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Run-lan YU

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An Electrochemical Study of DDTC Adsorption Jamesonite

YU Run-lan^{*1,2}, HU Yue-hua¹, QIU Guan-zhou¹, QIN Wen-qing¹

(1. School of Minerals Processing and Bioengineering,
Central South University, Changsha 410083, China

2. Department of Chemistry and Material Science, Hengyang Normal University,
Hengyang 421008, China)

Abstract: The interactions of jamesonite with diethyl dithiocarbamate (DDTC) were studied by AC impedance measurement and cyclic voltammetry. Several electrode processes under different potential conditions were observed. There mainly is the absorption of hydrophobic DDTC. PbD_2 , S^0 etc on the surface of jamesonite mineral from -178 mV to 472 mV (vs. SHE) and the interfacial capacitance also is small. When the electrode potential is over 472 mV, the surface of jamesonite mineral is of hydrophilicity due to the fact that hydrophobic PbD_2 , S^0 etc are oxidized into hydrophilic products such as Pb^{2+} , SO_3^{2-} , SO_4^{2-} , $PbSO_4$. So it was deduced that the potential range of jamesonite flotation using diethyl dithiocarbamate as a collector is from -178 mV to 472 mV, and its optimum potential range is between 122 mV and 222 mV due to the passive action by the hydrophobic species.

Key words: Jamesonite, Flotation, Electrochemistry

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1 Introduction

The idea that chemical interactions on the surface would occur by an electrochemical mechanism was first put forward by Salamy and Nixon. Since then, the electrochemical interactions for thio-collectors/ sulfide mineral systems have been the focus of numerous investigations and often with conflicting results for the same mineral system, thus highlighting the complexity of sulfide mineral flotation chemistry. A mixed potential model was established

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* To whom correspondence should be addressed, Tel:(86-731)8879815 E-mail:HYH@mail.csu.edu.cn

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and widely recognized during past 30 years. Based on the mixed potential model, there existed a potential at which an anodic reaction of xanthate to form metal xanthate or dithiolate and the cathodic reduction of oxygen proceed at finite rates, underlying the basis of the researches on the interaction mechanism between thio collectors and sulfide minerals. The flotation of sulfide minerals is possible only under certain redox potential and the separation of poly-metal sulfide minerals can be accomplished by Eh control (Wang, 1992). It is important for potential-controlled flotation to study the electrochemical mechanisms of the mineral/collector interactions under different potentials because the flotation recovery is dependent on the potential across the mineral/solution interface. Various electrochemical methods such as linear potential sweep voltammetry, cyclic voltammetry (Woods, 1997 for a review) and various surface analysis apparatuses such as infrared spectra, X-ray photoelectron spectroscopy etc. have been developed to investigate the electrochemical reaction mechanism involved in flotation of sulfide minerals.

Jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$) is the most important, useful and complex sulfide mineral in Dachang mine in Guangxi Autonomy. In order to separate jamesonite, marmatite ($\text{Zn}_{1-x}\text{Fe}_x\text{S}$), pyrrhotite ($\text{FeS}_{1.13}$), and pyrite (FeS_2) by potential-controlled flotation, it is imperative to understand the electrochemical behavior of interactions of jamesonite with thio collectors. There are few reports in this aspect. This paper provided significant information of interactions of jamesonite with diethyl dithiocarbamate by impedance measurement under extensive potential conditions and cyclic voltammetry.

2 Experimental

Lumps of jamesonite from Dachang Mine in Guangxi Autonomy were handpicked and crushed. Fraction of -0.15 mm was obtained by screening. Working electrode was a kind of carbon paste electrode consisted of 80 % of -0.15 mm particles of jamesonite, 10 % of graphite powder and 10 % of paraffin. The diameter of its working face exposed to the solution was 15 mm, about 1 cm^2 , and other faces were covered by epoxy resin. $0.1\text{ mol}\cdot\text{dm}^{-3}$ KNO_3 solution was used as a supporting electrolyte. Diethyl dithiocarbamate (DDTC) was used as a collector. All the solution used in experiments was prepared from analytical grade reagents and distilled water. The graphite power is spectrum grade.

