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The Effect of Organic and Inorganic "Addition-Agents" upon the Electro-Deposition of Copper from Electrolytes Containing Arsenic

BY

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Submitted in Partial Fulfilment of the Requirements for
the Degree of Doctor of Philosophy, in the Faculty
of Pure Science, Columbia University

Univ. of
California

The New Era Printing Company
Lancaster, Pa.
1911

ACKNOWLEDGMENT.

INTRODUCTION.

In the production of good and pure copper by electrolysis, the composition of the electrolyte is one of the important factors. The causes of poor copper deposits are chiefly due to the impurities which accumulate in the electrolyte, and which, under usual conditions, are precipitated along with the copper. Of those impurities, the most harmful and troublesome ones are arsenic and antimony, the presence of which in the deposited copper makes it brittle and nodular. It has been a known fact that during electrolysis, part of the arsenic and antimony contained in the anode dissolves and remains in solution. These two elements, especially the arsenic, are allowed to accumulate in the electrolyte till a critical point is reached, which has not yet been definitely determined. When this point is passed, they begin to be deposited with the copper on the cathode and render the deposit bad and brittle. To prevent this, it is therefore of utmost importance to maintain the electrolyte within a certain degree of purity, in other words, to keep the amount of arsenic and antimony in the electrolyte below the critical point. This is usually accomplished in practice by withdrawing a certain portion of the electrolyte and replacing it with an equal quantity of fresh solution, and the copper in the impure electrolyte recovered either by crystallization or by electrolysis with insoluble lead anodes. This not only complicates the process of electrolytic refining of copper, but also entails an extra item of expenditure in the production of electrolytically refined copper.

Another thing that is observed during the electrolysis is that "sprouts" or dendritic "trees" often form, especially along the edges of the cathode. The formation of such "trees" interferes with the work, renders it more difficult to operate, and prevents the electrodes from being placed close together; as there is danger that the electric current would be short-circuited. In conducting the electrolysis in a commercial way, the removal of these "trees" becomes absolutely necessary and is usually done by the tank inspectors, thus increasing the cost of refining.

The object of the present investigation is, therefore, twofold: first, to prevent the deposition of arsenic and antimony on the cathode, and second, to prevent the formation of dendritic "trees." This problem was worked out, having in mind the production of solid and smooth deposits, from copper electrolytes containing high percentages of arsenic, by means of organic and inorganic "addition-agents."

ABSTRACTS OF LITERATURE.

In reviewing the literature regarding both organic and inorganic addition-agents little was found.

Kiliani[1] was, perhaps, the first man, who had conducted systematic experiments to investigate the behavior of impurities present in the copper anode, and to study the effect of inorganic salts on the character of the copper deposit. For the latter case he used an electrolyte containing 15 grams of copper sulphate and 5 grams of sulphuric acid, in 100 c.c. solution with a current density of 20 amperes per square meter. He observed the fact that, with a small amount of tin salt in the electrolyte, good smooth, malleable copper was produced while, in the case when the electrolyte contained no tin salt, the deposit was extremely bad and brittle. He noted also the fact that the presence of a small amount of tin in the anode caused the potential difference between electrodes to be greatly reduced.

W. Borchers[2] performed experiments with the object of preventing the crystalline growth of copper on the deposit, by adding to the electrolyte a sufficient amount of sodium chloride, or magnesium chloride. He found, however, by the addition of these reagents, only a diminution of the evil could be effected.

H. O. Hoffman[3] has pointed out that hydrochloric acid is used in practice to precipitate the antimony in the electrolyte. This is accomplished by the addition of a sufficient quantity of crude hydrochloric acid to the head tank to maintain 0.04 gram of chlorine per liter in solution. The hydrochloric acid reacts with the antimony and precipitates it as oxychloride. When there is deficiency of hydrochloric acid the sample-plate becomes streaked, tarnished, black and brittle.

It is said that ammonium sulphate[4] has been used in the

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[1] *Berg und Hüttenmannisches Zeitung*, 1885, p. 249.

[2] W. Borchers, "Electrolytic Smelting and Refining," p. 206 (translated by McMillan).

[3] *T. A. I. M. E.*, 1904, Vol. 34, p. 312.

