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SURFACE REACTIVITY
AND COLLECTORLESS FLOTATION OF GALENA

Significant differences in collectorless flotation of eight galena samples of different origin have been found from microflotation test. Cyclic voltammetry measurements in pure base electrolyte and electrochemical impedance spectroscopy (EIS) measurements in the solution of lead nitrate were performed to explain the observed differences. A correlation between polarization resistance (Rp), determined from EIS spectra, and flotation was demonstrated indicating that less reactive samples of galena (higher values of Rp) floated evidently better than those of low Rp.
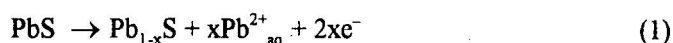
INTRODUCTION

Galena is undoubtedly the most intensively examined sulfide mineral. For a long time it has been treated as a "model mineral" for verification of various flotation theories (Granville et al. 1972). It is however well known (Lekki and Chmielewski 1987, 1987a, 1989; Chmielewski and Lekki 1989) that various galena samples, originating from different deposits, exhibit different collectorless flotation and other properties. For this reason there is no such thing as a "model galena" sample representative for galena as a mineral. Collectorless flotation of galena and other sulfide minerals (except MoS_2) has not been utilized (Arbiter and Gebhardt 1992), but a potential application of it still exists. Furthermore, the natural floatability of galena (and other sulfide minerals) may play an important (negative) role, when those minerals accompany other (nonsulfide) minerals (barite, coal). Thus, despite its theoretical importance, the investigations of the natural floatability of galena also presents the great practical interest.

It is generally believed, that sulfide minerals are not naturally floatable and a requirement for their collectorless flotation is the formation of either elemental sulfur or sulfur-enriched layer at the mineral surface (Arbiter and Gebhardt 1992, Hayes and Trahar 1987, Buckley and Walker 1986). On the other hand, the formation of coating of the surface by hydrophilic metal hydroxy and metal sulfoxy species lowers their
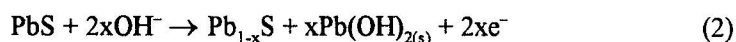
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collectorless flotation (Smart 1991). Both the formation of sulfur (or sulfur-enriched surface) and oxidized metal compounds result from electrochemical reactions. The kinetics of such reactions influences the collectorless flotation of sulfide minerals. For galena, the reactions can be written as follows:

$$PbS \rightarrow Pb_{1-x}S + xPb^{2+}_{aq} + 2xe^- \tag{1}$$

or

$$PbS + 2xOH^- \rightarrow Pb_{1-x}S + xPb(OH)_{2(s)} + 2xe^- \tag{2}$$

The deficit of lead (or excess of sulfur) at the surface may be compensated by diffusion of sulfur to the bulk of sulfide sample. Simultaneously, depending on whether the formation of oxidized lead species proceeds according to reaction 1 or reaction 2, hydrophilic coating of the surface by hydroxides (and/or carbonates) may form. Consequently, the final state of lead sulfide surface results from the competition between the process of the enrichment of the surface in sulfur and the formation of the hydrophilic lead species at the surface.

The suitable method of investigation of this type of reaction seems to be electrochemical impedance spectroscopy (EIS), which has already been successfully applied to study the reaction of the exchange of metal ions between the sulfide surface and the solution (Nowak 1993). The method was employed in this work along with cyclic voltammetry, to examine the electrochemical properties of the surface of natural galena samples from various sources.

EXPERIMENTAL

Eight dissimilar samples of natural galena of different origin were used in the investigations. The sources of the examined galena samples are given in Table 1.

Table 1. Characteristics of the galena samples

No. of sample	Symbol used	Sourse	Remarks
1	BC	Brushy Creek, Missouri, USA	suppl. by Wards Sci. Est.
2	OB	Orzeł Biały, Poland	–
3	TR	Transvaal, South Africa	–
4	BL	Rodopy, Bulgaria	–
5	TB	Trzebionka, Poland	–
6	KV	Cornwall, England	–
7	LB	Lubin, Poland	copper ore deposit
8	OK	Olkusz, Poland	–

Microflotation experiments for galena samples specified in Table 1 were conducted in the Hallimond tube equipped with a calibrated receiver for continuous monitoring of the recovered PbS particles during the course of a test. 1.1 g of galena sample was placed in the Hallimond tube and conditioned for 10 min. in 120 cm³ of distilled water at natural pH of 6.55. Flotation was then initiated at air flow rate of 37.5 cm³/min. In order to reduce excessive surface oxidation the time between sample preparation and flotation was kept less than 45 minutes.

To avoid the influence of mechanical carryover on the flotation results, the particle size fraction of 0.20–0.25 mm was selected, according to the flotometric approach elaborated by Drzymała and his co-workers. (Drzymała and Lekki 1989; Drzymała, Chmielewski et al. 1992).