A conventional three-electrode cell was used in our experiments. A platinum piece served as the counter electrode, and an Ag/AgCl electrode as the reference electrode, but all of the potential values in this paper have been calibrated vs. SHE. The reference electrode was placed in a Luggin capillary, which was placed just above the surface of the working electrode. The temperature was maintained at 25°C . After each measurement, the working electrode surface was gently polished on the abrasive papers of different types, then washed by distilled water. Experimental device was the Pottentiostat/Galvanostat Model 273A and 5210 Lock-in Amplifier from EG&GPAR Company. M398 soft system was employed for measuring electrochemical impedance spectrum (EIS)

with the amplitude of 5 mV from 10^5 to 5×10^{-3} Hz, and M270 soft system for measuring cyclic voltammograms.

3 Results and Discussion

3.1 Electrochemical Process of Interaction of DDTC with Jamesonite

What reactions can happen depends on their electrode potentials that may be calculated from Gibbs free energies of involving the matters in the reactions. E_h -pH diagram also is a method for investigating an electrochemical system. It has been identified by electrochemical measurements and X-ray photoelectron spectroscopy (XPS) that sulfide minerals such as pyrite (FeS_2), galena (PbS), chalcopyrite (CuFeS_2), and so on, can be oxidized into metal-deficient sulfides, elemental sulfur, oxy-sulfur species and sulfate salts in anodic processes under some definite potential conditions (Vanghan, 1997).

Jamesonite is a very complicate sulfide mineral containing Sb, Pb, Fe. The electrochemical reaction of various metal ion species and their interactions with DDTC may be different and complicated. Fig. 1 is the voltammograms for jamesonite electrode in the absence of DDTC (dash curve) and in the presence of DDTC (solid curve). When the concentrations of the ions are assumed as $10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ (Hamilton, 1985), according to thermodynamic calculation, HSbO_2 (aq.), Pb^{2+} and Fe^{2+} are the stable species in the solution of pH 6.86. Seen from the formula (1), it is impossible for Fe^{2+} to oxidize into $\text{Fe}(\text{OH})_3$ at pH 6.86 and $10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ Fe^{2+} conditions.



$$E_h = 1.406 - 0.177\text{pH}$$

In the absence of DDTC, the reactions of various anodic peaks in Fig. 1 (dash curve) may be as follow according to the diagram of E_h -pH (Qin Wenqing, 1997) and thermodynamic calculation. Although the reactions (4) and (5) are thermodynamically favored over the reactions (2) and (3), the anodic peaks of the reactions (4) and (5) will kinetically occur at high potential due to existing over-potentials (wang Dianzuo, 1988; Jiang Hao, 2000). Anodic current becomes positive from "A" dot at the potential 378mV. This probably implies that a metal-deficient sulfid begins forming due to Fe^{2+} in the sulfide lattice entering the solution. A current peak begins occurring at "B" dot (about 60 mV), and the peak current occurs at "C" dot (about 60 mV), corresponding to the corrosive reaction (2). Elemental sulfur ab-

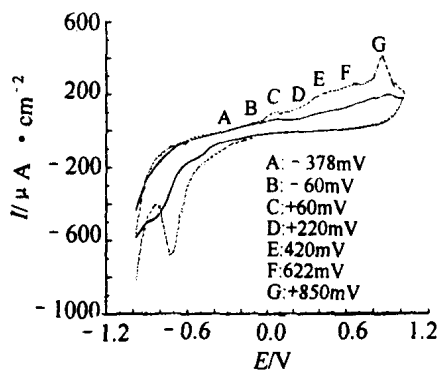
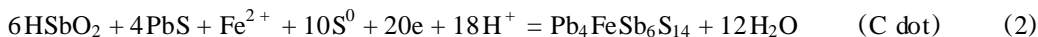


