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ZETA POTENTIAL OF POLISH COPPER-BEARING SHALE IN THE ABSENCE AND PRESENCE OF FLOTATION FROTHERS

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Abstract: In this paper, zeta potential as a function of pH of copper-bearing shale, which is mined in Poland by KGHM, was investigated. The measurements were conducted in water and aqueous solutions of selected flotation frothers. It was established that for investigated copper-bearing shale, after dispersion in water, the isoelectric point (*IEP*) occurs at pH=3.5. Addition of frothers decreased the *IEP* on the pH scale and the *IEP* for butanol was 1.93, for MIBC 2.90 and for eicosaethylene glycol hexadecyl ether (C₁₆E₂₀) 2.76. In the case of introducing frothers changed, the zeta potential becomes less negative. An empirical equation, having two adjustable parameters, was used in the paper to approximate the course of the zeta potential-pH curve. The equation showed a very good approximation of the zeta potential of the investigated shale either in water or frother aqueous solutions.

Keywords: zeta potential, frother, flotation, shale, pH, isoelectric point, IEP, empirical equation

INTRODUCTION

Zeta potential is an important parameter describing surface properties of materials. It is the electric potential within the interfacial double layer located at the slipping plane. The zeta potential indicates the difference in electrical potentials between the slipping plane and interior of an object suspended in a medium. The structure of electrical double layer is shown in Fig. 1.

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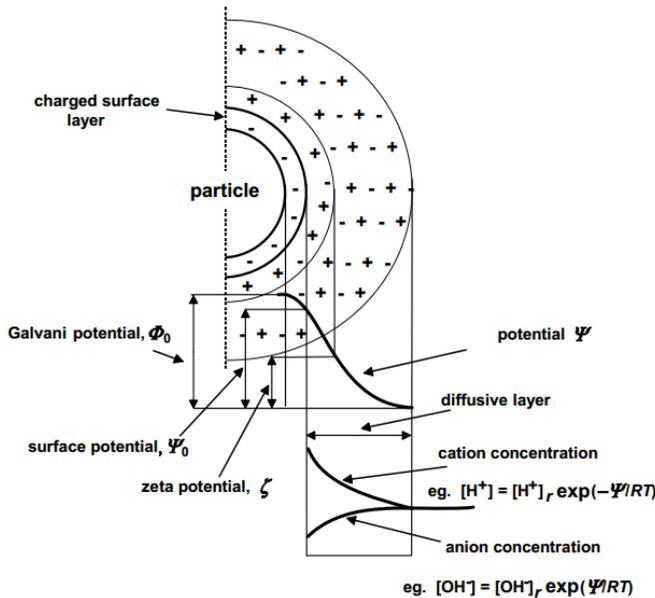


Fig. 1. Electrical double layer (edl) model consisting of a charged surface layer within the solid and neutralizing the charge rigid, and next, diffused layers of the edl in solution. The slipping plane, determining the zeta potential and located near the border between the rigid and diffused parts of the edl is also shown (Drzymala, 2007)

The zeta potential plays an important role in minerallurgy, especially in flotation. Performance of many flotation systems is the most effective at the isoelectric point on pH scale, called iep, at which the electric potential at the slipping plane is zero.

Copper bearing shale occurring as a Kupferschiefer Zechstein layer in South West Poland, called Lubin-Glogow Copper Basin, or LGOM, is mined and processed by KGHM Polska Miedź SA. The shale layer, together with a sand stone layer located below shale and a dolomite layer located above shale, forms copper ore which is an important raw material containing many valuable chemical elements including Cu, Ag, Au, Pb, Zn, As, Co, Ni, Mo, V, Re, S, and Se.

There are some difficulties in processing of copper bearing shale because in flotation process some gang minerals report with shale to the concentrate making it low in quality. In addition to that, certain amounts of metals are lost to the tailing with shale particles. Therefore, new approaches to shale processing are needed. To develop more efficient processes, knowledge on principal properties of shale is needed, including its zeta potential. Therefore, the aim of this paper was to determine the zeta potential of the copper bearing shale from LGOM. The zeta potential of shale was measured not only in water but also in aqueous solutions of selected frothers because there is a concept of processing of the shale-containing ore by so called pre-flotation of shale with

only frother, before proper flotation of sulfides in the presence of xanthate and frothers (Konieczny et al., 2013).

