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

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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. SO₄²⁻ 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.

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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.,...
concentration of SO$_4$ and Koldas, 2006). When pH is changed from 2.5 to 4.2, 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 ng/g 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 ferricyanide has been demonstrated by Mössbauer spectra (Williams and Scherer, 2004), and the Fe(III)–Fe(II) redox cycle between ferrous 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)$_2$(aq) 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
stirring. The reaction lasted for 30 min, and then the suspension was aged for 12 hr at 60°C. The mineral was washed with deionized water until the conductivity of the filtrate was below 20.0 μS/cm, and subsequently dried in an oven at 60°C for 12 hr. The as-prepared birnessite was ground in an agate mortar to pass through a 75-mesh sieve for use in the redox experiments.

Fig. S1a, b shows the XRD patterns and SEM images of prepared pure-phase birnessite. Typical three-dimensional hierarchical microspheres composed of disk-shaped plates were observed for the as-synthesized birnessite (Fig. S1b). The average oxidation state of Mn in birnessite was calculated to be 3.97, and the chemical formula was written as K_{0.056}MnO_2.013·0.709H_2O. The specific surface area of the synthesized birnessite was determined to be 98.8 m²/g.

1.3. Characterization methods

The prepared birnessite was characterized by an X-ray diffractometer (XRD, Bruker D8 Advance) using Cu Kα radiation at a scan rate of 4° min. The average oxidation state (AOS) of manganese was measured by an oxalic acid method (Hem, 1981). The content of K in birnessite was determined by a flame photometer (HG-3 blaze photometer). BET surface areas of as-obtained birnessite and pyrite were measured by a Micromeritics ASAP2020 system using nitrogen adsorption measurements.

After a period of reaction time, filtration and separation was conducted, and the wet solid products were identified soon after the reaction by an X-ray diffractometer. Before and after redox reactions, their morphologies were characterized by scanning electron microscopy (SEM, JEOL, JSM-6700F Field Emission) and transmission electron microscopy (TEM, Hitachi, H-7650). Fourier transform infrared spectroscopy (FT-IR, Nicolet 8700) was used to characterize the functional groups of redox products with a DTGS detector by making pellets with KBr powder. The content of crystal water in birnessite was calculated by mass balance using thermo-gravimetric analysis (TGA) with a NETZSCH TG 209 thermal analysis system.

The concentrations of Fe(II) ions and Cr(VI) in the filtrate were directly determined by ultraviolet-visible spectrophotometry (UV-1800, Shanghai Mapada Instruments Co., Ltd., China) using 1,10-phenanthroline and diphenylcarbazide as color developers, respectively. The total concentration of Fe(II) and Fe(III) in the filtrate was also determined using a spectrophotometric method by adding hydroxylamine hydrochloride to reduce Fe(III) to Fe(II) ions. The total concentrations of dissolvable Cr(III, VI), Fe (II, III) and released Mn(II) ions in the filtrate and the manganese content in birnessite were quantified by atomic absorption spectroscopy (Varian AAS240FS). It was noted that there was almost no difference in the concentration of total Fe determined using the spectrophotometric method vs. the atomic absorption method. The concentration of Cr(III) and Fe(III) ions could be calculated by subtraction of Fe(II) and Cr(IV) concentrations from the total concentrations of Cr(III, VI) and Fe(II, III), respectively.

The concentration of S(-II) in the filtrate was determined using a spectrophotometer (721/SP-721, Shanghai King Tech Industry Co., Ltd.), and the standard concentration of S(-II) was calibrated by iodometry and back-titrating with standard sodium thiosulfate solution (Caldwell and Krauskopf, 1929). The concentrations of SO_3^{2-}, S_2O_3^{2-} and SO_4^{2-} were analyzed by ion chromatography ( Dionex ICS-1100) using a conductivity detector with a resolution of 0.003 nS/cm. 1 mmol/L Na_2CO_3/ 36 mmol/L NaHCO_3 solution was used as eluent with a flow rate of 1.5 mL/min. The current was controlled at 142 mA, and the column temperature was kept at 30°C.

