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Effect of Fe-Ions on Pyrite-Xanthate Interaction in Chemically Manipulated Electrochemical Conditions

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ABSTRACT

The effect of ferrous and ferric ions on pyrite-xanthate interaction was investigated with contact angle measurements and UV-visible spectroscopy studies. Experimental works were conducted in chemically manipulated electrochemical conditions between 0-500 mV potential ranges. $KMnO_4$ and $Na_2S_2O_5$ were used to manipulate potential as oxidizing and reducing agents, respectively. Xanthate improved hydrophobicity of pyrite due to coverage of mineral surface with dixanthogen, but the contact angle decreased with the addition of ferrous and ferric ions. Pyrite displayed hydrophobic property in mild to moderately oxidizing conditions, whereas lower contact angle values were obtained at higher potentials due to the increase in the number of hydrophilic sites on the surface both in the absence and presence of xanthate and Fe-ions. UV spectroscopy study and contact angle measurements proposed that although the ferric hydroxy xanthate complex species could form at highly oxidizing potentials, the main hydrophilic species inhibiting the collector adsorption would be ferric oxyhydroxides in pyrite-xanthate system in the presence of ferric and ferrous ions.

Key Words: Pyrite; Flotation reagents; Redox reactions; Potential control

INTRODUCTION

Pyrite, FeS_2, is the undesired gangue part of most complex sulfide ores. Various surface active agents are used to separate valuable sulfide minerals selectively from pyrite by changing their surface properties in the flotation of these ores. Xanthate is the most commonly employed collecting agent of sulfide flotation systems due to its powerful collecting ability. To satisfy selectivity and depress pyrite, high conditioning pH, long conditioning time and, therefore, extensive surface oxidation are usually required in the flotation with xanthate [1]. However, traditional application may not be enough for a commercially efficient separation due to the similar surface properties of sulfide minerals. Therefore, for a few decades, a great interest has focused on the electrochemistry of pyrite flotation due to its semiconducting property.

There has been consensus on the adsorption of xanthate on pyrite in dixanthogen form in alkaline conditions. Since, pyrite has a rest potential greater than the reversible potential of xanthate/dixanthogen couple. Therefore, pyrite surface behaves as a catalyst promoting the anodic and cathodic reactions [2-5]. Kuopanportti et al [6] identified that O_2 increased pulp potential and reduced xanthate concentration based on UV-visible spectroscopy. Guo and Yen [7] manipulated surface potential of chalcopyrite potentiostatically and observed the adsorption peaks of dixanthogen at 241 nm and 286 nm indicating the coverage of mineral surface with dixanthogen. Jiang et al [8] stated that Fe ions reduced the floatability of pyrite with xanthate in neutral and mildly alkaline conditions, which was related with ferric hydroxy xanthate compounds. Fuerstenau et al [9] suggested the pyrite depression with ferrous ions which reduced pulp potential and then inhibited dixanthogen formation on the mineral surface.

Pyrite-xanthate interaction has been investigated extensively, especially at rest potential, but the research works on the role of redox conditions on xanthate adsorption are restricted. In this study, role of ferrous and ferric ions on the electrochemistry of pyrite-xanthate interaction was investigated in chemically manipulated redox condition under atmospheric environment. UV-visible spectroscopy and contact angle measurements were the tools.

EXPERIMENTAL

Samples

Experimental works were performed by using pyrite crystals from Artvin-Murgul deposits of Black Sea Copper Works, Co., Turkey. UV-visible spectroscopy and contact angle measurements were conducted in pH 9.2 buffer solutions (0.05 M $Na_2B_4O_7$) except stated otherwise. Pulp potential (Eh) was adjusted chemically with $KMnO_4$ and $Na_2S_2O_5$ to oxidizing and reducing potentials, respectively. Potassium amyl xanthate (KAX) was examined as collecting agent, while $FeCl_2.7H_2O$ and $FeCl_3.7H_2O$ were used as sources of ferrous and ferric ions, respectively.

Contact Angle Measurements

Contact angle measurements were performed in an electrochemical cell (Figure 1.a) containing working and reference electrodes by using a goniometer made in our laboratory. Goniometer (Figure 1.b) works as follows: number 1 handle allows left-right positioning of the cell; number 2 shaft permits the adjustment of the height of the cell platform; the spring mechanism, composed of four tension springs, under the cell platform provides leveling adjustment of the cell; height of the camera can be adjusted with the number 3 shaft.

