

# A STUDY ON THE ANODIC DISSOLUTION OF LEAD SULPHIDE AND CUPRIC SULPHIDE

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## I. Introduction

The extraction of metal from the metal sulphide concentrate is made by pyrometallurgy or hydrometallurgy that are operated through the processes of roasting or sintering. These processes are complicated and troublesome, so that many investigators go on with the studies on the direct extraction of the metal sulphide concentrate. These studies are the ammonia or oxygen pressure leaching and the direct electrolysis of these concentrate mixed with carbon or graphite powder and so on.

In this work, the metal sulphide concentrate which filled up around the anode carbon electrode was directly electrolyzed. The dissolution efficiencies for metal and the production efficiency for elemental sulphur and the anodic polarization were studied. (Elemental sulphur produced by this direct electrolysis is useful). Further, the anodic polarization behaviour was measured and the anodic reaction of the metal sulphide concentrate with the active oxygen that was produced by discharging at the anode, were discussed.

## II. Experimental

### *II-I. Experimental apparatus and specimen*

Experimental apparatus is shown in Fig. 1. Electrolytic cell was made from acryl-resin and temperature was controlled by electrical method. This electrolyte was stirred by stirrer. Reference electrode was saturated calomel electrode and

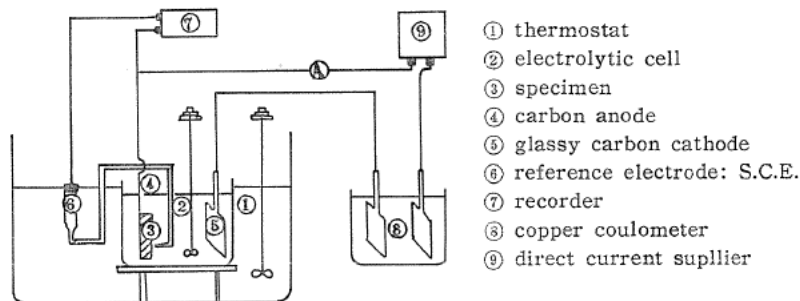


FIG. 1. Experimental apparatus

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copper coulometer was used to measure the quantity of electricity. The surroundings of carbon electrode which was anode, were filled up by specimen and the specimen was closed by the filter cloth not to fall down. Glassy carbon electrode was used as cathode, because the quantitative analysis of cathode deposit was easily carried out. The grain size distribution of the specimens used is shown in Table 1. Besides, elemental sulphur was not included in these specimens.

TABLE 1. The grain size distribution of specimen

Mesh→ Reagents↓	<100	100~150	150~170	170~200	200~250	250~325	325<
PbS (%)	19.88	34.39	23.32	18.69	3.02	0.43	0.27
CuS (%)	5.01	8.56	6.82	16.47	56.81	5.11	1.22

### II-2. Experimental procedure

The block diagram of the experimental operations is shown in Fig. 2. The surroundings of the anode carbon electrode was filled up by the specimen and it was closed by the filter cloth and it was electrolyzed at the conditions of the specified temperature and constant current density for 3 hours. After electrolysis, anode residue was washed and filtrated. Elemental sulphur in the residue was analyzed quantitatively (Lead sulphate was analyzed quantitatively in case of Pb sulphide). The dissolution quantity of metallic ion was obtained from the electrolyte, the washing solution and the cathode deposit. Besides, the anodic polarization was measured by means of the constant current method.

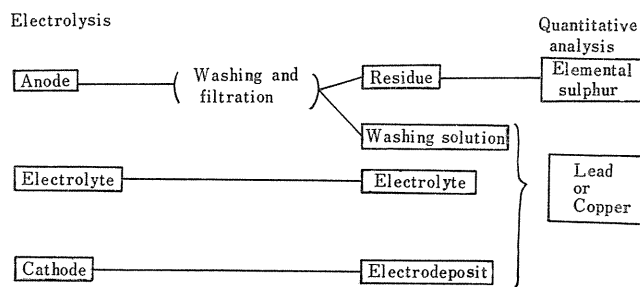


FIG. 2. Block diagram of the experimental operation.

