

THE EFFECT OF THE GRINDING MEDIA ON XANTHATE ADSORPTION ON GALENA IN FLOTATION SYSTEM

M. Kostović * and D. Stanković **

* University in Belgrade, Faculty of Mining and Geology,
Djusina 7, 11000 Belgrade, Serbia and Montenegro

** University in Belgrade, Faculty of Electrical Engineering,
Bulevar kralja Aleksandra 73, 11000 Belgrade, Serbia and Montenegro

(Received 15 September; accepted 18 November)

Abstract

The galvanic contact between grinding media (mild and stainless steel) and sulphide mineral (galena) has been studied. Galena frothless flotation tests for conditions before and after its galvanic contact with steels have shown that mild steel exerted a higher depressing effect on galena than stainless steel. The electrochemical nature of interaction was investigated by electrode potential and short circuit current measurements. Also, zeta potential measurements were employed to identify interaction between galena and grinding media. The tests indicated the cathodic behaviour of galena (reduction) and the anodic behaviour of steel (oxidation) in the galvanic contact. It was postulated that an iron hydrated oxide or hydroxide type compounds formed on galena surface upon galvanic contact with grinding media, decreased its floatability.

Keywords: galena, galvanic contact, grinding media, flotation

1. Introduction

Sulphide lead-zinc ores are usually concentrated by flotation, which is preceded by wet grinding in steel ball or rod mills. During wet grinding, there appears to be an interaction between grinding media and sulphide minerals which adversely affects the flotation responses of the sulphide minerals. The electrochemical nature of interaction between grinding media and sulphide minerals have additional implications in grinding manifesting in accelerated corrosion of the grinding media. Beside this, galvanic (electrochemical) contact directly influence on sulphide mineral flotation behaviour, especially on the ability of the mineral surface to be collected xanthates.

The effect of grinding media on sulphide minerals floatability have been studied by many researches under different, dynamic or stationary, laboratory or industrial conditions, and in various mills (porcelain, cast iron, steel) and using varied steels of which grinding materials can be made. Also, investigations were conducted on various sulphide minerals (pyrite, pyrrhotite, galena, chalcopyrite, sphalerite) [1 - 5]. All tests proved an active part of the grinding media on sulphide minerals, and mostly adverse effects on changes of the mineral surface as well as on floatability of sulphide mineral.

This work is referred to the influence of the effect of electrochemical interaction in galvanic contact between galena and grinding media on floatability of this mineral [6,7]. Also, this investigation was carried out in order to characterize the type of electrochemical reaction and the surface (galena and steel) species formed in galvanic contact. Galena was selected for present work because it has been little studied among other sulphide minerals (pyrite, pyrrhotite, and chalcopyrite).

2. Experimental

A pure galena mineral sample from Lece lead-zinc deposit was used in this study. The sample density was $7,548 \text{ g/cm}^3$ and chemical analyses showed that galena contained 86,12% Pb and 13,29% S. For the frothless flotation tests and for zeta potential measurements size fractions $-0,149+0,104 \text{ mm}$ and $100\%-0,010 \text{ mm}$ were used, respectively. The specific surface area of the sample used to measured electro kinetic potential was determined by Coulter Multisizer and gave the value of $0,188 \text{ m}^2\text{g}^{-1}$.

The reagents used in the experiments were potassium-butyl-xanthate (KBX) as a collector and Na_2CO_3 as pH regulator. All reagents were of p.a. purity grade. Distilled water used throughout the work. The concentration of collector was $1,5 \times 10^{-4}$ mol/dm³ in all flotation tests because it was concentration required to achieve maximum galena floatability and determined by a series of a preliminary flotation tests. pH of solutions varied from 5,3 to 11,1.

Frothless flotation tests were carried out at a modified Hallimond tube in time of 5 minutes, before and after the contact between galena and various type of steels or glass.

