



The electrochemistry of pyrite in chloride solutions

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ABSTRACT

A detailed study of the anodic and cathodic behaviour of natural pyrite in acidic chloride solutions containing various oxidants has been conducted as part of an overall program on the fundamental aspects of the heap leaching of copper sulphide minerals.

The stoichiometry of the anodic dissolution reaction depends on the potential in that it varies from less than 4F/mol Fe dissolved at potentials below 0.8 V(SHE) to 15F/mol Fe at potentials above about 1.0 V(SHE).

The mixed potentials of pyrite in chloride solutions containing iron(III) are greater than those in the presence of copper(II) and both increase with agitation as a result of enhanced transport of iron(II) and copper(I) from the surface of the dissolving mineral. The mixed potentials are unaffected by the presence of dissolved oxygen confirming the low reactivity for the cathodic reduction of oxygen.

The rate of anodic dissolution of pyrite in chloride solutions is independent of the acid and chloride concentration except at high chloride concentrations when the rate decreases slightly. The potential dependence of the anodic reaction roughly follows Tafel behaviour up to about 1.0 V but mechanistic conclusions are excluded due to the variable stoichiometry.

Cathodic reduction of oxygen is some 30 times slower than that of 1 g/L iron(III). The reduction of copper(II) is also less significant in the leaching of pyrite due to the lower formal potential of the copper(II)/copper(I) couple than that of the iron(III)/iron(II) couple in concentrated chloride solutions.

Comparative measurements have shown that pyrite will dissolve more slowly than chalcopyrite in chloride solutions and, this coupled to the low sulfate yield at low potentials, suggests that oxidation of pyrite as a source of heat in abiotic heap leaching is unlikely.

1. Introduction

The recovery of copper by heap leaching of low-grade ores containing secondary and tertiary copper sulfide minerals is becoming increasingly important as the easily leached oxide ores are being depleted.

Although it is well known that the rate of leaching of the secondary copper sulfides is more rapid than that of the primary minerals such as chalcopyrite and enargite under strongly oxidizing conditions, the rates are considerably slower than those for the most common oxide minerals. In addition, an oxidant is required for the sulfides and bacterially-assisted oxidation in sulfate solutions has been the generally accepted method for heap leaching of such minerals. An alternative approach using dilute chloride solutions has been applied in at least one case (Aroca, 1999) and more concentrated chloride solutions are currently being used in an operation in northern Chile. Chloride is an attractive alternative which can also make use of copper(II) as an oxidant. The rapid (relative to that of iron(II)) rate of the re-oxidation of copper

(I) by dissolved oxygen in chloride solutions (Miki and Nicol, 2008a, 2011) permits the use of aerated heaps without external regeneration of the oxidant.

Pyrite commonly occurs with the copper sulfide minerals and can potentially also be leached during chloride leaching. This can be a disadvantage in terms of higher oxygen demand and higher iron concentrations in the pregnant leach solutions. On the other hand, oxidation of pyrite has the potential to generate heat in the heaps thereby increasing the rate of leaching of the copper minerals. It was therefore considered important to undertake an electrochemical study of the behaviour of pyrite under chloride leaching conditions. A similar electrochemical study aimed at bacterial leaching of copper sulfides in sulfate media has previously been published (Nicol et al., 2013).

Although there have been many published reports on the electrochemistry of pyrite in both sulfate and chloride media (Peters and Majime, 1968; Biegler et al., 1975; Biegler and Swift, 1979; Misra and Osseosare, 1988, 1992; Zhu et al., 1993; Kelsall et al., 1996; Ahlberg and Broo, 1997; Lin and Say, 1997; Lehmann et al., 2000; Nicol and Liu,

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2003; Rimstidt and Vaughan, 2003; Antonijevic et al., 2005; Lehner et al., 2007; Miki and Nicol, 2008a, 2008b; Bryson and Crundwell, 2014; Lin et al., 2014; Nicol et al., 2016), none of these have addressed in any detail the electrochemistry under conditions appropriate to the heap leaching of pyrite under chloride conditions. In a detailed electrochemical study (Holmes and Crundwell, 2000) presented useful information on the electrochemistry of pyrite under various conditions in sulfate solutions at low temperatures and the authors developed a conventional mixed-potential model for the oxidative dissolution of pyrite in sulfate solutions containing iron(III), iron(II) and dissolved oxygen which correlated well with the observed electrochemical data. In a subsequent paper (Bryson and Crundwell, 2014), the same authors treated similar electrochemical data obtained in hydrochloric acid solutions in terms of the semi-conducting properties of pyrite. However, their data is of limited value as it was focussed on results at potentials higher than would be experienced by pyrite under heap leach conditions. The same considerations in terms of the potential region investigated apply to the other studies (Lehmann et al., 2000; Lin et al., 2014) conducted in chloride solutions.

This paper presents the results of a study of the anodic and cathodic electrochemistry of pyrite over a wide range of chloride concentrations at potentials relevant to the dissolution of the mineral under ambient conditions appropriate to heap leaching.

