TANNIC ACID AS A HYDROPHOBICITY MODIFIER FOR GALENA IN THE PRESENCE OF METAL IONS

Taki GULER, Ercan POLAT

Mugla Sitki Kocman University, Department of Mining Engineering, 48000 Mugla, Turkey, epolat@mu.edu.tr

Abstract: This study was performed to determine the effect of tannic acid (TA) on hydrophobicity of galena using Taguchi's design of experimental methodology. Roles of metal ions, dithiophosphinate (DTPI) concentration, and conditioning time on TA-galena interaction were tested by contact angle measurements. Results were evaluated by analysis of variance (ANOVA) test. DTPI was found to be the most effective parameter on the hydrophobicity followed by TA and nobility of metal ions. Effect of conditioning time was statistically insignificant. Electrochemical activity of metal ions became effective on TA-galena interaction: more active metals exhibit synergic effect with TA on the hydrophilicity of galena whereas more noble metals reduced the adverse impact of TA. Taguchi's design revealed that interactions between experimental variables were not statistically significant.

Keywords: tannic acid, galena, hydrophobicity, dithiophosphinate, standard formation potential, conditioning time

Introduction

Selectivity in flotation process is generally achieved by the aid of modifiers having inorganic origin like metal ions (Fe^{2+}, Pb^{2+}, Cu^{2+}, etc.) and inorganic complex ions (CN^-, $Cr_2O_7^{2-}$, SiO_3^{2-}, etc.). They have been used extensively and effectively since the first quarter of 20th century. These reagents have some adverse effects on the ecosystem due to their high toxicity and poisoning properties, which prevail as a result of incremental accumulation in water resources and earth. High costs of inorganic reagents may also be mentioned as another disadvantage for flotation processes. Increasingly stringent environmental restrictions force mineral processors to pay attention with an environmentalist perspective on concentration processes, and to use eco-friendly organic reagents (Bicak et al., 2007; Chandra and Gerson, 2009; Guler et al., 2013, 2014; Laskowski et al., 2007; Qiu, 2013).

Starch, dextrin, tannic acid (TA), albumin and arabic gum are outstanding macromolecular organic depressants. Among these, TA is the least known. It is a plant

derived hydrolysable active polyphenolic compound with the hydrophobic core and hydrophilic shell of polyphenolic structure. It behaves as a reducing agent in electrochemically active sulfide mineral pulps (Ahmad, 2014; Aromal and Philip, 2012; Hem, 1960; Qiu, 2013). The hydrolyzed hydrophilic active groups of TA have high affinity for heavy metal ions. TA reduces ferric species, and forms complex ferrous-TA compounds if the concentration of organic depressant is above a certain minimum dosage (Hem, 1960). TA was proposed to adsorb on galena through complex formation with Pb^{2+} ions, not with hydroxyl complex on the mineral surface (Qui, 2013). So that galena could be selectively depressed by TA in chalcopyrite flotation process.

Fe^{2+}, Pb^{2+} and Cu^{2+} ions are the most commonly encountered metal ions in the flotation system of galena ore or complex sulfide ores containing galena. They may intentionally be added as modifying agents, or be present as system variables. For the second case, ions of those metals may be present in flotation pulp as dissolved species from the constituent of ore while Fe^{2+} ions may also come from the milling circuit as dissolved species from milling media or mill linings (Chandra and Gerson, 2009; Peng et al., 2002; Peng et al., 2003). Presence of metal ions in flotation pulp may contribute selectivity, but may also decrease separation efficiency due to inadvertent activation and misreporting the unwanted mineral into the wrong stream (Bogusz et al., 1997; Chandra and Gerson, 2009; Finkelstein, 1997). Guler et al. (2014) stated that the effect of metal ion on the hydrophobicity of pyrite was dependent on its standard formation potential since more active metal ions reduced hydrophobicity while the nobility of modifying metal ions exhibited positive impact on the hydrophobicity of pyrite.

