

FOUNDAMENTAL STUDY ON PRODUCTION OF COPPER POWDER BY DIRECT ELECTROLYSIS (1)

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1. Introduction

Copper powders for power metallurgy are now produced by electrolysis process, spraying process, mechanical grinding process etc., (especially electrolytic process.) However, the source material for these process is copper metal, which is produced through many complex process. In this study, we tried to produce the copper powder by direct electrolysis of acidic copper sulfate solution using copper concentrates and lead pole as an anode, whereas the cathode is copper plate. Thus the old complex processes can be omitted. We investigated the anode reaction mechanism of this process and the behaviours of impurities in this electrolysis system. Chalcopyrite concentrates were used as copper concentrates.

2. Experimental

2.1. Materials

Copper concentrates (chalcopyrite) used for main reaction mechanism in this experiment consist of CuFeS_2 (mainly), FeS_2 , $\beta\text{-ZnS}$ (little). The chemical compositions are Cu: 12.30%, Fe: 22.35%, S: 38.80%, Si: 2.20%, Zn: 2.40% and so on.

2.2. Experimental procedure

The experimental apparatus is shown in Fig. 1. Electrolytic current source is 20 volt DC and a copper voltameter is used as voltameter, and as sealing cloths of anode and cathode for many purpose salans (co-polymer) are used.

Procedure: Construct the above apparatus and connect the lead wire as Fig. 1 and flow such DC current as fit the experimental specified condition (anodic current density, cathodic current density, electrolytic potential etc.).

The electrolytic conditions are as follows:

Initial pH valuc: 1.40, Temperature: 50°C

Experiment	Initial Cu content in electrolyte, g/l,	Cathodic current density, A/dm ²
a	33.5	1.87
b	0	2.50
c	0	1.30

Then, Cu content in electrolyte and pH is measured by spectrophotometry and pH meter.

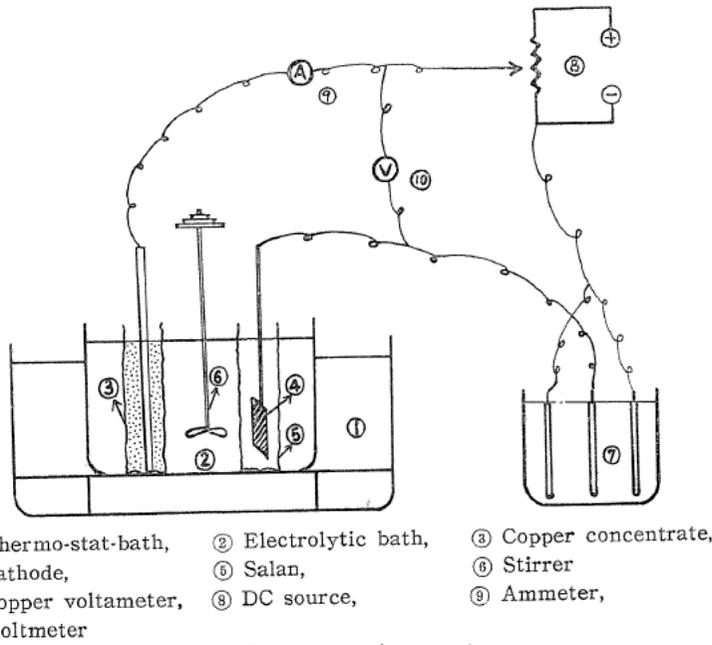


FIG. 1. Experimental apparatus.

