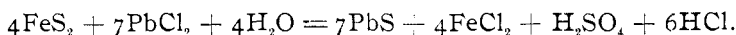


water in sealed tubes filled with carbon dioxide for 12 hours at 180°. The solid product contained large quantities of galena and lead sulphate, the latter being decomposed and its SO₄ extracted by treatment with sodium carbonate solution.

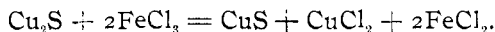
The reaction is therefore presumably :



From these experiments it would seem that the formation of free sulphuric acid through the action of neutral, air-free copper and lead solutions on pyrite and marcasite is a factor which can not be neglected.

Note on the Identification of Chalcocite.

Chalcocite is readily attacked by ferric salts thus :



The CuS thus formed shows the blue color of covellite. A fragment of chalcocite boiled for a moment with 10 per cent. ferric chloride solution acidified with hydrochloric acid becomes blue. The color appears to particular advantage on compact smooth chalcocite, but the rough mineral also becomes decidedly blue. A gray coating on chalcopyrite took on a deep indigo-blue color. The same effect is produced, but not as satisfactorily, by boiling with 1-1 hydrochloric acid or allowing to stand a short time with concentrated hydrochloric acid, but this is apt to dissolve the coating completely. Enargite is entirely unaltered in appearance by the above treatment¹.

BUREAU OF STANDARDS,
Washington, D. C.

THE ELECTROLYTIC DEPOSITION OF NICKEL-ZINC ALLOYS.

BY EUGENE P. SCHOCH AND ALCAN HIRSCH.

Received December 10, 1905.

Some time ago, while making some general experiments on the electrolytic deposition of alloys, we were surprised to find that, although zinc has a greater electrolytic solution tension than nickel, yet a bath which contains much more nickel than zinc yields an alloy which contains much more zinc than nickel. This fact appeared worthy of study and the paper presented below embodies the results which have been obtained so far.

The apparatus and arrangement used were as follows:— a paraffined wooden trough 49 x 13 x 10 cm. was filled with the electrolyte to a depth of about 7 cm. The anodes were placed at the ends of the trough, the active surface of each anode being 13 x 7 cm. The cathode was a cylinder of thin sheet metal with its axis vertical; it was placed approximately midway between the anodes. Its active surface was as nearly 1

¹ Knop. N. J' b. 1861, S. 533.

sq. dcm. as it could be made, which with a height of 7 cm., gives a diameter of 4.4 cm. The distance of the nearest point of the cathode from either anode was 22.5 cm., hence the distribution of the current over the cathode surface was assumed to be uniform.

The cathode was clasped around a paraffined wooden cylinder of about the same diameter. This wooden cylinder was suitably fastened to a vertical brass shaft supplied with pulleys. By this means the cathode was rotated at a rate of 160 revolutions per minute.

In order to investigate the electrolytic deposition of these nickel-zinc alloys four series of alloys were made. For the four series the ratios of nickel to zinc in the electrolyte were radically different, but during each series the ratio was kept practically constant by running nickel and zinc anodes the necessary ampere hours. At one end of the bath was placed a zinc anode and at the other end both a nickel and a zinc anode. The current from each side was half of the total required; and the distribution of the total current over the nickel and zinc anodes respectively was such as to re-supply the nickel and the zinc in the solution in approximately the same amount as deposited. The common source of current (storage cells) was connected to each of the three anodes through separate circuits, each circuit supplied with ammeter and rheostat, and all three connected through the common cathode. The temperature of the solution was maintained at about 25° and was not allowed to vary more than a degree or two. The results are tabulated below.