Hydrophobicity of galena may vary, depending on the presence of electrolytes in the flotation system particularly coming from ore itself and/or grinding circuit. Effect of electrolytes on the hydrophobicity and selectivity may be manipulated by TA exploiting its electrochemical activity property. This study aimed to identify the role of TA on galena hydrophobicity by contact angle measurement at different collector concentrations, metal ions, and conditioning time. Experimental system was designed by applying the Taguchi approach.

Materials and methods

Materials

Highly mineralized galena rock specimens were supplied from a galena-sphalerite ore deposit in Koyulhisar-Sivas, Turkey. Mineralogical and chemical characterizations of galena specimen were performed by XRD, AAS, SEM and optical metal microscopy. XRD measurement clarified that used sample was highly pure and the sole determined mineralogical phase was galena (Fig. 1). Sphalerite was found to be the trace impurity from chemical analysis and optical microscopy studies.
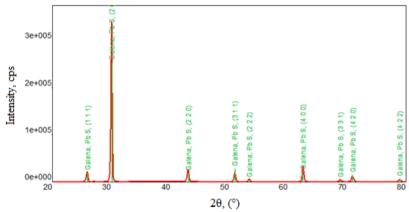
Fig. 1. XRD pattern of galena sample

Massive galena specimen was cut into a rectangular cross-section with surface area of approximately 9 mm^2. The shaped specimen was used in the preparation of galena electrode. It was mounted into a glass tube with an electrochemically inert epoxy resin. The surface of galena electrode was polished wet using 800-grit silicon carbide paper and 1 μm size diamond paste before each run. After polishing the mineral electrode surface, it was rinsed with distilled water, and transferred into the cell.

Experimental works were conducted using buffer solution (pH 9.2). Solution was prepared by 0.05 M Na-tetra borate ($Na_2B_4O_7 \cdot 10H_2O$) and distilled water. Experiments were performed at ambient temperature (about 20°C) in open atmosphere conditions.

$FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ and $Pb(NO_3)_2$ were used as inorganic modifying agents as sources of Fe^{2+}, Cu^{2+} and Pb^{2+} cations, respectively. Used inorganic modifiers were of analytical grade. Sodium di-isobutyl dithiophosphinate (DTPI) was used as thiol collector. DTPI is a commercial product of Cytec under the trade name "Aerophine 3418A" promoter. It contains about 50% w/w of DTPI with the traces of tri-isobutyl phosphine sulfide impurity (the rest is water). Tannic acid ($C_{76}H_{52}O_{76}$), supplied by Merck, was tested as organic modifying agent. Stock solutions of all reagents were prepared for daily consumption, as there is evidence that the polymer solution degrades over time (Bogusz et al., 1997).

Contact angle measurement

Contact angle measurements were made in-situ using a glass cell. An air bubble was placed on the mineral electrode surface by a micro syringe and photographed by Samsung S85 camera. Contact angle measurement set-up can be found elsewhere (Guler et al., 2009). MB-Ruler 3.3 software program (http://www.markus-bader.de/MBRuler) was employed in reading the contact angles from both sides of bubble on camera images. Final contact angle data was obtained taking the arithmetic mean of measured values.

Experimental design and statistical analysis

Experimental work was designed by applying the Taguchi approach. It was first introduced by Dr. Genechi Taguchi to provide reliable results by conducting relatively less experiments. Number of experiments is reduced by applying Taguchi's orthogonal array, which was derived from classical full factorial design. For complete analysis, Taguchi suggests to use signal-to-noise (S/N) ratio for multiple runs. The S/N ratio is a dimensionless performance measurement, and determines the most robust set of operating conditions from variation within the results. Noise factors are uncontrollable ones that cause variations in the quality property. On the other hand, signal factors are known as controllable and decrease the effects of uncontrollable factors. Taguchi's approach was applied for "the larger is better" case to maximize the response. The S/N ratio was calculated using following equation, where "y" is the experimental result

$$(S/N) = -10\log(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}). \qquad (1)$$