To study the effect of galvanic interaction among galena and stainless or mild steel ball material, a crucible made out of the grinding media (mild and stainless steel) was used. Besides grinding media, contact was provided with electrochemical inert material - glass. All tests were carried out under stationary conditions as follows: 1 g of mineral was placed in the steel crucible or glass along with 40 ml distilled water or Na_2CO_3 solution regulated pH. After a constant period of time for 3 h of galvanic contact in presence of air, galena was floated. Time of 3 hours of galvanic contact also was selected after series of a preliminary tests in which it was determined that longer contact than 3 h has no significant influence on galena decreasing floatability, irrespective of the steel type.

Zeta potential of galena was measured to establish the galena surface charge and to define the possible occurrences and phenomena at the mineral/solution boundary in the double electric layer as a consequence of galvanic contact. Electrokinetic measurements of the galena before and after the contact with tested material were carried out with a Riddick Zetameter electrophoretic apparatus.

To determine the respective oxide-reduction (anodic or cathodic) behaviours of galena and steels and possible electrochemical reactions in galvanic contact, electrode potentials (Eh) were measured. For these measurements Radiometer pH-meter type 61-62 was used. Also, the electrodes of mineral and stainless or mild steel were used as working electrodes, while calomel saturated electrode was used for reference. The measurements were carried out with single galena, stainless or mild steel electrodes, as well as short circuiting galena electrode with stainless or mild steel electrodes. The potential was measured immediately after dipping the electrodes into a

solution and the potential was read when equilibrium was established. The steady state values of the obtained potentials were converted to the standard hydrogen electrode.

In order to determine the kinetics of electrochemical reactions in galvanic contact of galena and steel, the short circuit current was measured. The short circuit current was measured in the closed circuit, using an automatic measuring and computer based system. Technique of short circuit current measurement by means of operational amplifier OP 01 is used in examinations. Digital multimeter Hewlett-Packard 3457 A provided with GPIB interface is used as measuring instrument. This instrument is connected by IEEE 488 BUS with PC 386SX having GPIB Interface card. For acquisition of measuring data, the software package Instrument manager is applied [8]

3.0. Results and discussion

3.1. Floatability tests

Figure 1 shows floatability of galena in solution of KBX, for pH range from 5,3 to 11,1 regulated with Na_2CO_3 . The tests were carried out under conditions of prior galvanic contact with each of the tested materials (glass, stainless and mild steel) during three hours (curves 2, 3 and 4) and without this contact (curve 1). The obtained results about galena floatability are graphically represented as floatability (%) - pH relations.

From Fig. 1 it is obviously that galena after contact with glass and stainless or mild steel reduces more or less its floatability. The contact with inert material (glass) in solution at pH=6-9 have very little effect to mineral floatability (curve 2) as compared with that under the same conditions, but without preliminary galvanic contact (curve 1). However, when galena was in galvanic contact with stainless or mild steel, its floatability decreased through the tested pH range (curve 3 and 4). Consequently, the galena contact with mild steel had a greater effect on galena floatability reduction than the contact with stainless steel.

The reduced floatability of galena in galvanic contact with stainless or mild steel is particularly notable in solutions of the natural pH (pH=5,3) or in

solution of pH=7-10. In a solution of pH about 10,5-11,0, galena is almost equally floatable as if it was not in a preliminary galvanic contact with the tested materials (R»58-62%).

