Hydrophobicity of Galena with Ovalbumin and Dithiophosphinate in Relation to its Potential Response

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Abstract

This study was performed to elucidate the role of ovalbumin (OVA) on the hydrophobicity and potential response of galena in the presence of dithiophosphinate (DTPI). OVA was tested as environmentally friendly depressing agent due to its electrochemically active behavior in aqueous medium. Contact angle measurements were performed in a three-electrode system electrochemical cell in pH 9.2 tetraborate buffer solution. Experimental works revealed that galena exhibited certain degree of natural hydrophobicity. DTPI significantly improved galena hydrophobicity especially by the extended conditioning. In contrast, OVA reduced contact angle, even overcame the hydrophobicity impact of DTPI on galena. Potential measurements indicated that adsorption of both OVA and DTPI on galena was electrochemical process. They reduced potential response of galena electrode.

Keywords: galena hydrophobicity; dithiophosphinate; ovalbumin; potential response; conditioning time

Introduction

Galena is the main source of metallic lead. It has semiconducting property and can easily oxidize in electrochemically active flotation pulp medium. Most encountered problem related with the recovery of clean galena concentrate in the complex sulfide ore flotation circuits is the concentrate dilution with other associated minerals of galena. Since, base metal sulfides show similar electrochemical behavior, and their flotation is potential dependent process (Bogusz et al., 1997; Chandra and Gerson, 2009; Finkelstein, 1997). Selectivity has generally been achieved by inorganic modifying agents in spite of their several disadvantages like problems related to handling, high cost, toxicity resulting in poisoning and several environmental hazards (Bicak et al., 2007). Regardless, inorganic depressants consumption has been forced to increase day by day due to need to process more complex and lower grade problematic ores with acceptable recoveries to meet demand. Then, organic modifiers have taken great interest in last few decades to satisfy selectivity in flotation processes due to environmental concerns (Bicak et al., 2007; Chandra and Gerson, 2009; Guler et al., 2013, 2014; Laskowski et al., 2007; Pugh, 1989; Qiu, 2013). Ovalbumin (OVA) is an environmentally friendly cheap surface active modifying agent. It constitutes the major part of chicken egg white. It is a high molecular weight monomeric glycoprotein with a chemical composition having backbone structure and side-chains. Unit building block of OVA, amino acid, contains carboxyl (-COOH) and amine (-NH$_2$) groups. Protein structure of OVA is

formed by bonding the 385 amino acids to each other via peptide linkages between C of carboxyl group and N of amine group. Proteins differ from each other depending on the number of amino acids constituting the molecule, and type and chemical composition of side-chains bonded to amino acids. Distinguishing characteristic of OVA is the presence of electrochemically active residues in its molecular structure: it has one disulfide (S-S) bond in cystine and four sulfhydryl (-SH) bonds in cysteine groups (Fothergill and Fothergill, 1970).

OVA has high tendency to interact with metallic species (Bastrzyk et al., 2008; Liu et al., 2006).