Four process parameters were tested at three different levels: concentrations of TA (5, 20, 50 mg/dm^3) and DTPI (10^{-5}, 10^{-4}, 10^{-3} M), type of metal ion (Fe^{2+}, Pb^{2+} and Cu^{2+}), and conditioning time (2, 10, 30 minutes). Metal ion was added into cell at constant concentration (10^{-4} M) when required. TA and metal ions were used as modifying agents while DTPI was tested as collector. Preliminary experiments were performed to determine TA levels while assumptions were made for conditioning time, type and concentration of metal ions, and concentration of collecting agent based on the previous findings (Bogusz et al., 1997; Chandra and Gerson, 2009; Peng et al., 2002). Types of metal ions were determined both considering the abundance in sulfide mineral pulps and their standard formation potentials. Among selected ones, ferrous ion was the most active ($E^{\circ}_{Fe^{2+}/Fe^0} = -440$ mV) whereas cupric ion was the most noble one ($E^{\circ}_{Cu^{2+}/Cu^0} = 337$ mV). Standard formation potential of lead is between them ($E^{\circ}_{Pb^{2+}/Pb^0} = -126$ mV).

Taguchi's L$_{27}$(3^4) orthogonal array was applied in experimental works to test four parameters (concentrations of TA and DTPI, formation potential of metal ions, and conditioning time) at three levels (Table 1). The number 27 means the number of experiments to be conducted to analyze all variables and their levels. Three images were taken from each bubble placed on mineral electrode surface both to calculate signal/noise ratio (S/N), and to eliminate man-made errors in order to obtain optimum results. The S/N ratios and mean contact angles of each run were calculated, and analysis of variance (ANOVA) table was drawn from the calculated data using Minitab software (Version 17.1.0) program.

Results and discussion

Contact angle measurements were made randomly and Taguchi's orthogonal array was constructed as seen in Table 1. Data given in the orthogonal array was analyzed by applying ANOVA test (Table 2), where DF is "degree of freedom", SS is "sum of squares", and MS represents "mean sum of squares". Following statistical results were recorded as model summary from ANOVA test: S = 0.7446; R-Sq = 98.88%; R-Sq(adj) = 95.14%. The applied Taguchi experimental design exhibited significantly high R-Sq value. The higher the F value and the lower the *P* value mean the greater the impact of variable on experimental results. Moreover, it is known well that if the calculated *P* value is lower than significance level *α*, in which case calculated *F* value is greater than $F_{Table,α}$ value, found elsewhere (Montgomery and Runger, 2007), then the influence of independent variables (experimental parameters) on dependent variable (contact angle) is statistically significant, and vice-versa (Guler and Akdemir, 2012; Montgomery and Runger, 2007).

ANOVA test revealed that maximum *F* value was obtained in the case of DTPI (F_{DTPI}: 184.05). So, collector concentration was the most effective factor, followed by TA concentration, while conditioning time was the least. Taken the significance level (*α*-level) as 0.05 (95% confidence or 5% significance) and magnitude of calculated *F* value as a criterion, then the effects of DTPI, TA and metal ions on the hydrophobicity were found to be statistically significant.

DTPI adsorption on galena is expected to occur in two steps (Pecina et al., 2006): electrochemical oxidation of galena surface and then chemical adsorption of DTPI ions on mineral surface as metal-collector species. First step is the release of Pb^{2+} ions according to the reaction given below. Surface oxidation proceeds spontaneously further around open circuit potential and Pb-sulfoxy and/or hydroxy complexes may form on galena (Guler, 2012; Kocabag et al., 1990). These excess oxidation products reduce mineral-collector interaction. So, slightly oxidizing condition is appropriate situation for DTPI adsorption where ionic form of lead present on the surface. Release of elemental sulfur also exhibits positive impact on hydrophobicity for which

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

TA was found to be second dominating experimental variable, and reduced hydrophobicity (Table 1). Its effect became more apparent at higher concentrations causing reasonably high *F* value (Table 2). Calculated *F* value for TA (F_{TA}) is much lower than F_{DTPI}, and much larger than $F_{metal\ ions}$. Metal ions have been known to be effective modifiers, and used to satisfy selectivity in the flotation of complex sulfide ores (Chandra and Gerson, 2009; Finkelstein, 1997; Peng et al., 2002, 2003). So, larger F_{TA} value demonstrated that TA was more effective modifier on galena than metal ions.