### II-3. Analytical procedures

#### a) The quantitative analysis of elemental sulphur

The residue which was washed and filtrated was dried enough in the dry oven controlled below 50°C. After dring, about 1 gram of it is weighted exactly and it was put into a 100 ml beaker. After about 50 ml of pyridine was added into it, it was heated to the boiling point. After heating, it was filtrated into a 100 ml messflask. Again about 50 ml of pyridine was added in its residue, and the above-mentioned operation was repeated. Finally, pyridine was added in order to make exactly 100 ml solution. A part of this pyridine solution was mixed with two parts of the supporting electrolyte, and the polarographic analysis was carried out. This calibration curve is shown in Fig. 3. This half wave potential

is  $-0.65$  V.

*b) The quantitative analysis of lead*

After electrolysis, the sum of the electrolyte (3% HBF 500 ml) and the washing solution of the anode residue, was diluted to the proper concentration of lead by 3% hydrofluoroboric acid. Three parts of this dilute solution were mixed with a part of 0.3% gelatin solution as maximum suppressor, and the polarographic analysis was carried out. This calibration curve is shown in Fig. 4. This half wave potential is  $-0.60$  V. The lead deposited at the cathode was solved in 100 ml of 1 N nitric acid. By the above-mentioned method, the polarographic analysis was carried out. This calibration curve is shown in Fig. 5. This half wave potential is  $-0.78$  V.

*c) The quantitative analysis of lead sulphate*

About 500 mg of the anode residue dried was exactly weighted and about 50 ml of 1 N sodium hydroxide was added on it and was heated. After heating, the

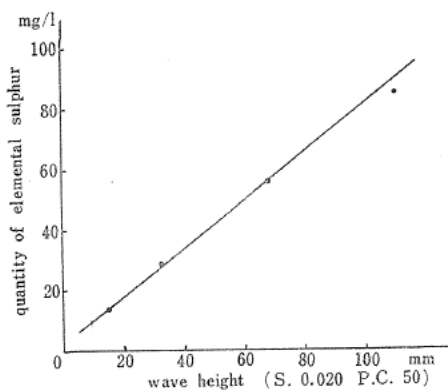


FIG. 3. The calibration curve of elemental sulphur.

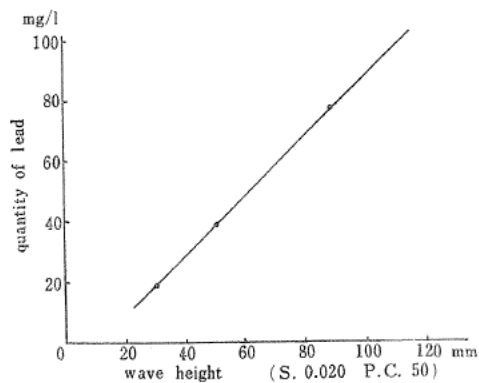


FIG. 4. The calibration curve of lead in the  $\text{HBF}_4$  solution

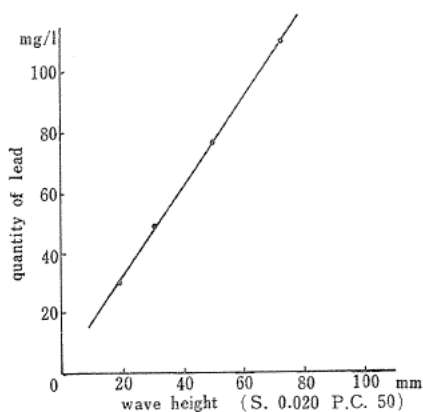


FIG. 5. The calibration curve of lead used 1 N  $\text{HNO}_3$ .