EXPERIMENTAL

The shale samples used for the measurements were hand-picked from the run-of-mine Legnica–Glogow Copper Basin copper ore processed by KGHM in southwest Poland near Rudna. There are many varieties of LGOM copper-bearing shales (Spalinska et al., 2008). The chemical analysis of copper-bearing shales (Banaszak and Banas, 1996) and additional information on copper-bearing shales (Spalinska et al., 1996) are presented in Tables 1 and 2, respectively.

Table 1. General information on chemical compositions of LGOM copper shale (Banaszak and Banas, 1996)

Chemical content	SiO ₂	Al ₂ O ₃	CO ₂	CaO	MgO	Na ₂ O	K ₂ O	C _{org.}
Percentage	30.63	10.01	9.90	7.94	4.05	0.32	2.18	8.04
Chemical content	S _S	S _{SO3}	FeS ₂	FeO	Fe ₂ O ₃	MnO ₂	Cu	Pb
Percentage	2.64	1.81	0.66	0.49	1.01	0.15	10.48	0.41

Table 2. Cu and other elements content (in %) in LGOM shale in comparison to other fractions of copper ore (Spalinska et al., 1996)

Element	Sandstone fraction	Shale fraction	Carbonate fraction
Cu	1.58	5.45	1.82
Pb	0.01	0.67	0.11
Zn	0.02	0.02	0.04
Ag	0.0080	0.0134	0.0048
Co	0.0054	0.0156	0.0028

Zeta potential measurements (Peng, 2014) for the sample were carried in distilled water and in frother aqueous solutions using ZETASIZER 2000 (Malvern, UK), which uses the laser Doppler electrophoresis method. The measurement is based on the movement of colloidal particles induced by electric field. The movement is recalculated into electrophoretic mobility and next into zeta potential using the known Smoluchowski equation.

The shale and quartz samples were, and ground in a mill for ultrafine particle producing. The shale sample was first crushed with a hammer and next ground in an im-

pact mill to obtain particles for the zeta potential measurements. A 0.5 g sample of shale was dispersed in 30 cm³ of dispersion medium (solids content was about 1.7%), which was either 0.001 M NaCl or 0.001 M NaCl and a frother having concentration equal to the air bubble critical coalescence concentration (*CCC*) (Laskowski, 2004) multiplied by two. The *CCC* and other properties of frothers used in this study are presented in Table 3. After 2 h of conditioning shale and the aqueous solution, several drops of a representative sample from the top of the suspension were transferred to another, 30 cm³ in volume, dispersion medium for eliminating large particles. This step is very important because Zetasizer 2000 does not tolerate any particles larger than 10 μm.

The diluted solutions were transferred into a transparent glass cell for the zeta potential measurements. The measurements and results were automatically performed by the machine. The measurements were repeated 5 times for each experimental point on the pH scale.

The pH of each suspension was adjusted by adding HCl or NaOH. The stabilization of pH of the suspension after each adjustment usually took more than 10 min due to carbonates which acted as a buffer. The pH values of the suspension were adjusted from 2 to 9 to get a meaningful relation between pH and zeta potential.

Table 3. *MW*, *HLB* and *CCC* values for frothers used in experiment. *CCC* of MIBC and butanol were taken from Zhang et al. (2012), and *CCC* of C₁₆E₂₀ was calculated from an equation proposed by Kowalczyk (2013)

Frothers	<i>MW</i> (g/mol)	<i>HLB</i>	<i>CCC</i> (mmol)
MIBC	102	6	0.851
Butanol	74	7	0.110
C ₁₆ E ₂₀	1124	16	0.032

RESULTS AND DISCUSSION

The results of the zeta potential measurements for the shale samples in the presence of water and different frothers at the concentration equal to 2·*CCC* are shown in Fig. 2.

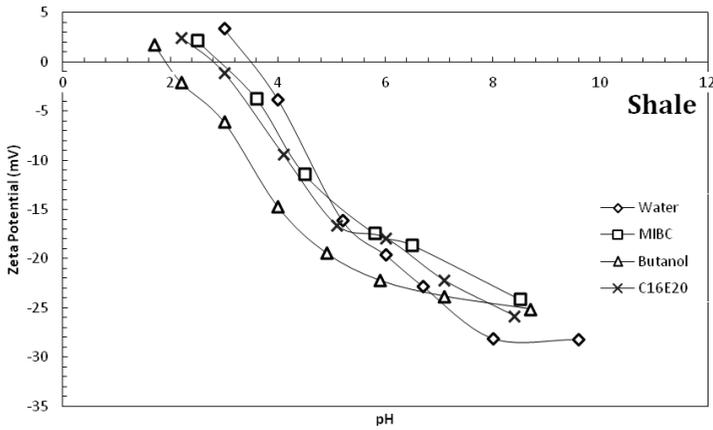


Fig. 2. Zeta potential profile of shale as a function of pH in water and frother aqueous solution

According to Fig. 2, the *IEP* of shale in water is about 3.5. At this pH, the zeta potential of shale is zero and shale shows maximum adsorption of nonionic reagents from aqueous solutions and maximum velocity of coagulation. This *IEP* value agrees well with the pH of the maximum ratio of shale settling, which occurs at $\text{pH} < 3$ (Kruszakin, 2014).