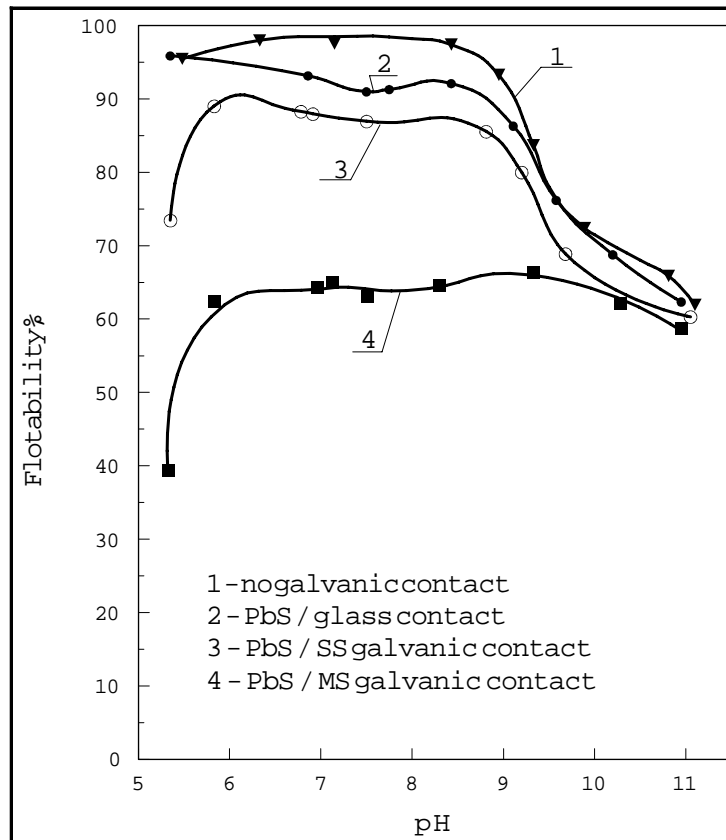


Fig. 1. Floatability of galena in solution of $1,5 \times 10^{-4} \text{ mol/dm}^3$ KBX for different pH range regulated with Na_2CO_3 , without and after 3 h of

3.2. Electrophoresis measurements

Galena zeta potential measured both before and after contact with tested materials in distilled water and Na_2CO_3 solutions of different pH (from 5,1 to 11,1) are shown on Figs. 2 and 3. Results are graphically represented as zeta

potential (mV) - pH relations. On Fig. 3 (curve 1), it was shown zeta potential of the precipitate formed at galvanic contact of galena and mild steel was. It was necessary because a colloidal brown precipitate was noted in the liquid phase only after this contact. All tests were performed without the presence of a collector.

Figure 2 (curve 1) shows that galena have negative charge through the entire pH range. Zeta potentials of galena increase with the increasing pH of the solution (from 5,1 to 11,1) without reaching point of zero charge (pzc). In strong basic solution (pH=11,1) galena have a very high negative zeta potential (even -72 mV). Also, a negative zeta potential and very similar change of potential of galena was determined at all pH after contact with glass as an electrochemically inert material and with stainless steel (Fig. 2, curves 2 and 3).

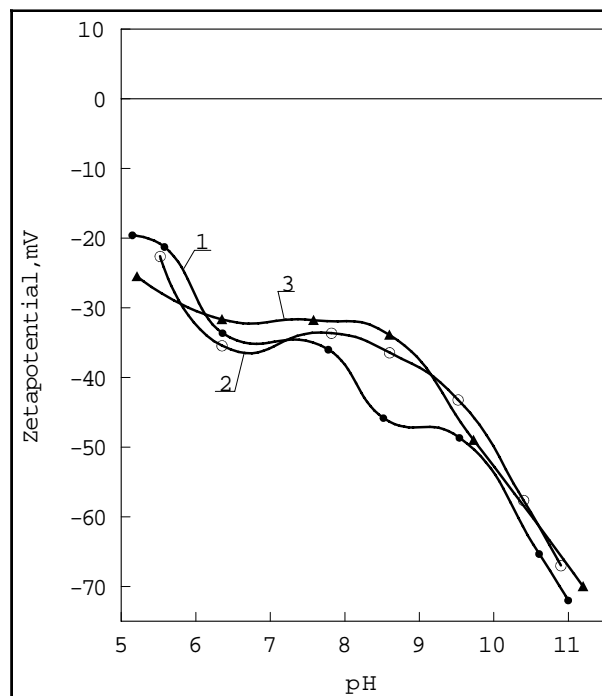


Fig. 2. Zeta potentials of galena in Na_2CO_3 solutions for different pH range: 1) before contact with tested materials; 2) after contact with glass and 3) stainless steel

