

Electrochemical and spectroscopic studies of pyrite–cyanide interactions in relation to the depression of pyrite flotation



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ARTICLE INFO

Article history:

Received 5 December 2015

Revised 25 February 2016

Accepted 1 March 2016

Available online 7 March 2016

Keywords:

Pyrite

Flotation

Free cyanide

Depression

Surface reaction

Redox potential

ABSTRACT

Cyanide is the most commonly used depressant to reject pyrite as a gangue mineral at alkaline pH in differential flotation. However, the depression mechanism of cyanide still remains uncertain. The depression effect has been proposed as the preferential adsorption of cyano species on pyrite, which has, however, not been confirmed experimentally. It is also believed that cyanide inhibits the chemisorption of thiol collectors due to the decrease of surface redox potential. In order to clarify the controversial depression mechanisms, the interactions between pyrite and cyanide at pH 10 were investigated in this study. Preferential adsorption of cyanide on pyrite rather than the decrease of surface redox potential was determined to be the depression contributor. Surface cyanoferric species were identified, both electrochemically and spectroscopically, on pyrite surface in the presence of cyanide, inhibiting the oxidation of pyrite and the oxidation/chemisorption of xanthate. This study provides new insights into the depression of pyrite flotation by cyanide.

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1. Introduction

Pyrite is the most abundant sulfide mineral which requires being separated from other base metal sulfide minerals in differential flotation. The chemistry for pyrite flotation and depression was reviewed by Ball and Rickard (1976). In general, pyrite flotation and depression strongly depend on pH. Pyrite is normally hydrophobic at mildly acidic pH (2–5.5), and partial recovery of pyrite can also be achieved with increasing the pH up to alkaline region (7.5–11) despite hydrophilic oxy-hydroxide coating on the surface (Wang et al., 1989). Cyanide can significantly depress pyrite flotation using thiol collectors (Grano et al., 1990; Guo et al., 2015; Hodgkinson et al., 1994). The depression of pyrite flotation by cyanide is more effective with increasing pH due to an increasing amount of alkali ions (OH⁻) and dissociated cyanide ions (CN⁻) (Sutherland and Wark, 1955; Wark, 1938). The electrochemical activities including the oxidation and chemisorption of thiol collectors which are essential for the establishment of hydrophobic surface of pyrite are inhibited by cyanide at alkaline pH (Janetski et al., 1977; Prestidge et al., 1993). It has also been reported that the depression effect of cyanide is more effective when it is added prior to the addition of collectors (Prestidge et al., 1993).

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Despite a number of studies, the depression mechanism of cyanide on pyrite flotation at alkaline pH still remains uncertain. There are two prevailing mechanisms proposed according to the literature review by Guo et al. (2014). Firstly, cyanide was proposed to preferentially adsorb on pyrite surface as hydrophilic iron cyanide compounds, inhibiting the subsequent formation/adsorption of hydrophobic species (Wang and Forsberg, 1996). Wang and Forsberg (1996) proposed that soluble iron-hexacyanide complexes Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻ dominated at neutral to alkaline pH in Fe–CN–Xanthate–H₂O system based on their thermodynamic calculations. However, the adsorption of cyanide on pyrite surface has not been successfully confirmed by experimental methods either spectroscopically (Prestidge et al., 1993), or electrochemically (Janetski et al., 1977; Wet et al., 1997).

In addition, the flotation of pyrite is only significant at a redox potential above a critical value which enables the chemisorption of thiol collectors. The chemisorption of typical collector, xanthate, on pyrite surface is a kinetic control process with charge transfer (Buckley and Woods, 1977). The oxidation of xanthate to dixanthogen on pyrite surface occurs above the reversible potential of xanthate/dixanthogen couple which may be slightly higher than that for its chemisorption (Buckley and Woods, 1977; Janetski et al., 1977; Leppinen, 1990). The decrease of redox potential on pyrite surface was generally observed as a result of cyanide addition to flotation pulp (Wet et al., 1997; Kocabag and Guler, 2007;

Woods, 1972; Hodgkinson et al., 1994). For example, the potential recorded on pyrite electrode decreased from 195 mV to 125 mV (SHE) with the addition of 200 mg/L NaCN at pH 11, at which pyrite recovery from the flotation decreased from 90% to 10% (Wet et al., 1997). Based on these observations, the depression mechanism of cyanide was also proposed as the decrease of surface redox potential, inhibiting the chemisorption of thiol collectors (Kocabag and Guler, 2007; Woods, 1972). However, few studies have been conducted to correlate the chemisorption of xanthate with the decrease of redox potential associated with the addition of cyanide.

In this study, electrochemical and spectroscopic measurements were applied to investigate the interactions between cyanide and pyrite. It is observed that alkaline flotation pH is typically used in plants when cyanide occurs in process water. Therefore, this investigation was carried out at pH 10 which is also in line with the previous study (Guo et al., 2015). Ultimately, the underpinning mechanism of cyanide in depressing pyrite flotation using xanthate as collector was determined.

