IMPACT OF OVALBUMIN ON PYRITE FLOTATION IN THE ABSENCE AND PRESENCE OF METAL IONS

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Abstract: Recovery of gangue pyrite and its accidental activation are vital issues in flotation of complex sulfide ores. This work was performed by cyclic voltammetry (CV) and flotation tests to elucidate applicability of ovalbumin (OVA) as depressant for pyrite. The synergetic effect of metal ions in addition to its possible use in case of accidental activation by metal ions. CV tests stated that OVA adsorbed irreversibly on pyrite, and restricted electron transfer up to moderately oxidizing potentials due to electrostatic interaction together with weak hydrophobic interactions. At highly oxidizing potentials, adsorption occurred through electrochemical mechanisms through formation of metal-OVA chelates. Rate of pyrite depression with OVA was found to be potential dependent reaching its peak point around moderately oxidizing potentials both in absence and presence of metal ions. Electrochemically active metals display synergetic effect with OVA on pyrite depression, whereas noble metals activate pyrite and reduced depressing potency of OVA.

Keywords: *pyrite, ovalbumin, metal ion, flotation, redox potential*

Introduction

Pyrite (FeS_2) is the most widespread sulfide mineral in earth crust. It is the major gangue of most sulfide ores and is rejected in flotation processes. Flotation practices revealed that there is a potential problem arising from concentrate dilution with recovery of gangue-pyrite in froth even in alkaline pulp due primarily to accidental activation. Its hydrophobization may result from dissolved metal ions from constituent of ore, and/or intentionally used ions as modifying agent to satisfy selectivity (Chandra and Gerson, 2009). Commonly encountered metal ions in flotation pulps are Cu^{+2}, Pb^{+2} and Fe^{+2}. First two of them may come from constituent of ore in addition to

intentionally added ones to improve selectivity, while a comminution circuit is major source of Fe^{+2}. Iron ions significantly depress ore-pyrite from neutral to mildly-alkaline pHs (Jiang et al., 1998). Activation by Cu-ions occurs through direct adsorption instead of one-to-one exchange with lattice. Cu^{+2} ions reduce into Cu^+ on pyrite by reducing components chiefly coming from grinding circuit and new Cu^+-sulfide phase forms (Weisener and Gerson, 2000; Chandra and Gerson, 2009). Similarly, activation by Pb^{+2} ions does not obey exchange with lattice cation. Lead activation occurs by deposition of dissolved or precipitated lead oxidation species on pyrite. In contrast to Cu^{+2}-activation, electrochemical potential was found to have no effect on pyrite activation by Pb^{+2} ions (Peng et al., 2012).

Various inorganic agents were used as pyrite depressant despite environmental concerns. Their consumptions have increased day by day due to need to process more complex and lower grade ores. However, selectivity has still remained as significant problem. By the time, researchers engaged more on the use of environmentally-friendly organic depressants as a result of strict environmental regulations and necessity to process low grade complex ores at low cost. However, ovalbumin (OVA) has not taken enough interest as a modifying agent in spite of being a good candidate as an adsorbent of metal ions (Maruyama et al., 2007).

OVA is a chicken egg protein having a molecular weight of 45000 g/mol. It is composed of amino acid subunits forming backbone structure and sidechains. The backbone structure contains 385 amino acids having carboxyl (–COOH) and amine (–NH$_2$) groups. The chemical structure and elemental constituent of sidechains of amino acids determine protein type. OVA exhibits electrochemically active behavior in aqueous environment due to presence of one disulfide (S-S) in cystine and four sulfhydryl (-SH) bonds in cysteine groups in sidechains (Fothergill and Fothergill, 1970).

Investigations on the use of OVA in mineral processing are limited. Bastrzyk et al. (2008) separated magnesite from quartz with anionic collector by using OVA as modifier. Guler et al (2013) emphasized importance of redox potential on OVA-pyrite interaction based on FTIR spectroscopy and cyclic voltammetry (CV). Ying et al (2004) stated that adsorbed albumin was stable on Au at potential range −200+600 mV, and could partly block redox reactions. Liu et al. (2006) attributed cysteine adsorption on pyrite to chemical interaction. Rojas-Chapana and Tributsch (2001) explained cysteine-pyrite interaction with disulfide formation between sulfhydryl groups of cysteine and free-SH groups from pyrite.

