

OXIDATION OF GALENA IN AMMONIUM CARBONATE SOLUTION AND APPLIED REACTOR^①

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ABSTRACT Anodic behaviour of galena in ammonium carbonate solution and products of anodic reaction resulting in passivation have been studied by electrochemical technologies including rotating ring-disc electrode etc. and physical detects. The effects of impurities in galena such as pyrite, pyrrhotite on converting galena to lead carbonate have been explained. The conversion rate can be accelerated by addition of some cupric ions to the ammonium carbonate solution and can be expressed by $a = K \log t + B$. The optimum reactor suitable for the conversion is a propeller agitation reactor without baffles, which has been proved in enlarged experiments with the reactor charged 50 kg ore.

Key words galena carbonate reactor

1 INTRODUCTION

Galena is used as the raw materials to recover lead. At present pyrometallurgy is generally used to extract lead at home and abroad. Now due to the rigorous demands in the conditions of environment and labour protection, recovery of lead by a hydrometallurgical process is being widely researched. But up to date none of the processes proposed is practicable economically and technically.

The process proposed by Lu, Keyuan^[1] in which conversion of galena to PbCO_3 in ammonium carbonate solution is simple and realizable. But very fine particles of ore and longer leaching time are required for the complete conversion of galena into PbCO_3 . The conversion percent of galena in ores originating from different mining areas had markedly difference, so that it is necessary to make thorough research on the conversion of galena. In order to accelerate the conversion, the Hydrometallurgical Research Laboratory, the Institute of Chemical Metallurgy have widely researched the conversion process. It involved reaction kinetics and mechanism, reaction products causing passivation, how to accelerate the

process and the reactor required for realizing the conversion.

2 ELECTROCHEMISTRY ON OXIDATION OF GALENA

2.1 *Anodic Polarization of Galena With a Ring-Disc Electrode*^[2]

The behaviour of anodic polarization of galena in ammonium carbonate solution was measured using ring(Ag)-disc(PbS) electrode with potential scanning. Three sharp current peak of 0.49 V (SHE), 0.86 V and 1.19 V were found under some experimental conditions on the anodic polarization curve in Fig. 1. The responded current occurred on Ag ring was also shown in Fig. 1. The actual collect efficiency N_{app} was much less than the theoretical value $N_{\text{th}} = 0.35$, showing the reaction products corresponding with the disc current were not mostly soluble or were not collected by the ring. It can be guessed according to the experimental results obtained by ring-disk electrode that the anodic polarization of galena probably goes through the steps of $\text{S}^{2-} \rightarrow \text{S}^0 \rightarrow \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-}$.

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2.2 Polarization Behaviour of Galena at Low Potential Region Using Stationary Electrode^[3]

In low potential region and low scanning rate, the voltammogram of artificial PbS is shown in Fig. 2^[3, 4]. The polarization curve can be divided into three segments. *a b* section

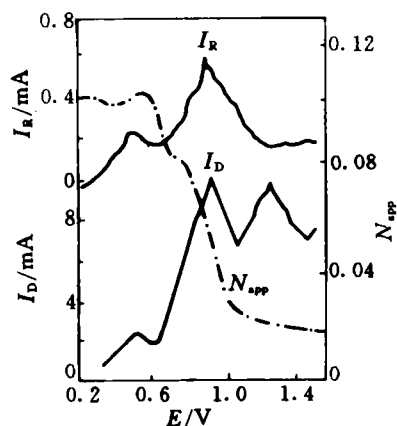


Fig. 1 Linear potential sweep Voltammogram obtained at a galena-Ag RRED and ring collection efficiency

note: $C_{(\text{NH}_4)_2\text{CO}_3} = 0.5 \text{ mol/L}$; $\text{pH} = 9.5$;
 $E_R = 0.7 \text{ V}$; $T = 298 \text{ K}$; 750 min^{-1} ; 10 mV/s