Elemental S in 3.0 mL of the reaction solution was filtered and dissolved in methanol, and then further filtered and quantified by high-performance liquid chromatography (HPLC) using an Agilent 1200 instrument with a UV-Vis detector at 254 nm. The samples were injected into a 50 μL loop and passed through an Eclipse XDB-C18 analytical chromatographic column, and the column temperature was maintained at 25°C. A standard sample was prepared by dissolving powered elemental sulfur in pure methanol, and a methanol solution containing...
5% water was used as the eluent (Schippers et al., 1996; Herszage and Dos Santos Afonso, 2003). All chemical analyses for each sample were repeated three times.

2. Results and discussion

2.1. Oxidation of pyrite by air (oxygen)

Air was continuously bubbled into the suspension of pyrite (1.0 g/L), and the pH was respectively adjusted daily to pH 3.0 and 5.0 with small volumes of 1.0 mol/L NaOH during the experiment. Fig. S2 shows the XRD patterns of solid products from the oxidation of pyrite by air (oxygen) in aqueous systems at different times. The typical diffraction peaks of pyrite were observed, and there was no significant change in crystal structure. The degree of crystallinity of pyrite decreased with time when pH was adjusted from 5.0 to 3.0 in the reaction systems, which was likely due to the difference in reaction mechanisms, because ferric (hydr)oxides were easily formed when pH was controlled at 5.0 (Gartman and Luther, 2014). In order to further examine the possible composition, FT-IR spectroscopy was used to identify the chemical groups present in the solid intermediates, as shown in Fig. 1. The absorption bands of pyrite are located in the range of 240–450 cm\(^{-1}\), and absorption band at 414 cm\(^{-1}\) corresponded to the stretching of the dimeric (S–S)\(^{2-}\) in pyrite (Montoro et al., 2004). This band did not disappear after 60 days, suggesting the incomplete oxidation and decomposition of pyrite during the redox processes. The bands at 3430, 1639 and 1400 cm\(^{-1}\) are attributed to bending modes of surface water molecules and carbonate ions, respectively (Chiriţă et al., 2008). In the present work, ferric hydroxide precipitate was obtained after filtration, and the wet samples tended to adsorb and react with carbon dioxide when exposed in air during the process of sample-taking and FT-IR characterization.

The absorption peaks at 1215 and 1090 cm\(^{-1}\) are assigned to SO\(^{2-}\) ions possibly formed during the redox processes (Chiriţă et al., 2008). The characteristic bands at 803 and 475 cm\(^{-1}\) are attributed to the Fe–O–H bending vibrations of Fe(OH)\(_{3}\) and goethite (Chiriţă et al., 2008), suggesting the formation of ferric (hydr)oxides. As seen from the FT-IR spectra, there was no significant change in chemical composition of intermediates when the pH was controlled at 3.0 and 5.0, respectively. During the oxidation processes, pulverization occurred, with a remarkable decrease in the particle size of pyrite (Fig. S3). After 60 days of reaction, some particle sizes decreased from more than 10 μm to less than 1 μm, as shown in the inset of Fig. S3e. However, pyrite of large particle size could be seen due to the incomplete reaction, and some small particles were also observed, likely due to the newly formed ferric (hydr)oxides.

The changes in the concentrations of elemental S and the dissolvable Fe(II), S(–II), SO\(^3\)\(^-\), SO\(^2\)\(^-\), and SO\(^4\)\(^-\) were determined and exhibited in Fig. 2. S\(_2\)O\(^3\)\(^-\) and SO\(^2\)\(^-\) could not be detected, and the concentrations of elemental S were determined to 0.023 and 0.018 mmol/L when the pH was respectively controlled at 3.0 and 5.0 after 60 days of reaction. As reported, elemental S was formed as a byproduct coating on pyrite surfaces during similar oxidation processes (Singer and Stumm, 1970; Mazumdar et al., 2008; Lindsay et al., 2015). SO\(^2\)\(^-\) ions were formed as the major oxidation product, with the concentrations of 0.58 and 0.79 mmol/L when pH was controlled at 3.0 and 5.0, respectively, after 60 days of reaction. Compared with the concentration of SO\(^2\)\(^-\) in the pyrite oxidation process, elemental S was slowly generated with a low yield. In this work, the concentration of S(–II) could not be determined due to the rapid oxidation of dimeric (S–S)\(^2-\) in pyrite to elemental S and SO\(^3\)\(^-\). Although S(–II) could be volatilized as hydrogen sulfide gas, the volatilized S(–II) could be ignored due to its rapid oxidation by oxygen and manganese oxides with high oxidation activity (Qiu et al., 2011; Gao et al., 2015b). In the present work, the oxidative dissolution of pyrite was likely coupled with the oxidation of dimeric (S–S)\(^2-\) to elemental S and SO\(^3\)\(^-\).