Since OVA is easily suppliable, abundant and cheap in addition to its affinity to interact with heavy metals depending on redox condition, its use as an environmentally friendly depressant with metal ions has rather not been considered yet. This work was made to elucidate impact of electrochemical condition on pyrite depression with OVA in absence and presence of metal ions by CV and flotation tests.

Experimental

Pyrite sample was supplied from Artvin-Murgul deposits in Turkey. Chemical and mineralogical analysis showed that pyrite was highly pure (>98% FeS_2) and major impurity was quartz. Mineralogical analysis was made by Bruker D8 Advance X-ray diffractometer. Pyrite was ground in a ceramic mill for flotation tests, sized (-212+75 µm) and stored in glass tubes under nitrogen atmosphere to eliminate surface oxidation.

Tetraborate (0.05 M $Na_2B_4O_7 \cdot 10H_2O$) buffer solution (pH 9.2) was used in experimental works. O_2 content of buffer was reduced down to 1 ppm by intensive bubbling of nitrogen (>99.998% N_2) for at least 15 minutes. It was controlled by a YSI-5100 oxymeter. $CuSO_4 \cdot 5H_2O$, $Pb(NO_3)_2$ and $FeCl_2 \cdot 7H_2O$ were used as sources of Cu^{+2}, Pb^{+2}, Fe^{+2} ions. Highly pure OVA (98%) supplied by Merck was tested as the environmentally-friendly organic modifier. Metal ion concentration was applied as 10^{-4} M and 250 g/Mg in CV and flotation tests, respectively. A 500 ppm of OVA in CV tests and 50 g/Mg in flotation study was used.

Three-electrode system cells were used in polarization works. Calomel electrode and Pt-foil were used as reference and counter electrodes, respectively. The working electrode was Pt-wire (150 cm) for flotation tests mounted to inner side of cell, while it was a shaped pyrite crystal in CV setup. Electrochemical works were performed using Gamry PCI-750 potentiostat and PHE-200 Physical Electrochemistry software of Gamry Co. Flotation tests were carried out in a specially designed closed cell system (Güler et al., 2013). Polarization was applied potentiostatically for 10 minutes, and then, froth was collected for 5 minutes.

Results and discussions

Pyrite reacts with surroundings in aqueous medium due to its semiconducting property, and surface state is established through electrochemical mechanisms in addition to possible chemical reactions. Electrochemistry of pyrite is a well-documented issue. Pyrite oxidizes first to release Fe^{+2} and S° (Ekmekci and Demirel, 1997). Fe^{+2} ion is not stable, and oxidizes to form ferric oxy-species at higher potentials, which reduces to ferrous hydroxides at lower potentials during cathodic scan. Fe^{+2}/Fe^{+3} redox of iron hydroxides drew distinctive oxidation (A1) and reduction (C1) peaks on pyrite voltammogram (Fig. 1a). Peak A2 arose chiefly from oxidation of S° to sulfate. Further oxidation of pyrite surface to Fe^{+3}-oxyhydroxides, and decomposition of H_2O to release O_2 did also contribute to charge transfer, which shaped peak A2. Oxidation products were reduced in cathodic scan, and increased current flow at lower potentials. Therefore, size of C1 ($Q_{C1} = 821$ µC) was greater than that of A1 ($Q_{A1} = 615$ µC) (Güler et al., 2013).
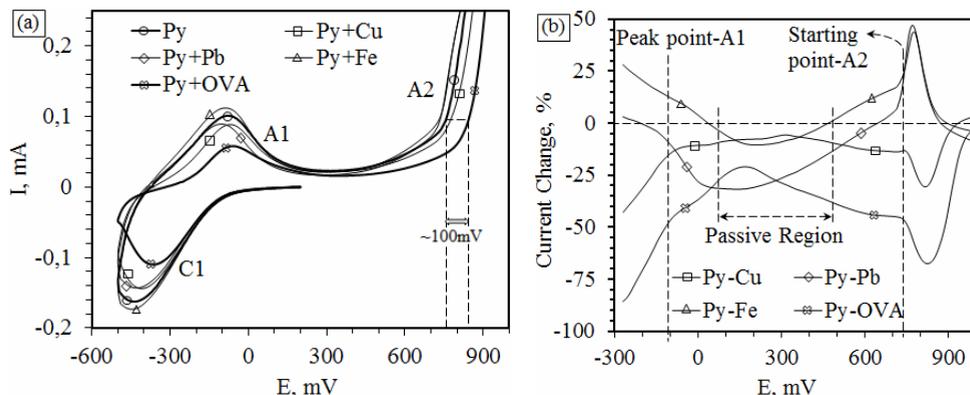
Fig. 1. Effect of metal ions and OVA on (a) electrochemical behavior of pyrite,
and (b) percentage change in anodic current respons of pyrite electrode