Table 1. Taguchi's $L_{27}(3^4)$ orthogonal array for contact angle measurement

Run	TA mg/dm^3	DTPI M	E_{Metal}° mV	Conditioning Time, min	Contact Angle Measurement (M), (°)				S/N Ratio
					M1	M2	M3	Mean	
1	5	10^{-5}	337	2	17	19	19	18.33	25.23
2	5	10^{-5}	−126	10	20	18	19	19.00	25.55
3	5	10^{-5}	−440	30	19	22	21	20.67	26.26
4	5	10^{-4}	337	10	43	41	40	41.33	32.31
5	5	10^{-4}	−126	30	35	35	36	35.33	30.96
6	5	10^{-4}	−440	2	30	30	28	29.33	29.33
7	5	10^{-3}	337	30	45	46	45	45.33	33.13
8	5	10^{-3}	−126	2	40	41	38	39.67	31.96
9	5	10^{-3}	−440	10	36	37	35	36.00	31.12
10	20	10^{-5}	337	2	17	19	18	18.00	25.08
11	20	10^{-5}	−126	10	16	17	15	16.00	24.05
12	20	10^{-5}	−440	30	13	14	15	14.00	22.88
13	20	10^{-4}	337	10	31	29	30	30.00	29.53
14	20	10^{-4}	−126	30	28	29	30	29.00	29.24
15	20	10^{-4}	−440	2	25	24	23	24.00	27.59
16	20	10^{-3}	337	30	38	40	39	39.00	31.82
17	20	10^{-3}	−126	2	32	32	33	32.33	30.19
18	20	10^{-3}	−440	10	30	29	30	29.67	29.44
19	50	10^{-5}	337	2	15	15	16	15.33	23.70
20	50	10^{-5}	−126	10	13	14	14	13.67	22.70
21	50	10^{-5}	−440	30	11	10	9	10.00	19.91
22	50	10^{-4}	337	10	25	25	24	24.67	27.84
23	50	10^{-4}	−126	30	22	23	23	22.67	27.10
24	50	10^{-4}	−440	2	19	20	18	19.00	25.55
25	50	10^{-3}	337	30	33	32	34	33.00	30.36
26	50	10^{-3}	−126	2	25	27	26	26.00	28.29
27	50	10^{-3}	−440	10	23	22	23	22.67	27.10

Table 2. ANOVA analysis for S/N ratio

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value	$F_{Table, \alpha=0.05}$
TA	2	61.614	30.807	55.57	0.000	5.14
DTPI	2	204.056	102.028	184.05	0.000	5.14
Metal ion	2	21.875	10.937	19.73	0.002	5.14
Conditioning time	2	1.257	0.629	1.13	0.382	5.14
TA-DTPI	4	0.321	0.080	0.14	0.959	4.53
TA-Metal ion	4	2.537	0.634	1.14	0.420	4.53
TA-Conditioning time	4	1.486	0.372	0.67	0.636	4.53
Residual error	6	3.326	0.554			
Total	26	296.472				

