



Effects of different oxyanions in solution on the precipitation of jarosite at room temperature

Yeongkyoo Kim

School of Earth System Sciences, Kyungpook National University, Daegu 41566, Republic of Korea



ARTICLE INFO

Keywords:

Jarosite
Oxyanion
Acid mine drainage
Coprecipitation
Heavy metal

ABSTRACT

The effects of five different oxyanions, AsO_4 , SeO_3 , SeO_4 , MoO_4 , and CrO_4 , on the precipitation of jarosite at room temperature were investigated by X-ray diffraction, scanning electron microscopy, and chemical analysis. Different amounts (2, 5, and 10 mol%) of oxyanions in the starting solution and different aging times (1 h–40 days) were used for the experiment. In the initial stage, only the amorphous phase appears for all samples. With increasing aging time, jarosite and jarosite with oxyanions start precipitating at room temperature with different precipitation rates and crystallinities. Jarosite with AsO_4 shows the lowest precipitation rate and lowest crystallinity. With increasing amounts of oxyanions, the crystallization rate decreases, especially for jarosite with AsO_4 . The jarosite samples with CrO_4 and SeO_4 show the fastest precipitation and highest crystallinities. For the jarosite samples with a low precipitation rate and low crystallinity, the amorphous phase contains high concentrations of oxyanions, probably because of the fast precipitation of the amorphous iron oxyanion phase; however, the phase with fast jarosite precipitation contains fewer oxyanions. The results show that coprecipitation of jarosite can play a more important role in controlling the behavior of CrO_4 than AsO_4 in acid mine drainage.

1. Introduction

Many iron minerals produced by the oxidation of pyrite, such as schwertmannite, ferrihydrite, goethite, and jarosite, precipitate in acid mine drainage (AMD) because of the dissolved ion species and their concentrations, and pH conditions [1–3]. Among these minerals, jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$, which is common in the weathered zone of sulfide ore deposits and in acid sulfate soil, is the only mineral belonging to the alunite group, and it precipitates with a high concentration of SO_4 and at $\text{pH} < 3$ [4,5]. Previous field studies showed that arsenate and other heavy metals could be naturally attenuated by the precipitation of mineral phases containing iron [2,6–13]. One of the main processes is the sorption of these metals on the surface of goethite and other mineral phases [14,15]. In addition, laboratory work showed that sulfate in schwertmannite can be replaced by arsenate and attenuated in AMD [6,13,16,17]. Jarosite is another mineral phase that could play an important role in attenuating arsenate; surface sorption, rather than replacement of arsenate, was suggested as a possible process [11,18]. However, other studies proposed that jarosite could contain arsenate substituting for sulfate within its structure and contribute to the attenuation of arsenate in AMD [2,7,8,12,14,15,19]. Previous X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) studies confirmed that arsenate could

substitute for sulfate within the jarosite structure in AMD [15,20,21]. Other oxyanions can affect the precipitation of jarosite and the resultant mobility of these oxyanions. The micro-EXAFS spectrum of acid sulfate soils formed from the weathering of pyritic shale revealed that a higher percentage of Se(VI) is related to jarosite occurrence [22]. Jarosite-type compounds containing SeO_4 instead of sulfate can also be synthesized by precipitation in the laboratory, suggesting that it is highly possible for oxyanions to coprecipitate with jarosite and decrease the mobility of the oxyanions [23].

Chromium is an important toxic element, and a CrO_4 analog of jarosite was identified in contaminated soils [24]. Laboratory studies have shown that in addition to selenium and arsenate, chromate-type jarosite could also precipitate at high temperatures, and this has been characterized [25,26]. This suggests that coprecipitation and replacement of oxyanions in jarosite can play important roles in attenuating heavy metals in AMD and other environments.

However, most studies on arsenate in jarosite have focused on the arsenate concentration in jarosite [2,7,8,12,14,19]. The studies on the substitution and coprecipitation of oxyanions in jarosite mostly focused on the formation of jarosite above 80°C or the hydrothermal synthesis and structure of these oxyanions in the lattice of jarosite [15,20,21,23,25–27]. In addition, there was no comparison between different oxyanions coprecipitated with jarosite. Therefore, no

E-mail address: ygkim@knu.ac.kr.