2.3. Pre-experimental results and consideration

The experimental results are shown in Fig. 2. In the case (a) of the appli-

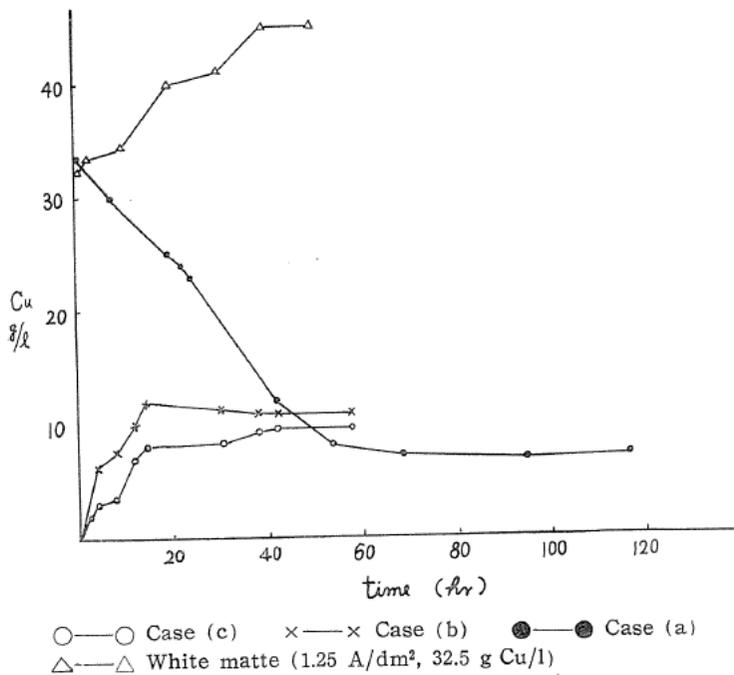


FIG. 2. Cu (g/l) in electrolyte-time (hr) curves in pre-experiments.

cation of the experimental optimum condition for white matte to copper concentrate, copper content in electrolyte reduces with time and becomes constant later, owing to low anodic current efficiency of this experiment. In the cases (b) and (c), Cu content in electrolyte becomes constant at 6-10 g/l.

3. Experimental Results and Consideration

3.1. Influences of cathodic current density

Electrolytic conditions are; Temperature: 40° C. Initial copper content in

TABLE 1. Experimental data for influences of cathodic current density

Cathodic current density, A/dm ²	5.62	5.00	2.50	1.25	0.31
Electrolytic (Ini.) potential, v (Fin.)	20 6	20 7.5	12.0 6	6.8 3.0	2.8 2.4
Cu content, g/l (Ini.) (Fin.)	7 5	7 5	7 5.5	7 4.5	7 4.5
pH (Ini.) (Fin.)	1.6 0.4	1.6 0.5	1.7 0.65	1.7 0.5	1.7 0.4
Time, hr	7.00	9.15	18.00	35.00	140.00
Cathodic current efficiency, %	71.30	74.40	71.50	81.10	97.80
Deposit Cu plate, %	0.02	0.83	11.11	28.59	90.58
Deposit Cu powder, %	99.98	99.17	88.89	71.41	9.42
Deposit condition of Cu powder	Good	Good	Good	No good	No good

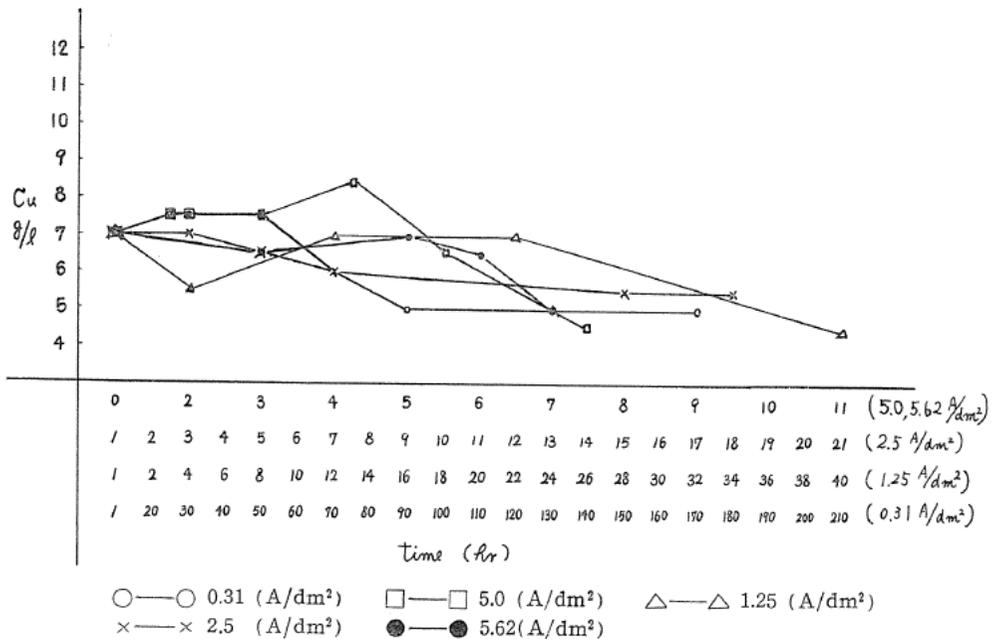


FIG. 3. Cu content-time curves for several cathodic current densities.