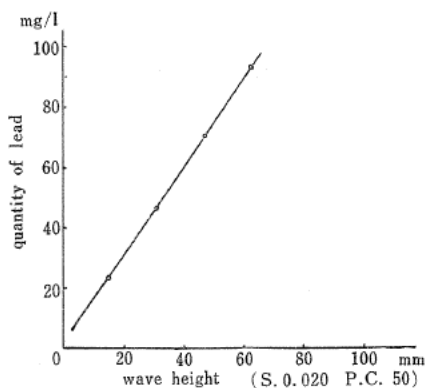


FIG. 6. The calibration curve of lead sulphate.

solution was filtrated. Then the filtrated solution was diluted exactly to 100 ml by 1N sodium hydroxide. Three parts of the dilute solution were mixed with a part of 0.3% gelatin solution, and the polarographic analysis was carried out. This calibration curve is shown in Fig. 6. This half wave potential is  $-0.75$  V.

*d) The quantitative analysis of copper*

After electrolysis, the electrolyte (3%  $\text{HBF}_4$  500 ml), the washing solution of the anode residue and the solution obtained by dissolution of cathode deposit copper into conc. nitric acid, were each analyzed by the atomic absorption method.

*II-3. Experimental conditions*

The experimental conditions are shown in Table 2.<sup>1)2)</sup>

TABLE 2. Experimental conditions

Conditions ↓	Reagents →	PbS	CuS
Electrolyte		3% $\text{HBF}_4$	3% $\text{HBF}_4$
pH		1.0	1.0
Electrolytic temperature		50°C	40°C
Current density		0.3 A/dm <sup>2</sup>	1.3 A/dm <sup>2</sup>
Electrolytic time		3 hour	3 hour

*II-4. Experimental results*

The anode polarization curves of lead sulphide and cupric sulphide for the variation of the specimen density are shown in Fig. 7 and 8. Table 3 and 4 show respectively the results of the constant current electrolysis for lead sulphide and cupric sulphide, where the dissolution efficiency for lead and copper (II) and production efficiency for elemental sulphur are defined as follows.

In main reactions, the active oxygen which discharged at the anode, acted with lead sulphide, and lead oxide and cupric oxide are produced. These dissolve

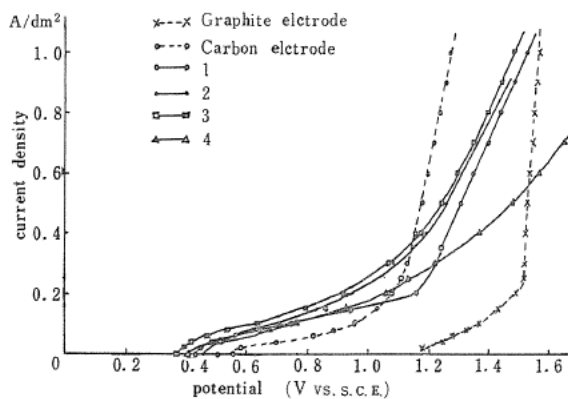


FIG. 7. The anodic polarization curve of PbS in 3%  $\text{HBF}_4$  solution.

into the electrolyte. By this overall reaction ( $\text{PbS} = \text{Pb}^{2+} + \text{S}^0 + 2e$ ,  $\text{CuS} = \text{Cu}^{2+} + \text{S}^0 + 2e$ ), those efficiencies are defined.