The first difficulty encountered was in the choice of a suitable metal to be used as cathode. Since it was desirable to determine the ratio that the amount of alloy obtained bears to the theoretical current yield, copper could not be used because it is impossible to dissolve the alloy from the copper surface without dissolving some of the copper, and the alloys did not peel completely from the copper sheeting even when the latter had been coated with a thin layer of graphite. Aluminum was tried because the alloys could be dissolved in nitric acid leaving the aluminum practically unattacked. However, it changes weight owing to oxidation, and hence could not be used. Platinum could not be employed because the alloys were all high in zinc, and the well known effect of platinum upon zinc soon showed itself. The most suitable metal for the purpose was found to be lead; the cathodes used were of thin sheet lead. They were thoroughly cleaned by treatment with concentrated hydrochloric acid, washed with tap and distilled water, alcohol and ether. Finally the cathode was dried in a desiccator and weighed. The back of the lead plate was covered with a thin layer of low melting paraffin. When the plate with the deposited alloy was taken from the bath the paraffin was removed with petroleum ether. The plate and alloy were washed, dried and weighed and then placed in dilute sulphuric acid and heated

until all the alloy was dissolved. The lead plate was then washed, dried and re-weighed. This weight was compared with the weight of the cathode before the alloy was deposited upon it; the difference between the two weights was never more than a few milligrams, and the average error was within 0.1 per cent. Therefore, the use of lead as cathode material was deemed sufficiently accurate. The solution in which the alloy had been dissolved was diluted to a definite volume and aliquot portions were taken for analysis.

Various methods of analytical separation were tried, but abandoned as unsuitable. Among these may be mentioned precipitating the zinc as sulphide in the presence of gallic acid, and precipitating the nickel as hydroxide with caustic soda. It is well known that zinc sulphide is not easily washed and filtered, and as all the alloys were very high in zinc, it was impracticable to use the hydrogen sulphide method. The precipitate of nickelous hydroxide contained zinc hydroxide which was not completely removed by re-solution and re-precipitation. Furthermore it was very difficult to wash the precipitate free from alkali. Hence this method left much to be desired. The following method was finally adopted as the most reliable and expeditious:

The determination of nickel depends upon the fact that in a weak ammoniacal solution, nickel may be titrated with potassium cyanide, silver iodide being used as an indicator. The method is well known and is described in Sutton's Volumetric Analysis (1896) p. 243. In the presence of sodium pyrophosphate, zinc exercises no influence. The accuracy of this method is confirmed by the following results:—

250 cc. contain 1.9981 grams electrolytic nickel dissolved in dilute sulphuric acid. 25 cc. of this solution were taken for each trial.

No. of trial	cc. KCN (.1827 N.) used	cc. AgNO ₃ 1/10 N. used	cc. KCN used by nickel	1 cc KCN = grams nickel
1	37.25	2.45	35.95	0.00556
2	37.3	2.8	35.8	0.00558
3	39.4	6.1	36.1	0.00554

NOTE:—The concentration of the potassium cyanide solution was determined by titration with the silver nitrate solution. By calculation 1 cc. KCN = 0.00558 gms. nickel. In the third trial some zinc chloride and sodium pyrophosphate were added to the solution.

The precautions which should be taken in this volumetric determination of nickel are: the solution should be distinctly, but not strongly, alkaline, and the temperature should be kept below 20°.

The zinc was determined from another sample of the alloy after first removing the nickel by precipitating with sodium hydroxide, dissolving and re-precipitating, and subsequently titrating the zinc in acetic acid solution by means of potassium ferrocyanide. The end-point was deter-

mined colorimetrically with uranium acetate as an indicator. This method was not very accurate owing to the difficulty of determining the end-point, and because some of the zinc was invariably carried down with the nickelous hydroxide as already stated. This method was found to be accurate only to 1 per cent. As the nickel determination was so much more accurate, the zinc was mostly found by difference.

In the four series of alloys described below, only the good plates that were obtained have been presented. The reasons for this are the following: powdery and warty deposits favor the evolution of hydrogen in an *irregular* manner as shown by the fact that results could not be duplicated. Such deposits also showed not the least regularity in the variation of their composition as compared with the variation of the compositions of the solutions.

In each series, the limiting current-densities were first determined with great care. The plates obtained with these current-densities were made in duplicate, and each was analyzed several times. In each series the highest and lowest current-densities are the critical current-densities. In the first series with the stationary cathodes, the limits within which satisfactory plates were obtained are closer together than with the rotating cathodes, as was to be expected.

