The galvanic interaction between gold and pyrite in the presence of ferric ions

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ABSTRACT

The current study investigated the galvanic interaction between gold and pyrite in the presence of Fe^{3+} to identify a means of facilitating the exposure of gold from its carrier mineral pyrite. It was found that gold was nobler than pyrite in the presence of ferric ions and a static current was generated once gold and pyrite were coupled. Dynamic polarization studies indicated that gold could catalyse the reduction of Fe^{3+}, and Fe^{3+} provided a more oxidizing effect on pyrite coupled with gold than that on pyrite without the coupling. This resulted in a significant increase in the oxidation rate of pyrite coupled with gold. Electrochemical characterization of pyrite surface and aqueous solution was also conducted after pyrite was oxidised with and without coupling with gold. A more extensive sulphur-rich layer was formed on pyrite after coupled with gold. The solution from galvanic oxidation also contained a much higher amount of oxidation products dissolved from pyrite surface. This study suggests that Fe^{3+} can enhance the oxidation and dissolution of pyrite coupled with gold.

1. Introduction

Gold is commonly associated with sulphide minerals, in particular, pyrite and arsenopyrite (Flatt and Woods, 1995). Due to the fact that gold can exist in solid solution with a diameter typically smaller than 1 μm and a concentration ranging from 0.2 to 132 ppm (Chryssoulis and Cabri, 1990), recovering gold by the conventional grinding-flotation/ cyanidation process is inefficient. These ores are known as refractory gold ores. Ultra-fine milling (UFM), producing particles with sizes in the range of 1–20 μm, has been proven to be able to expose the gold from its carrier minerals and hence significantly improve gold flotation and cyanidation or lower the temperature and pressure required for the subsequent oxidation process (Celep et al., 2011; Corrans and Angove, 1991). However, the prolonged milling process results in a high energy consumption and operating cost which generally limit its application only to high gold grade concentrates, for example, flotation and gravity concentrates (Corrans and Angove, 1991; La Brooy et al., 1994).

To more efficiently recover gold from refractory gold ores, accelerating the exposure rate of gold from its carrier minerals is an important option. It has been documented that gold is very noble and electrochemically inert as reflected by its lack of reactivity in air and the majority of aqueous solutions (Marsden and House, 2006), while the water/gold interface is catalytic (Zope et al., 2010). Therefore, a galvanic interaction between pyrite/arsenopyrite and gold is expected when they are electrically combined, which would enhance the dissolution rate of pyrite/arsenopyrite while exposing gold.

In the previous study, it has been found that the galvanic interaction between gold and pyrite exists and can be enhanced in the presence of oxygen (Huai et al., 2017). Additional formation of elemental sulphur, iron hydroxyl-oxide and iron sulphate has been observed on the pyrite surface after galvanic coupling with gold in oxygen-enriched conditions. However, under these conditions, a significant pyrite dissolution has not been observed, probably due to the lack of enough oxidizability of oxygen and the formation of Fe-oxy/hydroxide during oxidation which hinders the dissolution of pyrite in the neutral pH environment (Descostes et al., 2004). In this study, to facilitate the dissolution of pyrite and the exposure of gold, the galvanic interaction between gold and pyrite was initiated in the presence of Fe^{3+}. Fe^{3+} is more effective than O_2 for pyrite oxidation (Chandra and Gerson, 2010). Moses et al. (1987) proposed that pyrite oxidation rate in the presence of Fe^{3+} was two orders higher than that in oxygen-saturated solution at a low pH range. Economically, it is more favourable to use Fe^{3+} as an oxidant as it is generally available in gold processing plants (Li and Miller, 2007).

Pyrite oxidation by Fe^{3+} can be described by the following reaction (Holmes and Crundwell, 2000; Williamson and Rimstidt, 1994):

$$FeS_2 + 8H_2O + 14Fe^{3+} \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (1)$$
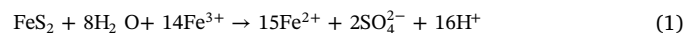
which can be further divided into two electrochemical half-reactions

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(Holmes and Crundwell, 2000). The anodic half reaction and the cathodic half reaction are shown in Reaction (2) and Reaction (3), respectively:

$$FeS_2 + 8H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- \tag{2}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3}$$

When both Fe^{3+} and O_2 are present, the cathodic product Fe^{2+} can be oxidized back into Fe^{3+} according to Reaction (4):

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{4}$$
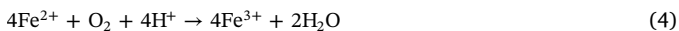
It is worth noting that Reaction (4) is much slower than Reaction (1) (Descostes et al., 2004; Moses et al., 1987; Sasaki et al., 1995) and cannot compensate the consumption of Fe^{3+}. Importantly, Reaction (3) is the rate-determining step of pyrite oxidation in the presence of Fe^{3+} (Moses et al., 1987) and the formation of under-potential deposited metal layers on polycrystalline gold electrodes can catalyse the Fe^{2+}/Fe^{3+} redox reaction, especially in the presence of chloride ions (Nagy et al., 1992). Taking into account this catalytic effect, it is expected that the coupling of pyrite with gold can accelerate pyrite oxidation and in turn facilitate the dissolution of pyrite and therefore gold exposure.