Pyrite floatability curves were thought to be shaped by dominating surface hydroxy species in the examined range (Fig. 2). The recovery curve drew an arch-shape. It reached a plateau around 200 mV owing to formation of hydrophobic elemental sulfur S°, together with possible hydrophobic polysulfides. Self-induced floatability left at lower rates in moderate to highly oxidizing potentials due to presence of ferric-hydroxides and hydrophilic sulfoxy species while ferrous species and HS⁻ inhibited pyrite flotation at reducing potentials (Ekmekci and Demirel, 1997).
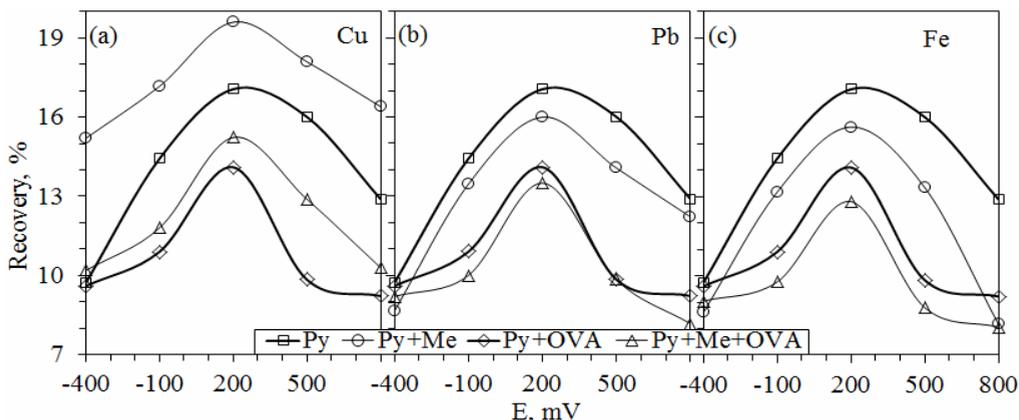
Fig. 2. Pyrite flotation in the absence and presence of metal ions (Me) and OVA

Electrochemistry of pyrite-metal ion interaction was investigated both in absence and presence of OVA. Examined metal ions were opted depending on abundance in sulfide ores, and their standard formation potentials $E°$. From the selected ions Fe ($E°$ for Fe^{+2}/Fe is –440 mV) is the most active one, while Pb ($E°$ for Pb^{+2}/Pb is –126 mV) is ready to oxidize around open circuit potential (OCP) of pyrite, and Cu ($E°$ for Cu^{+2}/Cu is 337 mV) is the most noble one.