In the first series two methods of operation were employed: first, the cathodes were stationary, but the liquid was stirred vigorously except in one case especially noted; second, the cathodes were simply rotated. In the second, third, and fourth series only the latter method of operation was employed.

Series 1.

Composition of electrolyte:

Zinc sulphate	143 grams
Nickel sulphate	235 "
Aluminum sulphate	75 "
Volume of solution	5000 c.c.
Ratio of nickel equivalents to zinc equivalents, 1.68 : 1	

A. With stationary cathodes.—In making this series the anodes were placed in the center of the bath with one cathode at each end connecting with two separate sources of electromotive force so that two different alloys could be made simultaneously. The liquid was stirred vigorously by means of rotating glass stirrers just in front of each cathode.

TABLE 1A.

No.	C. D.	Wt. Alloy	Amp. Hrs.	Per cent. of Theoretical Yield	Per cent. Nickel
1	0.5	4.2989 gm.	3 $\frac{1}{4}$	100	15.1
2 ¹	0.5	4.4344 "	3 $\frac{3}{8}$	100	16.6
3	0.5	3.6560 "	3 $\frac{1}{2}$	91	15.7
4	1.0	4.9786 "	4	100	12.8
5	1.5	6.5764 "	5 $\frac{3}{4}$	100	12.2

¹In (2) the liquid was not stirred.

B. With rotating cathodes.—In making this series the revolving cathodes were placed in the center of the bath with the anodes at the ends.

TABLE 1B.

No.	C. D.	Wt. Alloy	Amp. Hrs.	Per cent. of Theoretical Yield	Per cent. Nickel
6	0.2	2.6570 gm.	2 $\frac{9}{10}$	80	20.6
7	0.4	5.9134 "	5 $\frac{6}{10}$	92	16.4
8	2.0	6.0920 "	6 $\frac{1}{2}$	76.2	12.0
9 ¹	2.5				11.5
10	4.0	6.0890 "	5 $\frac{1}{3}$	98	9.3

¹ Plate 9 peeled from the cathode.

Series 2.

Composition of electrolyte :

Zinc sulphate	71.5 grams
Nickel sulphate.....	235. "
Aluminum sulphate.....	100. "
Volume of solution.....	5000. cc.
Ratio of nickel equivalents to zinc equivalents, 0.336 : 1.	

TABLE 2.

No.	C. D.	Wt. Alloy	Amp. Hrs.	Per cent. of Theoretical Yield	Per cent. Nickel
11	0.5	3.7157 gm.	3 $\frac{1}{2}$	93	8.4
12	1.5	5.4042 "	6	77	6.8
13	4.0	5.4662 "	4 $\frac{2}{3}$	100	6.6

Series 3.

Composition of electrolyte :

Zinc sulphate.....	71.5 grams
Nickel sulphate.....	23.5 "
Aluminum Sulphate.....	75. "
Volume of Solution.....	5000 cc.
Ratio of nickel equivalents to zinc equivalents, 3.36 : 1.	

TABLE 3.

No.	C. D.	Wt. Alloy	Amp. Hrs.	Per cent. of Theoretical Yield	Per cent. Nickel
14	0.5	1.0895 gm.	3 $\frac{1}{2}$	30	32.2
15	1.5	6.7526 "	6	95	18.9

Series 4.