Fe(II) ions were released during the redox processes, and their concentrations approached 0.29 and 0.048 mmol/L, at pH 3.0 and 5.0, respectively. In the present work, low pH facilitated the release of Fe(II) ions, and high pH accelerated the oxidation rate of pyrite to SO\(^3\)\(^-\). When pH was further adjusted to 7.0, the concentration of SO\(^3\)\(^-\) increased to 0.93 mmol/L after 60 days.

Fig. 1 – FT-IR spectra of solid products from the oxidation of pyrite suspension (1.0 g/L) by air at pH 3.0 (a) and 5.0 (b). FT-IR: Fourier transform infrared spectroscopy.
During the oxidation of pyrite in abiotic systems, the oxidation of Fe(II) to Fe(III) ions is suggested to be the rate-determining step, and is a function of pH (Singer and Stumm, 1970). In this work, the rate of Fe(II) oxidation by oxygen was remarkably increased when pH varied from 3.0 to 7.0, likely due to the different kinetic models in different pH ranges (Singer and Stumm, 1970).

The redox potential (Eh) values of reaction systems were periodically monitored in the first 6 days. As shown in Fig. 3a, there was no remarkable change in Eh values during the reaction processes due to the slow oxidation rate of pyrite. When FeS was oxidized in oxygen-bearing acidic solutions, Eh decreased from about 600 to 500 mV (vs SHE) in the first 6 days due to the higher reactivity under similar conditions (Chiriţă et al., 2008). The Eh values of the reaction systems were measured to be about 700 and 620 mV (vs SHE) when the pH was controlled at 3.0 and 5.0, respectively. The Eh decreased with an increase of pH in aerobic systems likely due to the different pH values and concentrations of Fe(II) ions in the reaction systems. In this work, air (oxygen) participated in the redox reactions, and played a major role in controlling the redox potential in the reaction systems (Singer and Stumm, 1970; Lowson, 1982).

As indicated by the FT-IR spectra (Fig. 1), Fe(OH)$_3(s)$ and goethite were possibly formed in the processes. Eh affects the crystal structures of ferric oxides in reaction systems, because Eh is related to the redox couples of Fe(OH)$_3(s)/$Fe$^{2+}$ and goethite ($\alpha$-FeOOH$_{am}$/Fe$^{2+}$). According to the redox equations of Fe(OH)$_3(s)/$Fe$^{2+}$ and $\alpha$-FeOOH$_{am}$/Fe$^{2+}$, Eh is a function of pH and the concentration of Fe(II) (Chiriţă et al., 2008). The equilibria between Fe(II) ions and amorphous Fe(OH)$_3(s)$ Eq. (1) and between Fe(II) ions and goethite ($\alpha$-FeOOH$_{am}$) Eq. (2) are, respectively, listed as follows (Chiriţă et al., 2008).

$$E_h = 1.065 - 0.177pH - 0.059\log[Fe^{2+}]$$

$$E_h = 0.740 - 0.177pH - 0.059\log[Fe^{2+}]$$

In the present aqueous systems, the concentration of Fe(III) ions was determined to be near zero due to the rapid reduction by pyrite and the formation of precipitate at high pH.

![Fig. 2](image_url) – The concentrations of Fe(II), SO$_4^{2-}$ and elemental S during the oxidation of pyrite suspension (1.0 g/L) by air at pH 3.0 (a) and 5.0 (b) as a function of time.