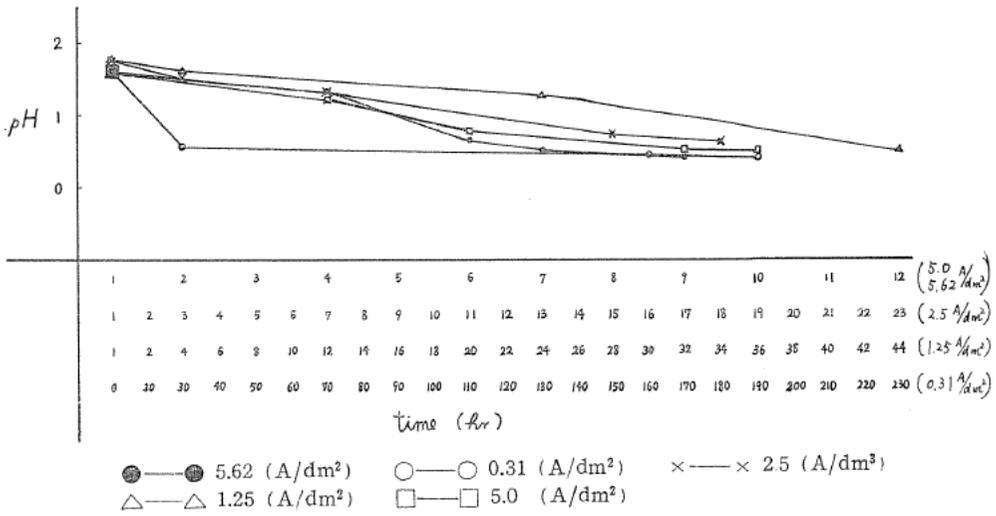


FIG. 4. Voltage-time curves for several cathodic current densities.

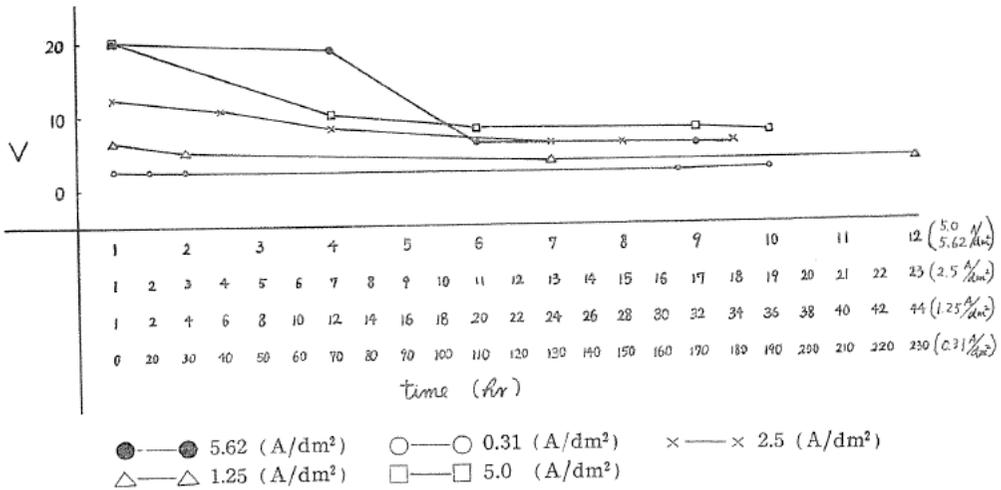
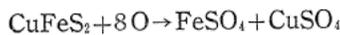


FIG. 5. pH-time curves for several cathodic current densities.

electrolyte: 7 g/l, Initial pH: 1.6-1.7, and cathodic current density: 5.62, 5.00, 2.50, 1.25 and 0.31 A/dm². The experimental results were shown in Table 1, Fig. 3, 4 and 5.