This interaction may either be physical or chemical depending on the mineralogical properties of minerals present in ore. Adsorption of OVA on oxide/oxidized surface is explained by the electrostatic forces through positively charged amino (-NH$_3^+$) groups and negatively charged oxide surfaces, or negatively charged carboxyl (–COO$^-$) groups and positively charged cations (Fothergill and Fothergill, 1970; Rezwan et al. 2005). On the other hand, Liu et al. (2006) observed chemical interaction between cysteine and pyrite by FTIR spectroscopy tests. Guler et al (2013, 2014) investigated OVA adsorption on pyrite by FTIR spectroscopy, cyclic voltammetry and flotation tests. They showed that pyrite-OVA interaction was potential-dependent process: OVA adsorbed on mineral surface physically in reducing to slightly oxidizing potentials, and electrochemically at highly oxidizing potentials through the formation of metal-OVA chelates. Use of active metal
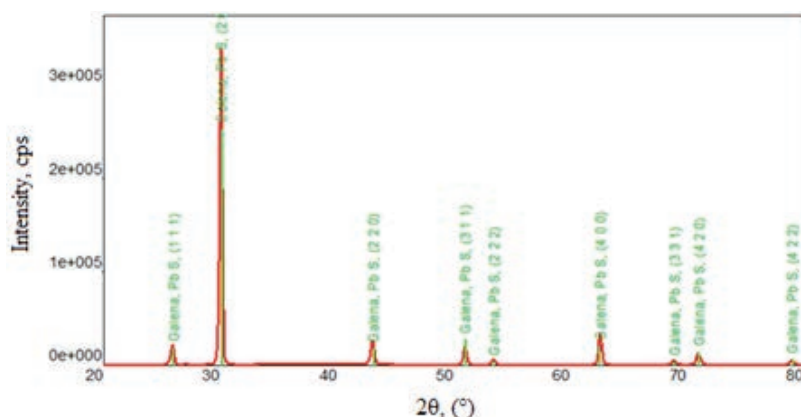
Fig. 1. XRD pattern of galena sample
Rys.1. Obraz XRD próbki galeny

ions like Pb^{+2} was found to increase OVA adsorption on pyrite (Guler et al., 2014). In spite of its numerous advantages as stated above, OVA has not taken enough interest possibly due to the presence of positively charged amino ($-NH_3^+$) groups and negatively charged carboxyl ($-COO-$) groups in the molecular structure, which might adversely affect the selectivity and flotation performance. Effect of OVA on the hydrophobicity of galena has not been taken into consideration, yet. This study was performed to elucidate the role of OVA on hydrophobicity and potential response of galena in the absence and presence of dithiophosphinate (DTPI).

Materials and methods

Experimental works were performed by using highly mineralized galena rock specimens from a galena concentrator in Sivas, Turkey. Sample was characterized mineralogically by XRD measurements and optical metal microscopy works, and chemically by SEM-EDS measurements. Galena crystal sample was found to be highly pure with trace impurity – sphalerite (Figure 1).

Experimental works were performed in an electrochemical cell, in which galena-working electrode, Ag/AgCl reference electrode and a micro-syringe for bubble creation were dipped. Working electrode was prepared cutting galena rock specimen into a rectangular cross-section, and then mounting it into a glass tube by an electrochemically inert epoxy resin. Exposed electrode surface was renewed polishing by 800-grit silicon carbide paper and 1 μm size diamond paste before each test. Experiments were made in tetraborate buffer solution (pH 9.2), which was prepared by distilled water. Polarization and contact angle measurement tests were made at room temperature (about 20°C) in open atmosphere conditions.

Contact angle was measured in-situ in the electrochemical cell. Air bubble was placed on galena elec-

trode surface by a micro syringe. Contact angle was monitored by a digital camera, and measured by using a freeware (http://www.markus-bader.de/MBRuler).

Tested collecting agent was sodium di-isobutyl dithiophosphinate (DTPI), a commercial product of Cytec under the trade name "Aerophine 3418A" promoter. Active chemical content of Aerophine 3418A was about 50% w/w of DTPI with the traces of tri-isobutyl phosphine sulfide impurity (the rest is water). Highly pure OVA (98%), chicken egg albumin, was supplied from Merck as organic modifying agent.

It was soluble in cold water, and has a reasonably high molecular weight.

Results and discussions

Effects of OVA and DTPI on the hydrophobicity and potential response of galena were investigated in open atmosphere condition at pH 9.2. Rest potential of galena was measured around 150 mV, at which condition contact angle was obtained as 37° indicating reasonable hydrophobicity of electrode surface. Galena is thought to oxidize releasing Pb^{+2} ions and elemental sulfur-S° according to reaction 1 (Gardner and Woods, 1979; Kocabağ and Guler, 2007; Rath and Subramanian, 1999). Surface hydrophobicity was attributed to the presence of S° in addition to lead ions, which satisfy porous electrode surface to proceed oxidation reaction (Cassaignon et al., 1998; Nava et al., 2002).