2. Experimental methods

2.1. Electrochemical measurements

A hand-picked natural massive cubic pyrite specimen of a high purity originating from Spain was used as the working electrode. Energy Dispersive Spectroscopy (EDS) analysis showed 66.35 at.% sulfur and 33.17 at.% iron with minor carbon contamination. XRD analysis also showed little impurities of the pyrite specimen. The pyrite electrode was connected with a copper wire using a silver-loaded conducting epoxy, and then mounted into a non-conducting epoxy resin exposing only one side with a geometric surface of approximately 0.25 cm².

A conventional three-electrode system was employed for the electrochemical measurements. A platinum plate with a surface area of 1 cm² 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 +0.194 V against a standard hydrogen electrode (SHE) (Bates and MacAskill, 1978). A Radiometer PGZ100 potentiostat was used in combination with a Frequency Response Analyzer (FRA). Open circuit potential (OCP), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed in solution with a volume of 200 mL at room temperature in the absence and presence of 0.1 mM PAX (potassium amyl xanthate) and 0.1 mM NaCN, individually and in combination. The background electrolyte was 0.1 M potassium perchlorate (KClO₄) solution and the pH was adjusted to 10 with 1 M KOH solution. All solutions were made with AR grade chemicals and de-ionized (DI) water, and purged with nitrogen for 30 min prior to each experiment. The electrochemical measurement system was sealed to prevent the possible return of oxygen.

A fresh electrode surface was generated before each experimental run by wet abrading with silicon carbide abrasive paper (1200 grits), following the procedure published in the literature (Hicyilmaz et al., 2004). The potential scan rate was 20 mV s⁻¹ for all cyclic voltammetry measurements. The variations in the current were recorded as a function of scan potential and reported as current density. The alternating current (AC) voltage (amplitude) for EIS was 10 mV. The initial and final frequencies were 10^{-1.5} Hz and 10⁴ Hz, respectively, with a frequency per decade as 5. Typically, the working electrode surface was allowed to react with chemicals for 5 min at the desired potential or, if necessary, until a steady state current was observed, after which the EIS was obtained. The good reproducibility of the electrode pretreatment and electrolyte preparation was confirmed by carrying out measurements in separate solutions.

2.2. Surface enhanced Raman spectroscopy measurements

Raman spectroscopy measurements were conducted on 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 spectral resolution of 2.7 cm⁻¹. The laser and scattered radiation were focused through the spectrometer objective with a long working distance. The laser spot size was measured at ~1.3 μm with power at the sample measured at 6 mW. Spectra were collected for 10 s × 20. Raman spectra were calibrated using the 520 cm⁻¹ silicon band.

Recently, surface enhanced Raman scattering (SERS) techniques have been extended to enable the observation of collector adsorption on sulfide surface which has been decorated with a sputtered film of gold (Hope et al., 2007). This highly sensitive technique is very promising to detect the possible modification of pyrite surface interacting with cyanide. In order to achieve the enhanced Raman signal, the surface of pyrite electrode was sputtered with fine gold (99.5% Au) using K550X sputter coater. The specimen was placed in a chamber that was then evacuated to a vacuum of 10⁻⁴ mbar. The pyrite electrode was transferred to the chamber in a nitrogen box to minimize oxidation. Gold was sputtered from the target of 60 mm Dia × 0.1 mm located 4 cm away from the sample for 2 min at the coating current of 25 mA. Then a drop of 0.1 mM NaCN solution at pH 10 was placed on the electrode surface for Raman spectroscopy measurements.

3. Results and discussion

3.1. The effect of cyanide on pyrite-xanthate interactions

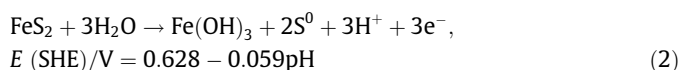
In the previous study, it was found that pyrite flotation was completely depressed by only 10 ppm cyanide at pH 10 (Guo et al., 2015). The cyanide anion in aqueous solution forms hydrocyanic acid according to the following dissociation reaction (Marsden and House, 2006).



The logarithmic exponent of the dissociation constant pK_a of HCN at 25 °C is 9.21 (Lu et al., 2002). The cyanide concentration indicated in the present paper refers to total cyanide including a portion of HCN. However, the effects of HCN and CN⁻ was not distinguished in the present work. In this section, the electrochemical behavior of pyrite exposed to xanthate and/or cyanide solution was studied with an emphasis on the response of pyrite surface to a variation of redox potential.

3.1.1. CV measurements

The effect of 0.1 mM NaCN and/or 0.1 mM PAX on the voltammograms of pyrite electrode at pH 10 is shown in Fig. 1. PAX and NaCN were added individually or simultaneously with the electrode being potentiostated at -550 mV. Then the voltammogram was recorded in a positive-going direction and only the second cycles of voltammograms are illustrated in Fig. 1. Peak A1 on the positive-going sweep as shown in Fig. 1a is attributed to the oxidation of pyrite. The oxidation products in the form of ferric hydroxide and a monolayer of elemental sulfur in alkaline media were proposed by Hamilton and Woods (1981) based on an electrochemical study. Their conclusion was also supported by Chernyshova (2003). The surface reaction is shown in Eq. (2).



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