<https://doi.org/10.1016/j.jhazmat.2018.04.016>

Received 12 May 2017; Received in revised form 28 March 2018; Accepted 7 April 2018

Available online 09 April 2018

0304-3894/© 2018 Elsevier B.V. All rights reserved.

systematic studies have examined the effects of oxyanions on the formation of jarosite at room temperature, which can provide useful information on the behaviors of heavy metals in natural environments, including AMD.

This paper presents the experimental results of the effects of different oxyanions on the precipitation of jarosite at room temperature and jarosite phases coprecipitated with oxyanions. The behaviors of oxyanions during the precipitation of jarosite are also compared.

2. Experimental methods

Jarosite containing K was synthesized for comparison with other precipitated jarosite phases. The jarosite synthesis method reported by Baron and Palmer was adopted [28]. Jarosite was synthesized by dissolving 13.98 g of $\text{Fe}_2(\text{SO}_4)_3$ and 5.6 g of KOH in 100 mL of deionized water, and the solution was boiled for 4 h at 95 °C. The precipitates were filtered through a 0.20 μm membrane filter and washed several times with deionized water during filtering.

For the jarosite samples coprecipitated with oxyanions at room temperature, five oxyanions (AsO_4 , SeO_3 , SeO_4 , MoO_4 , and CrO_4) were chosen as the representative oxyanions. H_2KAsO_4 , K_2SeO_3 , K_2SeO_4 , K_2MoO_4 , and K_2CrO_4 were selected as the sources for the five oxyanions, respectively. Different mixing orders for the three chemicals (KOH, $\text{Fe}_2(\text{SO}_4)_3$, and the oxyanions) led to the formation of different phases. In this experiment, KOH and the oxyanions were added to deionized water first, and then, $\text{Fe}_2(\text{SO}_4)_3$ was added and aged for different times, which precipitated jarosite phases. Different amounts of oxyanions (mol%) and aging times were used to investigate their effects on the formation of jarosite. Three different amounts of oxyanions (2, 5, and 10 mol%, based on the total anions in solution) and seven different aging times (1 and 6 h; 1, 3, 10, 20, and 40 days) were used for the experiments. At room temperature, the same aging times were additionally used for the precipitation of jarosite.

After the planned aging time, the precipitates were filtered through a 0.20- μm membrane filter and dried at 40 °C in an oven for 24 h. X-ray diffraction (XRD, Phillips X'pert APD) was used to identify and characterize the jarosite samples. The data were collected from $2\theta = 10$ to 60° with steps of $2\theta = 0.016^\circ$ and a counting time of 1 s per step with Ni-filtered Cu-K α radiation at 40 kV and 30 mA at the Daegu Center of Korea Basic Science Institute. The full width at half maximum (FWHM) of the XRD peak at 17.5° (5.09 Å, d(012)) was measured for each jarosite sample. This peak was chosen because it is the largest peak without any overlap. The morphology and size of the precipitated phases were investigated using field-emission scanning electron microscopy (FE-SEM, Hitachi model S-4200) at the Daegu Center of Korea Basic Science Institute. In addition, the chemical compositions of the precipitates were analyzed by energy-dispersive spectroscopy (EDS).

The concentrations of oxyanions in the precipitates prepared from 10 mol% oxyanions and aged for 40 days were analyzed by dissolving samples in a digestion acid mixture ($\text{HNO}_3:\text{HF}:\text{HClO}_4 = 4:4:1$). Four elements (As, Se, Mo, and Cr) in the precipitated samples were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) at the Seoul Center of Korea Basic Science Institute.