### III. Experimental consideration

#### III-1. On the polarization curves

The anode polarization curves of lead sulphide in Fig. 7, especially the curves of number 2 and 3, suggest that the active oxygen at the anode reacted conveniently to sample under the condition of this apparent current density 0.3 A/dm<sup>2</sup>. And the dissolution efficiency for lead and the production efficiency for elemental sulphur in Table 3 somewhat supported this suggestion. In the cupric sulphide case, the curves of number

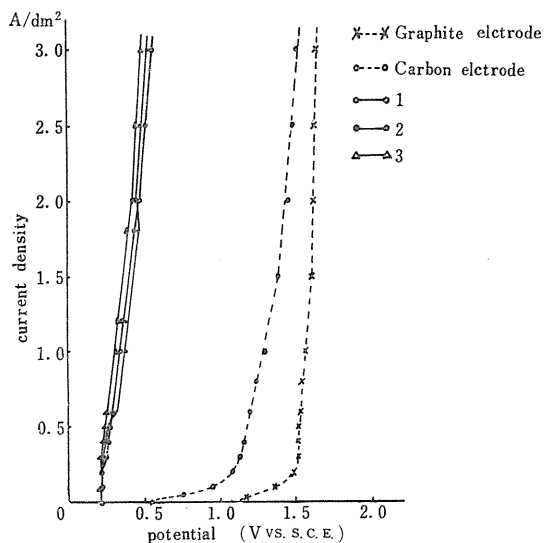


FIG. 8. The anodic polarization curve of CuS in 3% HBF<sub>4</sub> solution.

TABLE 3. The experimental data for PbS

Experimental number	Density (g/cm <sup>3</sup> )	Dissolution efficiency for Pb (%)	Production efficiency for S <sup>0</sup> (%)	Content of PbSO <sub>4</sub> (%)
1	0.69	79.4	49.3	16.0
2	1.16	74.0	80.0	17.3
3	1.67	77.0	40.0	17.6
4	2.23	76.5	79.7	17.5

TABLE 4. The experimental data for CuS

Experimental number	Density (g/cm <sup>3</sup> )	Dissolution efficiency for Cu (%)	Production efficiency for S <sup>0</sup> (%)
1	1.37	138	24.9
2	1.78	108	16.8
3	2.72	93.8	4.95

1, 2 and 3 in Fig. 8, suggest that the active oxygen reacted conveniently to sample under the condition of this apparent current density 1.3 A/dm<sup>2</sup>. The active oxygen reacts better to the sulphides on the graphite electrode than the carbon electrode showing in Fig. 7 and 8.

#### III-2. On the data of electrolysis

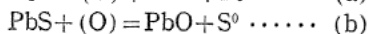
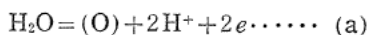
Lead sulphide; the dissolution efficiencies for lead shown in Table 3, was nearly 80% with no relation to the various specimen densities. The content of lead sulphate in the anode residue was about 18%, and was almost equal to the values before the electrolysis. This was indicated by quantitative analysis and by X-ray

diffractionometry. Therefore, the lead sulphate effected hardly to the anode reaction in this experimental. Cupric sulphide; Table 4 indicates that the smaller the density of specimen was, the larger the dissolution efficiency for copper and the production efficiency for elemental sulphur were. We suppose that the dissolution efficiency for cupric rose over 100% according to additional reaction of the cupric sulphide to the dissolved oxygen. And the smaller the density of specimen was, the better the permeation of electrolyte was, so that the dissolution efficiency for copper was high, we suppose. Besides, the grain size of metal sulphide concentrate showing in Table 1, may have an important effect upon the reactive effect. It is considered on the size of sulphides that the smaller the size of specimen is, the better the reaction occurs.

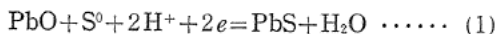
III-3. Consideration from potential-pH diagrams

a) PbS-H<sub>2</sub>O system

The potential-pH diagram of PbS-H<sub>2</sub>O system at 25°C is shown in Fig. 9. Each activity is defined respectively  $a_{Pb^{2+}}=10^{-4}$ ,  $a_{HSO_4^-}=10^{-3}$ ,  $a_{H_2S}=10^{-3}$ , and  $a_{PbO}=1$ , according to the last concentration of lead in the electrolyte in the PbS-H<sub>2</sub>O system. Though the experimental results indicate that the elemental sulphur is produced, it isn't produced at view of equilibrium at the point (⊗ in Fig. 9) of pH=1 and E=1.2 V in this work. Therefore, the reaction mechanisms which specimen acted with the active oxygen are considered as follows, where (O) is active oxygen.