The electrolyte solution becomes more acidic, because the following reaction occurs on the surface of anode:



Mixed deposit of copper powder and plate is produced because of the difference of current and concentration distribution of the cathode surface. When the deposit of copper powder dropped from cathode, the copper powder became to easily oxidize

and to change the colour to black. From these results, the optimum value of initial copper content in electrolyte is 7 g/l.

3.2. Influences of electrolytic temperature

Electrolytic conditions are; Initial copper content in electrolyte: 7.0 g/l, cathodic current density: 5.0 A/dm², initial pH in electrolyte: 1.50-1.70, and temperature: 20, 30, 40, 50 and 60 °C.

TABLE 2. Experimental data for influences of temperature

Temperature, °C	20	30	40	50	60
Potential, v (Ini.)	16	10	20	18	14
Potential, v (Fin.)	10	6	7.5	10	8
Cu content, g/l (Ini.)	7.0	7.0	7.0	7.0	7.0
Cu content, g/l (Fin.)	7.0	6.5	5.0	7.0	7.0
pH (Ini.)	1.45	1.50	1.60	1.50	1.50
pH (Fin.)	0.90	0.70	0.50	0.85	0.70
Cathodic current efficiency, %	79.5	83.7	74.4	86.4	89.3
Deposit Cu plate, g	0.051	0.051	0.053	0.057	0.166
Deposit Cu powder, g	6.143	7.104	5.989	5.966	6.967
Percentage of particle (10 mesh)	86.9	80.4	83.8	82.9	85.0
Deposit condition of Cu powder	Good	Good	Good	Good	Good

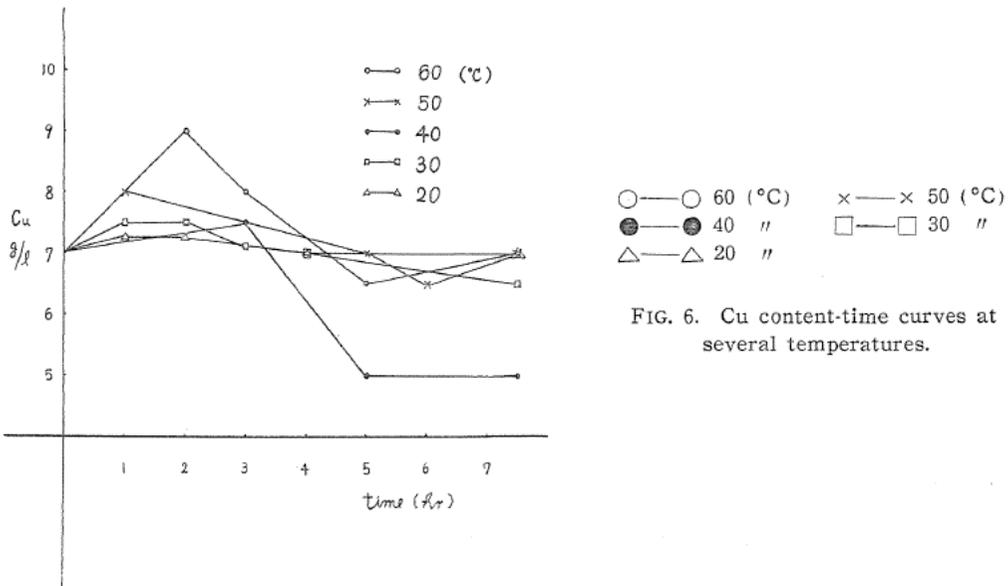


FIG. 6. Cu content-time curves at several temperatures.