Metal ions did not significantly alter pyrite voltammograms (Fig. 1a) except slight changes in current flow rate. Then, percentage variation in anodic current by metal ions with respect to reference value of bare pyrite was also considered (Fig. 1b). Positive values mean that modifying agents increase electron transfer rate, while negative ones show inhibition of charge transfer and passive layer formation. Electrochemical activity of pyrite was at minimal level in slight to moderately oxidizing potentials, in which region, amount of charge transferred was out of significance regardless of percentage magnitude of calculated value. Beyond this range, all the constituents affected current flow. Fe-ions displayed added-effect on the activity of Fe^{+2}/Fe^{+3} redox couple, and enhanced anodic current flow (Fig. 1). Depressing effect of Fe^{+2} ions became more predominant at oxidizing potentials. Since, number of surface sites covered by hydrophilic ferric species increased at higher potentials. Pb^{+2} ions adsorbed onto pyrite as Pb-complexes independent of applied potential. Adsorbed layer has porous structure (Nava et al., 2002; Güler, 2012), and does not inhibit anodic processes occurring on pyrite at moderate to highly oxidizing potentials. Therefore, Pb^{+2} ion also increased anodic current flow at moderate to highly oxidizing potentials. On the other hand, Cu-ions confined electron flow at changing rate among potential range. Potential icerased from reducing to slightly oxidizing values. Electrochemical activity increased on the surface. Redox processes completed at certain rate releasing ferric hydroxide and S°, at which point passivation by Cu^{+2} was significantly overcome (Fig. 1). Simultaneously, Cu-ions adsorbed on pyrite as hydrophobic CuS-like species and upgraded recovery. They are not stable at moderate to highly oxidizing potentials, and then Cu-hydroxides form on mineral surface. Hence, recovery started to decrease again at higher potentials with combined effect of ferric species and Cu-oxyhydroxides (Peng et al., 2012; Weisener and Gerson, 2000).

Isoelectric point of OVA is at pH 4.6 (Bastrzyk et al., 2008) and it has net negative charge at pH 9.2. Pyrite is also negatively charged in alkaline condition at OCP, which is around 200 mV at pH 9.2 (Kocabağ and Güler, 2008). Therefore, amount of adsorbed OVA on pyrite is expected to increase at positive potentials above OCP due to supply of more binding sites (Ying et al., 2004). OVA adsorption under reducing to slightly oxidizing conditions is also possible due to conformational changes in protein structure, which occurs at lower rates since OVA is hard protein (Nakanishi et al., 2001). OVA has electrochemically active sulfhydryl groups in addition to amine and carboxyl functional groups (Fothergill and Fothergill, 1970). These groups are anticipated to influence OVA-pyrite interaction related to potential.

Role of sulfhydryl residues on OVA-pyrite interaction did not appear on E-I spectrum up to about 750 mV besides passivation (Fig. 1). Since both OVA and pyrite have the same sign at lower potentials and around OCP, the passivation was not expected due to electrostatic repulsion. Therefore, the passivation would mainly be referred to irreversible adsorption of OVA during repeated cycling. The flotation results clarified role of OVA and passive layer formation (Fig. 2). Although weak

conformational changes in OVA molecule verified protein-pyrite interaction under OCP, electrostatic repulsion restricted the adsorbed amount (Ying et al., 2004). The monolayer coverage was thought to be satisfied at low OVA concentrations in slightly reducing condition due to large molecular size and side-on-type configuration (Liu et al., 2006). OVA loses only a small fraction of its secondary structure (α-helix) during adsorption on hydrophilic surface, which takes long time to reach equilibrium when conformational change or rearrangement of molecular structure occurs (Nakanishi et al, 2001). Moreover, collectorless flotation of pyrite was already achieved at its minimum value under reducing condition, and then electron blocking and depressing effect by electrostatic interaction could be only partially reflected on self induced floatability.

Figure 3 shows depression rate of pyrite with respect to applied potential drawn using experimental data:

$$Depression\ rate = (R_{M+Py} - R_{PY})/R_{PY},$$

where $R_{M+Pyrite}$ and R_{PY} are pyrite recovery with and without modifying agent(s), respectively. Hydrophobic redox products made pyrite more floatable around OCP, and reduced depressing effect of OVA (Figs. 2 and 3). Conversely, hydrophobic redox products may behave as tools for OVA adsorption through hydrophobic interaction in addition to weak conformational changes (Nakanishi et al., 2001; Bastrzyk et al., 2008; Güler et al., 2013). At moderately oxidizing potentials, OVA accumulation took place through ionic interaction between OVA and OH^- group of oxidized surface (Parida et al., 2006) and recovery drop reached peak point (Fig. 3). Effect of sulfhydryl groups became apparent at highly oxidizing potentials (Fig. 1). OVA shifted peak A2 to higher potentials, which was attributed to formation of metal-OVA chelate (Maruyama et al., 2007). OVA adsorption might also proceed through disulfide bond formation between sulfhydryl groups of OVA and –SH, oxidation product of pyrite (Rojas-Chapana and Tributsch, 2001). Although rate of recovery drop with OVA was significantly high at cited potentials, role of electrochemical interaction could not be clarified due to lower recovery values in collectorless condition both in absence and presence of OVA.