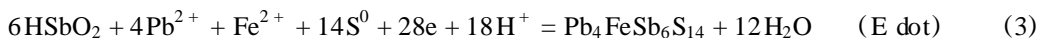
Fig. 1 Voltammograms for jamesonite electrode in $0.1 \text{ mol} \cdot \text{dm}^{-3}$ KNO_3 buffer solution of mixed phosphate at pH 6.86 (scan rate: 50 mV/s) solid line: $0.001 \text{ mol} \cdot \text{dm}^{-3}$ DDTC, dash line: without DDTC

sorbed on electrode surface results in the passive action so that the current does not increase with the enhancement of the potential from "C" to "D" dot. With the potential rising, the oxidation of jamesonite surface promotes. E, F and G dots correspond, respectively, to reactions (3), (4) and (5).



$$G^0 = -994.02 \text{ kJ/mol} \quad E^0 = 0.5150 \text{ V}$$

$$E_h = 0.4049 - 0.0531 \text{pH} = 0.04063 \text{ V}$$



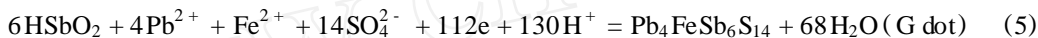
$$G^0 = -1267.22 \text{ kJ/mol} \quad E^0 = 0.4690 \text{ V}$$

$$E_h = 0.3447 - 0.0379 \text{pH} = 0.08447 \text{ V}$$



$$G^0 = -2522.48 \text{ kJ/mol} \quad E^0 = 0.4668 \text{ V}$$

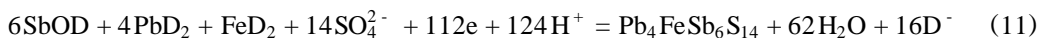
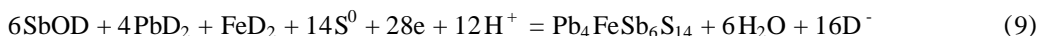
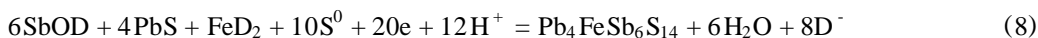
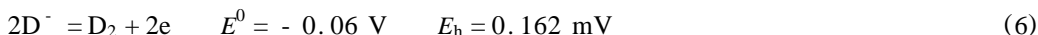
$$E_h = 0.3661 - 0.0634 \text{pH} = -0.06903 \text{ V}$$



$$G^0 = -4161.62 \text{ kJ/mol} \quad E^0 = 0.3850 \text{ V}$$

$$E_h = 0.3179 - 0.0685 \text{pH} = 0.1519 \text{ V}$$

In the presence of DDTC, the current of anodic peaks (solid curve) are lower than that without DDTC. This is unanimous with the principle of corrosion and inhibition. Because the equilibrium potential for the reaction (6) in 10^{-3} mol/L DDTC at pH 6.86 is 0.162 mV, which potential value is higher than the potential of first anodic peak (C dot: about 60 mV) in cyclic voltammogram without DDTC (dash curve), DDTC would be chemically absorbed and D_2 can not be formed on jamesonite surface according to the mixed potential model. Consequently, the anion of DDTC (in term of D^-) chemically absorbs on the surface of jamesonite electrode so that the corrosive reactions are inhibited and anodic current decreases. With the electrode potential rising continuously, the electrochemical reactions such as (8 ~ 11) probably happen. These hydrophobic products such as elemental sulfur, PbD_2 etc., will adhere to the surface of jamesonite electrode. These products will further be oxidized electrochemically according to these reactions such as (12 ~ 13). So the electrode process is very complicated. It is necessary to investigate the change of the interfacial structure of jamesonite electrode with the potential by AC impedance method



$$\begin{aligned}
 G^0 &= -118.79 \text{ kJ/mol} & E^0 &= 0.6155 \text{ V} \\
 E_h &= 0.6155 + 0.0298 \lg[\text{Pb}^{2+}] = 0.4563 \text{ V} \\
 2\text{HSbO}_2 + \text{D}_2 + 2\text{e} + 2\text{H}^+ &= 2\text{SbOD} + 2\text{H}_2\text{O} & (13) \\
 G^0 &= -210.37 \text{ kJ/mol} & E^0 &= 1.090 \text{ V} \\
 E_h &= 1.090 + 0.059 \lg[\text{HSbO}_2] - 0.059 \text{ pH} = 0.3772 \text{ V}
 \end{aligned}$$

3.2 Variation of Interfacial Structure of Jamesonite/ Solution with Potential

Electrochemical impedance method is very effective for investigating corrosive reaction, absorption and its film phase on solid surface (Shi Meilen 2001, Yang Huaiyu 2000, Cheng Yufeng 1997). The EIS curves of jamesonite electrode in $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ KNO}_3$ buffer solution of mixed phosphate at pH 6.86 are shown in Fig. 2 to Fig. 4. The results of EIS not only are in agreement with the results of the voltammograms, but also clearly reveal the variation of the interfacial structure of jamesonite/ solution with the potential of jamesonite electrode.