Synergic effects of tested variables on the hydrophobicity of galena were plotted in terms of contact angle on contour maps using data given in Table 1 (Figs. 2-4). Because of the applied experimental design, all variables made some more contributions on the magnitude of contact angle. For this reason, trend lines on the maps were regarded instead of magnitudes shaping them. ANOVA test revealed that dual effects of factors were statistically insignificant. In general, DTPI increased the hydrophobicity whereas TA displayed depressing action (Fig. 2). DTPI significantly overcame the depressing property of TA at higher concentrations, especially above 10^{-4} M DTPI. TA adsorption is favorable on unoxidized surface chemical state. Hydrophilic effect of TA arises from the formation of metal-TA complexes through chelate formation between polyphenolic hydroxyl of TA and metal ion on the mineral surface (Pugh, 1989; Qiu, 2013). Due to its reducing property. TA was thought to inhibit the surface excess oxidation (Ahmad, 2014; Aromal and Philip, 2012; Qiu, 2013). Reducing capacity of TA was reported to decrease at higher pHs (Hem, 1960). In spite of the presence of TA, galena surface might still continue to oxidize slowly after metal ion release. In case of surface excess oxidation, metal-TA complexes might not form, and full effect of TA could not be obtained. TA might still reduce hydrophobicity in such conditions due to adsorption by columbic attraction, hydrogen bond formation or hydrophobic association (Pugh, 1989). Hydration shell forms a mesophase on oxidized galena surface in alkaline condition. Hydrophilic TA molecules may adsorb on hydration shell by hydrogen bonding (Wang et al., 2013, 2014). Bond energy of hydrogen bonding is known to be weak. Then, wetting ability of TA depends on the number of the hydrophilic groups that can form hydrogen bond with water molecules (Wang et al., 2013) in addition to the rate of adsorbed collecting species. Moreover, TA is not expected to adsorb selectively on hydrated layer if the mineral surfaces are covered by metal hydroxyl species (Liu and Zang, 2000).
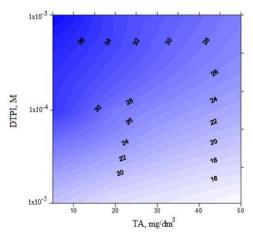

Fig. 2. Variation in the hydrophobicity of galena
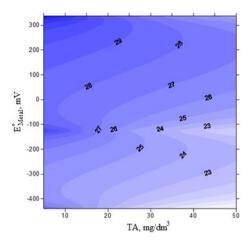depending on the concentrations of TA and DTPI

Fig. 3. Variation in the hydrophobicity of galena depending on
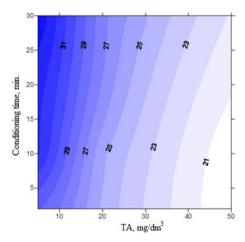TA concentration and standard formation potential of metal ions

Fig. 4. Variation in the hydrophobicity of galena
depending on TA concentration and conditioning time

Effect of metal ions varied depending on the standard formation potential (Fig. 3). The more noble metals behaved as activator whereas hydrophilicity became predominant by a decrease in the formation potential of metal ions with the synergic effect of TA. Fe^{2+} ions increased TA adsorption on galena while Cu^{2+} ions reduced TA adsorption, and inhibited the appearance of the full effect of TA on the degree of hydrophobicity (Finkelstein, 1997). Activation power became superior in the presence of Cu^{2+} ions (Chandra and Gerson, 2009; Rath and Subramanian, 1999). Copper ions reasonably overcame the hydrophilic effect of TA. Regular variation in the hydrophobicity on contour map was interrupted around the standard formation potential of Pb^{2+} possibly due to synergic effect of other experimental parameters. As a member of mineralogical formula, Pb^{+2} ions may be defined as the main system

variable of galena flotation. In addition to dissolved ions from galena surface, intentionally added Pb^{2+} ions into the system may slightly increase the hydrophobicity probably due to the increased activity of lead species on mineral surface, which favors the formation of the metal–collector compounds (Pecina et al., 2006). However, excess use may exhibit adverse effect. Lead ion is not stable in pulp medium at open circuit potential, and then oxidizes further to form hydrophilic Pb-oxyhydroxy species on the surface (Guler, 2012; Kocabag et al., 1990; Peng et al, 2003). Moreover, excess unoxidized lead ions are expected to provide additional adsorption centers for TA molecules (Laskowski et al., 2007). TA covers mineral surface in the form of lead-TA complexes. Pentacyclic chelates are thought to form between two neighboring phenolic hydroxyls of TA and metal ions (Wang et al, 2013). Fe^{2+} ion displayed detrimental effect on galena hydrophobicity. It is the most active component added to the system, and easily oxidizes to hydrophilic ferric oxyhydroxides. These redox products reduces collector adsorption rate on galena (Pecina, 2006; Peng et al., 2002, 2003). When added, TA retards the oxidation of ferrous species to ferric species, and forms hydrophilic Fe^{+2}-TA complexes (Hem, 1960).