![Fig. 3](image_url) – Open circuit potential for the oxidation of pyrite suspension (1.0 g/L) by air at pH 3.0 and 5.0 (a), and the relationship between log[Fe(II)] and pH (b).
(Singer and Stumm, 1970; Chirijă et al., 2008), and it could be assumed that \([\text{Fe}_{\text{total}}]\) equaled \([\text{Fe}^{II}]\). When pH was controlled at 3.0 and 5.0, Eh values were determined to be about 700 and 620 mV (vs SHE), respectively. The linear relationship between pH and the concentrations of Fe(II) ions is illustrated in Fig. 2b. When pH was controlled at 3.0 and 5.0, the corresponding concentrations of Fe(II) were recorded at different times (Fig. 2), and the changes of \(\log[\text{Fe}^{II}]\) are exhibited in Fig. 3b.

When pH was controlled at 3.0 and 5.0, the corresponding pH and the concentrations of Fe(II) ions is illustrated in Fig. 3b. It can be seen that pH 3.0 and 5.0 facilitated the formation of goethite and Fe(OH)₃, respectively. When the concentration of Fe(II) ions further increased, \(\alpha\)-FeOOH tended to transform into Fe(OH)₃(s), likely due to dissolution and re-precipitation (Fig. S4a), which were pulverized and disappeared into Fe(OH)₃(s), likely due to dissolution and re-precipitation (Fig. S4b), likely due to dissolution and re-precipitation (Williams and Scherer, 2004).

### 2.2. Oxidation of pyrite by birnessite

As one of the most common manganese oxides, birnessite can oxidize pyrite in supergene environments. In this work, birnessite (0.5 g/L) was added to a pyrite suspension (1.0 g/L) in a nitrogen atmosphere to simulate an anoxic environment, and pH was controlled at 3.0. Fig. 4 shows the XRD patterns and FT-IR spectra of the solid intermediate products at different times. Birnessite was not completely reduced after 1 day of reaction, and it disappeared after 7 days (Fig. 4a). Elemental S was formed as an intermediate and identified by small diffraction peaks (ICPDS card ID: 83-2284). As seen from the FT-IR spectra (Fig. 4b), the absorption bands at 513, 461 and 428 cm⁻¹ could be assigned to birnessite (Cui et al., 2009), which suggested that a mixed phase of birnessite and pyrite was observed after 1 day of reaction. Birnessite was completely reduced and dissolved after 7 days. The characteristic absorption peaks of ferric (hydr)oxides including Fe(OH)₃ and \(\alpha\)-FeOOH were observed, suggesting their possible role as intermediates. The solid intermediates were further characterized by SEM (Fig. S4). Flower-like microspheres of birnessite were observed after 1 day of reaction (Fig. S4a), which were pulverized and disappeared after 7 days (Fig. S4b). After 28 and 60 days, there was no significant change in the morphology of pyrite, indicating the slow reaction rate.

The elemental S and dissolvable products were further quantitatively analyzed as shown in Fig. 5a. The concentrations of released Fe(II), Mn(II) and SO₄²⁻ approached 0.07, 4.32 and 1.15 mmol/L, respectively, within 10 days of reaction. Elemental S was formed with a low concentration of about 0.06 mmol/L after 60 days. That is to say, SO₄²⁻ was also the major oxidation product when the oxidant birnessite was used instead of air. Compared with the concentration of SO₄²⁻ generated from the oxidation of pyrite in aqueous systems at pH 3.0, birnessite exhibited higher oxidation activity than air (oxygen) (Figs. 2a, 5a).

Usually, Mn oxides almost cannot be abiotically formed due to the extremely slow rate of Mn(II) oxidation by oxygen in open systems (Hem, 1981). Oxygen exhibits higher oxidation activity than Mn oxides in a strong alkali solution (Qiu et al., 2011). In the present work, birnessite showed higher oxidation activity than oxygen in air, likely due to the presence of a lower partial pressure of oxygen and acidic aqueous reaction system.