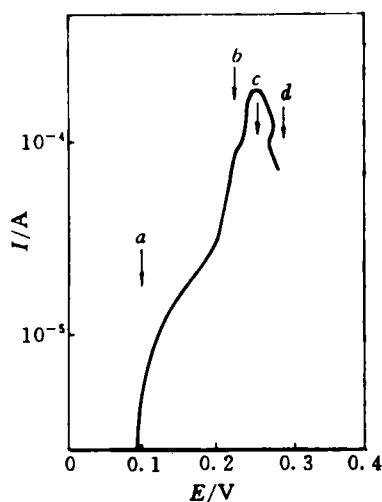


Fig. 2 Steady state anodic polarization of galena

note: $C_{(\text{NH}_4)_2\text{CO}_3} = 1 \text{ mol/L}$; $T = 298 \text{ K}$; 0.1 mV/s ; N_2

is a straight line; *cd* section is resulted from the products causing passivity; *bc* section is departure from the straight line toward the direction of increasing current. The level of the pit corrosion on the surface of electrode is probably responsible for the current departure from the straight line. The following equations

$$\partial \lg I / \partial \lg [\text{NH}_4^+] = 2.0$$

$$\partial \lg I / \partial \text{pH} = 0.92$$

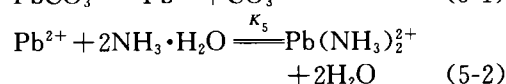
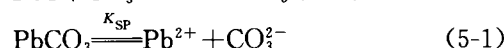
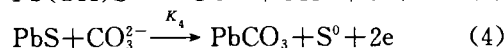
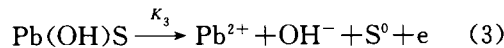
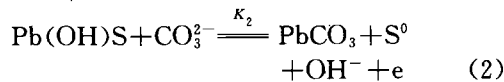
can be acquired from the polarization curves obtained in the solution with different concentration of $(\text{NH}_4)_2\text{CO}_3$ or different pH ^[2].

2.3 Physical Identification of Reaction Products on Surface of Galena^[5]

The reaction products on the surface of galena were identified by X-ray diffraction, SEM and AES. These experimental results showed there was PbCO_3 and amorphous sulfur on the surface of galena.

2.4 Mechanism of Reaction^[6]

According to the experimental results described above, the following mechanism was proposed:



According to the mechanism of reaction, at low potential region, the following equations can be obtained:

$$[\partial \lg i / \partial \lg [\text{NH}_4^+]]_E = 2$$

$$[\partial \lg i / \partial \text{pH}] = 1$$

It is consistent with the experimental results above.

A computer program was designed and used to evaluate the constants of these equations on the basis of the data obtained from voltammograms. The results are listed as fol-

lows:

$$K_1 = 0.4 \sim 7 \times 10^{-1};$$

$$K_2 = 1.2 \sim 3.1 \times 10^{-11};$$

$$K_3 = 0.4 \sim 1.6 \times 10^{-12};$$

$$K_4 = 3.2 \sim 6.2 \times 10^{-11};$$

$$K_5 = 1.6 \sim 4.3 \times 10^7$$

The theoretical curve obtained with these constants is in agreement quite well with the experimental curve, indicating that the reaction mechanism proposed by the authors is reasonable.

3 INTENSIFICATION OF CONVERSION OF GALENA TO LEAD CARBONAT

3.1 Effects of FeS_2 , Fe_7S_8 on the Conversion process of Galena^[7]

It had been experimentally found that the content of pyrite in ore affected remarkably on the conversion rate and the conversion ratio of galena. The results measured by electrochemical technologies showed that both Fe_7S_8 and FeS_2 can accelerate the conversion process of galena and that the acceleration of Fe_7S_8 on the oxidation of galena is larger than that of FeS_2 , this being attributed to larger catalytic activity of the surface of Fe_7S_8 on the reduction of oxygen^[8]. With the practical conversion process, the effects of impurity pyrite and pyrrhotite on the conversion ratio of galena can be expressed by the following formula^[9]:

$$i_{\text{Pbs}} = A(1 + BW_1)^{\beta_1}$$

where $A = i_{1d}$

$$B = i_{1d}/i_{1d} \times 10^{(E_{1r} - E_{1r})/b_c};$$

$$\beta_1 = b_c/(b_c + b_{1a});$$

i_{Pbs} —dissolved current density of galena;

i_{1d} —under rest potential, dissolved current density of galena;

i_{1d} —under Rest Potential, dissolved current density of impurity sulfides;

