The surface properties of pyrite coupled with gold in the presence of oxygen

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ABSTRACT

Gold often exists with pyrite and there is an urgent need to separate the low-gold-content pyrite from the high-gold-content pyrite when gold is recovered from refractory pyritic ores. This separation may be achieved by exploring the change of surface properties on pyrite upon contact with gold. For the first time, the current study investigated the galvanic interaction between gold and pyrite in the presence of oxygen as well as the oxidation products formed on pyrite surfaces with and without the galvanic coupling. It was interesting to find that gold was slightly more active than pyrite under ambient conditions, and the coupling of gold with pyrite generated a low negative galvanic current. However, under oxygen-enriched conditions, gold became much nobler than pyrite, and the coupling of gold with pyrite generated a high positive galvanic current resulting in an oxidation layer on pyrite. It is evident that oxygen can change the surface reactivity of gold and enhance the galvanic interaction between gold and pyrite. A combination of cyclic voltammetry measurements and Cryo-XPS (X-ray Photoelectron Spectroscopy) analyses was used to characterize pyrite surfaces after self-oxidation and galvanically induced oxidation. Additional oxidation products consisting of elemental sulphur, iron hydroxyl-oxide and iron sulphate, in particular the latter two, formed on pyrite surfaces when coupled with gold especially under oxygen-enriched conditions. This indicates that gold can alter pyrite surface properties once in contact with pyrite under oxygen-enriched conditions. This study provides new insights into the electrochemistry of base metal and precious minerals as well as the separation of different types of pyrite during the process of gold recovery.

1. Introduction

Gold is commonly associated with sulphide minerals, in particular pyrite and arsenopyrite (Flatt and Woods, 1995). To recover gold from pyritic ores, flotation is an important process to enrich gold and pyrite while rejecting non-sulphide gangue minerals. For refractory pyritic gold ores which predominate over free-milling counterparts nowadays, flotation concentrates are often fed to pressure oxidation which oxidizes the pyrite to release gold, followed by gold leaching and recovery (Ketcham et al., 1993; Thomas, 1991). The use of flotation concentrates as pressure oxidation feeds minimizes plant costs by allowing lower temperatures and pressures in the autoclaves, and by lowering greatly the tonnage of solids to be treated. Some sulphide sulphur is required to reduce or eliminate the need for external heating (e.g. steam injection). However, a too high sulphide sulphur content, above the point at which the process becomes autothermal (about 8%), necessitates dilution of the slurry in order that the additional heat may be dissipated (Mason, 1992). Thus, the autoclave capacity necessary to oxidize a fixed quantity of sulphide sulphur decreases significantly as the sulphide grade is increased beyond the autothermal point. This is a major problem in gold processing plants with a significantly higher sulphide sulphur content in autoclave feeds.

A refractory pyritic ore typically contains different types of pyrite with various gold concentrations (Ketcham et al., 1993). Thus, removing the low-gold-content pyrite including barren pyrite would decrease the sulphide sulphur content and increase the gold content in the autoclave feed, thereby maximizing gold production per tonne and minimizing the operation cost (Ketcham et al., 1993; King and Knight, 1992; Mao et al., 2010). Gold is the most noble metal and the water/gold interface is catalytic (Zope at al., 2010). A galvanic interaction between pyrite and gold may enhance pyrite oxidation. This will allow different surface properties to occur between the high-gold-content pyrite and the low-gold-content pyrite. These different surface properties can allow the separation of these two types of pyrite by flotation. For example, the high-gold-content pyrite can be floated in the absence of a collector if hydrophobic sulphur-rich products predominantly form on the surface, while the low-gold-content pyrite is rejected. If hydrophilic ferric hydroxides predominantly form on the high-gold-content pyrite after strong oxidation, it can be rejected in the flotation in the presence of a collector, while the low-gold-content pyrite is floated.

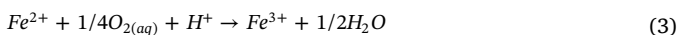A number of studies have investigated the galvanic interaction between gold and pyrite in the presence of a complex agent such as cyanide (CN-) or thiourea ($SC(NH_2)_2$) (Azizi et al., 2011; Lorenzen and Van Deventer, 1992a,b) and the galvanic interaction between gold and pyrite occurs and enhances the dissolution of gold at the initial stage, followed by the passivation of iron oxides (Aghamirian and Yen, 2005; Azizi et al., 2010; Lorenzen and Van Deventer, 1992a). However, all these previous studies were carried out in leaching environments. In the absence of any complex agent, studies on the galvanic interaction between gold and pyrite are limited in the context of mineral flotation. This may be due to the fact that pyrite and gold both present high surface inertness and similar rest potentials in the absence of complex agents. The rest potential of gold and pyrite in salt water is 200 mV and 220 mV (vs. SHE), respectively (Moslemi et al., 2011; Ramachandra, 2004; Zhang, 2011). Such a small potential difference may not be enough to serve as a driving force to push the electron flow efficiently to have an impressive galvanic interaction and, hence, change the surface properties of pyrite.

