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Research Article

Formation of Iron(III) oxyhydroxy sulfate mineral and mobilization of arsenic during oxidative decomposition of a natural pyrite (FeS_2)

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Abstract: The mobilization of arsenic (As) during the oxidative decomposition of a natural pyrite (FeS_2) containing As was examined using hydrogen peroxide as an oxidizing reagent. The release of As into aqueous solution, however, was apparently inhibited during the oxidation process, suggesting the formation of a secondary mineral that can entrap As. From the powder X-ray diffractogram and SEM-EDX observation for solid material remained after the decomposition of FeS_2, schwertmannite was detected. The fact suggests that As released during the oxidative decomposition of FeS_2 may be instantaneously sorbed to schwertmannite because of more rapid sorption rate than that by goethite.

Keywords: pyrite, oxidation, schwertmannite, arsenic, sorption

INTRODUCTION

Arsenic (As) is a ubiquitous element found in the atmosphere, soils, rocks and natural waters. As can mobilize in environment through natural processes such as weathering reactions of rocks, biological activity, volcanic emissions and through anthropogenic activities. Most of environmental problems for As result from its mobilization and accumulation under natural conditions. For an example, high As concentration has been found in groundwater, especially in southeast Asian countries. Arsenic contamination of groundwater has become the major concern since millions of people are drinking groundwater with higher As concentration than the standard of World Health Organization (10 ppb As) (Nriago *et al*., 1994 and Muehe *et al*., 2014).

Arsenic commonly occurs in many minerals, usually in conjunction with sulfur and metals. Among them, pyrite (FeS_2) constitutes a major source of As in the groundwater and surface waters (Smedely and Kinniburg, 2002, Garelick *et al*., 2008). Under acidic conditions, FeS_2 undergoes oxidation and releases large amount of As, generating Acid Mine drainage (AMD). As is released by the oxidation of FeS_2 by atmospheric oxygen or dissolved oxygen and secondary iron(III) minerals are also formed during the oxidation. Some researchers have postulated that the released As by the oxidation reaction of FeS_2 would be adsorbed on the mineral surface rather than be present in water as dissolved As (Nguyen *et al*., 2009, Carlson *et al*., 2002 and Fukushi *et al*., 2003). Under reducing conditions the secondary minerals adsorbing As undergoes reductive dissolution releasing As in the surrounding aquifers (Neil *et al*., 2012 and Cheng *et al*., 2009).

However, only a few quantitative experiments on the mobilization of As during the oxidative decomposition of FeS_2 has been reported. The purpose of this investigation is to examine the relationship between the secondary iron(III) minerals and behavior of As through a mimic experiment of oxidative decomposition of FeS_2 using hydrogen peroxide (Dimitrijevic *et al*., 1999). This study can give direct evidence that metal sulfide minerals containing As is a source of As in groundwater.

MATERIALS AND METHODS

Materials

Pyrite used in this study was collected from Lubuk Mandi gold mine tailings in Terengganu Malaysia. Chemical composition of the FeS_2 was determined by dissolving in nitric acid. The concentrations of Fe, As and S were determined by ICP-AES (Perkin Elmer Optima 5300 DV). The concentrations of Fe, S and As were found to be 48.80 wt%, 50.06 wt% and 0.01 wt%, respectively. All reagents used were of analytical grade. Solutions were prepared with deionized-distilled water.

Procedure

The oxidative decomposition experiment of FeS_2 was performed using hydrogen peroxide as an oxidizing reagent to accelerate the oxidation reaction. A 0.1 g of FeS_2, which was crushed and ground into powder, was added in a 100 cm^3 of 1:1 aqueous solution of hydrogen peroxide. The suspended solution was allowed to stand for 24 h and then filtered with a 0.45µm membrane filter. The concentrations of Fe, S and As in the filtrate were determined by ICP-AES. The residue on the filter was freeze-dried and characterized by XRD (Rigaku, Rint 2000, X-ray diffractometer) and SEM (Shimadzu, SEM-EDX SS-550).

RESULTS AND DISCUSSIONS

Formation of secondary minerals during the oxidative decomposition of FeS_2

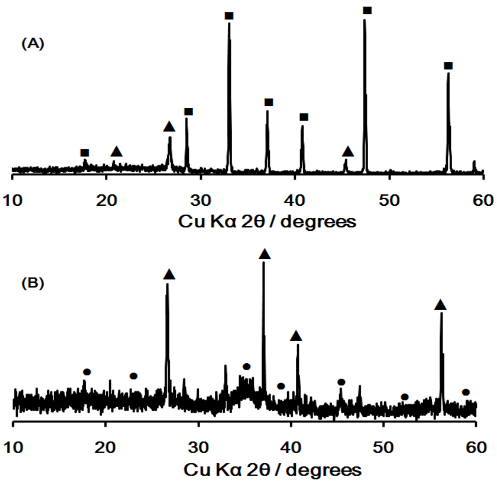

Figure 1: XRD pattern of the pyrite sample (A) before oxidation and (B)

after oxidation (■: pyrite, ▲: Quartz, •: schwertmannite).