$$PbS \rightarrow Pb^{2+} + S° + 2e^- \qquad E°=354 \text{ mV} \qquad (1)$$

OVA was tested as modifying agent to determine its effect on the hydrophobicity of galena. Contact angle (θ) decreased sharply with an increase in the OVA dosage up to 100 g/t (Figure 2). OVA was observed to manipulate rest potential behaving as a redox component in the galena-aqueous phase system. Equilibrium potential of galena electrode decreased almost linearly with OVA.
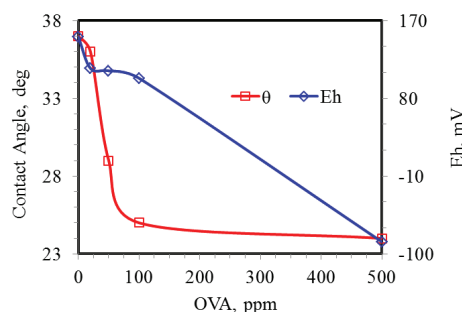
Fig. 2. Effect of OVA dosage on the contact angle and potential response of galena

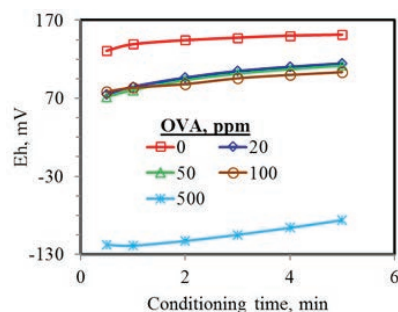Rys. 2. Wpływ ilości OVA na kąt zwilżania i flotowalność galeny

Fig. 3. Variation in the potential response of galena during conditioning with OVA

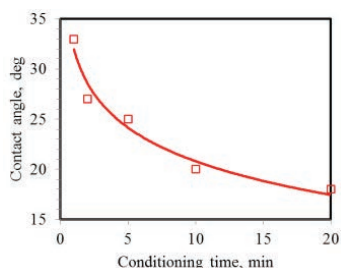Rys. 3. Zmiana flotowalności galeny w czasie kondycjonowania z OVA

Fig. 4. Effect of conditioning time on the hydrophobicity of galena (OVA: 100 ppm)

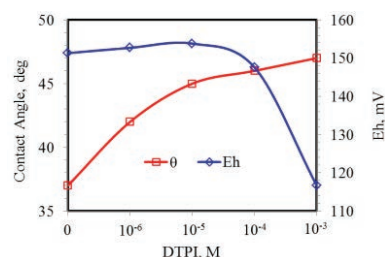Rys. 4. Wpływ czasu mieszania na hydrofobowość galeny (OVA: 100 ppm)

Fig. 5. Effect of DTPI concentration on the contact angle and potential response of galena

Rys. 5. Wpływ stężenia DTPU na kąt zwilżania i flotowalność galeny

But, rate of change of θ and Eh values with OVA did not exhibit similar tendency. Potential response of galena was recorded continuously during conditioning (Figure 3). Potential increased slightly both in the absence and presence of OVA. Equilibrium was almost reached at the 5th minute of conditioning. OVA decreased rest potential just after addition to the cell. Potential drop was limited to about 40 mV up to 100 ppm. It became considerably significant at 500 ppm OVA. At all tested dosages, potential increased continuously almost reaching equilibrium. Potential response drew steeper curve in the maximum OVA dosage as compared with lower ones.

Modifying effect of a flotation chemical depends both on the concentration and conditioning time. That is, enough time should be given for interaction of the agent with mineral surface (Chandra and Gerson, 2009; Finkelstein, 1997). Electrochemical works on the effect of OVA concentration revealed that optimum dosage was 100 ppm in collectorless condition (Figure 2). Then, effect of conditioning time was investigated at 100 ppm OVA (Figure 4). Hydrophobicity data drew a parabolic curve: at least 10 minutes of conditioning was observed to be necessary to make the impact of OVA on galena more apparent.