### 2.3. Oxidation of pyrite by birnessite in air

Usually, the oxidation of natural pyrite occurs in terrestrial surface environments, and the oxygen in air participates in this reaction. As for the above redox experiment of pyrite (1.0 g/L) and birnessite (0.5 g/L), air was continuously bubbled into the suspension instead of nitrogen. Fig. S5 shows the XRD patterns and FT-IR spectra of solid products from the oxidation of pyrite by birnessite in the presence of air at pH 3.0. A similar change trend in the chemical composition of solid products at different times was observed in the presence of nitrogen and air. The chemical stability of birnessite was improved, and some characteristic absorption peaks of birnessite were determined after 7 days of reaction (Fig. S5b). However, as indicated by the release rate of Mn(II) in the reaction systems, the reduction rate of birnessite became higher when air was bubbled into the reaction system instead of nitrogen in the initial stage (Fig. 5). The redox rate was increased with an increase in Fe(II) concentration. As reported in previous work, two-step reduction processes including Mn(IV) to Mn(III) and Mn(III) to Mn(II) occurred in birnessite during the reduction of Mn(IV) oxides by dissolvable sulfide, and the crystal structure stability of todorokite was significantly enhanced in the presence of oxygen due to the re-oxidation of Mn(III) to Mn(IV) in todorokite in the initial stage.
stage (Gao et al., 2015b). In the present work, the first step of Mn(IV) to Mn(III) occurs in the oxidation process of Fe(II), and Mn(III) tends to be re-oxidized to Mn(IV) in birnessite, possibly in the presence of air (oxygen), due to the low concentration of Fe(II) ions. The rate of pyrite oxidation by birnessite was slow, and the presence of oxygen enhanced the crystal structure stability of birnessite in the initial stage. The increase of Fe(II) concentration resulted in the further reduction and dissolution of birnessite in the later stage.

The effect of air (oxygen) on the chemical stability was further confirmed by SEM images as shown in Fig. 6. Irregular particles of pyrite and flower-like particles of birnessite were observed after 1 day of reaction, and they could also be detected after 7 days of reaction. The micro-morphologies

Fig. 5 – The concentrations of Fe(II), Mn(II), SO$_4^{2-}$ and elemental S during the oxidation of pyrite suspension (1.0 g/L) by birnessite (0.5 g/L) in nitrogen (a) and air (b) atmosphere at pH 3.0 as a function of time.

Fig. 6 – SEM images of solid products from the oxidation of pyrite suspension (1.0 g/L) by birnessite (0.5 g/L) in air atmosphere at pH 3.0 after 1 day (a), 7 days (b), 30 days (c), and 60 days (d).
and particle sizes remarkably changed after 30 and 60 days of reaction due to the further oxidation of pyrite.

The presence of oxygen facilitated the rapid oxidation of pyrite and improved the crystal structure stability of birnessite. The increase of oxidation rate was further confirmed by the change in the concentration of Fe(II), Mn(II), and SO$_4^{2-}$ (Fig. 5b). Within the first 3 days of reaction, the concentration of released Mn(II) increased linearly with time, and reached about 4.79 mmol/L. The concentration of released Mn(II) fluctuated with a small amplitude after 3 days, due to the increase in chemical stability of birnessite when oxygen participated in the redox process. After 3 and 60 days, the concentration of Fe(II) ions increased to 0.11 and 0.82 mmol/L, and the concentration of SO$_4^{2-}$ approached 1.20 and 1.99 mmol/L, respectively. After 60 days of reaction, elemental S was generated with a concentration of about 0.15 mmol/L. The concentration of SO$_4^{2-}$ and S significantly increased during the oxidation of pyrite by birnessite in the presence of air (oxygen).

