JOURNAL OF ENVIRONMENTAL SCIENCES 45 (2016) 164–176

Available online at www.sciencedirect.com

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www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Influence factors for the oxidation of pyrite by oxygen and birnessite in aqueous systems

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ARTICLE INFO

Article history:
Received 16 November 2015
Revised 7 January 2016
Accepted 12 January 2016
Available online 2 March 2016

Keywords:
Pyrite
Birnessite
Oxidation
Supergene environments
Catalysis
Soils

ABSTRACT

The oxidation of exposed pyrite causes acid mine drainage, soil acidification, and the release of toxic metal ions. As the important abiotic oxidants in supergene environments, oxygen and manganese oxides participate in the oxidation of pyrite. In this work, the oxidation processes of natural pyrite by oxygen and birnessite were studied in simulated systems, and the influence of pH, Fe(II) and Cr(III) on the intermediates and redox rate was investigated. SO_4^{2-} and elemental S were formed as the major and minor products, respectively, during the oxidation processes. Ferric (hydr) oxides including $Fe(OH)_3$ and goethite were formed with low degree of crystallinity. Low pH and long-term reaction facilitated the formation of goethite and ferric hydroxide, respectively. The rate of pyrite oxidation by birnessite was enhanced in the presence of air (oxygen), and Fe(II) ions played a key role in the redox process. The addition of Fe(II) ions to the reaction system significantly enhanced the oxidation rate of pyrite; however, the presence of Cr(III) ions remarkably decreased the pyrite oxidation rate in aqueous systems. The introduction of Fe(II) ions to form a Fe(III)/Fe(II) redox couple facilitated the electron transfer and accelerated the oxidation rate of pyrite. The present work suggests that isolation from air and decreasing the concentration of Fe(II) ions in aqueous solutions might be effective strategies to reduce the oxidation rate of pyrite in mining soils.

Introduction

Sulfide minerals are widely distributed and energetically exploited in the coal, metallurgy and chemical industries, resulting in large quantities of waste materials that have severe and widespread impacts on water and soil resources, such as acid mine drainage, soil acidification and the decrease of soil fertility (Johnson and Hallberg, 2005; Zhao et al., 2012; Lindsay et al., 2015). Sulfide minerals are also major sources of potentially toxic accessory elements including As, Pb, Cd, Tl and Hg. These elements may occur as discrete sulfides or trace impurities in other ore and gangue sulfide minerals (Zhao et al., 2012; Lindsay et al., 2015). As the most abundant of all metal sulfide minerals, pyrite is intensively involved in the oxidation processes in supergene environments (Singer and Stumm, 1970; Mazumdar et al., 2008; Konhauser et al.,

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http://dx.doi.org/10.1016/j.jes.2016.01.012

2011; Chen et al., 2014). For example, pyrite is usually enriched with arsenic, whose content can reach up to 10%, posing a potential threat to groundwater and drinking water during the oxidation processes (Wallis et al., 2010; Lizama et al., 2011; Kang et al., 2014). Therefore, the oxidation mechanism and kinetics of pyrite need to be studied under different conditions to prevent possible risks arising from its oxidative decomposition.

Natural pyrite can be oxidized by microbes (Konhauser et al., 2011), oxygen (Singer and Stumm, 1970), Fe(III) (Singer and Stumm, 1970), and ferric/manganese (hydr)oxides (Schippers and Jørgensen, 2001; Farnsworth and Hering, 2011) in open systems. However, the oxidation activity of bacteria was found to be remarkably affected by the acidity of the environment (Chen et al., 2014; Akcil and Koldas, 2006). For example, *Acidithiobacillus ferrooxidans* shows the highest activity in aqueous solutions with a pH of less than 3.2. If conditions are not favorable, the rate of acid generation by bacteria will remarkably decrease (Akcil and Koldas, 2006). When pH is changed from 2.5 to 4.2, the concentration of SO_4^{2-} in natural pyrite particles dramatically decreases from 69 to 27 g/kg with a decrease in Eh from 667 to 178 mV (*vs* Ag/AgCl) during the biochemical oxidation process (Chen et al., 2014). In fact, residual pyrite is randomly distributed in soils and sediments, being exposed to air in mining areas. Therefore, inorganic reactions would likely dominate in the initial stage of pyrite oxidation due to a near-neutral pH soil environment. The chemical oxidation process of pyrite first occurs, resulting in an increase in acidity and a consequent increase in the oxidation activity of bacterium. As reported, there was no remarkable decrease in pH after two years of oxidation experiments with natural pyrite; however, rapid oxidation and different mechanisms occurred when pH decreased below 3.0 (Chen et al., 2014). Therefore, in order to decrease the risk from the oxidation of pyrite, sufficient attention should be focused on the initial oxidation processes of pyrite with the participation of possible oxidants in natural environments.

