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Mechanisms of sulfide ion oxidation during cyanidation. Part II: Surface catalysis by pyrite

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ABSTRACT

The mechanisms and the reaction products for the oxidation of sulfide ions in the presence of pyrite have been established. When the leach solution contains free sulfide ions, oxidation occurs via electron transfer from the sulfide ion to dissolved oxygen on the pyrite mineral surface, with polysulfides being formed as an intermediate oxidation product. In the absence of cyanide, the polysulfides are further oxidised to thiosulfate, whilst with cyanide present, thiocyanate and sulfite are also formed from the reaction of polysulfides with cyanide and dissolved oxygen. Polysulfide chain length has been shown to affect the final reaction products of polysulfide oxidation by dissolved oxygen.

The rate of pyrite catalysed sulfide ion oxidation was found to be slower in cyanide solutions compared to cyanide free solutions. Mixed potential measurements indicated that the reduction of oxygen at the pyrite surface is hindered in the presence of cyanide. The presence of sulfide ions was also found to activate the pyrite surface, increasing its rate of oxidation by oxygen. This effect was particularly evident in the presence of cyanide; in the presence of sulfide the increase in total sulfur from pyrite oxidation was 2.3 mM in 7 h, compared to an increase of <1 mM in the absence of sulfide over 24 h.

1. Introduction

Most metal sulfides decompose in aerated, alkaline cyanide solution to form metal ions, metal oxides or metal cyanide complexes and various sulfur-containing species including thiocyanate, sulfide and thiosulfate ions, with polythionates and polysulfides having also been detected (Marsden and House, 1992). The negative impact that reactive sulfide minerals have on gold dissolution and cyanide and oxygen consumption has been widely studied, along with the addition of lead(II) ions to counteract their effect. A detailed description of this work can be obtained from the more recent publications and references cited within (Nicol et al., 1987; Dai and Jeffrey, 2006; Deschenes, 2005; May et al., 2005).

Reactive sulfides such as chalcocite undergo non-oxidative dissolution in cyanide solutions to form copper cyanide and sulfide ions in solution (Breuer et al., 2007), leading to passivation of the gold (Liu and Yen, 1995; Dai and Jeffrey, 2006). Thus, significant sulfide ion concentrations can be observed during cyanidation when appreciable reactive copper sulfides are present (Breuer and Rumball, 2007). For instance, at the Telfer operation in Australia, significant dissolution of reactive copper sulfides occurs in the pyrite concentrate leach circuit, and the addition of lead nitrate has been considered to overcome this effect. Therefore previous investigations reported by the authors in Part 1 of this series (Breuer et al., 2008b) focussed on the oxidation of sulfide ions in the presence of lead(II) ions (which precipitate to form PbS). The oxidation of sulfide ions was shown to occur via electron transfer from the sulfide ion to dissolved oxygen on the precipitated lead sulfide surface, with polysulfides being formed as an intermediate oxidation product. In the absence of cyanide, the polysulfides were further oxidised to thiosulfate and sulfite, whilst with cyanide present, thiocyanate was the major sulfur species formed from the reaction of polysulfides and cyanide.

During cyanidation of gold ores containing reactive sulfides it is likely that semi-conductive gangue minerals such as pyrite will be present in the ore. Thus, where reactive sulfide minerals dissolve, resulting in the formation of sulfide ions in solution, there is the potential for these semi-conductive minerals to catalyse sulfide ion oxidation via a similar mechanism to lead sulfide. Previous electrochemical studies have reported on the oxidation of sulfide ions on a range of semiconducting substrates, including pyrite, chalcopyrite and galena (Woods et al., 1989). Polysulfides were identified as a reaction intermediate in the sulfide-mineral systems investigated, with the rates of polysulfide formation and products from its further reaction found to vary with mineral surface. The highest concentration of polysulfides generated during the initial stages of sulfide ion oxidation was found to be at the galena surface, followed by chalcopyrite and then pyrite. Open circuit potential measurements though, indicated the rate of reaction of sulfide ions with air would be most favourable at a pyrite surface. However, this study and the conditions utilised were designed to inves-

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tigate the depressant action of sulfide ions during sulfide mineral floatation, and hence were quite different to those encountered during cyanidation. Thus, the present paper reports on the effect of pyrite during sulfide ion oxidation in cyanide leach solutions.

2. Experimental methods

2.1. Sample preparation

The pyrite sample was a selected mineral specimen ground to fine and intermediate particle sizes before use (see Table 1). Unless stated otherwise the fine pyrite was used in experiments. Chemical analysis of the sample and XRD confirmed it was almost pure pyrite, with minor silicate impurities. Goethite was obtained from a commercial source. Reactive trace impurities in the pyrite (for example chalcocite) were removed by leaching in 2000 mg L^{-1} NaCN for 24 h. An oxidised surface is also created in drying and storage of the pyrite. Therefore, before commencing each experiment, a weighed quantity of dried sample was acid washed for 10 min (3 M HCl) to remove the oxide layer on the mineral surface, then vacuum filtered and rinsed thoroughly with deionised water. The filter cake was allowed to stand under vacuum for approximately 20 min to remove excess water and then used immediately. This acid wash step was important in obtaining reproducible results that were otherwise affected by the degree of surface oxidation during drying and storage of the pyrite sample after impurity removal.