DTPI has been known to be an excellent sulfhydryl type collecting agent especially for Cu- and Pb-sulfides (Klimpell, 1999). Therefore, DTPI was selected to be tested with OVA. Figure 5 shows the effect of DTPI both on the hydrophobicity and potential response of galena. Adsorption of DTPI on galena is an electrochemical process (Pecina et al., 2006). Its adsorption was seen to be potential dependent process. Interestingly, potential response of galena did not differentiate up to 1x10-5 M DTPI whereas electrode potential decreased sharply in case of excess collector addition. DTPI became significantly effective on the hydrophobicity of galena at lower dosages, in which range contact angle increased sharply. Gradual increase continued at higher dosage. Potential response and contact angle curves drew antithetical curves: contact angle increased sharply at which concentration potential did almost not change, vice versa.

Electrode potential decreased almost exponentially by DTPI concentration just after addition (Figure 6). However, equilibrium potentials approached to the rest potential of galena after 5 minutes of conditioning except the curve for 1x10-3M. Therefore, effect of conditioning time was also tested on the hydrophobicity of galena with DTPI (Figure 7). Contact angle drew a curve reaching maximum value at 10 minutes of conditioning. In case of extended conditioning, hydrophobicity decreased slightly. Extended conditioning results in the excessive surface oxidation releasing hydrophilic Pb-oxides and sulfoxy species (Hemmingsen, 1992;
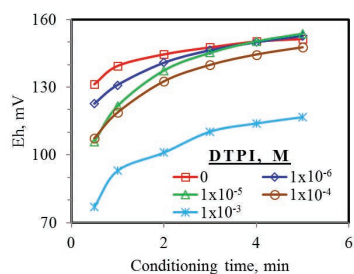
Fig. 6. Effect of DTPI conditioning at different dosages on the potential response of galena

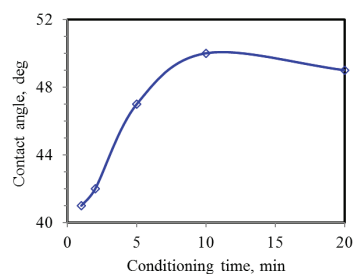Rys. 6. Wpływ mieszania różnych dawek DTPI na flotowalność galeny

Fig. 7. Effect of conditioning time on the hydrophobicity of galena (DTPI: 1×10^{-3} M)

Rys. 7. Wpływ czasu mieszania na hydrofobowość galeny (DTPI: 1×10^{-3} M)
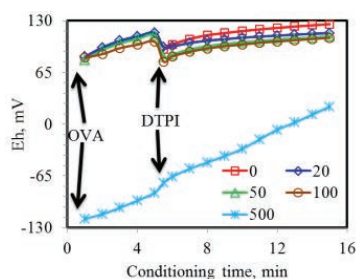

Fig. 8. Effect of OVA and DTPI addition on the potential response of galena

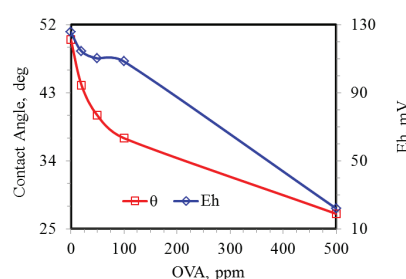Rys. 8. Wpływ dodatku OVA i DTPI na potencjalną odpowiedź galeny

Fig. 9. Effect of OVA concentration on the hydrophobicity and potential response of galena (DTPI: 1×10^{-3} M)

Ryc. 9. Wpływ stężenia OVA na hydrofobowość i potencjalną odpowiedź galeny (DTPI: 1×10^{-3} M)
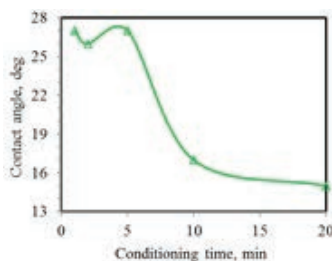

Fig. 10. Effect of condition time on the hydrophobicity of galena (OVA: 500 ppm; DTPI: 1×10^{-3} M)

Rys. 10. Wpływ czasu mieszania na hydrofobowość galeny (OVA: 500 ppm; DTPI: 1×10^{-3} M)

Kocabağ and Guler, 2007, 2008; Pritzker and Yoon, 1987; Rath and Subramanian, 1999).