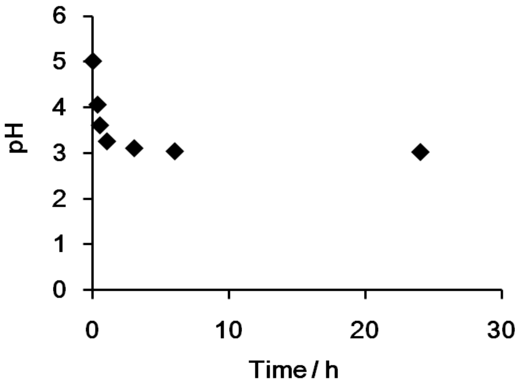

Figure 2: Variation of pH with time during the oxidation reaction of pyrite.

Fig.1 shows the powder X-ray diffractograms (XRD) for solid samples (A) before and (B) after the oxidative decomposition experiment of FeS_2. In the XRD pattern (A), peaks assigned to quartz and FeS_2 were observed, while, in the XRD pattern (B) peaks of FeS_2 disappeared after the experiment, suggesting that most of the FeS_2 was decomposed. Fig. 2 shows the variation of pH of the suspended solution with time during the oxidative decomposition experiment. The pH decreased from 5.0 to 3.0 because of the formation of sulfuric acid by the oxidation of S^{2-} to SO_4^{2-} and hydrolysis of $Fe(H_2O)_6^{3+}$ generated by the oxidation of $Fe(H_2O)_6^{2+}$. Fig. 3 shows the variation of Fe^{3+} and SO_4^{2-} concentrations in filtrates as a function of time. If no precipitation of secondary minerals occurred after the oxidative decomposition, final Fe^{3+} and SO_4^{2-} concentrations in filtrate can be estimated to be 8.33 mmol dm^{-3} and 16.6 mmol dm^{-3}, respectively. Even immediately after the decomposition reaction of FeS_2, the Fe^{3+} concentration was lower than 8.33 mmol dm^{-3} and was about 4 mmol dm^{-3} and then gradually decreased to near zero. Finally, most of the Fe^{3+} was precipitated. On the other hand, SO_4^{2-} concentration was about 12 mmol dm^{-3} immediately after the decomposition and was almost constant during the reaction. In Fig. 1(B), the peaks except those due to quartz can be assigned to schwertmannite from the comparison of XRD patterns of natural and synthesized schwertmannites (Bigham *et al.*, 1990, Schwertmann and Cornell, 2003).

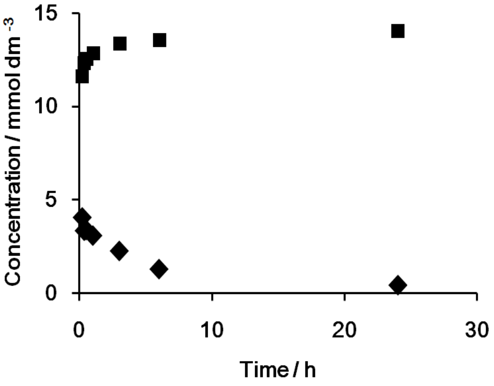

Figure 3: Variation of Fe (•) and sulfate (■) concentration with time during the oxidation reaction of pyrite.

Based on the result shown in Fig. 3, Fe^{3+} of 0.83 mmol and SO_4^{2-} of 0.26 mmol are considered to be precipitated as a secondary mineral. These amounts of Fe^{3+} and SO_4^{2-} interestingly correspond to the stoichiometry of schwertmannite ($(Fe_8O_8(OH)_x(SO_4)_y$; $x = 8 - 2y$, $1< y < 1.75$). Schwertmannite is a poorly crystalline oxyhydroxy iron(III) sulfate as shown in Fig. 1(B) and it precipitates under acidic pH (pH 2.5 – 4.5), Fe^{3+} and SO_4^{2-} rich water, which is a close condition shown in Figs. 2 and 3 (Bigham *et al.*, 1990, Jonsson *et al.*, 2006 and Regenspurg *et al.*, 2004). As well known, secondary iron minerals occur depending on pH. Under near neutral condition, goethite, which has highly crystalline nature, may be preferably precipitated (Luther *et al*., 1982, Bigham *et al*., 1996, Peretyazhko *et al*., 2009 and Regenspurg *et al*., 2004).

