Potential control flotation of galena in strong alkaline media

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Abstract: The electrochemical oxidation of galena in collectorless and collector flotation systems, particularly in strong alkaline media, was studied. The results show that, with pH value higher than 12.5 and potentials below 0.17 V, the oxidation products of galena are elemental sulfur and $HPbO_2^-$. Elemental sulfur was present on the mineral surface in excess of oxidized lead species due to dissolution of $HPbO_2^-$, which is beneficial to the flotation of galena. Under the same conditions, sphalerite and pyrite were depressed as a result of significant surface oxidation. Diethyldithiocarbamate (DDTC) was found to be the most suitable collector for galena flotation in strongly alkaline media. The very potential produced hydrophobic PbD_2—the surface reaction product of DDTC with galena, is 0 to 0.2 V. Meantime DDTC can depress the surface over-oxidation of galena. Investigations also indicate that, in the range of -0.9 V to 0.6 V, hydrophobic PbD_2 can be firmly adsorbed on galena.

Key words: galena; potential control flotation; collector

Document code: A

1 INTRODUCTION

At the early stage of sulfide flotation practice, the chemical theory and adsorption theory of flotation was proposed. The pulp pH was considered to be the most important control factor in flotation. In 1953, Salamy and Nixon[1] first put forward the idea that chemical interactions on the sulfide surface would occur by an electrochemical mechanism. It is now well established that the development of hydrophobicity by sulfide mineral particles in collectorless flotation arises from an anodic process involving the oxidation of mineral, coupled with the cathodic reduction of oxygen. When a collector is present in a flotation system, the anodic process is the charge transfer chemisorption of a thiol ion, and/or oxidation of the thiol ion to its disulfide, and/or the formation of a thiol compound with a metal component of the mineral. The pulp potential is now recognized to be another important factor in controlling flotation, which can be modified by addition of oxidizing or reducing agents or by an outside-polarized electrode connected with a potentiostat. There were lots of electrochemical studies on galena[2-7]. However, few investigations were related to the flotation behavior of galena in strong alkaline media.

In this paper, the authors study the electrochemical oxidation of galena in collectorless and collector flotation systems, particularly in strong alkaline media.

2 EXPERIMENTAL

Working electrodes are prepared using natural galena from Guangxi Province. The galena is a pure, homogeneous phase and a n-type semiconductor, whose diameter is 15 mm, and 3 mm in thickness, and the measured surface area is 1 cm^2. Before each experiment, the galena electrode was first polished with 600 grit silicon carbide paper and then rinsed with double-distilled water.

The reagents are sodium diethyldithio-carbamate (DDTC) with a purity of 99.5% and lime of reagent grade.

For electrochemical measurments, potential or current control was achieved with a Princeton Applied Research 273 potentiostat/galvanostat. All potentials reported are on the standard hydrogen electrode scale assuming that the potential of the calomel electrode on this scale is 0.244 V.

3 RESULTS AND DISCUSSION

3.1 Surface oxidation of galena in collector-less system

3.1.1 E-pH diagram

The researchers are interested in the element sulfur produced in the process of flotation, and take it as beneficial to flotation of sulphide minerals. The E-pH diagram of the $PbS-H_2O$ system at 25 °C, considering the barriers potential of SO_4^{2-} formed, is shown in Fig. 1.

It can be seen from Fig. 1, if potential is suitable, element sulfur exists on the galena surface in the whole pH range due to the oxidation of galena. When pH value is fixed, element sulfur produced has a corresponding potential range, beyond this scope, either the surface of galena is difficult to be oxidized or element sulfur is further oxidized to form SO_4^{2-} [8].