The frothers such as butanol, $\text{C}_{16}\text{E}_{20}$, and MIBC shift the *IEP* of shale to lower pH values. While MIBC and $\text{C}_{16}\text{E}_{20}$ ether showed no significant effect on the *IEP*, the most significant influence was observed for butanol.

The course of the zeta potential line versus pH for many systems can be empirically described using a special equation proposed by Ratajczak and Drzymala (2001) and used later by Drzymala (2007):

$$\zeta = 2 \frac{\zeta_{\max}}{1 + e^{f \times (\text{pH} - \text{iep})}} - \zeta_{\max} \quad (1)$$

which describes the zeta potential-pH curve with two parameters f and ζ_{\max} . Parameter f determines the decreasing rate of the curve and ζ_{\max} represents the maximum value of zeta potential. Equation (1) can also be applied for the zeta potential-pH curve of copper bearing shale. A comparison of the approximated and experimental data points for shale in water is shown in Fig. 3. It can be seen from Fig. 3 that the predicted values agree very well with the experimental data. However, there are small deviations at the beginning and at the end of the curve.

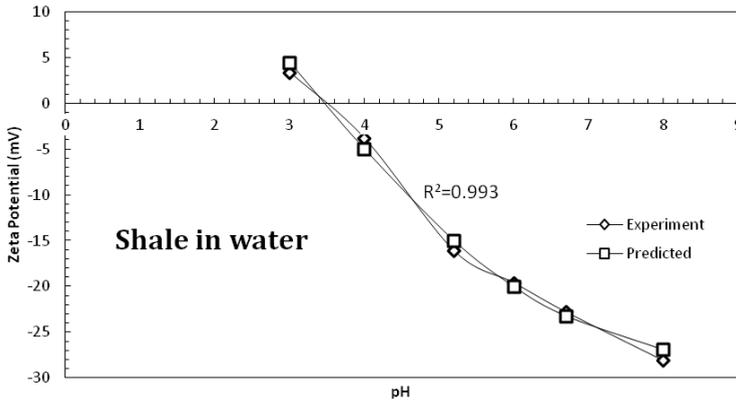


Fig. 3. Experimental (diamonds) and predicted (squares) values of zeta potential of shale in water

Also the data for shale in frother aqueous solutions, using the least squares method, were approximated with Eq. (1). Table 3 presents the results of calculations of f and ζ_{\max} as well as the coefficient of determination (R^2).

Table 2. IEP and empirical parameters f and ζ_{\max} needed for approximation of zeta potential of shale in water and in frother aqueous solutions as well as the coefficient of determination R^2

Solution	f	ζ_{\max}	IEP	R^2
Water	0.63	30.16	3.47	0.9931
MIBC	0.52	26.70	2.90	0.9930
Butanol	0.59	26.39	1.93	0.9936
$C_{16}E_{20}$	0.49	28.78	2.76	0.9899

Smaller value of f for zeta potential lines in the presence of frothers, when compared to that in water, indicates that frothers reduce sensitivity of the shale surface to pH. Smaller ζ_{\max} means that the shale surface is less charged. This may be caused by reduced activity of the surface modified by adsorption of the frother. The frothers used in the zeta potential measurements are non-ionic surfactants which do not change surface charge of particles but they make it closer to zero. The adsorbed surfactants molecules occupy some surface area of particles, therefore the total surface area of the particles having surface charge decreases, hence the zeta potential of the whole particles moves towards zero.

CONCLUSIONS

On the basis of the performed measurements and discussion, the following conclusions can be offered:

1. IEP of the investigated copper-bearing shale from LGOM (Poland) in water was found to be at pH=3.5. An addition of frothers shifted the IEP of shale to lower pH values while the change of the zeta potential of the shale was less negative,
2. the equation used to approximate the zeta potential-pH curve is useful for delineation of zeta potential of shale both in water and frother aqueous solutions.

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