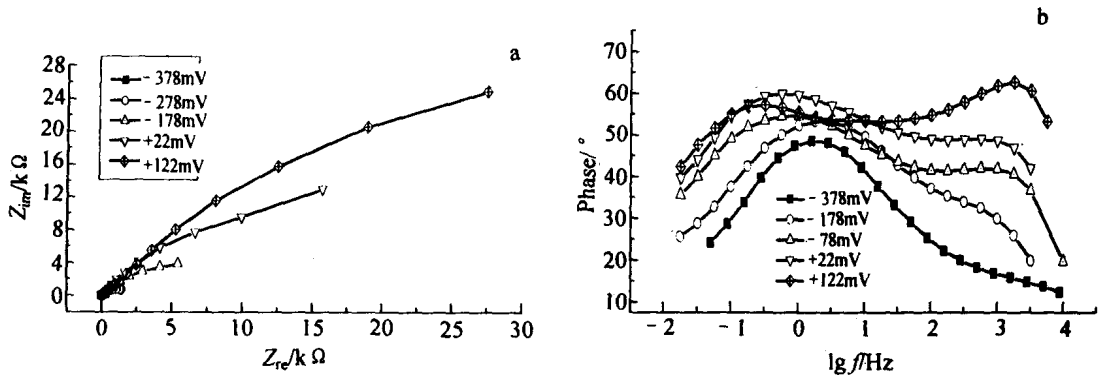


Fig. 2 The EIS of jamesonite electrode in $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ KNO}_3$ solution containing $0.001 \text{ mol} \cdot \text{dm}^{-3} \text{ DDTC}$ in the potential range from 378 mV to 122 mV

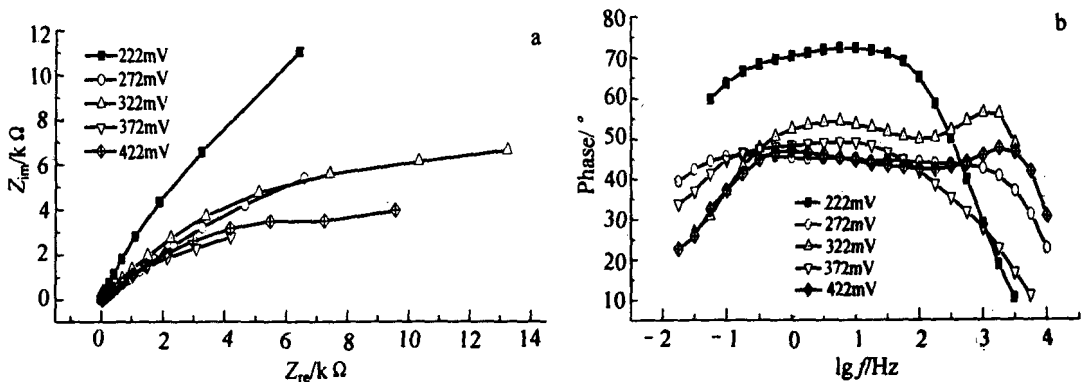


Fig. 3 The EIS of jamesonite electrode in $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ KNO}_3$ solution containing $0.001 \text{ mol} \cdot \text{dm}^{-3} \text{ DDTC}$ in the potential range from 222 mV to 422 mV