It is well known, the collectorless flotability of galena depends on the relative size of hydrophobicity of element sulfur and hydrophilicity of accompanying surface products, and the suitable pH and E value, i.e. weak acid solution and higher oxidation potential. However, considering the different thermodynamic stability of sulphide minerals, and the separation of galena with accompanying minerals (sphalerite and pyrite), flotation must be carried out in alkaline medium. In the weak alkaline media, hydrophobic sulfur and hydrophilic PbO (or Pb $(OH)_2$) exists simultaneously, while in the strong alkaline media (pH > 12.5), elemental sulfur present on the mineral surface in excess of oxidized lead species due to dissolution of $HPbO_2^-$ and making galena surface more hydrophobic, galena flotation can be carried out in the shadow part shown in Fig. 1.
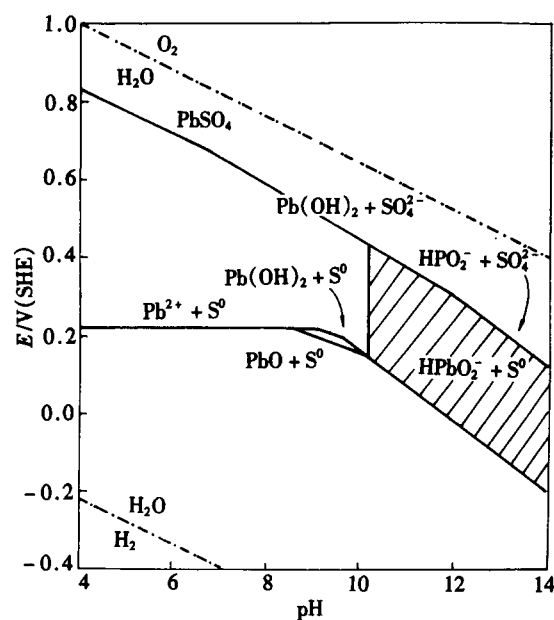

Fig. 1   E-pH diagram of $PbS-H_2O$ system at 25 °C

3.1.2 Electrode processes of galena oxidation in strong alkaline media

Voltammograms of a galena electrode in a saturated lime solution (pH 12.8 buffering solution) are shown in Fig. 2. The solution is transparent and contains no visible lime particles. The anodic current commences at the potential corresponding to the thermodynamic value for reaction (1):
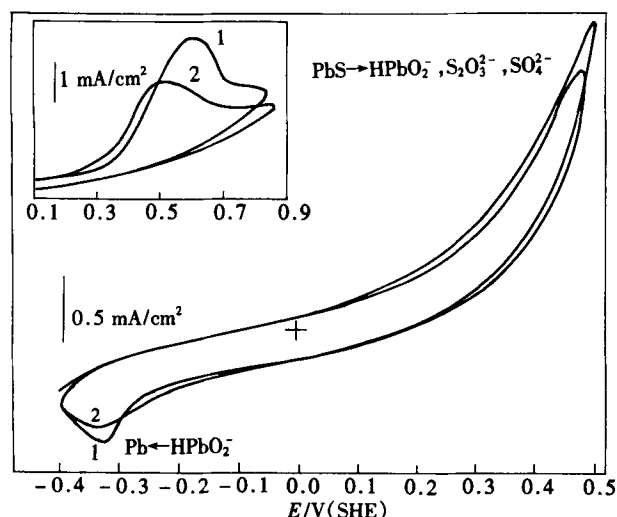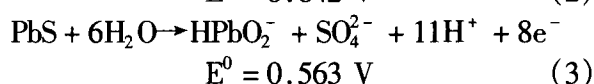
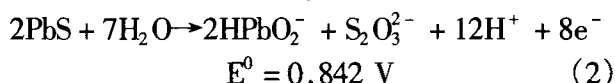$$PbS + 2H_2O \rightarrow HPbO_2^- + S^0 + 3H^+ + 2e^-$$