Conditioning time was left almost ineffective in the examined range (Fig. 4). Extended conditioning time slightly improve hydrophobicity, and reduced the influence of TA. Minimum hydrophobicity was observed at the highest TA dosage with lower conditioning times. Adsorption of metal ions on galena surface may need extended conditioning. Longer conditioning is known to be necessary particularly for Cu-activation to maximize metal-activation, and formation of hydrophobic Cu-S like new surface species (Chandra and Gerson, 2009; Finkelstein, 1997). However, excess conditioning may adversely affect hydrophobicity due to precipitation of metal ions as metal-oxyhydroxides on the surface. Especially in the presence of active metal ions like Fe^{+2}, hydrophilic oxyhydroxides are expected to form on the surface even at lower conditioning times (Finkelstein, 1997; Hem, 1960). Therefore, a significant effect of conditioning time on galena hydrophobicity could not be seen in Fig. 4 due to combined effect of factors and their levels as given in Table 1. Similarly, longer conditioning times may also be beneficial for TA adsorption (Wang et al, 2012). TA may gain time to interact both with unoxidized metal ions and/or hydrated mesophase. Minimum hydrophobicity was proposed to be possible at higher TA concentrations and lower conditioning times.

Optimum experimental conditions for the lowest and the highest hydrophobicity points were predicted by applying regression analysis (Table 3). Regression equation for the mean contact angle ($\Delta\theta$) was derived in terms of tested parameters (equation 3) using Minitab software program, where "E°" and "t" show standard formation potential of metal ion and conditioning time, respectively. Statistical data from regression analysis was obtained as follows: S = 2.24; R-Sq = 96.15%; R-Sq(adj) = 94.43%; R-sq(pred) = 91.33%. Mean predicted contact angle is calculated setting the tested parameter "1" in the equation 3, and the left is "0". According to applied Taguchi design, minimum hydrophobicity was seen to be obtained utilizing the

synergic effect of ferrous ion and TA. Optimized combination was determined as $(50 \text{ mg/dm}^3 \text{ TA}) + (10^{-5} \text{ M DTPI}) + (10^{-4} \text{ M Fe}^{+2}) + (2 \text{ minutes conditioning})$ to minimize the S/N ratio, and therefore for minimum hydrophobicity. Mean contact angle value for this condition was calculated as 6.15° from equation 3. Confirmation tests were also conducted, and closer θ values (8°, 7°, 8°) were obtained with a mean of 7.70° for the lowest hydrophobicity point. Hydrophilic effect of modifying agents was negligibly diminished by extended conditioning (Fig. 4). On the other hand, hydrophobic surface state of galena may be survived using cupric ion as modifying agent. Excess DTPI consumption, however, is necessary to overcome the depressing action of TA. Extended conditioning was seen to be slightly helpful to improve hydrophobicity. Experimental condition was determined to be "$(5 \text{ mg/dm}^3 \text{ TA}) + (10^{-3} \text{ M DTPI}) + (10^{-4} \text{ M Cu}^{+2}) + (30 \text{ minutes conditioning})$ for the highest hydrophobicity for the tested system. Mentioned combination was already present in the experimental design (Run 7), which was measured as 45.33°. Predicted contact angle was calculated as 44.30° from regression equation. These findings indicated that the Taguchi experimental design was applied properly determining the suitable variables together with their optimum levels.