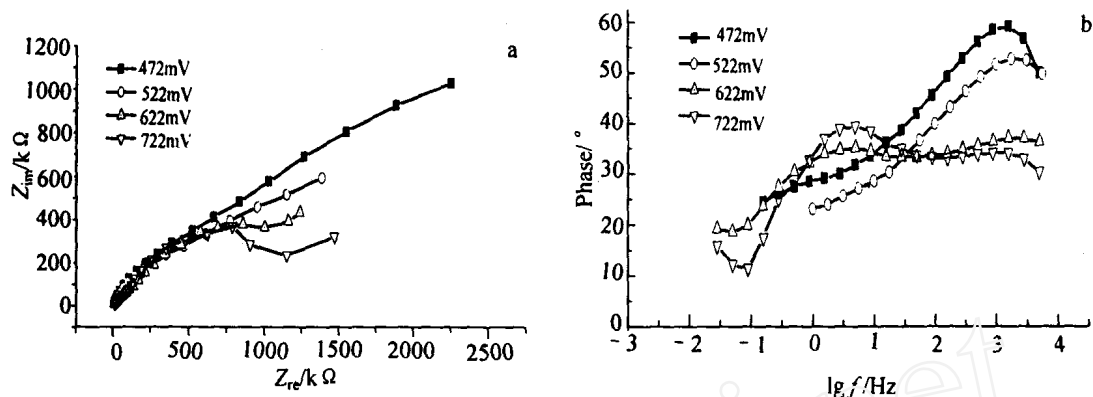


Fig. 4 The EIS of jamesonite electrode in $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{KNO}_3$ solution containing $0.001 \text{ mol} \cdot \text{dm}^{-3} \text{DDTC}$ in the potential range from 472 mV to 722 mV

Seen from Fig. 2 to Fig. 4, although the Nyquist diagrams appear single capacitive loop between -378 mV and 522 mV , the size of their capacitive loops are quite different, and phase-angle plots also are obviously different. This indicates that surface of jamesonite electrode is controlled by different electrochemical processes under extensive potential conditions (Yang Huaiyu, 2000). The diameters of capacitive loops increase rapidly with the enhancement of the electrode potential between -378 mV and 122 mV , so charge transfer resistance increases with the rising of potential. The electrode process is controlled by the growth of chemical absorption film of diethyl dithiocarbamate, which corresponds to reactions (7). The absorption of collector under low potential condition has been reported (Buckley and Woods, 1993, 1995, 1997, et al.). The sizes of capacitive loops are nearly same at 122 mV and 222 mV , which probably correspond to reactions (8,9). When the potential is over 222 mV , the diameters of capacitive loops as well as charge transfer resistance slowly reduce again from 222 mV to 472 mV . It indicates that passive film resulting from bulk precipitate of collector salts (such as S^0 , PbD_2 , SbOD etc.) breaks down gradually. The electrode process is controlled by the breakdown of passive film, which probably corresponds to reactions (12,13). When the potential is over 522 mV , the complicate capacitive loops implies that electrode process is of multiple intermediate products (Zhou Zhong-bo, 1987). Thereby, sulfur may be oxidized into $\text{S}_2\text{O}_3^{2-}$ and SO_4^{2-} ions, which are probably attributed to reactions (4,5). The reactions (10,11) may not exist. That peak current at high potential may result from the deposition of PbSO_4 and a small amount of the absorption of PbD_2 . It was reported that PbD_2 can not be completely decomposed even at high potential (Gu Guohua, 2002). If Nyquist plot is imitated into a half circle, the center of the circle lies below the Z_{re} axle. Consequently, the jamesonite electrode/solution is a system controlled by activated polarization, and

Nyquist curves appear the dispersed characterization (Wu Yinxun, 1995).