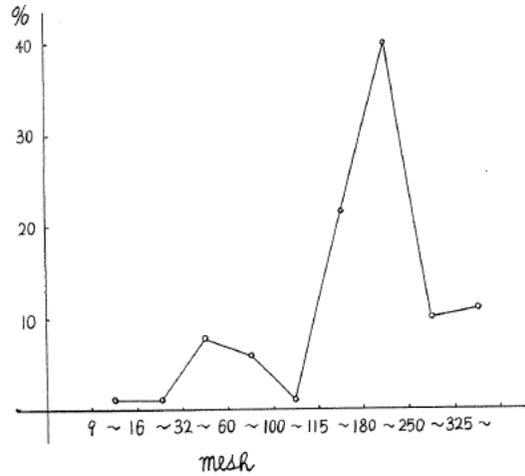


FIG. 7. Grain size distribution of deposit copper powder by 60°C-electrolysis.

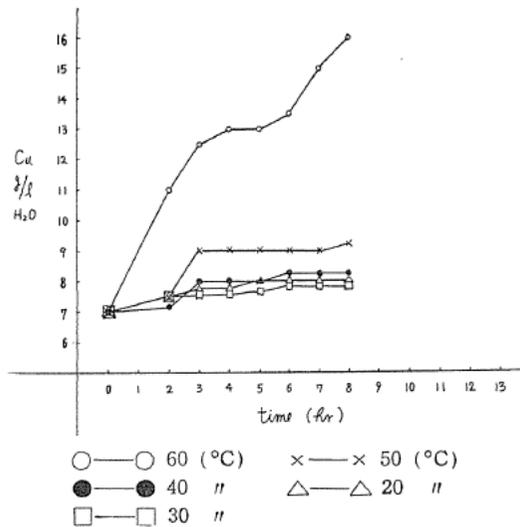


FIG. 8. Natural-dissolution curve of copper concentrate.

The experimental results are shown in Table 2 and Fig. 6. And grain size distribution of deposit copper powder (deposited at 60°C) are shown in Fig. 7 and natural-dissolution curves of copper concentrate are shown in Fig. 8. The copper powder produced at 60°C-electrolysis are suitable for copper powder metallurgy and most of them are in grain size between 180 and 250 mesh.

3.3. Influences of initial pH in electrolyte

Electrolytic conditions are; cathodic current density: 5.0 A/dm², initial copper

content in electrolyte: 7.0 g/l, temperature: 60° C, and initial pH in electrolyte: 0.7, 1.0, 2.5 and 3.65.

The experimental results are shown in Table 3, and Fig. 9. And grain size distribution of deposit copper powder are shown in Fig. 10.

TABLE 3. Experimental data for influences of initial pH

pH	0.70	1.60	2.50	3.65
Potential, v (Ini.) (Fin.)	13 6	14 8	12 6	10 6
pH (Fin.)	—	0.7	1.0	0.6
Cathodic current efficiency, %	86.2	89.3	89.8	90.7
Deposit Cu plate, g	0.044	0.166	0.132	0.242
Deposit Cu powder, g	7.063	5.966	7.943	7.247
Percentage of particle (100 mesh)	86.8	85.0	81.6	73.0

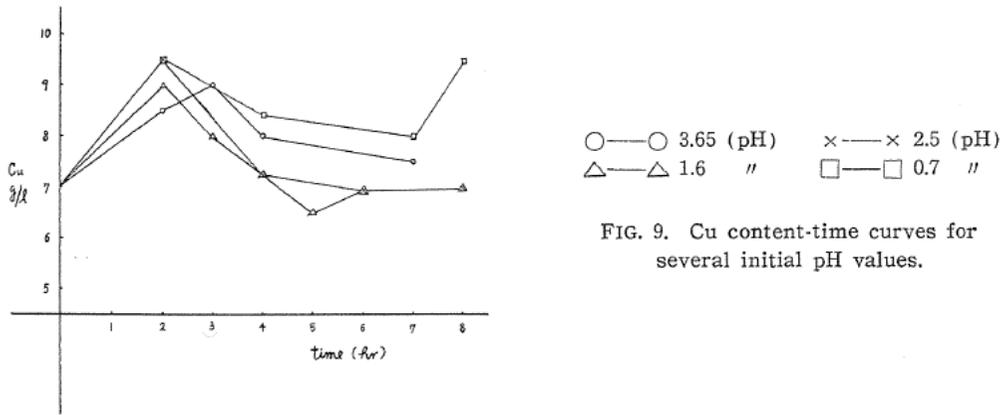
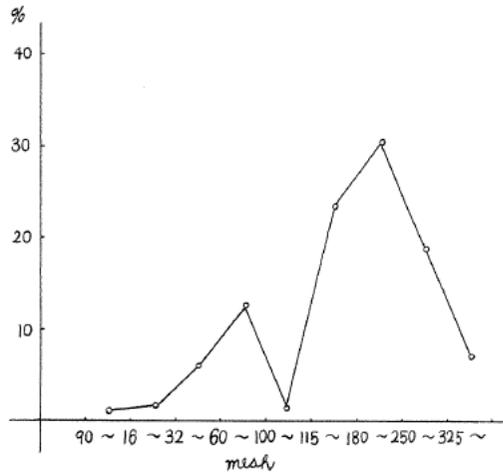