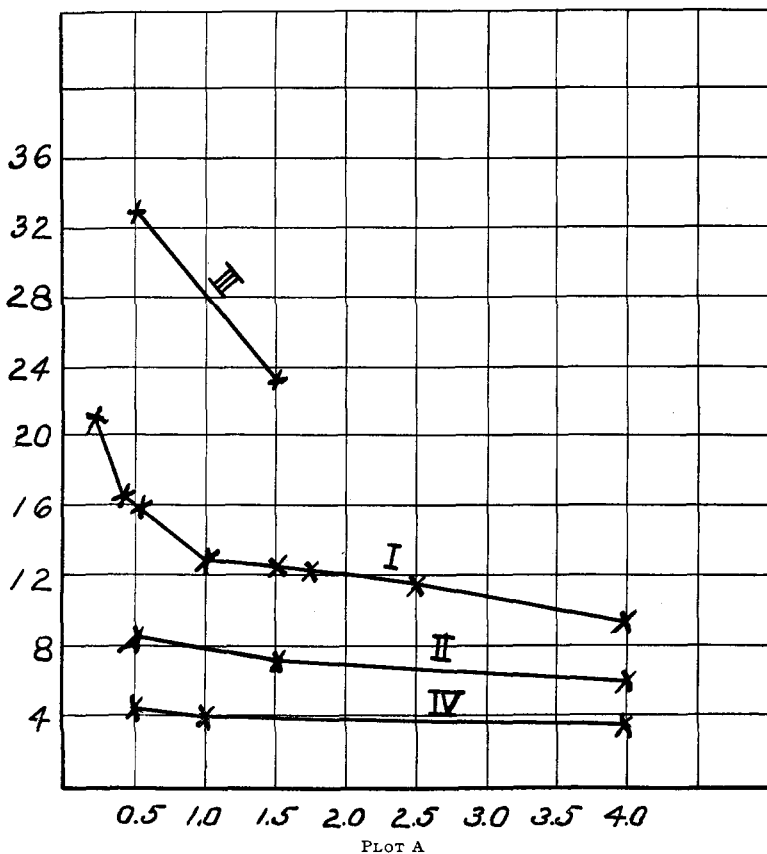
Composition of electrolyte

Zinc sulphate.....	834 grams
Nickel sulphate.....	235 "
Aluminum sulphate.....	110 "
Ammonia alum.....	25 "
Volume of solution.....	5000 cc.
Ratio of nickel equivalents to zinc equivalents, 0.29 : 1.	

TABLE 4.

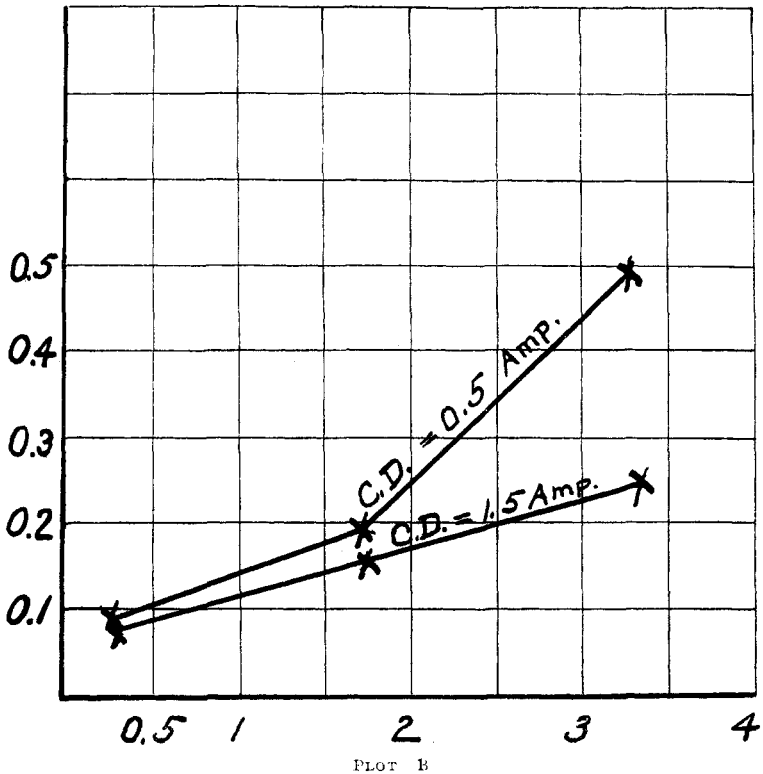
No.	C. D.	Wt. Alloy	Amp. Hrs.	Percent. of Theo. retical Yield	Percent. Nickel
16	0.5	4.0052 gm.	3 ⁷ / ₁₂	100	4.3
17	1.0	7.0860 "	6	100	3.9
18	2.0	15.4422 "	13	100	3.8
19	4.0	7.4031 "	5	100	3.6

The foregoing results are plotted as follows :



In plot A each series is represented by a curve. The different current-densities are plotted as abscissas, and the percents of nickel as ordinates. In plot B the abscissas are the ratios of equivalents of nickel to equivalents of zinc in the electrolyte; the ordinates are the ratios of the percents of nickel to zinc (in equivalents) in the alloy.