The Bode phase angle plots distinctly reveal the variation of the interfacial structure with the electrode potential. When the potential is at - 378 mV, there is only a phase angle at the edge of low frequency. From - 178 mV on, two phase-angles occur. This means that there are two time-constants (τ), namely, there are two different electrode processes on jamesonite electrode surface. The phase angle at the edge of low frequency may represent the anodic corrosion reaction of jamesonite electrode. and the phase angle at the edge of high frequency may have something to do with part passive action on electrode surface resulting from the chemisorption of DDTC, the absorption of elemental sulfur and the bulk precipitate of metal diethyl dithiocarbamate. Part passive action of jamesonite surface changes its interface structure and makes another time-constant occurring. The phase angle is the highest and passive phase angle occurs at 222 mV. When the potential is between 222 mV and 472 mV, seen from the curves of phase angles. the electrode processes should include the growth of absorbing film due to the chemical reaction and the breakdown of absorbed film due to the rising of electrode potential. Only a phase angle appears at 472 mV and 522 mV. So the passive film breaks down entirely, and products of chemical reactions can't be absorbed on electrode surface. When the potential is over 622 mV, there are multiple phase = angles. It may mainly result from the formation of $S_2O_3^{2-}$, $S_xO_y^{2-}$ and SO_4^{2-} ions, and the part deposition on PbS_2O_3 and $PbSO_4$.

3.3 Relationship of Jamesonite Floatability with its Electrochemistry

The floatability of a sulfide mineral mainly depends on the hydrophobicity of its surface, which is related not only to the oxidized products but also to its surface structure and medium charge constant. When a surfactant absorbs on electrode/ solution interface, its differential capacitance will decrease due to the decrease of medium-charge constant (ϵ) and the increment of the thickness of double charge layer. Generally speaking, the smaller the interface capacitance is, the stronger its surface hydrophobicity is. The bigger charge transfer resistance (R_t) is, the more difficult the electrode reaction is. Seen from the study of cyclic voltammogram, there mainly is the absorption of DDTC, PtD_2 , S^0 etc. on the surface of jamesonite mineral from 178 mV to 472 mV. These matters are of hydrophobicity. Seen from the study of EIS, the interfacial capacitance also is small. When the electrode potential is over 472 mV. The surface of jamesonite mineral is of hydrophilicity due to the fact that hydrophobic PbD_2 , S^0 etc are oxidized into hydrophilic products such as Pb^{2+} , SO_4^{2-} , $PbSO_4$. So it was deduced that the potential range of jamesonite floatation using diethyl dithiocarbamate as a collector is from 178 mV to 472 mV, and its optimum potential range is between 122 mV and 222 mV due to the passive action by the hydrophobic species.

4 Conclusions

The interaction behaviors of jamesonite with diethyl dithiocarbamate appeared different elec-

trode processes under different potential conditions. There mainly is the absorption of hydrophobic DDTc, PbD_2 , S^0 etc. on the surface of jamesonite mineral from - 178 mV to 472 mV, and the interfacial capacitance also is small. When the electrode potential is over 472 mV, the surface of jamesonite mineral is of hydrophilicity due to the fact that hydrophobic PbD_2 , S^0 etc. are oxidized into hydrophilic products such as Pb^{2+} , SO_3^{2-} , SO_4^{2-} , PbSO_4 . So it was deduced that the potential range of jamesonite flotation using diethyl dithiocarbamate as a collector is from - 178 mV to 472 mV, and its optimum potential range is between 122 mV and 222 mV due to the passive action by the hydrophobic species.

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电化学研究 DDTC 在脆硫锑铅矿表面的吸附

余润兰^{*1,2}, 胡岳华¹, 邱冠周¹, 覃文庆¹

(1. 中南大学资源加工与生物工程学院, 湖南 长沙 410033)

(2. 衡阳师范学院化学与材料科学系, 湖南 衡阳 421008)

摘要: 通过循环伏安法、交流阻抗法研究了二乙基二硫代氨基甲酸钠(以 D 表示)与脆硫锑铅矿的相互作用。在不同的电位条件下呈现出不同的电极过程。从 -178 ~ 472 mV (相对于标准氢电极), 脆硫锑铅矿表面主要是 DDTC, PbD_2 , S^0 等疏水性物质的吸附, 界面电容也比较小。当电极电位高于 472 mV 时, 由于 PbD_2 , S^0 等疏水性物质被氧化成 Pb^{2+} , SO_3^{2-} , SO_4^{2-} , $PbSO_4$ 等亲水性产物, 脆硫锑铅矿表面是亲水的。由此推测用 DDTC 做捕收剂浮选脆硫锑铅矿的电位范围为 -178 ~ 472 mV, 最佳电位范围为 60 ~ 222 mV。

关键词: 脆硫锑铅矿; 浮选; 电化学