FIG. 9. Cu content-time curves for several initial pH values.

FIG. 10. Grain size distribution of deposit copper powder by pH 2.5-electrolysis.



3.4. Behaviours of impurities

Electrolytic conditions are; Anode: copper concentrates (20% chalcopyrite) 200 g, lead (as an electrode), cathode: pure copper plate (8×2 cm²), copper content in electrolyte: 7.1 g/l, initial pH: 2.5, temperature: 60°C, and electrolyte are stirred. As for the electrolytic time, after each five hours the cathode plate are replaced during total 20 hours.

Electrolytic data are shown in Table 4.

TABLE 4. Electrolytic data for behaviour of impurities

Time, hr	0-5	5-10	10-15	15-20
Potential, v (Ini.)	9.0	7.9	7.1	6.2
(Fin.)	7.2	6.5	5.6	5.5
pH (Ini.)	2.50	2.10	1.28	1.28
(Fin.)	2.10	1.28	1.28	1.20
Cathodic current efficiency, %	92.6	72.1	38.7	16.6

* Cathodic current density: 5.0 A/dm²

Copper concentrates used have the following chemical compositions; Cu: 20.40%, Fe: 34.16%, S: 36.49%, Zn: 3.37%, Sb: 0.218%, Bi: 0.073%, As: 0.022%, Ni: none, Co: 0.090%, Pb: none, SiO₂ and H₂O etc: bal.

Compression ratio of concentrate is about 1.5-2.0 g/ml in order to investigate the behaviour of impurities.

3.4.1. Analytical methods

The analytical methods used in the experiment are shown as follows;

Element	Analytical method
Cu	Electrolytic analysis and spectro-photometry
Fe	X-ray fluorometry
Zn	X-ray fluorometry
Bi	Spectro-photometry (di-ethyl-di thiocalvamic acid method; 370 m μ)
Sb	Spectro photometry (rodamine B method; 565 m μ)
As	Drop micro analysis
Co	X-ray fluorometry and drop micro analysis
Pb	X-ray fluorometry and polarography
S	Gravity method

* In X-ray analysis, W target and LiF crystal are used.

3.4.2. Behaviours of iron, zinc, bithmus, antimony, arsenic, cobalt, nickel, and lead.

Changes of Fe and Cu in electrolyte and changes of Fe in deposit copper are shown in Fig. 11. Relation between iron ion content in electrolyte and deposit iron is not clear, but relation between iron ion content and copper ion content in electrolyte speaks something regarding to the deposit iron. Generally speaking, the deposit potentials for impurities and Cu are as follows;

$$E_{Cu} = E_{0Cu} + RT/2F \ln A_{Cu}$$

$$E_M = E_{0M} + RT/nF \ln A_M$$

- * E : Specified deposit potential
- E_0 : Standard deposit potential
- A : Activity in electrolyte
- Cu: Copper M: Metal

If M is divalent, the co-deposition occurs in $E_{Cu} = E_M$, i.e.

$$(E_{0Cu} - E_{0M}) + 0.0001984 T \log \sqrt{A_{Cu}/A_M} = 0$$

As for zinc and bithmns, the experimental results are shown in Fig. 12 and 13. Zinc and bithmus have the similar inclination as iron. As for antimony, the experimental results are shown in Fig. 14. The behavior of antimony is different from iron, zinc, bithmus. The more antimony content in electrolyte increases with time, the more deposited antimony content increases.