In connection with the foregoing results it should be mentioned that the relative amount of hydrogen discharged varies in an irregular manner from plate to plate, especially at the beginning of the formation of the alloy. Hence the current yield of the alloys obtained varies considerably. Yet it may be stated as the result of general observation, that in



PLOT B

deposition of all alloys containing less than 20 per cent of nickel and which present a bright, smooth surface, the evolution of hydrogen is comparatively slight.

On inspection, the tables and curves show three general results: —

(1) The proportion of zinc in the deposit is greater with a greater proportion of zinc in the electrolyte.

(2) The proportion of zinc in the deposit increases with the current-density and approaches "asymptotically" to a maximum; in series 2 and 4 the maximum is practically reached.

(3) The ratio of zinc to nickel (by equivalents) in the alloy is from 4.5 to 14 times their ratio in the electrolyte, according to the concentrations of the latter.

The first two results may be passed as being in accordance with established principles; they present nothing new. We shall pass, then, to the consideration of the third, which is really the main point of this paper. In order that this result may show itself properly, all influences that would help or hinder it should be excluded. The main, and perhaps the only influence that affects it is changes in concentration which

influence the relation between the degrees of dissociation of the zinc and the nickel salts respectively. Accordingly, two solutions were prepared, both fairly dilute, and differing not too extensively in the relative concentrations of the nickel and the zinc salts. The data for these solutions are:—

(a) Solution same as for Series 4, except that the total volume of the solution is fifteen liters (i.e. three times as much as before). With current densities above two amperes the alloys obtained were practically of constant composition. The alloy obtained with C.D. = 3 amp. contained 4.6 per cent. nickel. Hence the ratio of zinc to nickel (by equivalents) in the alloy equals 5.4 times their ratio in the electrolyte.

(b) Nickel sulphate	131.5 grams
Zinc sulphate	182 "
Ammonia alum	100 "
Volume of solution	5000 cc.
Ratio of nickel to zinc equivalents.....	0.74:1

With current-densities above two amperes, the alloys obtained were practically of constant composition. The alloy obtained with C.D. = 3 amp. contained 11.2 per cent. nickel. Hence, ratio of zinc to nickel (by equivalents) in the alloy equals 5.3 times their ratio in the electrolyte. This indicates that the cause produces a *constant* factor.

We are not ready to say anything as to the nature of the cause itself. We thought it might be due to a possible difference in the rates of migration of the nickel and zinc ions, but we have since learned that the equivalent conductivities of the sulphates and of the chlorides of these metals at corresponding concentrations are practically the same, and hence have given up this explanation.

Further work on this problem is in progress.

CHEMICAL LABORATORY,
THE UNIVERSITY OF TEXAS.

THE ELECTROLYTIC PREPARATION OF AMALGAMS.

BY GEORGE MCP. SMITH AND JAMES R. WITHROW.

Received December 28, 1906.

The older methods of preparing amalgams with the help of the electric current¹ require much time and somewhat complicated apparatus. Considerable labor is also frequently involved. E. S. Shepherd,² however, has proposed, as a lecture experiment, the electrolytic preparation of sodium amalgam. He points out that the amalgam formed is not so heavy as the mercury itself, and therefore serves to retard action by rising to the surface and thus separating the mercury from the electrolyte to

¹ Nernst, *Z. Electrochem.*, 3, 308 (1897); Kerp, *Z. anorg. Chem.* 17, 300 (1898); Reuter, *Z. Electrochem.* 8, 801 (1902).

² *J. Phys. Chem.* 7, 29, (1903).