Oxygen and manganese (hydr)oxides participate in the initial oxidation of pyrite in supergene environments. Manganese is abundant and ubiquitous in the Earth's crust and second only to iron as the most common heavy metal (Post, 1999). Manganese also exists as a trace element in the tailings mineral assemblage (Lindsay et al., 2015), and is often released at high concentration in acid mine drainage (Evangelou and Zhang, 1995; España et al., 2005; Akcil and Koldas, 2006). Near the Earth's surface, Mn(II) is easily oxidized, and biogeochemical processes are believed to have mainly governed the formation of Mn oxide minerals (Butterfield et al., 2013). Layered manganese oxides including birnessite can be formed by biologically induced mineralization of Mn(II) (Zhu et al., 2010; Butterfield et al., 2013). Birnessite and todorokite were also found in a former uranium mining area, contaminated by acid mine drainage and metals of high concentrations, which demonstrates that biogenic Mn oxides can be generated in both moderately acidic and neutral pH environments (Akob et al., 2014). Birnessite is the predominant naturally occurring manganese oxide in most environmental settings, adsorbing and oxidizing heavy metal ions and organic pollutants (Post, 1999; Zhu et al., 2010; Johnson et al., 2015). Natural birnessite affects the migration and transformation of sulfur, iron and other trace metals. In open systems, both oxygen and birnessite will participate in the oxidation of pyrite.

Ferrous ions effectively catalyze the oxidation of pyrite by manganese oxides and oxygen. During the oxidation of pyrite by oxygen, the rate-determining step is the oxidation of ferrous iron in aqueous solutions with pH below 3.5 (Singer and Stumm, 1970). An Fe(II)/Fe(III) shuttle transports electrons between the surfaces of manganese oxides and pyrite, and the reaction rate between Fe(II) and manganese oxides is faster than that between Fe(III) and FeS_2 (Schippers and Jørgensen, 2001). The electron transfer between the adsorbed Fe(II) and the underlying ferric oxides including goethite, hematite, and ferrihydrite has been demonstrated by Mössbauer spectra (Williams and Scherer, 2004), and the Fe(III)–Fe(II) redox cycle between ferrous ions and ferric oxides facilitates the biogeochemical cycles of C, N, S, and P (Li et al., 2012). As pyrite is usually exposed to air in tailings areas, both oxygen and manganese oxides can participate in its oxidation processes, and the effect of Fe(II) on reaction processes also needs to be further clarified.

Chromium is another important component in acid mine drainage, and affects the oxidation behaviors of pyrite. Cr is typically found in the soils of mining areas, and considered to be a known human carcinogen (España et al., 2005; Li et al., 2012; Marchand et al., 2012; Zhao et al., 2012). Cr(VI) can be formed from the oxidation of Cr(III) by Mn(IV) oxides, and participates in the oxidation of pyrite. Cr(III) is directly oxidized by manganese oxides to form Cr(VI) (Landrot et al., 2012). $Cr(OH)_3$(s) oxidation can be induced by surface-catalyzed Mn(II) oxidation in an oxygen atmosphere, and Mn(IV) oxide is formed as an intermediate during this process, resulting in a potential pathway for natural Cr(VI) contamination (Namgung et al., 2014). Cr(VI) oxidizes sulfide minerals, including pyrite and schwertmannite, in aqueous solutions (Lin and Huang, 2008; Graham and Bouwer, 2012; Zhou et al., 2012), and natural pyrite is used as a reactive material to form a permeable reactive barrier to remediate Cr(VI)-contaminated groundwater (Liu et al., 2015; Kantar et al., 2015). That is to say, Cr(III) possibly works as a catalyst during the oxidation of pyrite by manganese oxides. However, the catalytic effect of Cr(III) needs to be further examined to assess the potential risk factor for pyrite oxidation by manganese oxides in natural environments.

In this work, the oxidation processes of natural pyrite by oxygen and birnessite were simulated in the laboratory. The effects of pH, Fe(II) and Cr(III) on the reaction intermediates and redox rate were investigated, and the catalytic effects of Fe(II) and Cr(III) were compared during the reaction processes.

1. Materials and methods

1.1. Synthesis of birnessite

Birnessite was synthesized using the reduction of potassium permanganate by concentrated hydrochloric acid (Mckenzie, 1971). 0.2 mol of $KMnO_4$ was dissolved in 350 mL deionized water in a conical flask and boiled with an oil-bath heated at 110°C, and then 60 mL of 6 mol/L hydrochloric acid was added dropwise to the boiling solution at 0.7 mL/min with vigorous