As for arsenic, the following data show little dissociation of arsenic into electrolyte.

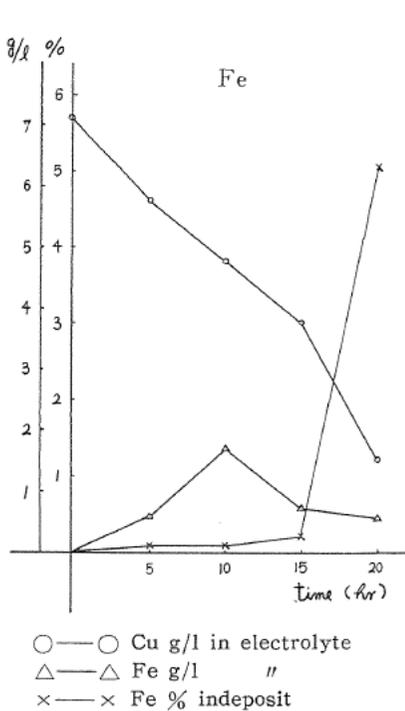


FIG. 11. Cu and Fe content-time curves.

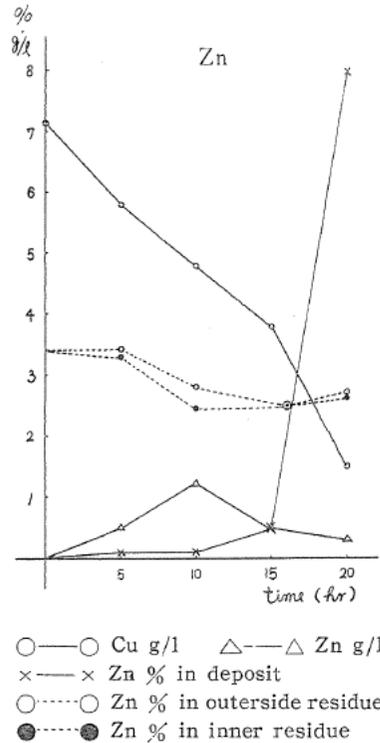
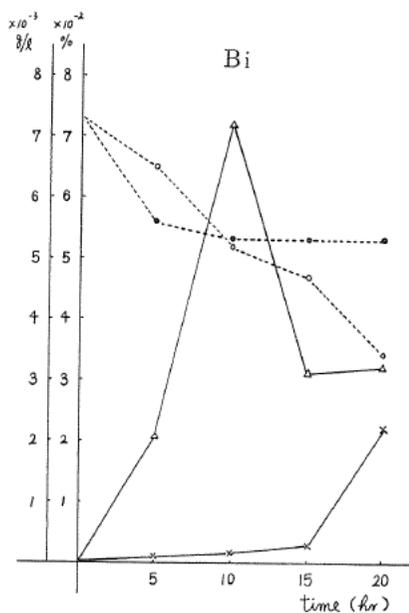
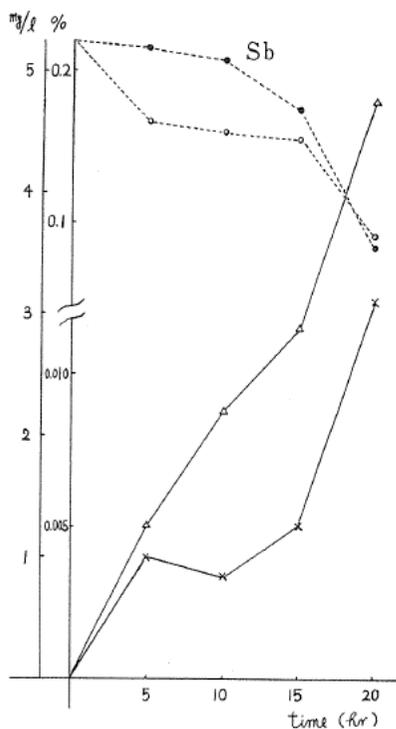


FIG. 12. Cu and Zn content-time curves.



×—× Bi % in deposit
 △—△ Bi g/l
 ●—● Bi % in inner residue
 ○—○ Bi % in outer residue

FIG. 13. Bi content-time curves.