A combined effect of OVA+metal ions on electrochemical behavior of pyrite was given in Fig. 4. No peculiar peak did appear besides present ones. Instead, metal ions enhanced passivizing effect of OVA. The maximum passivation was observed with OVA+Fe^{+2}. The polarization potential *vs*. rate of pyrite depression curve for OVA+Fe^{+2} did also exhibit similar results (Fig. 3). In general, curves in Fig. 3 assumed an "M-shape" and two maxima appeared at -100 mV and 500 mV. Recovery drop decreased down to minimum point at about 200 mV between two maxima due to hydrophobization of pyrite surface. Since hydrophilic surfaces bound significantly more protein than hydrophobic ones due to less charged property of hydrophobic surfaces, and binding of protein to hydrophobic surfaces by unspecific hydrophobic and van der Waals interactions. Under OCP, where first peak appeared, both OVA and

pyrite were negatively charged. Metal ions served as bridging medium between OVA and pyrite through ion attachment to peptide chain leading to unfolding (Nakanishi et al., 2001; Jansson and Tengvall, 2004; Ying et al., 2004). Conversely, OVA is known to have high internal stability, and there would be significant electrostatic repulsion between OVA and pyrite in alkaline condition. So, OVA adsorption by bridging action of metal ions occurred in limited rate, which referred to limited pyrite depression with OVA+metal ion as seen in Figs. 2 and 3. Positive applied potential satisfied significant electrostatic interaction of OVA with metal-oxyhydroxides (Parida et al., 2006). Rate of pyrite depression reached its maxima, and almost kept on at higher potentials with negligible decrease.
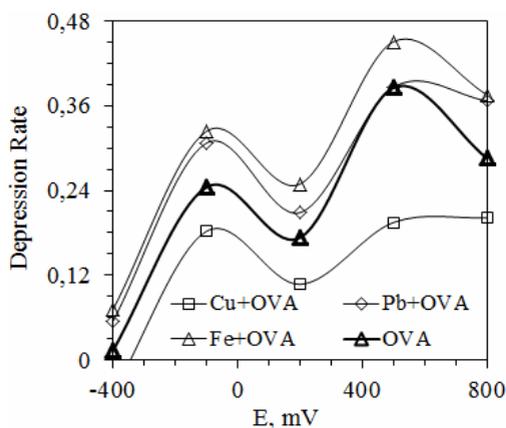
Fig. 3. Relationship between applied potential and depression rate
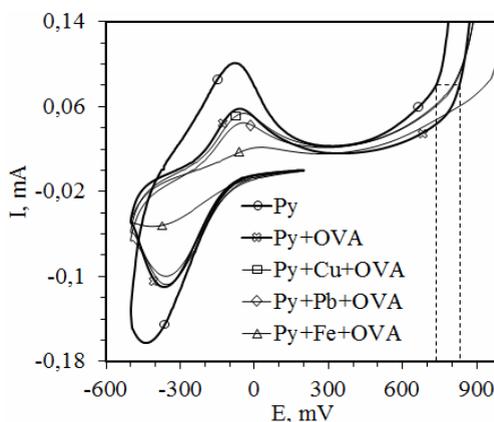
Fig. 4. Effect of modifying agents on voltammetric behavior of pyrite

Cu^{+2} ion activated pyrite (Fig. 2a) and reduced depressing potency of OVA from about 40% down to 20% at moderate to highly oxidizing potentials (Fig. 3). On the other hand, Pb^{+2} and Fe^{+2} exhibited synergetic effect with OVA except that depression effect of Pb^{+2} left at negligible rate in slight to moderately oxidizing potential range. Effect of metal ions on OVA-pyrite interaction was thought to depend mainly on their formation potentials. Then, impact of OVA on pyrite flotation was also depicted on contour maps concerning rate of pyrite depression with OVA+metal ion (Fig. 5a) and depression rate of metal-interacted pyrite with OVA (Fig. 5.b). In general, depressing effect of OVA+metal ion was in increasing order by applied potential, and a formed M-shape curve with peaks at slightly reducing and moderately oxidizing potentials almost for all E^o values. The curve for OVA from Fig. 3 was overlapped in Fig. 5a. This curve intersected E^o value of about 0 mV indicating that metal ion with positive E^o could not be applicable as depressant with OVA in pyrite flotation. Metal ions should have negative E^o to enhance depressing potency of OVA on pyrite, and flotation should be performed at moderately oxidizing potentials. The overlapped OVA curve did almost draw frontier line. More noble metals having positive $E°$