(a) + (b)



$$E = 0.728 - 0.0591 \text{ pH} + 0.0296 \log a_{PbO} \dots\dots (1)'$$

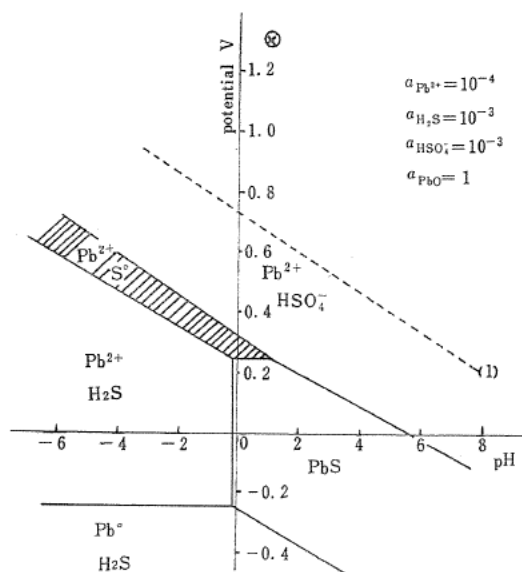
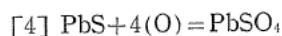
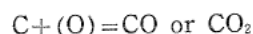
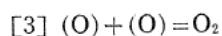
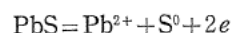
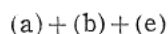
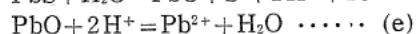
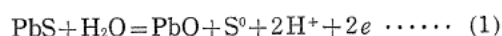
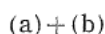
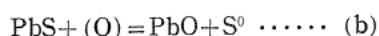
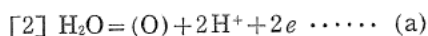
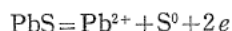
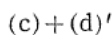
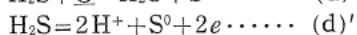
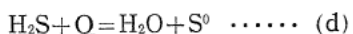
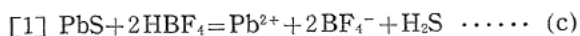


FIG 9. The potential-pH diagram of PbS-H<sub>2</sub>O system at 25°C.

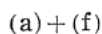
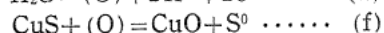
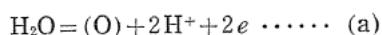
This reaction equation (1) entered in Fig. 9, is shown by the dotted line (1). At the point which a potential is higher than this dotted line, the elemental sulphur is produced. This illustrates fairly the experimental results. Therefore, the reactions of lead sulphide at the anode are considered as follows.



For the reaction [1], in this experiment, it is observed that lead sulphide acts with the dissolved oxygen in the electrolyte and produces the elemental sulphur according to the reaction (b). For this, it is considered that the activity of the dissolved oxygen in 3% hydrofluoroboric acid is a large, therefore the elemental sulphur is produced. Besides, during electrolysis, it is suspected that it is produced according to the reaction (d)'. Therefore, this reaction [1] is perhaps main possible reaction. For the reaction [2], as the above mentioned consideration at the potential-pH diagram, it is considered that this is also a main possible reaction. For the reaction [3], those productions were not observed. For the reaction [4], the content of lead sulphate didn't change before and after this experiment in Table 3. Therefore, the anode reactions of lead sulphide concentrate are controlled by [1] and [2].

#### b) *CuS-H<sub>2</sub>O system*

The potential-pH diagram of CuS-H<sub>2</sub>O system at 25°C defined by the same method of lead sulphide, is shown in Fig. 10. Though the experimental results indicated that the elemental sulphur is produced, it isn't produced at the view of equilibrium at the point (in Fig. 10) of pH=1 and E=0.6V in this experiment. Therefore, the anode-reaction-mechanisms of the reaction with the active oxygen, are considered as follows.



