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The interaction between copper species and pyrite surfaces in copper cyanide solutions

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ABSTRACT

The adsorption of copper ions and the formation of a copper sulfide phase on pyrite surfaces are of vital importance to alter the surface property of pyrite and determine its fate either to be rejected in the flotation of polymetallic sulfide ores or to be recovered in the flotation of pyritic gold ores. Cyanide and copper may coexist in the process water with complicated speciation. The objective of this study is to understand the interaction between copper cyanide species and pyrite and clarify the possible adsorption of copper on pyrite surfaces from cyanide-bearing solutions. Surface-enhanced Raman spectroscopy and electrochemical measurements were used to determine the reaction products formed on pyrite surfaces. It was found that Cu(I)-bearing species were incorporated into pyrite, forming a CuS-like sulfide from copper cyanide solutions at a more oxidizing potential, while a Cu_2S-like sulfide formed at a more reducing potential. The amount of copper deposited on pyrite was significantly improved at a more reducing potential at which the pyrite surface tended to be FeS-like. In addition, these Cu(I)-sulfides on pyrite surfaces were dissolved by cyanide-bearing species at a high CN/Cu ratio, compromising the total amount of copper uptake.

1. Introduction

Pyrite responds well to thiol collectors such as xanthates and its flotation presents two maximums at around pH 4 and 8 with a depression at around pH 7 (Fuerstenau et al., 2007; Wang et al., 1989a). The high flotation yield at pH 4 is due to the formation of sulfur-rich products and dixanthogen (Leppinen, 1990; Lopez Valdivieso et al., 2005). The yield at pH 8 is due to the formation of iron hydroxide-xanthate complexes on pyrite surfaces (Fornasiero and Ralston, 1992). The depression at around pH 7 is due to a high density of ferric hydroxides on pyrite surfaces, which, however, disappear with the increase of xanthate concentration due to the reduction of ferric hydroxides to ferrous species resulting from the oxidation of xanthate to dixanthogen (Lopez-Valdivieso et al., 2005). The depression above pH 11 is due to the thermodynamic instability of dixanthogen and the formation of ferric hydroxide islands on pyrite surfaces (Leppinen, 1990; Fuerstenau et al., 2007).

Cu^{2+} can activate pyrite and then enhance the adsorption of xanthate resulting in good floatability at neutral to alkaline pH (Chandra and Gerson, 2009; Finkelstein, 1997; Laajalehto, 1999; Leppinen, 1990; Weisener and Gerson, 2000a; Weisener and Gerson, 2000b; Wang et al., 1989b). The copper activation process on pyrite surfaces has been considered to be an electrochemical process involving the adsorption of Cu^{2+} onto pyrite surfaces and the reduction of Cu(II) to Cu(I) with simultaneous oxidation of pyrite resulting in the formation of a Cu(I)-sulfide phase (Weisener and Gerson, 2000a; Weisener and Gerson, 2000b). The adsorption of Cu^{2+} on pyrite is more favorable in reducing conditions (Chen, 1998). Cu^{2+} dissolved from copper minerals such as chalcopyrite and chalcocite through a galvanic interaction may activate pyrite inadvertently and deteriorate the separation of copper and other base metal sulfide minerals from pyrite in flotation (Peng et al., 2003). To ensure the selectivity between pyrite and other base metal sulfides in the presence of copper ions, the deactivation of copper ions on pyrite surfaces will be required.

Cyanide is added intentionally to depress pyrite or deactivate copper activation on pyrite surfaces in the flotation of copper, lead and zinc ores. The mechanism of pyrite-cyanide interactions has been generally accepted as cyanide preferentially adsorbing on pyrite with iron cyanide compounds inhibiting electrochemical activities on the surface (Elgillani and Fuerstenau, 1968; Janetski et al., 1977; Wang and Forssberg, 1996). Copper and cyanide co-existing in solution show complicated speciation, depending on the pH and cyanide-to-copper ratio (Dai et al., 2012; Lu et al., 2002; Lukey et al., 1999). Cuprous tetra-cyanide ($Cu(CN)_4^{3-}$), cuprous tri-cyanide ($Cu(CN)_3^{2-}$), and cuprous di-cyanide ($Cu(CN)_2^{-}$) are the most common cuprous cyanide species. Cuprous cyanide species are also present in the process water from gold cyanidation recycled to flotation circuits and may inadvertently affect the flotation of pyrite where precious metals are always associated with (Adams, 2013).

