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Electrochemical investigation of mineral electrodes in phosphate-buffered alkaline solution

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Abstract: Cyclic voltammetric methods have been applied to study the electrochemical behavior of the sulfide minerals in phosphate-buffered alkaline solution. The redox process of electrodes of sulfide ores was investigated using silicone-impregnated graphite electrode. The cathodic and anodic reaction products in alkaline solution were determined within the potential range of -2V to +2V (vs. Ag/AgCl). The several successive measurement cycles' voltammograms leads to the appearance of a new anodic peak at E = 450mV, which is absent in the first cycle and curves, as well as other features that appear in cycling, can probably be explained by secondary electrochemical transformations of the products formed by the oxidation of the original pyrite at the interface between the electrode material.

Keywords: electrochemical method, chalcopyrite, pyrite, sodium sulfide ,flotation

INTRODUCTION:

Copper is the one of the widely consumed metals in the world. An increased trend of copper consumption due to high development rate of the mining industry became apparent in the last decade [1]. Therefore it becomes important to improve existing methods of processing refractory ores or low copper content ores to cope with this consumption trend, and search for a development of a new processing technology in this area. Traditionally, copper ores have been recovered by three methods: the hydrometallurgy-electrometallurgy (SX-EW technology) and pyrometallurgy; and these methods are continuously improved in the last century [2]. From the previous studies, it was observed more works are devoted to the study of copper ore processing by the hydrometallurgical method [1, 3, 7-9]. Due to the specific crystal structure of chalcopyrite, the study of its surface, and change in composition and structure of reaction products became main study topics [6]. Processing of copper ores by flotation method is considered as more adequate technology among developed ones, therefore more studies are directed into the improvement of recovery process by flotation [4, 5]. Modern flotation process of hydrophobic mineral particles are based on their poorly wetted characteristic by the water and instant adherence to the air bubbles that allow flotation of formed foam layer [10-16].

Due to the increased depth of open pit mining, the primary sulfide ores are now more widely processed and its low copper content and finer particle size makes flotation process more difficult. Semiconductor properties of chalcopyrite and pyrite can be more beneficial in this case allowing easier flow of electron transfer through it. Hydrophobicity and degree of flotation of pyrite depends on redox oxidation capability [17-18].

Electrochemical techniques, especially cyclic voltammetry can detect the intermediate redox reactions on the mineral surface under certain potentials. Sulfide mineral oxidation arises from the reaction of species on the mineral surface with water and oxygen and it is inevitable during processing in plant conditions.

The main aim of the present work is to study the investigation on the electro-chemical behavior of mineral electrode (graphite and pyrite) in phosphate-buffered alkaline solution.

EXPERIMENTAL:

Electrochemical measurements were carried out in the laboratory of Irkutsk State University, by cyclic voltammetry on computer controlled potentiostat IPC-proM with three-electrode cell. As the reference electrode - Ag/AgCl in 3M KCl (BAS RE-1), as an auxiliary electrode – platinum is used. Working electrodes was prepared from natural sulfide ores

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that are named **Gr** and **Pyr**. Mineral electrodes immobilized in interchangeable pipette tips that has dosing volume of 0.2 ml. Electrical contact was achieved through a copper wire soldered to the lower end of the electrode that not exposed to the solution. It was 1-2 mm above the cutting tip. Then the tip filled with the active mass, gradually compacting it and seeking release of the material through the lower section of the tip. This arrangement allows multiple updates working electrode surface. Scheme electrode shown in Figure 1. Before each test, argon was purged for 5 min in the electrolytic cell in order to remove of oxygen from the electrode surface. Potential sweep rate was 50 mV/s. Initial potential was 0V; sweep direction in the first cycle - the anode in an alkaline phosphate-buffered saline (APB, 0.1M, pH 7.4) at room temperature. The active mass of the electrodes prepared from graphite powder (**Gr**), a sample of pyrite (**Pyr**) mixed with silicone liquid (Si-L). The mass ratio of components and the volume of liquid produced three electrodes are shown in the table 1. The data measurements obtained were processed by a computer program Dropview-2.1. Redox process of pyrite and chalcopyrite electrodes in alkaline solution of sodium sulfide was studied at a potential $-2V \sim +2V$, the potential sweep rate in this case was $50\mu V/sec$.

