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Study of the kinetics of pyrite oxidation under controlled redox potential

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ABSTRACT

An experimental study of the ferric oxidation kinetics of pyrite was conducted under controlled redox potentials of 700, 800 and 900 mV (vs. SHE). The rate of pyrite oxidation strongly depends on redox potential, increasing fivefold when redox potential is increased by 100 mV. Pyrite dissolution is significantly affected by temperature. Activation energies of 56.6, 55.9 and 51.9 kJ/mol calculated from pyrite dissolution at redox potentials of 700, 800 and 900 mV (vs. SHE) respectively confirmed a chemical or an electrochemical rate-determining reaction on the pyrite surface.

A mineralogical study of the residue after dissolution of pyrite confirmed that elemental sulfur formed during pyrite dissolution. Iron hydroxide/oxide precipitation and jarosite were not observed in residual pyrite by X-ray diffraction spectroscopy analysis. Results of scanning electron microscope analysis of residual pyrite indicated that oxidation readily occurred at specific sites with high surface energy, such as particle edges, corners, defects, and fractures. The products of pyrite dissolution were heterogeneously distributed on the pyrite surface. These results provide useful information for optimizing the conditions that could be used for heap bioleaching of refractory gold ores containing pyrite.

1. Introduction

Pyrite is the most abundant sulfide mineral, and is found in most mining environments, particularly in coals and in Cu, Pb and Zn sulfide ores. Ore minerals are intimately intergrown, which restricts the use of conventional techniques of mineral separation to produce bulk concentrates (Wiersma and Rimstidt, 1984; Dimitrijevic et al., 1996; Holmes and Crundwell, 2000). Pyrite is also the most prevalent host for gold. Gold is finely disseminated in the pyrite matrix to become refractory gold ore, which cannot be extracted by conventional cyanidation (Antonijević et al., 1997; Descostes et al., 2004; Bouffard et al., 2006). Therefore, effective oxidation of pyrite is necessary for the release of this type of gold.

In recent years, the mechanism of pyrite oxidation and the factors influencing the oxidation rate of pyrite have been studied extensively. The reactions of pyrite oxidation in solution have been defined as follows (Garrels and Thompson, 1960; Singer and Stumm, 1970):

$$2\,FeS_2 + 2H_2O + 7O_{2(aq)} \rightarrow 2\,Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{1}$$

$$4\,Fe^{2+} + O_{2(aq)} + 4H^+ \rightarrow 4\,Fe^{3+} + 2H_2O \tag{2}$$

$$FeS_2 + 8H_2O + 14\,Fe^{3+} \rightarrow 15\,Fe^{2+} + 2SO_4^{2-} + 16H^+. \tag{3}$$

Eq. (2) is the rate-controlling step (Singer and Stumm, 1970). The above equations indicate that both oxygen and ferric ion are oxidants for pyrite oxidation. However, ferric ion is confirmed to be a more effective oxidant than oxygen at all pH values (McKibben and Barnes, 1986; Moses et al., 1987; Nicholson et al., 1988; Holmes and Crundwell, 2000), and an increase in pyrite dissolution is achieved with increasing concentration of ferric ions. Reported rate laws involving ferric species generally follow half-order kinetics with a few studies reporting up to first-order kinetics (Holmes and Crundwell, 2000; Chandra and Gerson, 2010), which are detected under non-controlled redox potential. Reaction orders with respect to ferric are found to be 1.0, 0.5 and 0.62 in the reports (Wiersma and Rimstidt, 1984; McKibben and Barnes, 1986; Rimstidt and Newcomb, 1993), respectively. Reaction orders of 0.3 and 0.93 were determined under conditions of N_2-purged solution and dissolved oxygen, respectively (Williamson and Rimstidt, 1994). Sulfuric acid resulting from pyrite oxidation is a significant contributor to the environmental problem of acid rock drainage, which implies that increasing solution pH accelerates pyrite oxidation (Chandra and Gerson, 2011a; Heidel and Tichomirowa, 2011). Isotope studies indicate

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Table 1
Elemental analysis of pyrite sample.

Elements	Fe	S	Si	Al	K	Ca	Cu	As	Mg	Zn	Pb	Na
Wt.%	43.49	50.75	3.75	0.58	0.12	0.29	0.20	0.02	0.04	0.04	0.04	0.03

the preferential incorporation of oxygen from water molecules rather than molecular oxygen into sulfate during pyrite oxidation with high ferric iron/pyrite surface ratios. However, adsorbed molecular oxygen acts as a pyrite oxidant and is incorporated into the produced sulfate in anaerobic and low oxygen experiments with low ferric iron/surface ratios (Heidel and Tichomirowa, 2011). The rate of pyrite dissolution decreases with increased sulfate concentration and ferrous concentration, as verified by an electrochemical method (M.J. Nicol et al., 2013).