3. Results and discussion

3.1. Jarosite containing K

An XRD pattern and SEM image of jarosite precipitated at a high temperature are presented in Fig. 1. All XRD peaks are well matched to those of jarosite. The SEM image of the precipitate shows anhedral and mainly globular forms, which were also reported in other studies [29,30]. Some particles have cubic shapes. The particle size is relatively homogeneous in the range of 3–15 μm . The EDS analysis shows that the samples are composed only of Fe, O, K, and S, confirming that the synthesized precipitate is jarosite. However, the unit cell dimensions of

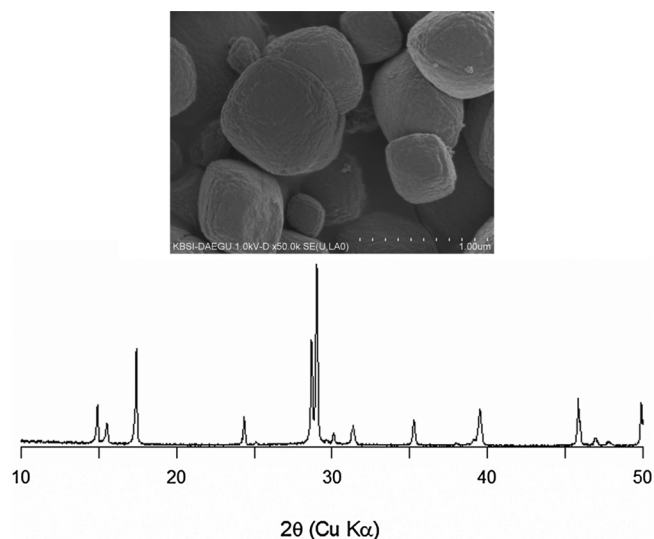


Fig. 1. SEM image and XRD pattern of jarosite synthesized at 95 °C.

jarosite precipitated at high and low temperatures and aged in this study were a: 7.306, c: 17.099 and a: 7.314, c: 17.042, respectively, indicating that not only K but also hydronium is included in the precipitated jarosite samples [21,31].

3.2. XRD patterns of jarosite coprecipitated with oxyanions

The XRD results show that the different oxyanions in solution, oxyanion concentration, and aging time affect the precipitation rate of jarosite (Figs. 2–4). The XRD patterns of the samples reacted with 2 mol % of oxyanions and jarosite show that they can precipitate at room temperature, implying that they can precipitate in a natural environment, such as AMD, even though more time is required than that for the synthesis of jarosite with oxyanions, above 95 °C [15,20,21,24,26,27]. After 1 h, the XRD patterns of most samples only show a broad background, indicating the presence of non-crystalline phases. After 6 h, major peaks of jarosite appear for all samples, except for that with MoO_4 ; a small peak near 30° is observed for the jarosite sample with CrO_4 , suggesting that part of the jarosite crystallized. Most jarosite samples show major XRD peaks after 1 day. The FWHM values are closely related to the crystallite dimensions and crystallinity of iron minerals, such as goethite, hematite, and magnetite [32–34]. The FWHM values of the 17.5° peak for all of the samples are listed in Table 1. The FWHM values of the samples that reacted with 2 mol% of oxyanions slightly decreased with increasing aging time, indicating that the samples become more crystalline or the particle sizes of the samples increase. The jarosite samples precipitated at room temperature also show decreasing FWHM values with increasing aging time. The values for the samples, except for those reacted with AsO_4 , are generally similar to or narrower than the jarosite that precipitated at room temperature. The values for the samples that reacted with AsO_4 are larger than the other samples, indicating that the samples with AsO_4 may have less crystalline phases than the other samples.

For the samples that reacted with 5 mol% of oxyanions, the XRD patterns show slightly different features (Fig. 3). Most samples do not form crystalline phases after 6 h, and it takes at least 1 day for the crystallization of jarosite. The samples that reacted with AsO_4 have slightly broader peak widths than those of the other samples, suggesting that this jarosite has lower crystallinity. These FWHM values generally show a similar trend for the samples reacted with 2 mol% of oxyanions, decreasing with respect to the aging time for all samples (Table 1). However, the FWHM values are larger for the samples reacted with 5 mol% of oxyanions than for the samples reacted with 2 mol% of oxyanions. The samples with AsO_4 have the largest FWHM, while those

Download English Version:

<https://daneshyari.com/en/article/6968416>

Download Persian Version:

<https://daneshyari.com/article/6968416>

[Daneshyari.com](https://daneshyari.com)