$$E^0 = 1.182 \text{ V} \qquad (1)$$
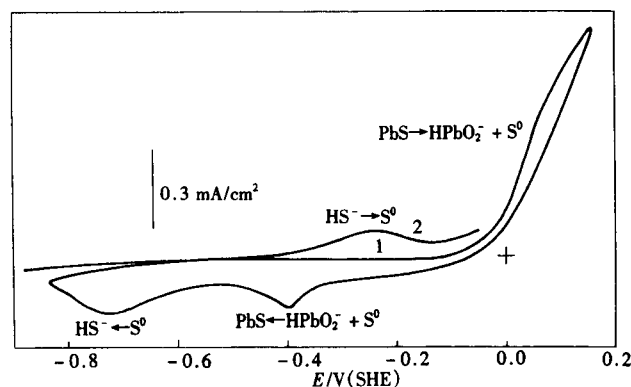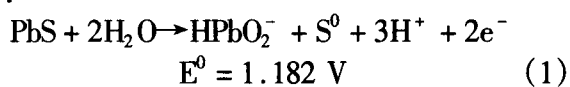
potential scan at 20 mV s^{-1}; pH: 12.8

Background solution: buffer solution

plus 0.5 mol/dm^3 KNO_3 at 25 °C

Fig. 2   Cyclic voltammograms of a galena electrode

Two cathodic current peaks are observed on the subsequent negative-going scan, one at the higher potential corresponds to the inverse reaction (1), and the other to the reduction reaction of surplus sulfur on the electrode surface. A new anodic current peak appears on the second cycles. This phenomenon is attributed mainly to HS^- remaining at the galena electrode.

Fig. 3 shows voltammograms for a galena electrode at pH 12.8 after raising the upper potential limit of the scan. At the higher potentials, sulfur is further oxidized:

$$2PbS + 7H_2O \rightarrow 2HPbO_2^- + S_2O_3^{2-} + 12H^+ + 8e^-$$
$$E^0 = 0.842 \text{ V} \qquad (2)$$
$$PbS + 6H_2O \rightarrow HPbO_2^- + SO_4^{2-} + 11H^+ + 8e^-$$
$$E^0 = 0.563 \text{ V} \qquad (3)$$

Background solution: pH 12.8 buffer solution
plus 0.5 mol/dm^3 KNO$_3$ at 25 ℃

Fig. 3 The first two consecutive cyclic voltammograms of galena electrode

Because the soluble anodic products such as $S_2O_3^{2-}$ and $HPbO_2^-$ transport to the liquid phase, the anodic current on the peaks increases steeply. Note that the peaks in Fig. 2 corresponding to the inverse of reaction (1), and to HS^- oxidation, do not appear in Fig. 3. When the negative-going scan is continued to − 400 mV, the cathodic current peak appears at − 325 mV, this is probably explained by the $HPbO_2^-$ reducing to form Pb. Also shown in Fig. 3 are two consecutive cycling voltammograms recorded when the upper potential

limit exceeds 0.8 V. The anodic current is less on the second scan due to part of the anodic product formed on the first cycle remaining on the electrode surface. This anodic product is attributed to PbO. When the potential exceeds 0.72 V, the anodic current increases again, and this results from the anodic dissolution of the passive product PbO:

$$2PbO + 2H_2O \rightarrow 2HPbO_2^- + 2H^+ \qquad (4)$$
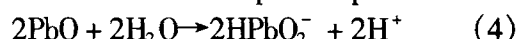
As discussed above, in strong alkaline media (pH 12.8), surplus elemental sulfur can be produced as a result of oxidation and dissolution of the galena surface at a lower oxidation potential (about 0.2 V). On the other hand, it has been reported[3,9] that, at pH > 12.5 and E > 0.2 V, sphalerite and pyrite surfaces are oxidized obviously. So, the flotation separation of galena from sphalerite and pyrite should be carried out in strong alkaline media (pH > 12.5) and the potential must be controlled below 0.2 V.