It was noted that the concentrations of SO$_4^{2-}$ were nearly positively correlated with those of Fe(II) ions during the redox processes of pyrite in different systems (Fig. 2, 5). Fe(II) ions of high concentration accelerated the oxidation of pyrite to SO$_4^{2-}$. The oxidation of pyrite results in the release and dissolution of Fe(II) ions (Akcil and Koldas, 2006). When the oxygen in air served as oxidant, the oxidation of Fe(II) to form Fe(III) was possibly the rate-limiting step for the oxidation of pyrite (Singer and Stumm, 1970; Evangelou and Zhang, 1995). Fe(III) ions formed by the redox reaction of Fe(II) and Mn(IV) oxide can react with pyrite before they precipitate as ferric (hydr)oxide, and electron transport occurs via the Fe(II)/Fe(III)-shuttle in the process (Schippers and Jørgensen, 2001). In order to study the influence of Fe(II) on the oxidation rate of pyrite, some Fe(II) ions were added to the reaction systems, and the effect of Fe(II) ions on redox rate was further compared by using Cr(III) ions instead.

2.4. Influence of Fe(II) and Cr(III) in closed systems

During the oxidation processes of pyrite, Fe(II) ions play an important role in controlling the reaction rate. Hexavalent chromium can also oxidize pyrite, which can be used for treatment of Cr(VI) (Lin and Huang, 2008; Graham and Bouwer, 2012; Zhou et al., 2012). Cr(III) ions can be oxidized by Mn(IV) oxide minerals to form Cr(VI) ions (Landrot et al., 2012), suggesting that Cr(III) can also catalyze the oxidation of pyrite by birnessite. The influence of Fe(II) and Cr(III) ions on the redox processes and kinetics was compared in closed systems.

Fig. S6 shows the XRD patterns and FT-IR spectra of solid products from the oxidation of pyrite suspension (1.0 g/L) by birnessite (0.5 g/L) with addition of Fe(II) ions (0.4 mmol/L) in a nitrogen atmosphere at pH 3.0. Similar change trends in the chemical compositions of solid products were observed with and without adding Fe(II) ions to reaction systems (Figs. 4, S6). After 7 days of reaction, birnessite was completely reduced, and elemental S was formed as an intermediate during the reaction process. SEM images further indicated the transformation processes of solid products (Fig. S7). The typical micro-morphologies of birnessite could be seen after 1 day, and it disappeared after 7 days. The pulverization of solid products was significantly intensified, and smaller particles were newly formed, likely due to the formation of iron oxides, which were confirmed by the FT-IR spectra. The absorption bands at 803 and 475 cm$^{-1}$ are assigned to the bending vibrations of Fe–O–H in Fe(OH)$_3$ and goethite (Chiriţă et al., 2008), which also could be seen in TEM images in later experiments.

The dissolvable intermediates were determined, as shown in Fig. 7a. Although Fe(II) ions of 0.4 mmol/L was added to the reaction systems, the concentration of Fe(II) ions in the initial stage almost approached zero due to their rapid adsorption on the surface of birnessite (Gao et al., 2015a). After 5 days of reaction, the concentrations of Fe(II), released Mn(II) and SO$_4^{2-}$ ions approached 0.17, 4.69 and 1.21 mmol/L, respectively. After 10 days, they reached 0.32, 4.75, and 1.21 mmol/L, respectively. After 10 days of reaction at pH 3.0, the concentration of newly generated SO$_4^{2-}$ increased from 1.15 to 1.42 and 1.21 mmol/L, and the concentration of released Mn(II) ions increased from 4.31 to 4.65 and 4.75 mmol/L. The concentration of Fe(II) was about 0.07, 0.26 and 0.31 mmol/L, when the reaction systems of pyrite and birnessite were admitted into nitrogen, air and Fe(II) ions of 0.4 mmol/L in

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Fig. 7 – The concentrations of Fe(II), Mn(II), SO$_4^{2-}$, S, Cr(III) and Cr$_2$O$_7^{2-}$ during the oxidation of pyrite suspension (1.0 g/L) by birnessite (0.5 g/L) with added Fe(II) (a) and Cr(III) (b) of 0.4 mmol/L at pH 3.0 in nitrogen atmosphere as a function of time.
nitrogen atmosphere, respectively. The results suggested that oxygen in air made some contribution to the oxidation of pyrite, and that Fe(II) accelerated the oxidation rate.