On the other side, precipitate have positive charge in solutions of low acidic, neutral or low basic pH, and negative charge in solutions of basic or highly basic pH and reached (pzc) at pH=8,2 (Fig. 3, curve 1). The precipitate generated by the contact of mild steel and galena represents the type of iron hydrated oxide compound or iron hydroxide compound. It was concluded from the fact that colloidal iron hydroxide type compounds have positive zeta potentials in acidic solution and negative zeta potentials in basic solution. It is interesting to note that various data about (pzc) for iron hydroxide exists in literature, but most authors established (pzc) at about pH 7 [9, 10]. Perhaps the presence of CO_3^{2-} and HCO_3^{2-} anions moved the (pzc) of the iron hydroxide precipitates.

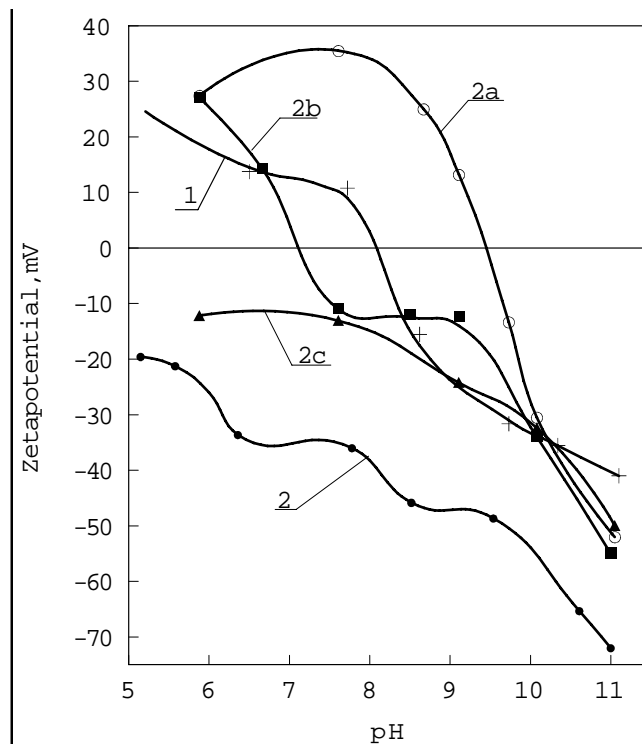


Fig. 3. Zeta potentials in Na_2CO_3 solutions for different pH range of:
 1) precipitate; 2a-2c) galena after galvanic contact with mild steel:
 2a) without decantation of precipitate, b) after decantation of
 precipitate, 2c) after decantation of precipitate and galena rinsing

Galvanic contact with mild steel leads to notable zeta potential variations (Fig. 3, curves 2a, 2b and 2c). After each galvanic contact with mild steel, galena changed the potential sign (from negative to positive) reaching even very high zeta potentials, and the IEP (curves 2a and 2b). However, decantation of the precipitate (curve 2b), and galena rinsing (curve 2c), reduced the potential negative values which approached those when galena was not in galvanic contact. This is approve that certain positive charged ionic species originating from the precipitate are surface active for galena. As a result they are most likely fixed as opposite-charged ions in the double electric layer, the Stern or compact layer, changing the surface charge of galena. Or in pH<8,2 solution, mineral and precipitate particles of opposite charges are attracted and associated by the electrostatic attraction (heterocoagulation).

3.3. Electrochemical measurements

The electrode potentials (single and common) (Eh, mV) and short circuit currents (I, mA) of galena, stainless and mild steels are shown in Table 1. The measurements were carried out in distilled water at natural pH 5,4, and in solutions at pH 7,5 and 10,1 adjusted by Na₂CO₃.