For electrochemical measurements, galena samples were cut with a diamond saw to the shape of a cylinder and then embedded in a glass tube with an epoxy resin. The electrical contact to the mineral was made with a silver containing conducting epoxy resin (Tra-duct). The surface of the electrode was subsequently abraded before the measurements with a steel blade. The solutions were made from a.r. grade lead nitrate and sodium nitrate. In all electrochemical tests solutions containing 2.0 mol/dm³ of $NaNO_3$ at pH 6.2 were used as a base electrolyte.

The impedance spectra and cyclic voltammetry curves were measured utilizing a system consisting of Frequency Response Analyzer 1250, Electrochemical Interface 1286 (Schlumberger-Solartron) connected to a Hewlett-Packard computer. The three electrode configuration was used with saturated calomel electrode (SCE) as a reference electrode. Potentials were measured and quoted in this work versus the saturated calomel electrode (SCE). Details regarding the measuring system, experimental procedure, sample preparation, handling as well as data processing were given in previous works (Chmielewski and Nowak 1992; Nowak 1993).

The electrical equivalent circuit (EEC) presented in Fig. 1 was used to describe and interpret the frequency dependence of measured impedance spectra. The least-squared equation describing the dependence of the EEC impedance on the frequency was fitted to experimental impedance data using the MINUIT (CERN Computer Program Library) program.
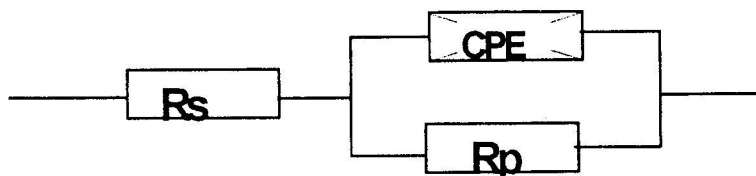

Fig. 1. Electrical equivalent circuit (EEC) for a galena electrode in lead nitrate
solution.   Rs – solution resistance,   Rp – resistance of the Faradaic reaction
(polarization resistanace), CPE – constant phase element, representing capacitance
of the electrical double layer at the electrode surface

RESULTS AND DISCUSSION

Figure 2 shows a typical cyclic voltammetry plot for the TB galena sample in well deoxidized, pure base electrolyte solution. Most of the investigated galena samples behaved similarly (Fig. 2). There is no peak during the first cathodic voltammetric cycle, indicating that the surface of galena did not contain a noticeable amount of the oxidation products. However, when the surface was then oxidized by changing the potential
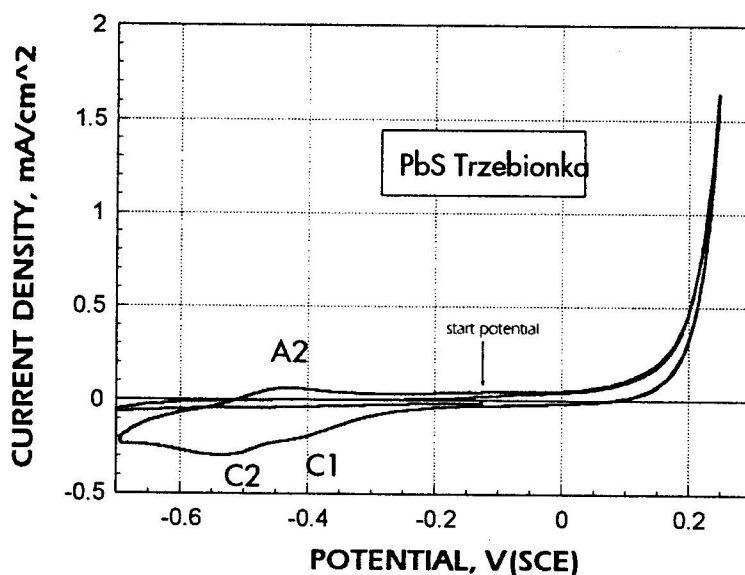

Fig. 2. Cyclic voltammetry curve of the TB galena in deoxygenated 2 mol/dm³
NaNO₃ solution (pH 6.2). Potential sweep rate 20 mV/s, first cycle commenced
from the rest potential in the cathodic direction

to the value of +0.25 V, the subsequent cathodic sweep showed a presence of two peaks (C1 and C2, Fig. 2). First peak (C1) can be attributed to the reverse reaction 1 (or 2), whereas the second peak (C2) was most likely due to the following reaction:

$$Pb_{1-x}S + 2xH^+ + 2xe^- \rightarrow (1-x)PbS + 2xHS^-_{aq} \qquad (3)$$
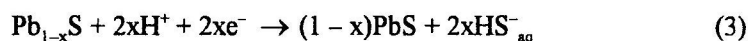
The anodic peak (A2 in Fig. 2) can be related to the oxidation of the HS⁻ ion, previously formed in cathodic reaction 3. It may be seen, that when the electrode is polarized to sufficiently high potential, the amount of sulfur species formed is much higher than the amount of oxidized lead available at the surface. It can be estimated from much higher electrical charge associated with the peak C2 in comparison with peak C1.