Contact angles were photographed by a Nikon Coolpix995 camera and read by using MB-Ruler 3.3 software program (http://www.markus-bader.de/MB-Ruler) as shown in Figure 2. Contact angle (θ) is read from the photographs directly from left side of the bubble ($\theta=\alpha$) or from the right side as $\theta=180-\alpha$.

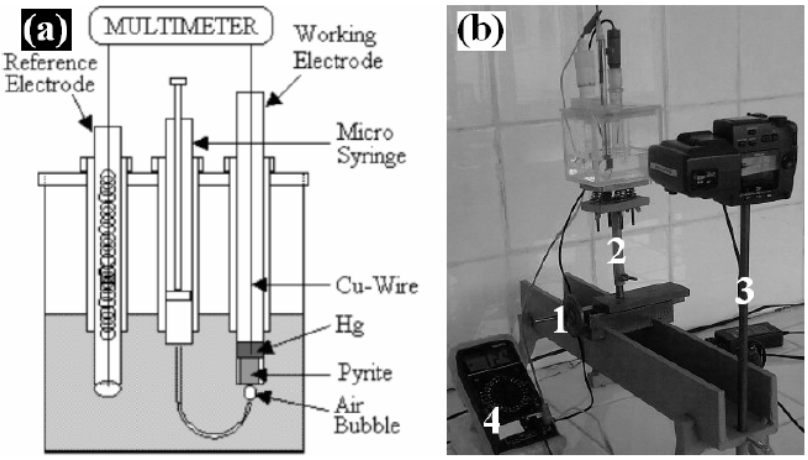

Figure 1. a) Electrochemical cell and b) goniometer for contact angle measurements

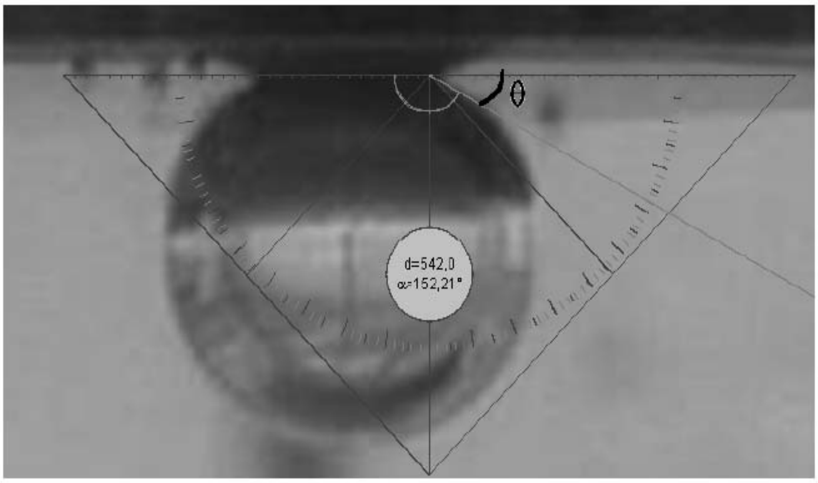

Figure 2. The measurement of contact angle from photograph

Working electrode was constructed from a pyrite crystal as described previously [10-11]. Pyrite working electrode was polarized for 10 minutes prior to each measurement. Redox potential of pyrite electrode was recorded with a multimeter (number 4 in Figure 1.a) using a saturated calomel electrode as a reference electrode. However, redox potentials were given in the standard hydrogen electrode (SHE) scale by adding 245 mV to measured values. Surface of working electrode was renewed polishing by 800-grit SiC paper and then by 1 µm diamond paste before each run.

UV-Visible Spectroscopy Measurements

Pyrite crystals were ground for 15 minutes in a ceramic mortar prior to UV-visible spectroscopy measurement. Then, sample was polarized at investigated experimental conditions. During polarization, potential was adjusted chemically and measured with a pH-meter using a Ag-AgCl ORP electrode. Potentials were converted to the standard hydrogen electrode (SHE) scale by adding 205 mV to measured values. 3 ml aliquot of supernatant liquid was withdrawn after the conditioning for 2, 5, 10 and 30 minutes, and centrifuged using Hettich Universal 16A model centrifuging apparatus. The clarified aqueous solution was put in a standard 10 mm light path quartz cuvette for UV spectroscopy analysis. UV spectra were obtained over a wavelength range of 190-400 nm using Shimadzu UV-1601 UV-visible spectrometer.