$$\Delta\theta = 26.074 + 5.593 \, (\text{TA}_5) - 0.296 \, (\text{TA}_{20}) - 5.296 \, (\text{TA}_{50}) - 9.963 \, (\text{DTPI}_{0.00001})$$
$$+ 2.296 \, (\text{DTPI}_{0.0001}) + 7.667 \, (\text{DTPI}_{0.001}) - 3.259 \, (\text{E}^{\circ}_{\text{Fe}^{2+}/\text{Fe}^{0}}) - 0.111 \, (\text{E}^{\circ}_{\text{Pb}^{2+}/\text{Pb}^{0}})$$
$$+ 3.370 \, (\text{E}^{\circ}_{\text{Cu}^{2+}/\text{Cu}^{0}}) - 1.407 \, (\text{t}_2) - 0.185 \, (\text{t}_{10}) + 1.593 \, (\text{t}_{30}) \tag{3}$$

Table 3. Prediction of possible combinations, and results of confirmation experiments

	TA, mg/ dm^3	DTPI, M	Metal ion	Conditioning time, min	Predicted contact angle, (°)	Measured contact angle, (°)			
						M1	M2	M3	Mean
Minimum contact angle	50	10^{-5}	Fe^{2+}	2	6.15	8	7	8	7.70
	50	10^{-5}	Fe^{2+}	10	7.37				
	50	10^{-5}	Fe^{2+}	30	9.15	11	10	9	10.00
Maximum contact angle	5	10^{-3}	Cu^{2+}	30	44.30	45	46	45	45.33
	5	10^{-3}	Cu^{2+}	10	42.52				
	5	10^{-3}	Cu^{2+}	2	41.30				

Conclusions

Effect of TA on the hydrophobicity of galena was investigated in the presence of metal ions and DTPI. Experimental design was made by applying the Taguchi approach to test for effects of four parameters (concentrations of TA and DTPI, standard formation potential of metal ions, and conditioning time) on the hydrophobicity of galena. Concerning the hydrophobicity, significance order of parameters was determined as follows: DTPI concentration, TA concentration,

nobility of metal ion, and conditioning time. TA was observed to be much more powerful modifier than metal ions, and reduced hydrophobicity of galena even in the presence of DTPI. Electrochemically active metals increased hydrophilic action of TA whereas noble ones diminished the adverse effect on the contact angle. So, TA was thought to exhibit negligible effect on the floatability of sulfide minerals of noble metals. Then, TA may be proposed as environmentally friendly, cheap and effective depressant for sulfide minerals releasing electrochemically more active ions like Pb^{2+} and Fe^{2+} for a selective flotation process, and to reduce the adverse effect of accidental activation on selectivity.

References

AHMAD T., 2014, *Reviewing the tannic acid mediated synthesis of metal nanoparticles*, Journal of Nanotechnology, 2014, 1-11.

AROMAL A.S., PHILIP D., 2012, *Facile one-pot synthesis of gold nanoparticles using tannic acid and its application in catalysis*, Physica E 44, 1692-1696.

BICAK O., EKMEKCI Z., BRADSHAW D.J., HARRIS P.J., 2007, *Adsorption of guar gum and CMC on pyrite*, Minerals Engineering, 20, 996-1002.

BOGUSZ E., BRIENNE S.R., BUTLER I., RAO S.R., FINCH J.A., 1997, *Metal ions and dextrin adsorption on pyrite*, Minerals Engineering, 10, 441-445.

CHANDRA A.P., GERSON A.R., 2009, *A review of the fundamental studies of the copper activation mechanisms for selective flotation of the sulfide minerals, sphalerite and pyrite*, Advances in Colloid and Interface Science, 145, 97-110.

FINKELSTEIN N.P., 1997,*The activation of sulphide minerals for flotation: A review,* International Journal of Mineral Processing, 52, 81-120.

GULER T., 2012, *Galena oxidation in alkaline condition*, 13th International Mineral Processing Symposium, Bodrum, Turkey, 239-246.

GULER, T., CETINKAYA, S., AKDEMIR, U., DOGAN, T., KOCABAG, D., 2009, *Effect of Fe-ions on pyrite-xanthate interaction in chemically manipulated electrochemical conditions,* International Journal of Natural and Engineering Sciences, 3(3), 1-7.