The investigated galena samples exhibited apparently different collectorless flotation (Fig. 3). Extreme differences in flotation recovery were found for galena samples. Galena labeled as LB and OB almost did not float after 30 minutes while almost 100%
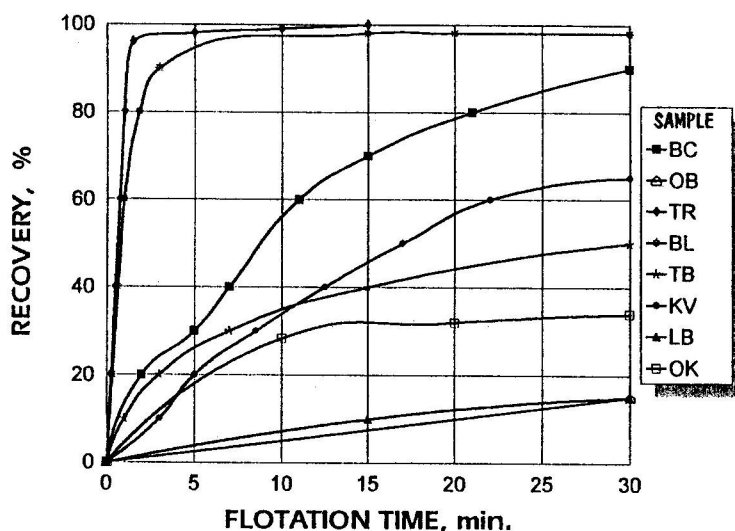
Fig. 3. Recovery vs. time relationships for the collectorless flotation of various
galena samples. Flotation test at natural pH and pulp potential. Size fraction:
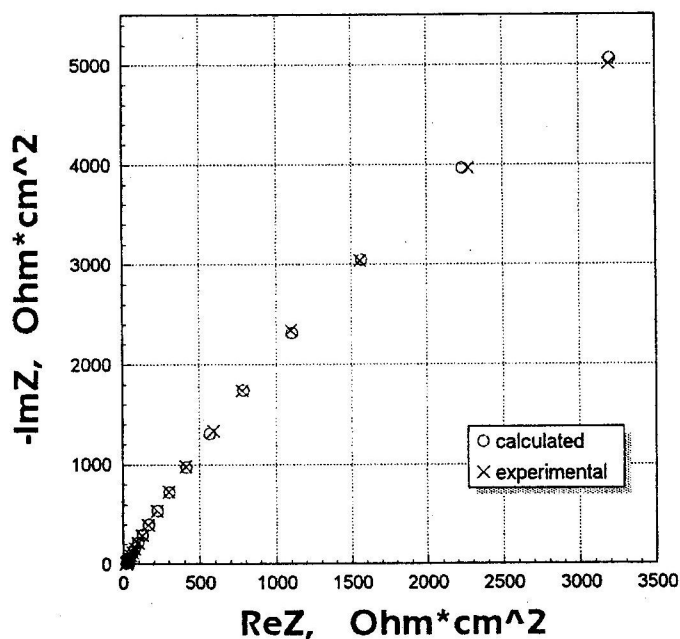0.20–0.25 mm

Fig. 4. An example of the fit of the equation describing the electrical equiva-
lent circuit from Fig. 1 to the measured impedance data for the electrode of ga-
lena TB. Thoroughly deoxidized solution of $Pb(NO_3)_2$ (0.1 mol/dm^3) and
$NaNO_3$ (2 mol/dm^3), pH 6.1. Frequency range 0.1 – 1000 Hz
+ – measured points, o – calculated values

flotation after a few minutes was recorded for galena BL, TR. No correlation was found between either the shape of a voltammetric curve in pure base electrolyte or the electrical charge related with particular processes and floatabilities. Moreover, the circumstances in the case of a "single particle" electrode are quite different than in the case of a particle's suspension. In the former case the ratio: (volume of the solution)/(surface area of the sample) is practically infinitely large, in the latter – the magnitude of this ratio is much lower. Therefore, in the case of the powdered mineral the solution may be saturated with the ions and molecules liberated from the solid surface. In the case of a "single particle" sample, such saturation is not possible. Accordingly, the measurements of the exchange current density for the reaction 1 (or 2) were conducted.