2. Experimental section

2.1. Electrodes

The pyrite sample was obtained from GEO Discoveries, Australia. The elemental composition of the sample determined by ME-XRF is shown in Table 1. The sample is mainly composed of Fe and S with trace amounts of other elements with a purity of 98%. The preparation of the electrodes has been described elsewhere (Huai et al., 2017). Briefly, the specimen was cut into rectangular slices with dimensions of approximately $15 \times 15 \times 5$ mm and mounted using epoxy resin. The slides were polished on both sides. An insulated copper wire was attached to the underside of the specimen using silver conductive epoxy (M.G. chemicals, AU). The section was attached to a PVC tube acting as a sample holder with a silicone sealant (Selleys, AU) to ensure that the sample was placed in the same position in the electrolyte each time. A fresh pyrite surface was created before each experiment by abrading with successively finer grades (600, 800, 1200, 1600 and 2000 grit) of silicon carbide paper followed by successively polishing with 3, 1 and 0.5 μm diamond suspensions (Dia-duo, Struers, AU) and rinsing with Milli-Q water in a nitrogen-filled vessel for 20 s.

A specimen of gold ($20 \times 10 \times 2$ mm) with a high purity of 99.99% was obtained from XRF Labware. A copper wire was soldered onto one end which was then sealed in a glass tube to prevent tin, lead and copper from affecting the properties of gold and pyrite. A fresh gold surface was created by abrading with 2500 grit silicon carbide paper followed by polishing with 1.0 and 0.5 μm alumina oxide compounds and rinsing with Milli-Q water in a nitrogen-filled vessel for 20 s. Before each test, the gold electrode was cleaned by electrochemically cycling the electrode in a weak sulfuric acid solution from -400 to 1400 mV (vs. Ag/AgCl) at a rate of 100 mV/s until a stable CV curve was achieved. This method has been proved to be able to generate a clean gold surface (Spégel et al., 2007).

Table 1
Elemental compositions of the pyrite sample determined by ME-XRF (Huai et al., 2017).

Mineral	Species present (wt.%)								
	Fe	S	Cu	Bi	Pb	Al_2O_3	SiO_2	Ti	Zn
Pyrite	46.7	> 50	0.01	0.02	0.02	0.02	0.12	0.04	0.02
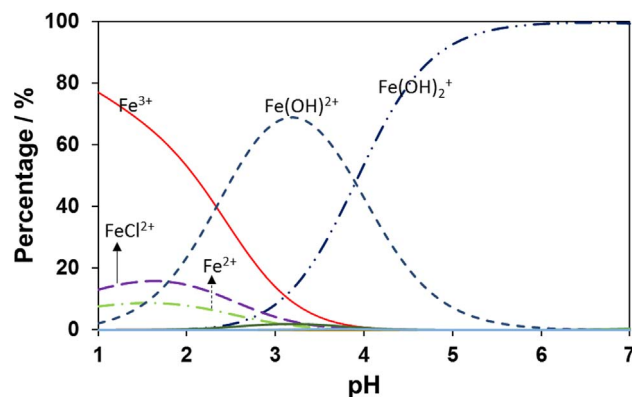
Fig. 1. Speciation of Fe^{3+} in the pH range from 1 to 7 at 25 °C (Fe conc. = 2 mM, Cl conc. = 26 mM, K^+ conc. = 10 mM, $\log K_{Fe(OH)2}^+ = -5.75$, $\log K_{Fe\ OH}^{2+} = -2.02$, Eh = 800 mV).

2.2. Solution preparation

ACS grade ferric chloride hexahydrate was used to prepare a ferric ion solution and ACS grade hydrogen chloride (Sigma-Aldrich, AU) was used to adjust the pH. The experimental solutions were prepared right before the tests with a 0.01 M support electrolyte to minimize the negative effect of potential drop (Hampton et al., 2011). Water used in the experiments was purified with an Ultrapure Academic Milli-Q system (Millipore, US). This water has a specific resistance of 18.2 MΩ cm^{-1}.

The investigation of galvanic interactions between gold and pyrite in the presence and absence of Fe^{3+} was carried out in an acidic environment at pH 2. Fig. 1 shows the ferric speciation as a function of pH from 1 to 7, which was simulated using a computer program Visual MINTEQ (version 3.0) (Guo et al., 2015; Gustafsson, 2012). In this modelling, the species other than Fe^{3+}, Fe^{2+}, $FeCl^{2+}$, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ were ignored due to their low concentrations, following the previous work (Machulek et al., 2012). At the region of pH less than 2, the dominant species is Fe^{3+} accounting for more than 60% of the overall iron species. When pH is greater than 2, an exponential decrease in Fe^{3+} concentration was observed with $Fe(OH)^{2+}$ taking over as the main ion species in the system due to the hydrolysis. The increase in $Fe(OH)^{2+}$ concentration ceases at pH 3.5 and it is replaced by its hydrolysate $Fe(OH)_2^+$ which dominates the system afterwards. Fig. 1 suggests that the suitable pH for the Fe^{3+} system is less than 2, above which the freshly prepared Fe^{3+} is supersaturated with the formation of colloidal iron hydroxides. In this study, pH 2 was used, which is also consistent with the previous work (Descostes et al., 2004; Sasaki et al., 1995).

2.3. Electrochemical measurements

All the electrochemical measurements were controlled by a CHI 920D (CH Instruments, Inc., US) potentiostat with a platinum counter electrode (Radiometer, AU) and Ag/AgCl reference electrode (Radiometer, AU) and conducted in an anaerobic environment with nitrogen purging during the conditioning and nitrogen blanketing during the measurements. The oxygen content of the solution was measured using a YSI-5739 dissolved oxygen sensor (TPS, AU) and logged in real-time using WinTPS software (TPS, AU). It decreased from 8 ppm to less than 1 ppm during the initial nitrogen conditioning. All the measured potentials were converted to standard hydrogen electrode (SHE) values by adding 220 mV (Mu et al., 2015).

2.3.1. Open circuit potential and galvanic current measurements

In order to validate the existence of a galvanic interaction between gold and pyrite, open circuit potential (OCP) and galvanic current measurements were conducted in a traditional three electrode jacketed