Among the factors that affect pyrite dissolution, the solution Eh is the most critical and is directly correlated with rate. A number of recent publications (May et al., 1997; Ruitenberg et al., 1999; Chandra and Gerson, 2010) have focused on the use of Eh to monitor the rate of reduction of iron(III) and as a means of controlling the rate of oxidation of the mineral. However, few investigations of pyrite oxidation have been conducted under controlled redox potential. M. Nicol et al. (2013) performed pyrite oxidation by controlling solution potential with potassium permanganate, showing that the rate of dissolution is significantly higher at a potential of 850 mV than it is at 800 mV (throughout this paper potentials are quoted with reference to the standard hydrogen electrode, SHE). Leaching studies (Chandra and Gerson, 2011a) have shown that the rate of pyrite dissolution is faster at a solution Eh of 900 mV than at 700 mV controlled by 15 wt.% hydrogen peroxide (H_2O_2) solution at pH 1 in the leach media of HCl, H_2SO_4 and $HClO_4$. These two investigations confirm that the solution Eh significantly affects the dissolution of pyrite. However, the effect of temperature on the kinetics of pyrite dissolution under controlled redox potential is rarely reported. Temperature is not uniform in a heap leaching pile, generally being higher at the center of the pile than near the edges. Thus, investigation of the effect of temperature on the kinetics of pyrite dissolution under controlled redox potential would provide useful information on the optimization of the parameters of pyrite heap leaching.

The main available pre-oxidation processes for refractory gold ores are roasting, pressure oxidation and bio-oxidation. Compared with other commonly applied oxidation techniques, bio-oxidation is the most promising economically and in terms of environment. However, the rate of heap bio-oxidation of pyrite that encapsulates gold is slow, forcing the mineral industry to seek improved processes for the treatment of refractory gold ores.

The indirect oxidation mechanism of pyrite bioleaching has been confirmed by many researchers (Sand et al., 2001; Tributsch, 2001; Heidel and Tichomirowa, 2011; Basson et al., 2013). The process of pyrite bioleaching involves two rate-controlling sub-processes: chemical leaching of pyrite by ferric ion and bacterial oxidation of ferrous ion to regenerate ferric ion (Boon et al., 1998). Microorganisms can rapidly oxidize ferrous ion to maintain the potential of the solution constant under appropriate conditions. For example, Eh of the leachate in the Zijinshan (China) bioheap is constant within the range of 710 mV to 740 mV (Ruan et al., 2011). According to typical heap bioleaching conditions, figuring out the effect of temperature on the kinetics of pyrite oxidation under the condition of constant potential is essential to improve the rate of pyrite heap bioleaching. This research aims to identify the effect of temperature on the rate of pyrite dissolution under constant solution Eh (700, 800 and 900 mV) controlled by 15% H_2O_2. The conclusions provide useful information on the heap bioleaching of refractory gold ore.

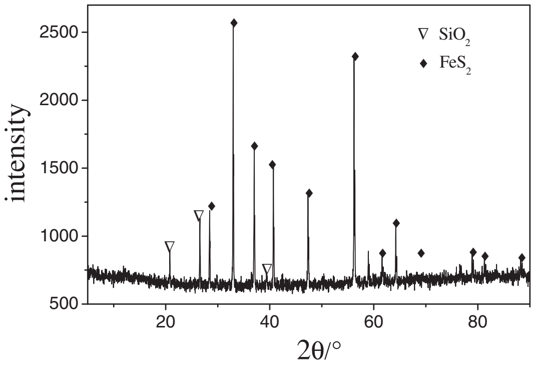

Fig. 1. XRD spectra of initial pyrite.

2. Experimental

2.1. Pyrite sample

The pyrite sample was manually sorted from Zijinshan copper ore. The sample was wet sieved and then dry sieved to particle sizes between 45 and 74 μm. The sample was washed by ultrasonication using HCl (1:1) solution and distilled water before the experiments. Inductively coupled plasma optical emission spectrometry analyses (ICP-OES; Table 1) indicated a S: Fe atomic ratio of 2.04 and a total impurity content of 5.76%. The phase composition was confirmed by powder X-ray diffraction (XRD) and the result is shown in Fig. 1. The XRD spectrum was recorded from 5°–90° 2θ with a scan rate of 0.2°/s. The result indicated that pyrite was the primary phase with a little silicate impurity present in the ore after the pretreatment. No other impurity phase was observed from the powder XRD analysis spectrum.

2.2. Leaching experiments

Fig. 2 shows the experimental setup for dissolution kinetics. To obtain a leaching solution potential of 900 mV, 4 g of ferric sulfate salt ($Fe_2(SO_4)_3$) were added to 400 mL of distilled water. The solution pH was adjusted to 1.0 ± 0.2 using 98% sulfuric acid. The initial potential of the solution was about 850 mV, and the Eh of the solution was adjusted to 900 mV with 15% H_2O_2 (Chandra and Gerson, 2011a). For experiments at potentials of 800 and 700 mV, 4.4 g of ferrous sulfate salt ($FeSO_4 \cdot 7H_2O$) were added to 400 mL of distilled water, and the solution pH was adjusted to 1.0 ± 0.2 with 98% sulfuric acid. The initial potential of the solution was about 460 mV, which was adjusted to the desired value using 15% H_2O_2. Solution pH was measured using a LIQ-GLASS TEMP BNC pH electrode with a PT100 temperature sensor. Eh was monitored using a platinum ring electrode with a combined Ag/AgCl reference electrode (3 M KCl). In all cases, 400 mL of ferric sulfate/ferrous sulfate solution (as described above) were added to a 1 L reaction kettle and the temperature was controlled using a water bath equipped with a digital thermostat. After temperature equilibration, about 4 g of treated pyrite were added to the reactor and agitation was set at a specified speed of 340 rpm using an IKA RW20 digital stirrer. To control the solution Eh within ±10 mV of the set value (700, 800 and 900 mV), peroxide solution was titrated into the reaction kettle using a peristaltic pump connected to a MR1-100 pH/ORP controller during the experiment. Analytical reagent grade chemicals and distilled water were used in all experiments.