behave as activator, whereas more active metals with lower $E°$ depress pyrite. On the other hand, OVA was found to be effective in depressing activated pyrite with more noble metals almost only at highly oxidizing potentials (Fig. 5b). Depression rate of activated pyrite with OVA did also form a peak around slightly reducing potentials for noble metals. In case of flotation application at slightly reducing potentials, OVA might then be preferred as pyrite depressant.
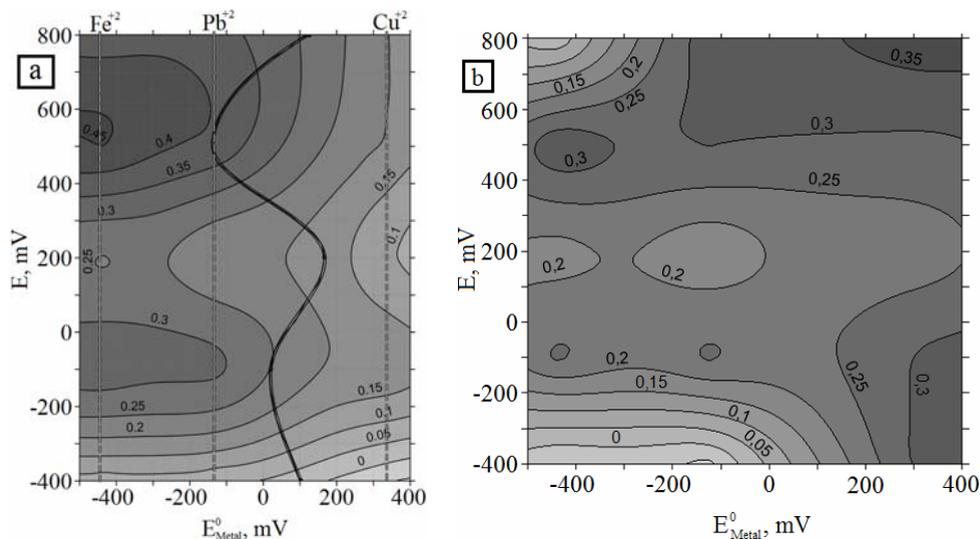
Fig. 5. Rate of recovery drop of (a) bare pyrite with the synergetic effect of metal ions and OVA, and (b) metal-interacted pyrite with OVA depending on standard formation potential of metal ion (E^0_{Metal}) and applied potential (E)

Conclusions

Adsorption and depressing effects of OVA on pyrite in absence and presence of metal ions were investigated by CV and flotation tests. The following conclusions can be drawn.

1) Flotation reached peak point around OCP of pyrite due to hydrophobization. Beyond this range, the hydrophilic redox products decreased pyrite recovery. Cu^{+2} activated pyrite, whereas Fe^{+2} exhibited depressing effect. Pb^{+2} did also depressed but at negligible rate.

2) OVA reduced flotation both in absence and presence of metal ions.

3) Pyrite depression with OVA can be controlled by applied potential. Electrostatic interaction as a result of conformational changes in OVA molecule, together with hydrophobic interaction, caused nearly insignificant depression in reducing to slightly oxidizing potentials. OVA adsorption through ionic interaction induced the maximum depression at moderately oxidizing potentials, which level was almost kept at highly oxidizing potentials due to formation of metal-OVA chelates.

4) Metal ions with more negative E° enhanced depressing potency of OVA, whereas those with positive E° could not be used as alternative depressant with OVA.

5) Activated pyrite with metal ions having positive E° can be depressed with OVA at moderate to highly oxidizing potentials. Reasonable depression might also be possible at slightly reducing condition.

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