of Ferrihydrite Transformation and As(V) Sequestration under the Effect of Humic Acids: A Mechanistic and Quantitative Study. *Environ. Sci. Technol.* **2018**, *52*, 11632–11641. [\[CrossRef\]](#)
28. Salama, W.; El Aref, M.; Gaupp, R. Facies analysis and palaeoclimatic significance of ironstones formed during the Eocene greenhouse. *Sedimentology* **2014**, *61*, 1594–1624. [\[CrossRef\]](#)
29. Wan, J.; Guo, C.; Tu, Z.; Zeng, Y.; Fan, C.; Lu, G.; Dang, Z. Microbial Reduction of Cr (VI)-loaded Schwertmannite by *Shewanella oneidensis* MR-1. *Geomicrobiol. J.* **2018**, *35*, 727–734. [\[CrossRef\]](#)
30. Fan, C.; Guo, C.; Chen, W.; Lu, G.; Shen, Y.; Dang, Z. Fe(II)-mediated transformation of schwertmannite associated with calcium from acid mine drainage treatment. *J. Environ. Sci.* **2023**, *126*, 612–620. [\[CrossRef\]](#)
31. Van Driessche, A.E.S.; Stawski, T.M.; Benning, L.G.; Kellermeier, M. Calcium Sulfate Precipitation Throughout Its Phase Diagram. In *New Perspectives on Mineral Nucleation and Growth: From Solution Precursors to Solid Materials*; Van Driessche, A.E.S., Kellermeier, M., Benning, L.G., Gebauer, D., Eds.; Springer International Publishing: Cham, Switzerland, 2017; pp. 227–256.
32. Yao, Q.; Guo, C.; Li, X.; Jin, X.; Lu, G.; Yi, X.; Huang, W.; Dang, Z. Synergy of oxalic acid and sunlight triggered Cr(III)-bearing Schwertmannite transformation: Reaction mechanism, Cr and C spatial distribution and speciation on the nano scale. *Geochim. Cosmochim. Acta* **2022**, *329*, 70–86. [\[CrossRef\]](#)
33. Paikaray, S.; Peiffer, S. Dissolution Kinetics of Sulfate from Schwertmannite Under Variable pH Conditions. *Mine Water Environ.* **2010**, *29*, 263–269. [\[CrossRef\]](#)
34. Boily, J.F.; Gassman, P.L.; Peretyazhko, T.; Szanyi, J.; Zachara, J.M. FTIR Spectral Components of Schwertmannite. *Environ. Sci. Technol.* **2010**, *44*, 1185–1190. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Ying, H.; Feng, X.; Zhu, M.; Lanson, B.; Liu, F.; Wang, X. Formation and transformation of schwertmannite through direct Fe³⁺ hydrolysis under various geochemical conditions. *Environ. Sci. Nano* **2020**, *7*, 2385–2398. [\[CrossRef\]](#)
36. Salama, W.; El Aref, M.; Gaupp, R. Spectroscopic characterization of iron ores formed in different geological environments using FTIR, XPS, Mössbauer spectroscopy and thermoanalyses. *Spectrochim. Acta A* **2015**, *136*, 1816–1826. [\[CrossRef\]](#)
37. Li, X.; He, C.; Liang, H.; Chen, K.; Yao, Q.; Guo, C.; Lu, G.; Dang, Z. Investigation of the Interactions Occurring Between Cr(VI) and Citric Acid-Schwertmannite Composites: A Macroscopic and In Situ ATR-FTIR Study. *ACS Earth Space Chem.* **2022**, *6*, 391–402. [\[CrossRef\]](#)
38. Ding, Z.; Fu, F.; Dionysiou, D.D.; Tang, B. Coadsorption and subsequent redox conversion behaviors of As(III) and Cr(VI) on Al-containing ferrihydrite. *Environ. Pollut.* **2018**, *235*, 660–669. [\[CrossRef\]](#)
39. Antelo, J.; Fiol, S.; Gondar, D.; López, R.; Arce, F. Comparison of arsenate, chromate and molybdate binding on schwertmannite: Surface adsorption vs anion-exchange. *J. Colloid Interface Sci.* **2012**, *386*, 338–343. [\[CrossRef\]](#)
40. Stumm, W.; Morgan, J.J. *Aquatic Chemistry*; John Wiley & Sons. Inc.: New York, NY, USA, 1996.
41. Wang, C.; Wu, R.; Guo, J.; Cui, Y. Effects of Cr(VI)-reducing bacteria on the behaviour of Cr(VI) adsorption by goethite and haematite: Speciation and distribution. *J. Soils Sediments* **2020**, *20*, 3733–3741. [\[CrossRef\]](#)
42. Mytych, P.; Ciesla, P.; Stasicka, Z. Photoredox processes in the Cr(VI)-Cr(III)-oxalate system and their environmental relevance. *App. Catal. B Environ.* **2005**, *59*, 161–170. [\[CrossRef\]](#)
43. Wu, W.; Wang, S.; Tzou, Y.; Chen, J.; Wang, M. The adsorption and catalytic transformations of chromium on Mn substituted goethite. *App. Catal. B Environ.* **2007**, *75*, 272–280. [\[CrossRef\]](#)
44. Cheng, H.; Jing, Z.; Yang, L.; Lu, A.; Ren, G.; Liu, J. Sunlight-triggered synergy of hematite and *Shewanella oneidensis* MR-1 in Cr(VI) removal. *Geochim. Cosmochim. Acta* **2021**, *305*, 19–32. [\[CrossRef\]](#)
45. Ni, M.; Ratner, B.D. Differentiating calcium carbonate polymorphs by surface analysis techniques—An XPS and TOF-SIMS study. *Surf. Interface Anal.* **2008**, *40*, 1356–1361. [\[CrossRef\]](#) [\[PubMed\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.