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Practical operations have demonstrated that pyrite can be activated on the one hand but depressed on the other hand in copper and cyanide-bearing environments. $Cu(CN)_3^{2-}$ was found to depress pyrite in the flotation of pyritic gold ores at pH 10 (Guo et al., 2015). However, the impact of cuprous cyanide on mineral flotation is rather complicated. Cuprous cyanide was found to activate mineral flotation as well (Prestidge et al., 1997; Seke and Pistorius, 2006). A distinctive aspect of pyrite is the occurrence of variable surface compositions subjecting to oxidizing or reducing aqueous solutions (Murphy and Strongin, 2009). Pyrite surfaces after fracturing show both S monomers (S(–II)) and S-S dimers ($S(-I)_2$) (Von Oertzena et al., 2006). The intermediate oxidation of pyrite leads to the formation of ferric hydroxides and a sulfur-rich layer (elemental sulfur (S^0), poly-sulfides (FeS_n) or metal-deficient sulfide ($Fe_{1-x}S_2$)) (Buckley and Woods, 1987; Hamilton and Woods, 1981; Yoon et al., 1991). The extensive oxidation of pyrite to sulfate occurs at more positive potentials while the reductive decomposition of pyrite to a FeS-like surface with dominant S monomers takes place at more negative potentials (Hamilton and Woods, 1981; Tao et al., 2003). The competitive adsorption between copper and cyanide may also change pyrite surface chemistry.

In this study, the adsorption of copper ions on pyrite surfaces from cyanide-bearing solutions was investigated via an electrochemical approach including voltammetry and impedance measurements by taking into account the redox potential and cyanide-to-copper ratio. The reaction products were determined by surface-enhanced Raman spectroscopy and the surface reactions taking place on pyrite surfaces were discussed from a thermodynamic aspect. This study suggests the chemical conditions for the activation and deactivation of copper ions on pyrite surfaces in copper and cyanide-bearing environments, which is valuable for the selective flotation of other base metal sulfide minerals against pyrite and also for the flotation of pyritic gold ores where gold is recovered with pyrite.

2. Experimental methods

2.1. Materials

Copper cyanide solutions were prepared by dissolving copper(I) cyanide powder (CuCN, 99.99%, Aldrich) to sodium cyanide (NaCN, 99.9%, Aldrich) solutions to give the final solutions with CN/Cu = 2/1, 2.5/1, 3/1, 3.5/1 and 4/1. A hand-picked natural massive cubic pyrite specimen originating from Spain was used as the working electrode. Energy Dispersive Spectroscopy (EDS) analysis on the pyrite specimen showed 66.35 at.% sulfur and 33.17 at.% iron with minor carbon contamination. XRD analysis also showed a high purity of the pyrite specimen with minor quartz and galena minerals.

2.2. Electrochemical measurements

The pyrite electrode was connected with a copper wire using a silver-loaded conducting epoxy, and then mounted into non-conducting epoxy resin exposing only one side with a geometric surface of approximately 0.25 cm^2. A platinum plate with a surface area of 1 cm^2 was utilized as the auxiliary electrode (counter electrode). Potentials were measured and reported against an Ag/AgCl reference electrode filled with 3 M KCl which has a potential of +0.1915 V against the standard hydrogen electrode (SHE). A Radiometer PGZ100 potentiostat was used in combination with a frequency response analyzer (FRA).