2. Experimental

The properties of the natural pyrite samples and fabrication into electrodes have been described in a previous publication (Nicol et al., 2013). The electrodes prepared with a normal cubic face exposed to the solution are labelled “pyrite1” and “pyrite3” while that with the diagonal face exposed is “pyrite2”. A fourth electrode, “pyrite4” was prepared from a local museum-grade single crystal with the cubic face exposed. The counter electrode was a thin, coiled platinum (Pt) wire of about 10 cm in length housed in a tube with a fritted glass end to isolate the solution from that in the cell. The reference electrode was either a mercury-mercurous chloride (sat. KCl) electrode with a potential of 0.254 V against the standard hydrogen electrode (SHE) at 25 °C or a silver-silver chloride (3MKCl) electrode with a potential of 0.210 V versus SHE at 20 °C. All potentials in this study have been reported against SHE.

Details of the conventional electrochemical methods and experimental procedures have been provided in a previous publication (Nicol et al., 2016). As previously described, electrochemical measurements were carried out using a standard three-electrode system with one of the above pyrite electrodes used as a rotating (100 to 500 rev/min) working electrode.

The above three-electrode system was used in conjunction with either a EG & G Princeton Applied Research Model 173 Potentiostat/Galvanostat and an EG & G Princeton Applied Research Model 175 Universal programmer or a Solartron 1720 potentiostat to conduct the electrochemical measurements. Current and potential readings from the former were captured using a National Instrument data acquisition card, which was controlled by Labview™ software while CorrWare software was used with the latter potentiostat.

The solutions used as electrolytes in this study were all prepared using analytical grade (AR) chemicals and Millipore-quality (Milli-Q) water.

Prior to each experiment, the electrode surfaces were very gently sanded with P1200 silicon carbide paper for a few seconds. Thereafter, the mineral was wet-polished in the same way using a finer grind (4000 grit) silicon carbide paper. Experiments were conducted at either 25 °C or 35 °C.

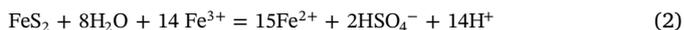
Analysis of iron in solution was conducted colorimetrically at 515 nm using the o-phenanthroline method (Vogel, 1961) in the presence of hydroxylamine to reduce any iron(III) to iron(II).

3. Results and discussion

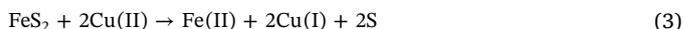
3.1. Thermodynamic considerations

It is known that pyrite can be oxidised in acid solutions to form either/or both sulfur and sulfate ions. The stoichiometry will be dealt with in a later section.

The overall oxidative dissolution of pyrite with iron(III) as the oxidant can be written as.



Oxidation can also be accomplished with copper(II) ions as the oxidant in chloride solution.



The potentials for the oxidation of pyrite in a solution of 4 M chloride containing 0.05 M iron(II), 0.1 M H^+ and 0.1 M HSO_4^- can be calculated using the Nernst equation and the standard electrode potentials (HSC Chemistry, Ver 7.1) as



These values have been calculated ignoring the weak complexation of iron(II) by either sulfate or chloride ions.

The formal potential of the iron(III)/iron(II) couple decreases from 0.740 V in the absence of chloride to 0.693 V in 4 M chloride while that of the copper(II)/copper(I) couple varies from 0.390 V in 0.1 M chloride to 0.572 V in 4 M chloride (Nicol et al., 2016).

Given that the potentials for the iron(III)/iron(II) couple are 0.3 to 0.4 V greater than those for reactions (4) and (5), there are no thermodynamic restrictions to the oxidation of pyrite by iron(III) with either sulfur or bisulfate as the oxidation products. In the case of copper (II) as the oxidant, this is also true at high chloride concentrations but not at low chloride concentrations except at high copper(II)/copper(I) concentration ratios.

3.2. Mixed potential measurements

Mixed potential measurements were made under various conditions by immersing the electrode in the relevant solution for up to 30 min under open-circuit conditions. These measurements provide information on the potential regions relevant to leaching and also a preliminary indication of the effectiveness of the oxidants. The effect of mass transport was evaluated by initially measuring the potential of a stationary electrode for a period after which the electrode was rotated at 500 rev/min. These measurements were made in solutions of various chloride concentrations and pH but only the data obtained in 1 M HCl solutions are shown below.

The results in the absence of an oxidant and in the presence of dissolved oxygen (solution sparged with pure oxygen) are shown in Fig. 1 from which it is apparent that the mixed potential is some 40 mV greater in the presence of oxygen suggesting that dissolved oxygen does act as an oxidant in this system. No effect of agitation was observed with oxygen as could be expected given the low reactivity of oxygen. This is confirmed by comparing the mixed potential of about 0.58 V with oxygen with those measured in solutions containing iron(III) and copper(II) in Figs. 2 and 3 that are significantly greater. The small increase in the potential with agitation in the case of the solution sparged with nitrogen is probably due to the entrainment of some oxygen from the air during agitation.

The mixed potentials in solutions containing 1 g/L of either iron(III) or copper(II) are shown in Figs. 2 and 3. The potential is higher in the presence of iron(III) than copper(II) as expected given the higher formal potential of the former. In a solution containing both oxidants (Fig. 4),

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