Effect of OVA on the potential response of galena was investigated in the presence of DTPI (Figure 8). Experimental works were conducted with 10-3M DTPI to distinguish clearly the modifying effect of OVA. Conditioning for DTPI was 10 minutes, which was determined from Figure 6 as an optimum value. Conditioning time for OVA was applied as 5 minutes. OVA reacted with mineral surface electrochemical and reduced electrode potential (Guler et al., 2013, 2014). After DTPI addition, sharp spikes in the potential curves were seen. Spikes occurred as drops at low OVA concentrations whereas an increase in the potential was observed in the presence of 500 ppm OVA. Inclination of potential curves for lower OVA dosages was not so high. Since, the measured equilibrium potential of

(OVA+DTPI)-interacted electrode surface was already closer to the open circuit potential of galena. Steeper increase in potential curve for 500 ppm OVA was attributed to the oxidizing effect of atmospheric oxygen. Since, experiments were conducted in open atmosphere condition.

Contact angle measurements indicated that OVA reduced the hydrophobizing effect of DTPI on galena (Figure 9). Contact angle decreased sharply at lower OVA dosages, and then gradually. Conversely, slight decrease on electrode potential was seen first, and then increased with an increase in OVA concentration. Minimum contact angle was measured at 500 ppm OVA in the presence of 10-3M DTPI. Therefore, effect of conditioning time was investigated at these values (Figure 10). Significant change in contact angle was not seen at shorter condition periods. Optimum value was reached at 10 minutes of

conditioning: contact angle was reduced from 50° (Figure 7) down to 17° (Figure 10) by using 500 ppm OVA. This figure demonstrated that OVA could depress galena even in the case of excess DTPI use.

Conclusion

Effects of OVA and DTPI on the hydrophobicity and potential response of galena were investigated in pH 9.2 tetraborate buffer solutions. Following conclusions were drawn from experimental works:

- Galena exhibits certain degree of natural hydrophobicity in alkaline condition.
- OVA interacts electrochemically with galena mineral. It reduces hydrophobicity of galena.
- DTPI improved hydrophobicity of galena. DTPI adsorption on galena is an electrochemical process. It reduces potential response of mineral.
- Optimum conditioning time should be given to make the actions of OVA and DTPI more apparent.

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Abstrakt

Badanie to zostało przeprowadzone w celu wyjaśnienia wpływu owalbuminy – albuminy jaja kurzego (OVA) na hydrofobowość i flotowalność galeny w obecność ditiofosfonianu (DTPI). OVA został przetestowany jako przyjazny dla środowiska środek depresyjny ze względu na właściwości elektrochemiczne i zachowanie w środowisku wodnym. Pomiary kąta zwilżania przeprowadzono w ogniwie elektrochemicznym z trzema elektrodami w roztworze buforowym tetraboranu o pH 9,2. Prace eksperymentalne wykazały, że galena wykazuje pewien stopień naturalnej hydrofobowości. DTPI znacznie poprawiło hydrofobowość galeny, zwłaszcza przez przedłużenie czasu kondycjonowania. Przeciwnie, dodatek OVA zmniejszył kąt zwilżania, nawet przezwyciężył wpływ hydrofobowości DTPI na galenę. Pomiary potencjału wykazały, że adsorpcja obu odczynników OVA i DTPI na galenę jest procesem elektrochemicznym. Zmniejszyły one wartość potencjału elektrokinetycznego galeny.

Słowa kluczowe: hydrofobowość galeny, ditiofosfonat, albumina jaja kurzego, potencjał, czas kondycjonowania