The influence of Cr(III) ions on the oxidation rate of pyrite was further studied by adding Cr(III) ions of 0.4 mmol/L to the reaction systems of pyrite (1.0 g/L) and birnessite (0.5 g/L) in a nitrogen atmosphere at pH 3.0. After 60 days of reaction, the characteristic diffraction peaks of birnessite could be detected as shown in Fig. S8a, and the corresponding chemical compositions of birnessite, pyrite and ferric oxides were further confirmed by FT-IR spectra (Fig. S8b). The flower-like particles of birnessite could be observed during the redox processes (Fig. S9), and some needle-like particles were also observed, likely due to the formation of ferric oxides after 60 days.

After 60 days of reaction, the concentrations of released Fe(II), Mn(II) and SO$_4^{2-}$ ions reached 0.01, 1.37 and 0.13 mmol/L, respectively, suggesting the very slow oxidation of pyrite after addition of Cr(III) ions (Fig. 7b). The concentration of Fe(II) ions decreased to near zero, and pyrite was almost not oxidized in the initial stage, which was also indicated by the low concentration of SO$_4^{2-}$. The release of Mn(II) ions took place owing to the reduction and ion exchange of birnessite by Cr(III) ions.

Fig. 8 – SEM images of solid products from the oxidation of pyrite suspension (1.0 g/L) by birnessite (0.5 g/L) with added Fe(II) (0.4 mmol/L) for 1 day (a), 7 days (b), 14 days (c), 30 days (d) and 60 days (e) in air atmosphere at pH 3.0.
Usually, the rate of Cr(III) ion oxidation is affected by pH and the crystal structures of manganese oxides (Carbonaro and Stone, 2015; Landrot et al., 2012). In this work, the adsorption of Cr(III) ions on the surface of birnessite might occur as the major reaction due to the similar standard redox potentials of MnO2/Mn2+ and Cr2O7^2-/Cr3+ (Cui et al., 2011). Although Cr(VI) ions were formed in this process, they slowly oxidized the pyrite due to the low concentrations. Therefore, Fe(II) ions played a more important role than Cr(III) in the catalytic oxidation of pyrite by birnessite.

2.5. Influence of Fe(II) and Cr(III) ions in open systems

The influences of Fe(II) and Cr(III) on the oxidation processes of pyrite by birnessite were further studied in open systems. Similar results were obtained when Fe(II) ions were added to the redox systems of pyrite and birnessite in the presence or absence of air. After 7 days of reaction, birnessite was completely reduced and dissolved (Fig. S10). It seemed that the presence of oxygen could not remarkably improve the stability of birnessite, possibly due to the rapid reduction of birnessite by the added Fe(II) ions.

The solid products were further characterized by SEM and TEM as shown in Fig. 8. The irregular particles of pyrite disappeared, and amorphous ferric oxides were formed after 1 day of reaction. For example, needle-like particles of goethite were formed after 30 days, and micro-morphologies characteristic of lepidocrocite was also observed after 60 days. As reported in our previous work, Fe(OH)3 of weak crystallinity would be transformed to lepidocrocite and goethite in an acidic environment (Gao et al., 2015a). Similar particles of ferric oxides were observed during these redox processes.

The concentrations of released Mn(II), Fe(II) and SO4^2− ions are illustrated in Fig. 9a. There was no obvious change in the concentrations of these components when the reaction systems were in the presence/absence of air. After 5 days of reaction, the concentrations of Fe(II), released Mn(II) and SO4^2− approached 0.22, 4.42 and 1.28 mmol/L, respectively. After 60 days, they approached 0.91, 4.41, and 2.11 mmol/L, respectively. The concentration of Fe(II) ions increased due to desorption from the birnessite surface and release from pyrite during the redox processes. When air (oxygen) was bubbled into the reaction system, the concentration of Fe(II) ions increased (Figs. 7a, 9a), resulting in a higher rate of pyrite oxidation. There was no remarkable change in the concentration of Mn(II) ions, suggesting that oxygen in air played a more important role in the later stage of pyrite oxidation.