The exchange current density for any galena electrode in the solution of lead ions is relatively low when compared with other metal sulfides (Nowak 1993). Only a small part of the EIS semicircle (Fig. 3), which is usually obtained in the case of an activation-controlled electrochemical reaction when the data are presented in the Nyquist scheme, was visible in the case of investigated samples (Fig. 4). Apparently quite a good fit was obtained for all galena samples. An example of the fit of the equation, describing the impedance of equivalent electrical scheme from Figure 1, to the experimental data for galena OK is presented in Fig. 4. The polarization resistance, Rp, which was determined from the EIS data assuming EEC from Fig. 1, is inversely proportional to exchange current density (Chmielewski and Nowak, 1992). Figure 5 presents the correlation between Rp calculated from the impedance measurements on all galena
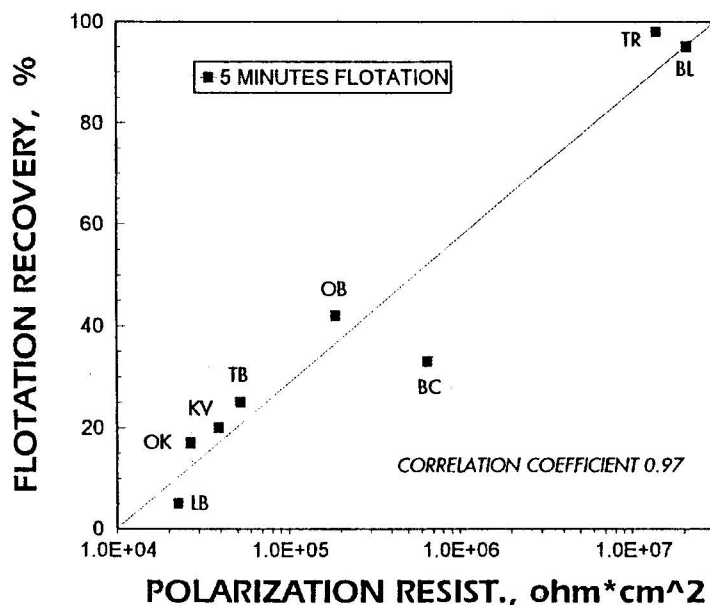

Fig. 5. The correlation between the polarization resistance, Rp, and flotation recovery after 5 minutes for examined galena sample

electrodes (and, hence, exchange current density) and the flotation of particular PbS samples (Fig.3).

Taking into account the possible sources of errors (differences in surface roughness factor, possible impurities in galena) the observed correlation is excellent (correlation coefficient = 0.97 for 5 minutes of flotation time). It is evident that the superficial properties of galena during collectorless flotation are controlled by the kinetics of the reaction of transfer of lead ions through the interphase boundary. The samples of lower Rp (or higher exchange current densities) exhibited at the same time remarkably worse floatability in relation to those of higher Rp.

If the dominating superficial process preceding the flotation was the formation of the layer of elemental sulfur on the galena surface, with the simultaneous liberation of lead ions to the solution (reaction 1), one would expect the opposite behavior. The obvious explanation is, that the process determining further superficial properties of PbS is the formation of a surface coating composed with oxidized lead species, which makes the surface hydrophilic. It explains why the more reactive (exhibiting evidently higher exchange current density) samples show, at the same time, worse floatability. A similar correlation was previously observed for various pyrite samples (Chmielewski and Nowak 1992). Pyrites showing higher reactivity (lower polarization resistance) floated evidently worse than those of lower reactivity (higher Rp).

CONCLUSIONS

Remarkably different collectorless flotation of various galena samples was observed during Hallimond tube flotation tests. The observed differences were related to the electrochemical phenomena taking place on the PbS surface prior to the flotation. The superficial properties of PbS during collectorless flotation were evidently controlled by the kinetics of the transfer of lead ions through the mineral/solution interface. The formation of hydrophilic oxidized lead species determines the galena collectorless floatability. The magnitudes of polarization resistance, Rp, determined from measured electrochemical impedance spectroscopy data, characterized the capability of galena to surface oxidation. The Rp values for various galena samples were within the range of three orders of magnitudes, what appeared to be the most surprising observation. The samples with the higher Rp floated better than those exhibiting low Rp. The behaviour of galena during the collectorless flotation can be, therefore, predicted from electrochemical data using EIS method.

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Na podstawie testów mikroflotacyjnych ośmiu naturalnych próbek galeny stwierdzono istotne różnice ich flotacji bezkolektorowej. Aby wyjaśnić obserwowane różnice wykonano pomiary woltamperometryczne na elektrodach galenowych w elektrolicie podstawowym oraz badania impedancyjne w roztworze azotanu ołowiu(II). Zaobserwowano dobrą korelację między oporem polaryzacyjnym (Rp) próbek galeny, określonym z pomiarów impedancyjnych, a ich flotacją. Próbki galeny wykazujące wyższą reaktywność powierzchniową (niższe Rp) flotowały zdecydowanie słabiej od próbek chrakteryzujących się mniejszą reaktywnością (wyższe Rp).