RESULTS AND DISCUSSIONS

Sulfide flotation has traditionally been applied in alkaline condition to satisfy the selectivity against pyrite. Since the oxidation of Fe-ions forms Fe-hydroxy species at alkaline pHs [12], which cover pyrite surface and reduce floatability [3,13]. Therefore, the role of pH on the hydrophobicity of pyrite was examined first (Figure 3). Both redox potential and contact angle decreased at higher pHs. The change of redox potential both in the absence and presence of xanthate is proportional to each other in the examined pH range. Xanthate caused a slight reduction in the rest potential [4]. This slight reduction in the surface potential towards cathodic values could be explained with the electrochemical behavior of xanthate in pyrite-xanthate system in alkaline condition: mineral surface (0.220 V) is more anodic as compared with the equilibrium potential of xanthate/dixanthogen couple (-0.159 V) which is 0.078 V for 10^{-4} M xanthate [14]. Therefore, pyrite surface behaves as catalyst, and the formation of dixanthogen would be expected from the thermodynamic considerations [2,5,15].

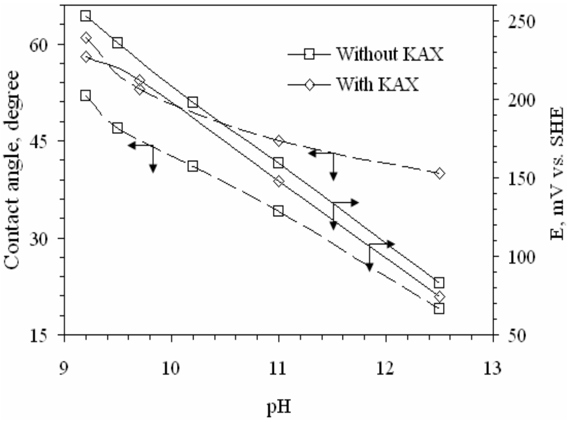

Figure 3. Role of pH on the contact angle and potential of pyrite in the absence and presence of 10^{-4} M KAX

On the other hand, contact angle data displayed different trend: in collectorless condition, contact angle decreased linearly by increasing pH while xanthate resulted in a considerable increase in the hydrophobicity of pyrite at highly alkaline pHs. Initial step in pyrite oxidation is the release of ferrous ions, and then formation of hydrophilic ferric species in addition to the exhibition of hydrophobic elemental sulfur (S°) and polysulfides as metastable phases, which form hydrophilic sulfate species as stable phase at longer conditioning period. Increase in the alkalinity resulted in extensive coverage of mineral surface with hydrophilic species [3-4,16-17] and reduced the contact angle.

In the presence of xanthate, contact angle values and therefore hydrophobicity improved in all the examined pH range as compared with the collectorless condition due to the increase in the number of sites covered by hydrophobic collector species [16]. There is always a competition on the adsorption of hydrophobic xanthate species and hydrophilic ferric species: stability of ferric species increases at higher pHs and inhibit xanthate adsorption on pyrite, and then, contact angle decreased [4,18-19]. The decrease is not considerable at highly alkaline pHs, which could be due to the formation of perxanthate by oxidation of xanthate or by decomposition of dixanthogen with hydroxide [20-21].

Fe ions may behave as potential controlling agent or as a modifier. Therefore, effect of ferrous ion concentration on the hydrophobicity and electrochemical behavior of pyrite was also investigated (Figure 4). Ferrous ions behaved as reducing agent at all pHs and caused a slight decrease in the surface potential of pyrite. This change in the potential increased with the increase of Fe^{+2} ion concentration and became considerable in the presence of 10^{-3} M Fe^{+2}. In the absence of ferrous ions, increase in the alkalinity affected the hydrophobicity adversely, and contact angle decreased linearly. Fe^{+2} ions decreased contact angle in mild to moderately alkaline conditions. Ferrous ions are not stable in alkaline condition and oxidize to hydrophilic ferric hydroxide, which has lower solubility, so, precipitate on mineral surface [3,5,10,22]. Similar results, however, were obtained with and without Fe^{+2} in highly alkaline conditions, because ferrous ions, added or formed by the oxidation of mineral surface, oxidize to ferric species and cover the pyrite surface with stable hydrophilic species.

