

# Stability of schwertmannite and ferrihydrite in the stream waters of Imgok and Osheep Creek polluted by acid mine drainage

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The precipitation of Fe-compounds from acid mine drainage (AMD) and stream water polluted by AMD plays a crucial role in regulating pollutant migration and determining the impacts of AMD on aquatic ecosystems. It is thus essential to identify the nature of precipitates that form and to understand their stabilities in order to assess their environmental impact. This is a necessary prerequisite before an appropriate treatment program can be prepared. Various kinds of Fe-compounds have been found to precipitate from AMD, but not all of them have been investigated in detail. Schwertmannite is one of the Fe-compounds which need more investigation. Its stability constant was reported only once (Bigham *et al.*, 1996).

The purpose of this study is to determine the stability of schwertmannite and ferrihydrite as a function of the composition of the stream water from which they precipitate. Schwertmannite and ferrihydrite have been found to precipitate respectively from the stream waters of Imgok Creek and Osheep Creek in Kangwon-Do, Korea (Yu, 1996; Yu *et al.*, 1996). Although Imgok and Osheep Creeks both drain what were once very actively operated mining areas and are polluted by AMD from the abandoned coal mines, their compositions are very different.

## Methods

Precipitate and stream water samples were collected along Imgok Creek in October 1995 and Osheep creek in July 1994. Each precipitate sample was transferred to a 250 ml acrylic bottle, tightly sealed with a cap, and then stored in a refrigerator at 4°C until later analyses. Stream water samples were filtered with a 0.45 µm micropore filter before being bottled in 500 ml polyethylene bottles presoaked in 1:1 HCl and HNO<sub>3</sub>. Approximately 200 ml of each filtered water sample was acidified with concentrated-HNO<sub>3</sub> and transferred in a separate 250 ml presoaked polyethylene bottle. All water samples

were also stored in a refrigerator until later analyses.

pH, Eh, conductivity, and temperature of the stream water were measured in the field wherever a precipitate and/or a water sample were collected. The chemical compositions of the water and precipitate samples were determined by ICP-AES, ICP-MS, and ion chromatography (IC) at the Korean Basic Science Center and Department of Chemistry of Kangwon National University (KWNU). Prior to chemical analysis, 0.2 g of each precipitate sample was washed three times with deionized water, dried at 120°C for 2 hrs, and dissolved in 50 ml of 5 N HCl.

For more accurate identification of the precipitates, X-ray diffraction (XRD), Infrared spectroscopy (IR) and thermal analyses including DTA, TGA, and DTGA were undertaken at the Department of Geology and the Department of Chemistry of KWNU. The thermal analyses were conducted on 20 mg samples dried at 60°C for two hours.

## Results and discussion

The chemical compositions of the precipitates suggest that all the samples from Imgok Creek except one mainly consist of Fe hydroxysulphates. Three samples, one is from Imgok Creek and the other two from Osheep Creek, contain insignificant SO<sub>3</sub> and are likely to mainly consist of Fe hydroxide. None of the analysed samples seems to have polycationic phases such as K-jarosite, because all of them have negligible amounts of cations other than Fe. H<sub>2</sub>O(+) contents of the precipitates were calculated from the thermal analyses. The molal Fe to S and Fe to H<sub>2</sub>O ratios of the samples mainly consisting of hydroxysulphate vary respectively from 4.31 to 7.12 and from 0.39 to 0.95. This variation may be caused by variable stoichiometry of a single Fe phase, mixing of more than two Fe phases of constant stoichiometry, or some combination of these two possibilities.

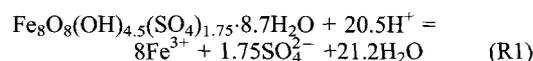
The results of XRD analyses indicate that most precipitate samples are mixtures of several minerals,

suggesting that the molal ratio variations discussed above are due to mixing of more than two Fe phases. XRD patterns show that one sample consists of almost schwertmannite with few impurities, another is mainly ferrihydrite with very minor quartz, while a third has not only ferrihydrite but also considerable amount of quartz and micas. The rest of the samples turns out to be the mixtures of schwertmannite, goethite, and small amount of others. It is believed that the goethite does not directly precipitate from the stream water but results from the later reaction between the stream water and schwertmannite after precipitated (Bigham *et al.*, 1996).