The influence of Cr(III) ions on the rate of pyrite oxidation by birnessite was studied in the presence of air. Compared with the similar systems with pyrite and birnessite, the chemical stability of birnessite was improved when Cr(III) was used instead of Fe(II) in the presence of air, and birnessite could be detected after 14 days (Fig. S11). In the redox system of pyrite and birnessite with the participation of Cr(III), the presence of air decreased the chemical stability of birnessite due to the increase of Fe(II) concentration (Figs. 7b, 9b, S8, and S11). Although oxygen (air) participated in the redox systems, large particles of pyrite could also be observed throughout the reaction, and the low concentration of Fe(II) improved the crystal structure stability of birnessite, which persisted after 60 days (Figs. 10, and S11).

The above results further indicated that Fe(II) accelerated pyrite oxidation by birnessite and oxygen in air. The oxidation rate of pyrite decreased in the presence of Cr(III) ions under similar conditions. When Fe(III), O2 and Cr(VI) worked as oxidants, the difference in pyrite oxidation rate was due to the different mechanisms involved (Luther, 1987; Kirk et al., 1990; Rimstidt and Vaughan, 2003; Lan et al., 2006). Fe(III) can chemically bind to the surface of pyrite readily whereas O2 cannot (Luther, 1987; Kirk et al., 1990). Electron transfer between adsorbed Fe(III) and Fe(II) in pyrite rapidly occurs, with the formation of Fe(II)-S2− and subsequently electrons are transported from S2− (II) to Fe(III) through a persulfide bridge, resulting in the oxidation from S2−(II) to S and SO4^2− (Luther, 1987). Although the direct reaction of pyrite and oxygen occurred, the coating of ferric (hydr)oxides on the surface of pyrite might inhibit this reaction, and Fe(II) possibly acted as an effective catalyst in the further oxidation processes. As for the reaction of Cr(VI) and FeS2, it seemed that a two-step reaction occurred. The one-step reduction of Cr(VI) by pyrite is slower than the two-step process consisting of rapid Cr(VI) reduction by Fe(II) to form Fe(III) and the oxidation of FeS2 by Fe(III) (Lan et al., 2006). In this work, Cr(III) ions were first oxidized to Cr(VI) by birnessite, and then the

![Fig. 9](image-url) - The concentrations of Fe(II), Mn(II), SO4^2−, S, Cr(III) and Cr2O7^2− in the redox reaction of pyrite suspension (1.0 g/L) and birnessite (0.5 g/L) with addition of Fe(II) (a) and Cr(III) (b) of 0.4 mmol/L at pH 3.0 in air atmosphere as a function of time.
newly formed Cr(VI) further oxidized pyrite. However, the rates of Cr(III) oxidation by birnessite and pyrite oxidation by Cr(VI) are slow due to the similar standard redox potentials and two-step process, respectively. The presence of air (oxygen) enhanced the oxidation rate of pyrite due to the increase of the concentration of the catalyst Fe(II), which could be formed from the oxidation/dissolution of pyrite. Therefore, isolation from air and decreasing the concentration of Fe(II) might be effective means to decrease the oxidation rate of pyrite. When manganese oxides participate in the oxidation of pyrite, the introduction of some transition metal ions with lower valence states might remarkably affect the reaction rate.

3. Conclusions

Oxygen in air and birnessite participate in the oxidation of natural pyrite, and pH, Fe(II) and Cr(III) ions affect the redox reaction rate. Elemental S, SO$_4^{2-}$, Fe(II) ions and ferric oxides are formed during the processes, and SO$_4^{2-}$ is the major product. pH 3 and 5 facilitate the formation of goethite and amorphous ferric hydroxides, respectively. Fe(II) ions act as a catalyst and play an important role in the oxidation rate of pyrite. In open aqueous systems, high pH accelerates the oxidation of pyrite to SO$_4^{2-}$ due to the rapid oxidation of Fe(II).
ions by oxygen, in spite of the low concentration of Fe(II) ions. As for the oxidation of pyrite by birnessite, the presence of Fe(II) ions significantly enhances the reaction rate. The participation of oxygen further improves the oxidation rate induced by the increase of Fe(II) concentration. The presence of Cr(III) ions remarkably decreases the rate of pyrite oxidation by birnessite in the presence or absence of air (oxygen).

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Appendix A. Supplementary data
Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.01.012.

REFERENCES