3.2 The interaction of collector with galena in strong alkaline media
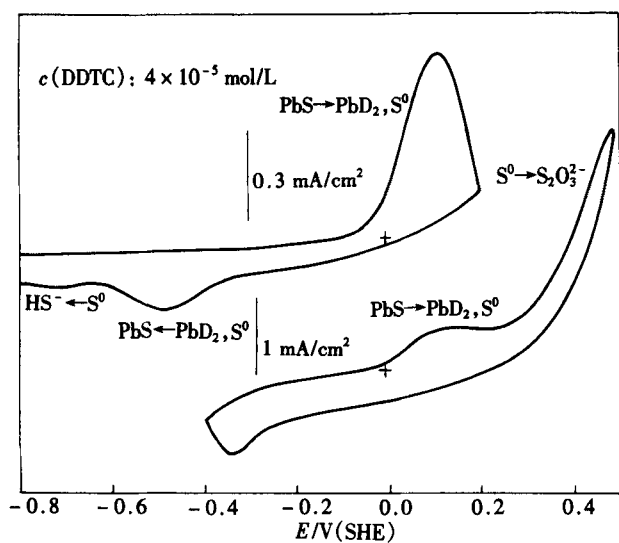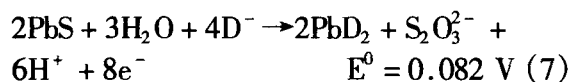
Voltammograms for a galena electrode in the presence of DDTC in strong alkaline media are shown in Fig. 4. It is evident that an anodic current peak arises between 0 to 0.2 V on scans to different upper potential limits. This peak is assigned to the anodic reaction (where D = DDTC):

$$PbS + 2D^- \rightarrow PbD_2 + S^0 + 2e^-$$
$$E^0 = -0.301 \text{ V} \qquad (5)$$
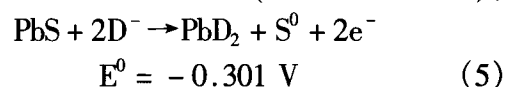
The reversible potential of reaction (5) corresponding to a DDTC concentration of 4×10^{-5} mol L^{-1} is calculated to be − 0.044 V, which is quite close to the initial oxidation potential in the voltammogram. The anodic peak for the formation of PbD$_2$ almost coincides with the peak for galena self-oxidation shown in Fig. 2. In this case, because the products of the oxidation of galena itself are $HPbO_2^-$ and S^0, there exists a chemical reaction in which PbD$_2$ is formed:

$$HPbO_2^- + 2D^- + 3H^+ \rightarrow PbD_2 + 2H_2O \qquad (6)$$
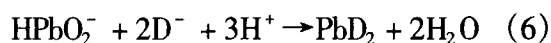
On the negative-going scan, the first cathodic peak corresponds to the formation of PbS again, and the other to the reduction of surface surplus sulfur. When the upper potential limit of the scan is above 0.4 V, the anodic current peak is due to two reactions in which PbD$_2$ is formed. One is reaction (5) and the other may be

$$2PbS + 3H_2O + 4D^- \rightarrow 2PbD_2 + S_2O_3^{2-} +$$
$$6H^+ + 8e^- \qquad E^0 = 0.082 \text{ V} \quad (7)$$

Background solution: pH 12.8 buffer solution
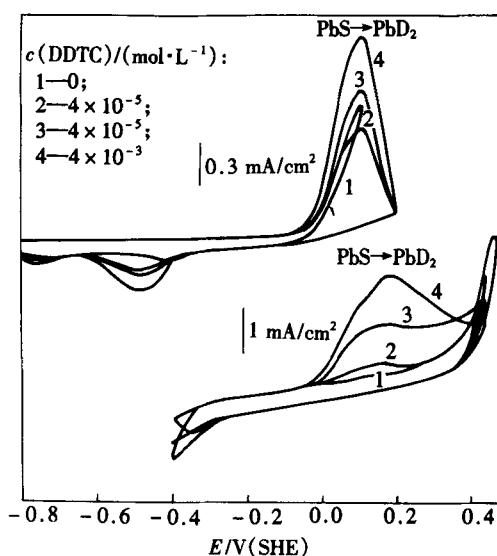plus 0.5 mol/dm³ KNO₃ at 25 ℃