E_{1r} —rest potential of galena;

E_{1r} —rest potential of impurity sulfides;

b_{1a} —Tafel slope of the anodic oxidation of galena;

b_c , b_{1c} , b_{1c} —Tafel slope of the cathodic reduction of oxygen on sulfide ores

3.2 Catalysis of Copper Ion on the Conversion of Galena to PbCO_3 ^[5]

It has been found experimentally the conversion percent of pure and natural galena was very low, only about 1%. If copper ion was contained in ammonium carbonate solution, the conversion percent was markedly increased while high concentration of $\text{Cu}(\text{NH}_3)_4^{2+}$ was also unfavourable, because CuS can be formed on the surface of galena. The further reaction of galena would be blocked.

4 KINETICS OF CONVERSION OF GALENA^[5]

In the presence of copper ion, the kinetics of conversing galena into lead carbonate can be described by $a = K \lg t + B$

where

a —conversion ratio of galena

t —reaction time(h)

K , B —constants which can be obtained from a plot of $a - \lg t$ curves and B can be regarded as a conversion ratio of galena at first hour of reaction.

At the initial stage of reaction, conversion ratio is directly proportional to the concentration of copper ion. The effects of the $(\text{NH}_4)_2\text{CO}_3$ concentration on the conversion ratio of galena is less. But with the prolongation of reaction time, the conversion ratio is directly proportional to the concentration of $(\text{NH}_4)_2\text{CO}_3$. At a high concentration of $(\text{NH}_4)_2\text{CO}_3$, the effect of the concentration of Cu^{2+} is less. But at low concentration of $(\text{NH}_4)_2\text{CO}_3$, the concentration of Cu^{2+} is increased, the conversion ratio is decreased. Apparent activation energy at the initial stage of reaction, $\Delta E_B = 36.8 \text{ kJ/mol}$, can be obtained from the drawing of $\lg B \sim 1/T$. The effect of temperature on K is irregular. As the size of ore particles increases, B decreases and K increases.

5 REACTOR USED IN OPERATION OF CONVERSION^[10]

It has been proved by enlarged experiments charged 50 Kg concentrate of PbS containing Au that the propeller agitation reactor without baffles is available for the conversion of galena into PbCO₃. The optimum parameters of the reactor are: $D/d = 3.5$, $H/C = 7$, the dip angle of paddle being 45°. Where D is the diameter of the reactor(m); d diameter of the paddle of the agitator(m); H height of the reactor(m); C distance from the paddle to bottom of the reactor. The conversion efficiency of the reactor is more than 99% and the energy consumption is lower.

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(From page 40) agglomerates are lower than those of the compacts, the sintered densities are quite close to theoretical density. Hence, in order to increase the sintered density, it is necessary to decrease the agglomerate density as much as possible.

4 CONCLUSIONS

(1) When chemical coprecipitation is used to prepare ultrafine ZrO₂ (Y₂O₃) powders, poor sinterability for the powder derived from direct drying and calcination of water-washed hydroxide gels is observed. Ball-milling is found to be an effective way to improve the sinterability of the powder, and the sintered density is increased from 89% to 96% of theoretical density.

(2) The powder sinterability can be greatly improved by adding some surfactants during the coprecipitation and before drying of hydroxide gels, and the sintered density high-

er than 98% is obtained, which is quite close to that of the powder derived from alcohol-washed gels.

(3) The key to increase the sintered density is to lower the agglomerate density and strength as well as to increase the compaction pressure.

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