2.2. Batch experiments

Unless stated otherwise, batch experiments were carried out in an enclosed 500 mL reactor fitted with an overhead stirrer rotating at 400 rpm. A solution volume of 300 mL was used and experiments were undertaken at room temperature and atmospheric pressure, with the oxygen sparge rate into the reactor maintained at 100 mL min^{-1}.

Solutions were prepared from analytical grade reagents and DI water. Where required, cyanide and mineral samples (pre-treated samples if needed) were added to the solution before a concentrated sodium hydrosulfide solution (sulfide ions added to simulate the rapid dissolution of a reactive metal sulfides such as chalcocite) was added to the reactor to start the experiment. The DO was monitored and the pH maintained at 11 for the duration of the experiments using a DataTaker and Metrohm Dosimat to dose NaOH. Samples (1 mL) were taken at regular intervals and filtered with a 0.45 μm Millipore filter, which removed all the solids prior to analysis by ion chromatography for sulfur and metal cyanide species.

Pre-oxidation (where indicated) was undertaken for 3 h at pH 11 and 100 mL min^{-1} oxygen prior to the addition of reagents to start the experiment. No attempt was made to optimise the pre-oxidation conditions.

2.3. Electrochemical investigations

The pyrite electrode was prepared from a natural massive specimen of the same origin as the ground material used. A selected piece was cut from the specimen, mounted on a stainless steel stub and encapsulated in an epoxy resin.

Table 1
Specifications for mineral samples.

Mineral	Particle size, P80	Sample weight (g)	Surface area ($m^2\ g^{-1}$)
Pyrite (fine)	<45 μm, 16 μm	5	2.45 ± 0.03
Pyrite (intermediate)	<317 μm, 161 μm	50	0.056 ± 0.001
Goethite	<4 μm, 1.2 μm	0.1	12.9 ± 0.2

A fresh surface was produced before each electrochemical run by wet polishing on 300 grit silicon carbide paper and rinsing with DI water. The freshly polished surface was then transferred immediately to the electrochemical cell and the experiment promptly started. The electrode was rotated at 300 rpm. Experiments were started from the open circuit potential of the system and the potential was swept at 1 mV s^{-1} in a positive direction. Potentials were measured against a Ag/AgCl reference electrode but are reported relative to the standard hydrogen electrode (SHE). The potential was controlled by a EG&G Model 362 scanning potentiostat with measurements recorded simultaneously using a PC.

Experiments were carried out in solutions of: (i) 1000 mg L^{-1} NaCN, (ii) 1 mM NaHS and (iii) 1000 mg L^{-1} NaCN plus 1 mM NaHS. A 50 mM CO_3^{2-}/HCO_3^- buffer/background electrolyte (pH 11) was utilised for each experiment. To study the oxidation processes, the electrolyte was degassed with high purity argon for 30 min prior to each experiment.

2.4. HPLC analysis of samples

For the previous investigation of the lead sulfide catalysed oxidation of sulfide ions (Breuer et al., 2008b), sulfate was not quantified, though it was indicated that little sulfate was formed directly from the oxidation of sulfide ions as all of the sulfur in solution was accounted for by sulfite, thiosulfate and that present as lead sulfide. Sulfate is formed from the direct oxidation of pyrite however (Breuer et al., 2008a), and so a new ion chromatography method was developed to quantify sulfate generation. It also allowed for the observation of any differences in the sulfide ion oxidation mechanism in the presence of pyrite compared to lead(II) ions.

A Waters 2695 HPLC separation module was used for the analysis of the non-UV active sulfate, by suppressed conductivity detection (Dionex AMMS 300 suppressor and Water 431 conductivity detector). The separation was effected using a Dionex IonPac AS17 anion exchange column equipped with a Dionex IonPac AG20 guard column. A pump flow rate of 1 mL min^{-1} was used, with the column temperature set to 25 °C. The Empower™ software package (Waters Corporation) was used to control the HPLC and calculate peak areas (from μS vs. time). A step change gradient elution method using a sodium hydroxide/acetonitrile mixture (with increasing percentage of hydroxide) was chosen as the mobile phase with this column as it facilitated the separation of sulfate and sulfite ions (low percentage hydroxide) as well as providing a rapid exchange of strongly adsorbing anion species (high percentage hydroxide) generated during the experiments, including thiosulfate, thiocyanate and trithionate.

The quantification of the UV active sulfur species (sulfide, sulfite, thiosulfate, thiocyanate and trithionate) was conducted as detailed previously (Breuer et al., 2008b) with some also able to be quantified by the suppressed conductivity method described above. This provided a check for the analysis results. Fig. 1 shows the conductivity chromatogram for an injection of solution containing chloride, cyanate, sulfite, sulfate, thiosulfate, thiocyanate and trithionate. Clearly, there is good separation of these species allowing for easy quantification, and all are eluted within 25 min. Strongly absorbed anions (tetrathionate and metal cyanides) are trapped in the guard column and back-flushed offline during the analysis by 0.1 M hydroxide to reduce the analysis time between samples.

3. Results and discussion

3.1. Effect of pyrite on sulfide ion oxidation rate

An initial test found that the homogeneous oxidation of sulfide ions by oxygen alone is relatively slow, with a 60% reduction in the sulfide ion concentration after 3 h (Fig. 2). The DO concentration