Fig. 4 Cyclic voltammograms of galena electrode on a potential scan at 20 mV s⁻¹

Fig. 5 represents voltammograms at different DDTC concentrations at pH 12.8 with the upper limit of potential scan being 0.2 V and 0.5 V, respectively. The anodic current peak resulting from the formation of PbD2 is increased when the DDTC concentration is increased; meanwhile the anodic current peak for the oxidation of galena decreases.

It can be seen from Fig. 5 that the increase in the charge associates with the cathodic current peak increased at a lower rate than that for the increase in the anodic peak. This indicates that PbD_2 is not reduced completely in the cathodic process. This behavior is also illustrated in Fig. 6, which shows voltammograms for three consecutive cycles.

It can be concluded that there exists a critical concentration of DDTC between 0 and 4×10^{-3} mol/L⁻¹ at a given pH value. Above this concentration, PbD_2 is formed by the anodic process (reaction (5)). Below the critical value, oxidation of galena occurs as the major anodic process. From Fig. 5 it can be seen that the cathodic peak appears on the voltammograms for the galena electrode at pH 12.8 is greatest at a DDTC concentra-

tion of 4×10^{-3} mol·L⁻¹. The oxidation of galena itself is depressed at the high DDTC concentration. The anodic current peak of PbD_2 is seen to appear at 0-0.2 V. However, the anodic current decreases continuously when the electrode is cycled between -0.9 V and 0.6 V, and the anodic peak shifts slightly to more negative potentials. These phenomena may be attributed to the incomplete reduction of PbD_2. The accumulation of PbD_2 at the galena surface on cycling may retard the anodic process.

Background solution: pH 12.8, buffer solution
plus 0.5 mol/dm³ KNO₃ at 25 ℃

Fig. 5 Cyclic voltammograms for galena electrode in solutions of different DDTC concentration on potential scans at 20 mV s⁻¹
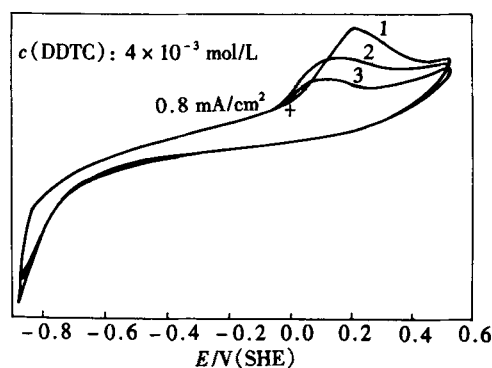
Background solution: pH 12.8 buffer solution
plus 0.5 mol/dm³ KNO₃ at 25 ℃

Fig. 6 The first three consecutive cyclic voltammograms for a galena electrode on potential scans at 20 mV s⁻¹

4 CONCLUSIONS

The analyses of the E-pH diagram of the PbS-H_2O system at 25 ℃ indicate that in the weak alkaline media, hydrophobic sulfur and hydrophilic PbO (or Pb(OH)$_2$) exist simultaneously, while in the strong alkaline media (pH > 12.5), elemental sulfur is present on the mineral surface in excess of oxidized lead species due to dissolution of $HPbO_2^-$ and making galena surface more hydrophobic, galena flotation can be carried out in strong alkaline media. All this is verified by the study of the electrochemical oxidation of galena.

Diethyldithiocarbamate (DDTC) is a suitable collector for galena flotation in strong alkaline media. The very potential produced hydrophobic PbD_2—the surface product of DDTC on galena, is 0 to 0.2 V. Meantime DDTC can depress the surface over-oxidation of galena. Investigations also indicate that, in the range of -0.9 V to 0.6 V, hydrophobic PbD_2 can be firmly adsorbed on galena.

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