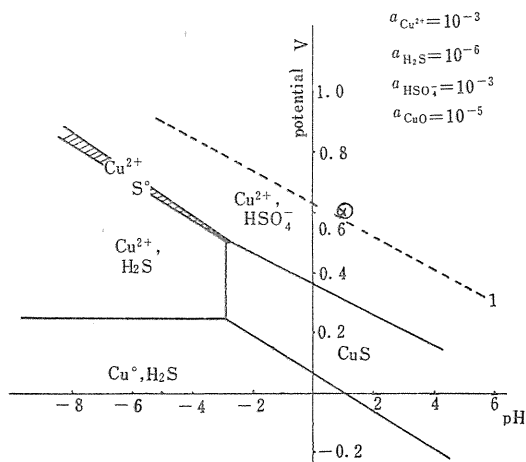
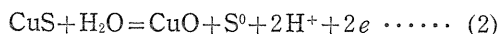
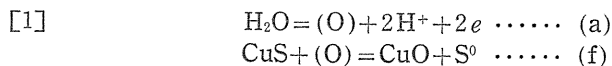


FIG. 10. The potential-pH diagram of CuS-H<sub>2</sub>O system at 25°C.

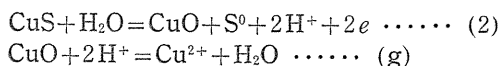


$$E = 0.778 - 0.591 \text{ pH} + 0.0296 \log a_{\text{CuO}} \dots\dots (2)'$$

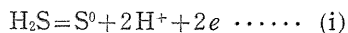
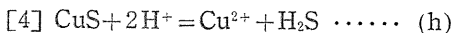
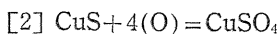
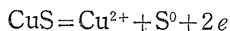
This reaction equation (2) entered in Fig. 10, is shown by the dotted line (1). At the point which the potential is higher than this dotted line, the elemental sulphur is produced. This illustrates the experimental results better. Therefore, the reactions of cupric sulphide at the anode are considered as follows.



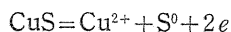
(a) + (f)



(a) + (f) + (g)



(h) + (i)



The reaction [1] is considered similarly as a main possible reaction. The reaction [2] isn't considered as a main possible reaction on account of the high dissolution efficiencies for copper from this experimental results. The reaction [3] isn't considered owing to no observation of the production. The reaction [4] isn't considered also, because it isn't observed that the elemental sulphur produces

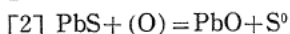
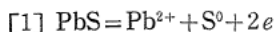


by the action of the dissolved oxygen. This phenomenon differs from lead sulphide. Also owing to the potential-pH diagram, this isn't considered as a main possible reaction. Therefore, the anode reaction of cupric sulphide concentrate is controlled by the reaction [1]. But, there is a question how sulphur except production of elemental sulphur reacts. One of answers for it will be the effect of the vacancy of cupric sulphide, we guess. It is considered that this question must, henceforth, be solved by the followed investigation.

#### IV. Conclusion

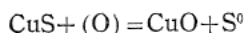
(1) For lead sulphide concentrate, the dissolution efficiencies for lead didn't change in this experimental region of density of specimen.

(2) The anode reactions of lead sulphide concentrate are controlled by the following reactions.



(3) For cupric sulphide, the smaller the density of specimen was, the larger the dissolution efficiency for copper and the production efficiency for elemental sulphur were.

(4) The anode reaction of cupric sulphide concentrate is controlled by the following reaction.



(5) Elemental sulphur is produced from lead sulphide concentrate by the dissolved oxygen which included the electrolyte. But, it isn't produced from cupric sulphide concentrate by the same process.

#### V. Reference

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