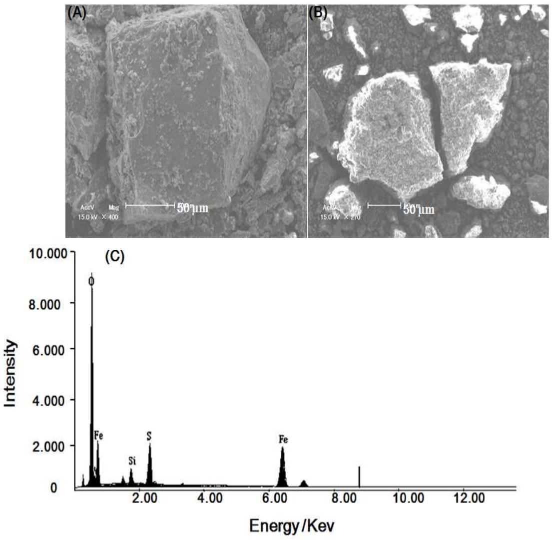

Figure 4: SEM photographs of pyrite sample before oxidation (A), after oxidation (B) and EDX signal of the solid material after oxidation (C).

Fig. 4 shows the result of SEM-EDX observation for solid samples (A) before and (B) after the oxidative decomposition. Fig. 4(A) shows the SEM image of FeS_2 sample with clear shape and smooth plane. On the other hand, Fig. 4(B) shows the SEM image of solid sample after the oxidative decomposition which seems to be aggregate of fine particles. The image in Fig. 4(B) is somewhat similar to that of the synthesized schwertmannite presented by Paikaray *et al*., (2011). According to Bigham *et al*., (1990), the Fe/S atomic ratio for naturally occurred schwertmannite ranges from 4 to 8. Fig. 4(C) shows the EDX result for a solid sample in Fig. 4(B). The Fe/S atomic ratio for the solid sample after the oxidative decomposition experiment was found to be 4.01 from the EDX result. The ratio of Fe/S calculated from the oxidative decomposition experiment (Fe/S = 3.2, in Fig. 3) was close to the ratio obtained from the EDX result (Fe/S = 4.01, in Fig. 4(C)). Judging from the experimental results, it can be reasonably concluded that schwertmannite $(Fe_8O_8(OH)_4(SO_4^{2-})_{2.0\sim2.5})$ was formed as a secondary iron(III) mineral during the oxidative decomposition of FeS_2 using H_2O_2.

Behavior of As during the oxidative decomposition of FeS_2

Although schwertmannite is a metastable mineral and transforms to goethite, which is thermodynamically more stable than schwertmannite, under oxic condition (Regenspurg *et al*., 2004 and Bruton *et al*., 2008), only schwertmannite was observed in Fig. 1(B). Both goethite and schwertmannite have high affinity toward As, however, schwertmannite has higher sorption capacity than goethite because of its unique structure and larger surface area (100–200m^2/g).Therefore, schwertmannite acts as a sink for many toxic anions especially As, Se, Cr etc. (Regenspurg *et al*., 2005).

Fig. 5 shows the variation of As concentration in filtrates as a function of time during the oxidative decomposition experiment. From the As content in FeS_2, if all of As remains in solution after the oxidative decomposition, the As concentration should be 1.3 mmol dm^{-3}. In Fig. 5, however, most of the As was not detected in solution. Therefore, it can be considered to be instantaneously sorbed by schwertmannite formed during the oxidative decomposition of FeS_2.

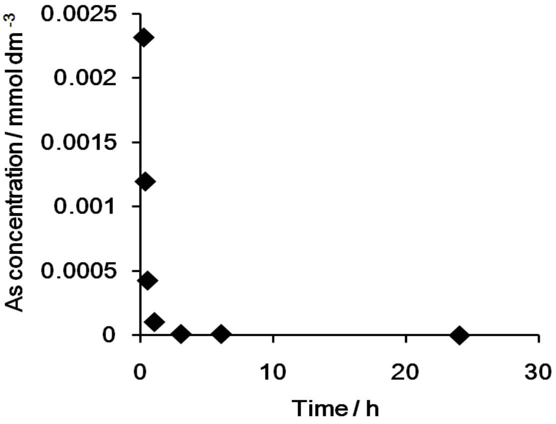

Figure 5: Variation of arsenic concentration with time during the oxidation reaction of pyrite.

According to the previous study on the sorption of As(V) ($AsO_3(OH)^{2-}$) to schwertmannite, As(V) can be rapidly sorbed to the tunnel cave of schwertmannite by exchange of As(V) with SO_4^{2-} (Bruton *et al.*, 2009). The sorption of arsenic on the schwertmannite and goethite showed that the sorption capacities of As to schwertmannite was significantly higher than that of goethite (Asta *et al.*, 2009).

Conclusion: FeS_2 containing As probably moves downstream through the weathering of rocks. Under oxidizing conditions in low place, the FeS_2 is decomposed to release As as As(V) in solution. However, schwertmannite, which is formed as a secondary mineral, rapidly sorbs the As(V). This naturally occurring attenuation mechanism reduces the amount of arsenic transport downstream. When the schwertmannite which sorbs As(V) reaches reducing conditions, it undergoes dissolution releasing As(V) in the surrounding aquifers. Thus, the contamination of As in groundwater are the result of oxidative decomposition of sulfide bearing minerals like pyrite and the dissolution of iron secondary mineral oxides such as schwertmannite.

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