It has also been found that the rest potential of gold in oxygen-saturated 2 N H_2SO_4 solution is 980 ± 20 mV, and under these conditions the gold surface is covered with a hydrated monolayer of adsorbed oxygen atoms rather than a layer of Au_2O_3 (Hoare, 1963). The possible oxygen reduction reaction (ORR) on gold consists mainly of a two-electron transfer process in acid solution, in which the first and rate-determining step is usually stated as the reaction below, resulting in the adsorption of $(HO_2)_{ad}$:

$$O_2 + H^+ + e^- \rightarrow HO_{2ads} \tag{1}$$

Reaction 1 is followed by either the desorption and release of $(HO_2)_{ad}$ into the water or the further reduction of hydrogen peroxide ions into OH^- with the former path dominating in acid solution (Andoralov et al., 2011). Meanwhile, it has been reported that the rest potential of a clean pyrite surface lies between 200 and 300 mV, and once exposed to oxygen it would increase up to 600 mV as a result of surface passivation (Peters and Majima, 1968). The oxidation process of pyrite in the presence of oxygen is generally expressed as follows (Chandra and Gerson, 2010; Singer and Stumm, 1970):

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

$$Fe^{2+} + 1/4O_{2(aq)} + H^+ \rightarrow Fe^{3+} + 1/2H_2O \tag{3}$$

It is clear that oxygen reacts differently on gold and pyrite surfaces and increases the rest potential of gold and pyrite to a different extent. As a result, oxygen may initiate or enhance the galvanic interaction between gold and pyrite.

In this study, the galvanic interaction between gold and pyrite under ambient and oxygen-enriched conditions in the absence of complex agents was studied by open circuit potential (OCP) and galvanic current measurements. In addition, the surface chemical changes after the galvanic interaction were characterized by cyclic voltammetry (CV) and cold stage X-ray Photoelectron Spectroscopy (Cryo-XPS, below −145 °C). This study provides new insights into the electrochemistry of base metal and precious minerals as well as the separation of different types of pyrite during the process of gold recovery by flotation.

2. Experimental section

2.1. Materials

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 was mainly composed of Fe and S with trace amounts of other elements with a purity of 98%. The specimen was cut into rectangular slices with dimensions of approximately 15 × 15 × 5 mm by a slow speed diamond saw, mounted using epoxy resin and then polished on both sides. An insulated copper wire was

Table 1
Elemental compositions of the pyrite sample determined by ME-XRF.

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

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 silicone sealant (Selleys, AU) to make sure 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 further polishing with 3, 1 and 0.5 μm diamond suspensions (Dia-duo, Struers, AU) successively and rinsing with Milli-Q water in a nitrogen-filled vessel for 20 s.

A specimen of gold (20 × 10 × 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 0.3 μm alumina 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 cleaning method has been proved to be able to generate a clean gold surface (Spégel et al., 2007).

A.R. grade dihydrogen orthophosphate and potassium chloride (Sigma-Aldrich, AU) were used to prepare a pH 5 buffer solution with a 0.1 M support electrolyte to minimize the negative effect of the potential drop from the buffer solution (Hampton et al., 2011). Water used in the experiments was purified with an Ultrapure Academic Milli-Q system (Millipore, US). The Milli-Q water has a specific resistance of 18.2 MΩ cm^{-1}.

2.2. Experimental

Electrochemical studies were conducted in a traditional three electrode jacketed cell controlled by a CHI 920D (CH Instruments, Inc., US) potentiostat with a platinum counter electrode (Radiometer, AU) and Ag/AgCl reference electrode (Radiometer, AU). All the measured potentials were converted to standard hydrogen electrode (SHE) values by adding 220 mV (Mu et al., 2015). The experimental procedure is shown diagrammatically in Fig. 1.

In order to validate the enhancement of galvanic interactions by oxygenation of the surrounding electrolyte, this study was conducted in two parts to enable a comparison to be made as shown in the two dash-dotted squares in Fig. 1: galvanic interactions under ambient conditions and oxygen purging conditions. The ambient condition refers to the condition of the immediate environment without surrounding atmosphere control. For each experimental protocol, the system was allowed a conditioning time of 1800 s before the experiment was commenced. 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). With oxygenation, it increased from 8 ppm to 31 ppm during the 1800 s pre-measurement conditioning.

2.2.1. Open circuit potential and galvanic current measurements

Open Circuit Potential (OCP) measurements were performed with the freshly prepared pyrite and gold electrodes in pH 5.0 buffer solution for 1200 s. The galvanic current between gold and pyrite was measured for 1200 s by connecting the two materials to the working clip and ground jack of the potentiostat individually, while at the same time the