×—× Sb % in deposit
 △—△ Sb g/l
 ○—○ Sb % in inner residue
 ●—● Sb % in outer residue

FIG. 14. Sb content-time curves.

Time, hr	As content near Pb pole of anode, %	As content in outside of anode, %
5	0.022	0.022
10	0.022	0.022
15	0.022	0.022
20	0.022	0.017

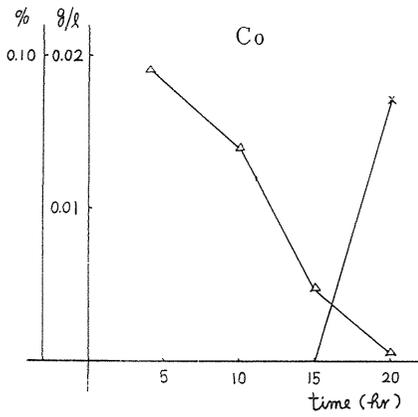
As for cobalt and nickel, the experimental results are shown in Fig. 15 and 16. If copper content in electrolyte decreases extremely, they may deposit into cathode metal (Nickel is not contained in concentrate, but in copper sulfate used).

As for lead, the data are shown in Fig. 17. Lead is dissolved out from lead electrode, and the dissolved lead did not give the deposit metal good effect.

4. Conclusion

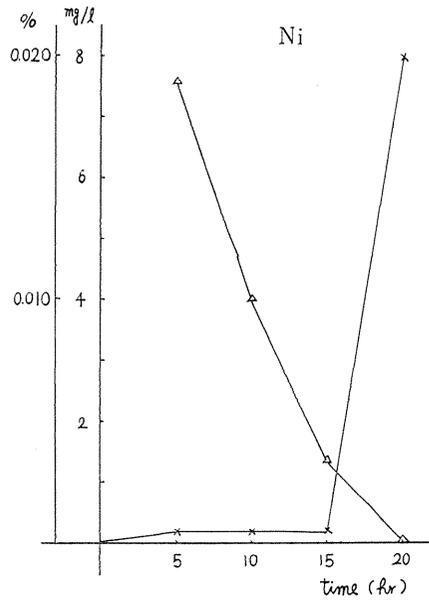
1) The optimum conditions for copper only in producing copper powder by direct electrolysis of copper concentrates are as follows;

Initial copper content in electrolyte: 0.7 g/l
 Cathodic current density: 5.0 A/dm²
 Temperature: 60°C
 Initial pH: 2.5
 Optimum cathodic current efficiency: 89.80%



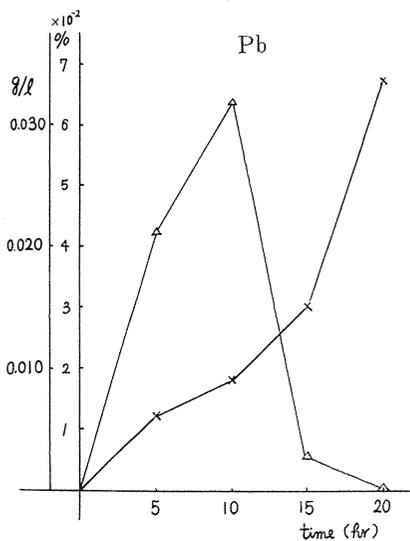
x — x Co % in deposit △ — △ Co g/l

FIG. 15. Co content-time curves.



x — x Ni % in deposit △ — △ Ni g/l

FIG. 16. Ni content-time curves.



x — x Pb % in deposit △ — △ Pb g/l

FIG. 17. Pb content-time curves.

Percentage of particle (100 mesh): 81.60%

- 2) Main anodic reaction is sulfation of chalcopyrite.
- 3) As for imprity elements, dissolution of iron, zinc, bithmus, antimony, cobalt and lead except arsenic occurred in anode.
- 4) In this experiment, when copper content in electrolyte is over 5 g/l, deposit copper powder had the purity of 99.9% Cu. If some process, for example, ion exchange resin film method, is done for removing the impurities of protecting cathode from impurities, the purity of the deposit copper powder may increase better.