A fresh electrode surface was generated before each experimental run by wet abrading with silicon carbide abrasive paper (1200 grits). The previous study on Cu^{2+} activation confirmed that the oxidation of pyrite during polishing did not have a strong influence on copper adsorption and similar results were obtained between the polished and in-situ fractured pyrite electrodes (Chen, 1998). A pretreatment of the pyrite electrode was conducted at a certain polarization potential in a deoxygenated solution containing copper cyanide at pH 7 for 10 min under stirring (50 rpm/m). The copper cyanide solution was then removed from the electrochemical cell which was then filled with a deoxygenated solution without copper ions for electrochemical measurements. Nitrogen gas was applied above the solution to expel the return of oxygen. The measurement system (electrochemical cell) was sealed to minimize the volatilization of HCN from aqueous phase to gas phase during the experiment. For a closed and static system, <0.05% of the total aqueous HCN volatilizes (Lotter, 2006). The actual volatilized HCN during mineral processing should be evaluated and monitored before any large scale application.

Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were performed in a 0.2 L background solution with 0.1 M potassium dihydrogen phosphate (KH_2PO_4, 99.9%, Aldrich) at room temperature. The pH was adjusted to 7 with a KOH solution. All solutions were prepared with deionized water. The potential scan rate for CV was 0.02 V s^{-1}. EIS was conducted at a DC applied potential of 0.1 V which was close to the open circuit potential of pyrite, and at an AC potential of 0.01 V. Typically, the electrode surface was stabilized at the desired DC potential for 5 min after which EIS was obtained.

2.3. Raman spectroscopy measurements

Raman spectroscopy measurements were conducted with a Renishaw Raman spectrometer using 632.8 nm red excitation from a He-Ne laser. The scattered light was detected with a CCD detector cooled to −50 °C with the spectral resolution of 2.7 cm^{-1}. The laser and scattered radiation were focused through the spectrometer objective lenses with a long working distance. The laser spot size was ~1.3 μm and the laser power at the sample was 0.6 mW (10% power). Spectra were collected for 10 s with 20 accumulations. The grating was calibrated using the 520 cm^{-1} silicon band. Surface enhancement was achieved by sputtering fine gold (99.5% Au) on pyrite surfaces using K550X sputter coater. The specimen was placed in a chamber which was then evacuated to a vacuum of 10^{-4} mbar. Gold was sputtered for 2 min at a coating current of 25 mA from a target located 60 mm away from and 4 cm above the sample. The gold-coated pyrite electrode was pre-treated at a certain polarization potential in a deoxygenated solution containing copper cyanide at pH 7 for 10 min under stirring at 50 rpm/m, and then transferred to the spectrometer chamber for measurements under nitrogen protection.

3. Results

This research started with understanding the copper adsorption on pyrite surfaces in the copper cyanide solution with CN/Cu = 2/1 at different polarization potentials. The reaction taking place on pyrite surfaces were studied by cyclic voltammetry, the reaction products formed were determined by surface-enhanced Raman spectroscopy and the properties of the surface layer structure as a result of copper adsorption was analyzed by electrochemical impedance spectroscopy. Then how Cn/Cu ratios affected the copper adsorption on pyrite surfaces was investigated.

3.1. Copper adsorption on pyrite surfaces at CN/Cu = 2/1

3.1.1. Cyclic voltammetry

The voltammogram of the untreated pyrite electrode exposing to the background solution at pH 7 is shown in Fig. 1(a). The anodic peak A1 commencing at −0.27 V is due to the intermediate oxidation of pyrite through Eq. (1), (2) or (3) (Buckley and Woods, 1987; Hamilton and Woods, 1981; Yoon et al., 1991).

$$FeS_2 + 3H_2O \rightarrow Fe(OH)_3 + 2S^0 + 3H^+ + 3e^- \quad (1)$$

$$nFeS_2 + 3(n-2)OH^- \rightarrow 2FeS_n + (n-2)Fe(OH)_3 + 3(n-2)e^- \quad (2)$$