Table 1. Composition of mineral electrodes

Composition Electrodes	Graphite, %	Pyrite, %	Si-L, %
Gr - electrode	~ 90	-	10
Pyr - 2 - electrode	~ 35	~ 55	10
Pyr - electrode	~ 35	~ 55	10

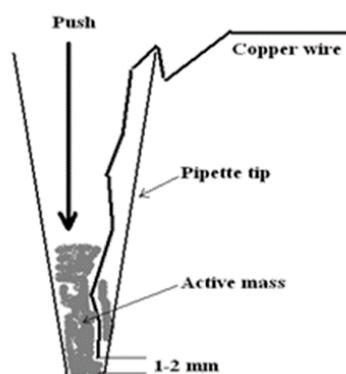
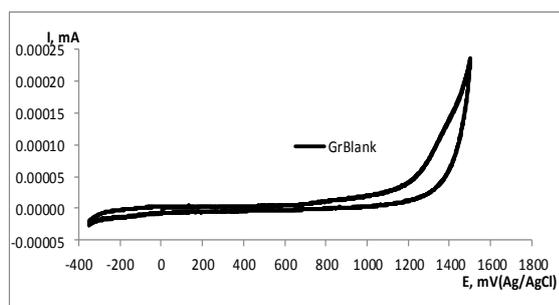


Fig. 1. Scheme of the electrode

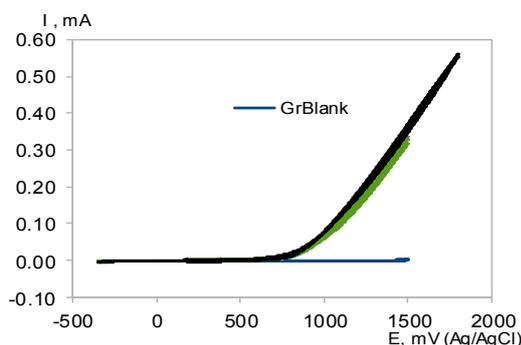
RESULTS DISCUSSION:

A. Cyclic voltammogram measured at a graphite electrode in an alkaline phosphate-buffered saline (APB, 0.1 M, pH 7.4) at room temperature: The results are shown in Figure 2-4.

Data shown in Figure 2 demonstrate that the voltammogram measured on the electrode of the background solution prepared from graphite and silicone-L, which are typical carbon electrode

Fig. 2. Cyclic voltammograms measured on electrode **Gr** alkaline phosphate-buffered saline in 0.1 M, pH 7.4, $v=50mV/sec$ three consecutive cycles.

materials. In a wide potential range -200 to 700mV registered only charging currents of the double layer. In the region of potentials more negative than -200mV marked increase in cathodic current that may be associated with reduction of oxygen functional groups on the electrode surface. Stability of the electrode is confirmed by the fact that three consecutive measurements voltammograms are virtually identical. Introduction to the electrode material pyrite significantly changes the form of the current-voltage curves (Fig. 3). For comparison, the curves measured with a graphite electrode is also presented in Figure 3 (blue).

Fig. 3. The cyclic voltammograms measured on electrode **Pyr-2** APB in 0.1M, pH 7.4, $v=50 mV/sec$ three consecutive cycles in the potential range -350 to 1500 mV, and then the two cycles in the potential range 350 - 1800 mV.

Obviously, the main differences are manifested in the anodic potential region. Thus, there is a clear increase of $\approx 300mV$ anodic current during voltammograms at a potential of 1500mV and values are 1000 times greater than voltammogram of a graphite electrode. Behavior of the electrode can be considered as the oxidation of pyrite from the electrode surface. Fig. 4 shows the same results, but the scale of the axis changed to make the visual features of the voltammograms that appear on the second and subsequent cycles.

It should be noted that the cathodic peak at $E= 300mV$ occurs during the voltammetric curves only in the second and subsequent cycles. The magnitude of the cathode current at this peak increases from

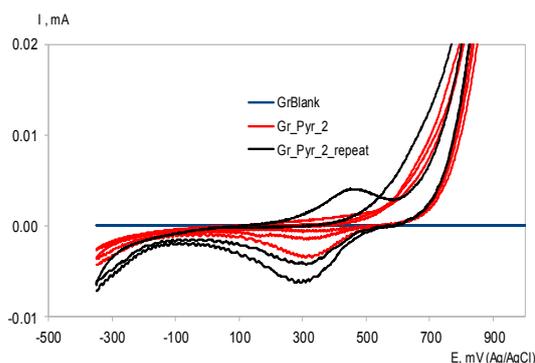


Fig. 4. Cyclic voltammograms measured on electrode **Pyr-2** APB in 0.1M, pH 7.4, $v=50\text{mV/sec}$ three consecutive cycles in the potential range -350 - 1500 mV, and then the two cycles in the potential range -350 - 1800 mV. The scale of the axes is changed from Figure3.

cycle to cycle. In addition, a slight increase of cathodic current compared to the background is registered in the *hydrogen* field at $E=-100$ to -350mV range. The magnitude of this current depends on the cathode potential, limiting anodic sweep. Finally, several successive measurement cycles' voltammograms leads to the appearance of a new anodic peak at $E=450\text{mV}$, which is absent in the first cycle and curves, as well as other features that appear in cycling, can probably be explained by secondary electrochemical transformations of the products formed by the oxidation of the original pyrite at the interface between the electrode material.

CONCLUSION:

Several successive measurement cycles' voltammograms leads to the appearance of a new anodic peak at $E = 450\text{mV}$, which is absent in the first cycle and curves, as well as other features that appear in cycling, can probably be explained by secondary electrochemical transformations of the products formed by the oxidation of the original pyrite at the interface between the electrode material.

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