GULER T., AKDEMIR U., 2012, *Statistical evaluation of flotation and entrainment behavior of an artificial ore*, Transactions of Nonferrous Metals Society of China, 22, 199-205.

GULER T., SAHBUDAK K., CETINKAYA S., AKDEMIR U., 2013, *Electrochemical study of pyrite−ovalbumin interaction in relation to flotation*, Transactions of Nonferrous Metals Society of China, 23, 2766-2775.

GULER T., SAHBUDAK K., AKDEMIR U., CETINKAYA S., 2014, *Impact of ovalbumin on pyrite flotation in absence and presence of metal ions,* Physicochemical Problems of Mineral Processing, 50, 31-40.

HEM J.D., 1960, *Complexes of ferrous iron with tannic acid*, Chemistry of Iron in Natural Water, Geological Survey, 75-94.

KLIMPEL R.R., 1999, *A review of sulfide mineral collector practice*, Proceedings of a Symposium Held at the Annual SME Meeting, Advances in Flotation Technology, Denver, Colorado, 115–127.

KOCABAG D., GULER T., 2008, *A comparative evaluation of the response of platinum and mineral electrodes in sulfide mineral pulps*, International Journal of Mineral Processing, 87, 51-59.

KOCABAG D., KELSALL G.H., SHERGOLD H.L., 1990, *Natural oleophilicity/ hydrophobicity of sulphide minerals, I. Galena*, International Journal of Mineral Processing, 29, 195–210.

LIU Q., ZHANG Y., 2000, *Effect of calcium ions and citric acid on the flotation separation of chalcopyrite from galena using dextrin*, Minerals Engineering, 13, 1405-1416.

MINGIONE P.A., 1990, *Use of AEROPHINE® 3418A Promoter for Sulfide Minerals Flotation*, American Cyanamid Company, Paper No. 26, USA, 485-508.

MONTGOMERY, D.C., RUNGER, G.C., 2007. *Applied Statistics and Probability for Engineers, 4th edition*. John Wiley and Sons, Inc.

LASKOWSKI J.S, LIU Q., O'CONNOR C.T., 2007, *Current understanding of the mechanism of polysaccharide adsorption at the mineral/aqueous solution interface*, International Journal of Mineral Processing, 84, 59-68.

PENG Y., GRANO S., RALSTON J., FORNASIERO D., 2002, *Towards prediction of oxidation during grinding I. Galena flotation,* Minerals Engineering, 15, 493-498.

PENG Y., GRANO S., FORNASIERO D., RALSTON J., 2003, *Control of grinding conditions in the flotation of galena and its separation from pyrite*, International Journal of Mineral Processing, 70, 67-82.

PECINA E.T., URIBE A., FINCH J.A., NAVA F., 2006, *Mechaism of di-isobutyl dithiophosphinate adsorption onto galena and pyrite*, Minerals Engineering, 19, 904-911.

PUGH R J., 1989, *Macromolecular organic depressants in sulphide flotation- A review, 1. Principles, types and applications*, International Journal of Mineral Processing, 25, 101-130.

QIU X., 2013, *A non-toxic depressant for galena in differential flotation of Cu-Pb sulfides*, Advanced Materials Research, 734-737, 1018-1021.

RATH R K., SUBRAMANIAN S., 1999, *Adsorption, electrokinetic and differential flotation studies on sphalerite and galena using dextrin*, International Journal of Mineral Processing, 57, 265-283.

WANG H., CHEN X., BAI Y., GUO C., ZHANG L., 2012, *Application of dissolved air flotation on separation of waste plastics ABS and PS*, Waste Management, 32, 1297-1305.

WANG H., WANG C., FU J., GU G., 2013, *Wetting behavior and mechanism of wetting agents on low-energy surfaces*, Colloids and Surfaces A, 424, 10-17.

WANG H., WANG C., FU J., GU G., 2014, *Flotability and flotation separation of polymer materials modulated by wetting agents*, Waste Management, 34, 309-315.