The role of chemically manipulated electrochemical condition on the hydrophobicity of pyrite was investigated at different collector concentrations as shown in Figure 5. Pyrite has remarkably high contact angle values in mild to moderately oxidizing potentials. Contact angle decreased at higher potentials. Effect of xanthate could not be observed at lower collector dosages in mild to moderately oxidizing conditions. Improvement in the hydrophobicity was clearly observed in the presence of 10^{-4} M xanthate in the examined potential range.

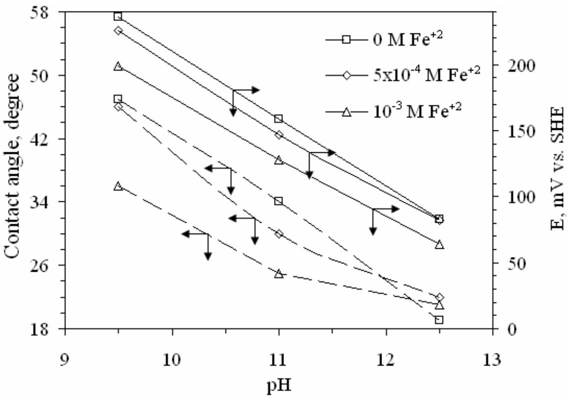

Figure 4. Role of Fe^{+2} ions on the contact angle and potential of pyrite in the absence and presence of 10^{-4} M KAX

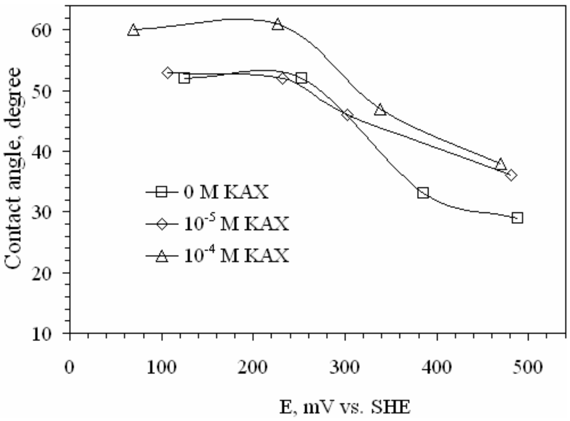

Figure 5. Role of KAX concentration on the hydrophobicity of pyrite at pH 9.2

Initially, oxidation of pyrite forms ferrous ions and polysulfides in alkaline pH producing a metal deficient surface. This iron deficient polysulfide rich surface improves the hydrophobicity in mild to moderately oxidizing potentials. But, Fe^{+2} ions are not stable at higher potentials, and precipitate as hydrophilic ferric oxyhydroxides and cover the mineral surface, which inhibit the hydrophobic effect of polysulfides [5,22]. In the presence of xanthate, similar trends were observed between contact angle and surface potential compared with collectorless condition: xanthate improved the hydrophobicity of pyrite and reduced hydrophilic effect of surface oxidation products of mineral in mild to moderately oxidizing conditions. However, reasonable decrease at higher potentials was also seen in the presence of xanthate, which was attributed to the increased stability of ferric species [4].

Xanthate is a most commonly employed thiol collector due to its strong collecting ability. But its selectivity is low. Therefore, various modifying agent have generally been used in the flotation of complex sulfide ores with xanthate to improve the selectivity.

In the present study, the effects of ferrous and ferric ions on pyrite-xanthate interaction were investigated in chemically manipulated electrochemical conditions (Figure 6). Contact angle values were obtained in the presence of 10^{-4} M xanthate with/without Fe ions. Both ferrous and ferric ions inhibited collector adsorption on mineral surface and reduced the hydrophobicity. Adverse effect of ferric ions became predominant at mildly oxidizing potential, whereas hydrophilic effect of ferrous ions was slightly higher in moderately oxidizing condition. They displayed similar behavior at highly oxidizing potentials, because under these conditions, ferrous ions oxidize to ferric ions, so xanthate affinity towards pyrite decreases in the presence of Fe-ions due to the formation of hydrophilic ferric hydroxy species [5].