Table 1. Electrode potentials and short-circuit currents of galena and stainless/mild steel galvanic contact as a functions of pH

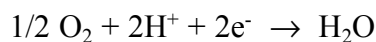
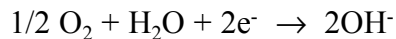
Galena - stainless steel				
Solution pH	Eh _{PbS}	Eh _{Com.}	Eh _{SS}	I (μA)
5,4 (d. w.)	268	269	273	0,97→0,15
7,5	258	222	195	3,44→0,29
10,1	138	115	91	6,81→0,42
Galena - mild steel				
Solution pH	Eh _{PbS}	Eh _{Com.}	Eh _{MS}	I (μA)
5,4 (d. w.)	268	251	233	6,27→2,67
7,5	258	215	149	17,58→3,29
10,1	138	119	80	19,09→5,98

From Table 1 it can be seen that highest potential value is possessed by galena and the lowest by mild steel. Also, all potentials have positive signs and decrease with the increasing pH of solution. Values of common potentials (measured at short circuit galena and stainless or mild steel) are between single potential values of galena and stainless/mild steel in almost all cases. These potentials in galvanic contact approach active areas or steel potentials.

It should be possible to predict the probable electrochemical reactions when galena is galvanic coupled with the stainless or mild steel in the flotation system. Namely, the behaviour of galena and steels in galvanic contact can be possible to predict based on the galvanic series of metals or minerals. Galena, having electrode potential higher than steel, behaves in galvanic contact as the cathode with the reduction reaction on its surface. On the other side, stainless or mild steel, having a lower electrode potential in the galvanic series, behaves as the anode with the oxidation reaction on it. The oxidation reaction means oxidation of elementary iron to ferrous ions:



and the reduction reaction means oxygen reduction to hydroxyl ion or water molecule:



However, this conclusion can't be taken with safety for galena and stainless steel galvanic contact, because electrode potentials of galena and stainless steel have almost same values in distilled water at natural pH of solution. Even stainless steel electrode potential value is insignificant higher than galena electrode potential value. So, in galena and stainless steel galvanic contact it couldn't be assumed appropriate cathodic or anodic behaviour of galena and stainless steel.

The higher current readings listed in Table 1 were observed immediately after the electrodes were dipped into the solution and the circuits were closed. The lower current readings are recorded when steady values were reached. The obtained results related to the galvanic current show that the measured

currents were higher in galena contact with mild steel than with stainless steel. Also, the currents are the highest in the moment of currents occurrences and decrease with the contact time until a state of equilibrium, which corresponds to the surface polarization of one of the electrodes in the system. This indicates as accelerated electrochemical reaction at galena/mild steel contact, when also a significant decreasing in mineral floatability was noted. Also, the data indicate that the currents are much higher in the basic solution than in distilled water. The higher obtained currents in Na_2CO_3 solution than in distilled water can be assumed is due to the higher conductivity of the solution.

4. Conclusions

Galvanic contact of galena with the grinding media represented by various steels (stainless and mild) affects floatability of the mineral in solutions of various pH regulated with Na_2CO_3 in the presence of KBX collector. Any change in the mentioned conditions at galena flotation is manifested in a notable reduction of galena floatability. Consequently, mild steel has a much greater depressing effect than the stainless steel, and higher values of measured current in short circuit between galena and mild steel in relation to stainless steel, indicating a faster electrochemical reaction. On the other side, the contact of galena and an inert material (glass) has no significant depressing affect on the floatability of this mineral.

In galvanic contact with steel, galena with the higher electrode potential acts as cathode, with the respective electrochemical reduction reaction on its surface, while stainless or mild steel with the lower electrode potential acts as an anode yielding the anodic reaction of oxidation. Electrochemical interaction between galena and stainless or mild steel are resulted in definite alterations on the mineral surface and iron hydrated oxides or hydroxides species coating on the surface of galena are occurred. These products are responsible for galena surface activity on collector adsorption and result lowering the mineral floatability.

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