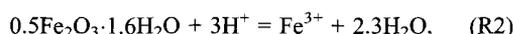
The IR spectra and thermal curves of the three precipitates with insignificant SO<sub>3</sub> content do not show the absorption band between 1,100–1,200 cm<sup>-1</sup> attributed to the stretching vibration of SO<sub>4</sub> (Bigham *et al.*, 1990) or the endothermic peak at 630°C caused by release of gaseous SO<sub>3</sub> from structural SO<sub>4</sub> (Bigham *et al.*, 1990). These features are observed all other precipitates. These results of the IR and thermal analyses are well consistent with the chemical and XRD analyses.

The chemical formulae of schwertmannite and ferrihydrite are determined from the chemical compositions of the precipitates consisting of schwertmannite with few impurities and ferrihydrite with very minor quartz: Their chemical formulae are Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>4.5</sub>(SO<sub>4</sub>)<sub>1.75</sub>·8.7H<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub>·1.6H<sub>2</sub>O, respectively. The chemical formula of the schwertmannite we determined has the value of SO<sub>4</sub> close to the maximum value suggested by Bigham *et al.* (1990).

The dissolution reactions of schwertmannite and ferrihydrite are usually represented as



and



respectively. The corresponding solubility lines for reactions (R1) and (R2) are

$$\text{pFe} = 2.563\text{pH} - 0.219\text{pSO}_4 + 0.125\text{pK}_s \quad (1)$$

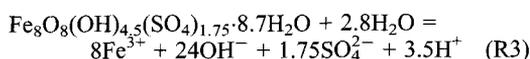
and

$$\text{pFe} = 3\text{pH} + \text{pK}_f \quad (2)$$

where p represents  $-\log_{10}$ , and K<sub>s</sub> and K<sub>f</sub> are the stability constants of schwertmannite and ferrihydrite, respectively. If pSO<sub>4</sub> is constant, plotting pFe against pH of the solution should give not only pK's of both phases but also the stability boundary between them as equations (1) and (2) indicate.

When pSO<sub>4</sub> varies over a wide range of values as is seen in the stream waters of this study, however, estimating pK's in this manner would give erroneous results.

Rreactions (R1) and (R2) may be rewritten as



and



The corresponding solubility lines for reactions (R3) and (R4) respectively become

$$\text{pFe} + 3\text{pOH} = -0.219(\text{pSO}_4 + 2\text{pH}) + 0.125\text{pK}'_s \quad (3)$$

and

$$\text{pFe} + 3\text{pOH} = \text{pK}'_f \quad (4)$$

As equation (3) and (4) suggest, pK's and the stability boundary can be determined by plotting pFe+3pOH against pSO<sub>4</sub>+2pH, which accounts for variations in pSO<sub>4</sub>. Figure 1 shows the activity data of the water samples and the solubility lines of schwertmannite (at pK<sub>s</sub> = 0, -10, and -18) and ferrihydrite (at pK<sub>f</sub> = -2.5, -4, and -5). The activities of the dissolved species in the stream water were calculated with the computer program MINTQA2 (Allison *et al.*, 1991), using the Davis equation, from the chemical compositions of the water samples. The activities plotted in Fig. 1 indicate that the stability constant of schwertmannite should be much lower than previously suggested (pK<sub>s</sub> = -18) (Bigham *et al.*, 1996) and can be as low as pK<sub>s</sub> = 0. If pK<sub>s</sub> = 0.0 for schwertmannite, the stability constant of ferrihydrite also should be lowered to pK<sub>f</sub> = -2.5 to maintain their relative stability boundary around pSO<sub>4</sub> + 2pH = 12 as indicated in Fig. 1.

## Acknowledgements

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