Role of ferrous and ferric ions on xanthate adsorption was also investigated with UV-visible spectroscopy. Pyrite sample was polarized in a cell open to the atmosphere. Polarization from rest potential to reducing condition was conducted with $Na_2S_2O_5$, and to oxidizing environment with $KMnO_4$. Figure 7 shows the solution concentration of xanthate ion after a certain polarization period. The highest adsorption density was observed in the absence of iron ions in oxidizing conditions. However, contact angle values gave the lowest hydrophobicity results in the worked experimental conditions. Hydrophilic complex Fe-xanthate compounds, such as $Fe(OH)X_2$, would be the cause of low contact angle values at highly oxidizing potentials under mildly alkaline pHs [8,23-24]. Effect of ferrous ions on xanthate adsorption on pyrite surface is not distinguishable except the results obtained at highly oxidizing potential. On the other hand, ferric ions hindered xanthate-pyrite interaction and reduced collector adsorption. Therefore, it can be conclude that the main mechanism for the decrease in contact angle was the inhibition of xanthate adsorption due to rigorous coverage of mineral surface with hydrophilic ferric oxyhydroxides instead of the formation of hydrophilic Fe-xanthate complexes [2-3].

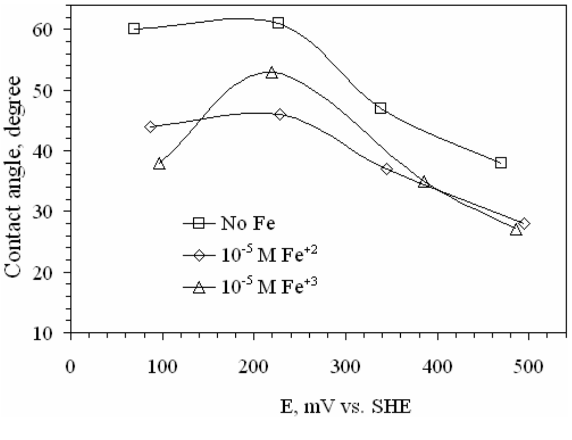

Figure 6. Role of Fe-ions on the hydrophobicity of pyrite with 10^{-4} M KAX at pH 9.2

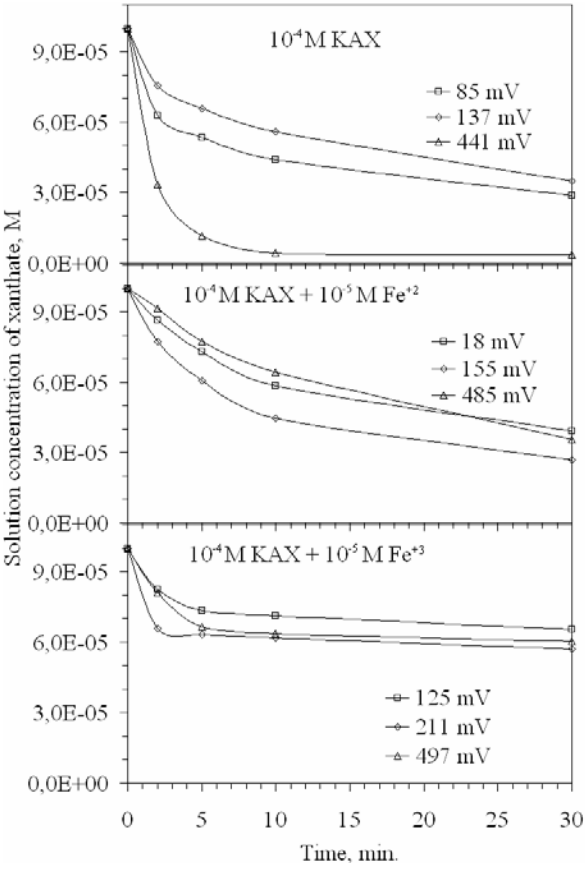

Figure 7. UV-visible results of xanthate-pyrite interaction in the absence and presence of Fe ions in chemically manipulated electrochemical condition

CONCLUSIONS

In the present work, role of chemically manipulated electrochemical condition and Fe ions (Fe^{+2} and Fe^{+3}) on pyrite-xanthate interaction was investigated with contact angle measurements and UV-visible spectroscopy studies. Xanthate improved hydrophobicity of pyrite due to coverage of mineral surface with dixanthogen, whereas ferrous and ferric ions decreased contact angle. Maximum contact angle values were obtained around 100-200 mV.

On the other hand, hydrophobicity decreased at highly oxidizing potentials due to the coverage of pyrite surface with stable hydrophilic ferric species, which were the oxidation products of preferentially dissolved ferrous ions from mineral surface or added Fe ions into the solution. UV spectroscopy study suggests that although the ferric hydroxy xanthate complex species formed at highly oxidizing potentials, the main hydrophilic species inhibiting the collector adsorption could be ferric oxyhydroxides in pyrite-xanthate system in the presence of ferric and ferrous ions.

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