[4] T. Ulke, "Modern Electrolytic Copper Refining," 1st ed., p. 18.

electrolyte to hinder the precipitation of arsenic on the cathode, and the amount usually added was from 0.5 to 20 per cent. The addition of this salt decreases the conductivity of the electrolyte.

L. W. Wickes[5] investigated the percentage of arsenic which the deposited copper would contain for a given potential between electrodes, and the relation between variations in the potential and the amount of arsenic in the copper deposited. For his experiments he used anodes containing 1 per cent., 2 per cent., and 4 per cent. arsenic, and an electrolyte containing 75 parts of water, 19 parts of copper sulphate, and 6 parts sulphuric acid, by weight, and also an electrolyte of the same composition, but containing 0.101 per cent. arsenic in the form of arsenic acid. The experiments were conducted with 0.4 volt, 0.6 volt, and 0.8 volt. He found that with different voltages and the same percentage of arsenic in the anode, the percentage of arsenic in the cathode copper was practically the same in all cases, and that the greater the percentage of arsenic in the anode, the more erratic were the results. The conclusion which he drew of his experimental data is that the percentage of arsenic in the deposited copper is not a function of the potential between electrodes, but of the degree of hydrolyzation of the sulphate of arsenic in the electrolyte.

Of the work on organic addition-agents, that of Edward F. Kern and Royal P. Jarves[6] should be mentioned. They conducted experiments to investigate the effect of the presence of tannin, pyrogallol, gelatine, and resorcinol upon the density and coherence of electrolytically deposited copper, lead, and silver. For their experiments on copper they used two kinds of electrolyte, the cupric sulphate and the cupric fluo-silicate. With the former electrolyte which contained 16 grams of cupric sulphate $CuSO_4 \cdot 5H_2O$) and 4 grams of sulphuric acid (H_2SO_4) per 100 c.c., they found that the presence of tannin, resorcinol or gelatine equally caused the copper to deposit more smoothly. The deposited copper formed at 30° C. was better than that at 20° C. With the fluo-silicate electrolyte, which contained 6.34 grams of copper, and 3.60 grams of free hydro-fluo-silicic acid (H_2SiF_6)

[5] E.M. thesis, Metallurgical Library, School of Mines, Columbia University.

[6] *School of Mines Quarterly*, 1909, Vol. 30, p. 119.

per 100 c.c., they observed that the deposits were rendered brighter and more smooth by the presence of tannin, pyrogallol, or gelatine. The first of these addition-agents was the most effective while the last two were somewhat less. Better results · were also obtained at 30° C. than at 20° C.

In regard to the function of organic addition-agents, Edward F. Kern[7] has also performed invaluable experiments for which the following electrolytes were used:

1. Cupric electrolytes, which consisted of cupric sulphate, cuprous chloride, and cupric fluo-silicate.
2. Lead electrolytes, which consisted of lead nitrate, and lead fluo-silicate.
3. Silver electrolytes, which consisted of silver nitrate and silver fluo-silicate.

The organic addition-agents employed were gelatine resorcinol, pyrogallol, and tannin. With the results of his experiments he concluded as follows: "That the most suitable organic addition-agents for copper, lead, and silver electrolytes are compounds of the benzene ring series, which have a large number of adjoining hydroxyl radicals; and also, the greater the molecular weight of the addition-agent, in other words, the larger the numbers of hydroxyls, the more effective it is in producing more satisfactory results."

"If it is the hydroxyl (and, as well, the amine) radicals of organic addition-agents, which cause deposits to form denser, smoother and less crystalline; then, no doubt, this effect may be attributed to the reducing property of the addition-agents. This statement was suggested by recalling a general rule of organic chemistry, which is: 'The most easily oxidizable organic compounds of the benzene ring series, and those which more readily precipitate metals from their solutions, are compounds which contain the largest number of hydroxyl or amine radicals; and the compounds which are most easily oxidized are those in which the hydroxyl and the amine radicals are the more closely grouped.'"

From his experimental data and the above generalizations he has deduced a theory regarding the function of an addition-agent, which reads: "The function of an addition-agent in an electrolyte is to maintain a reducing menstruum around the cathode, which, in turn, causes the electro-deposit to form denser and smoother."

[7] *Tran. Amer. Elect. Society,* 1909, Vol. XV., p. 441.

"The fact that the consumption of organic addition-agents is in proportion to the amount of metal deposited is an evidence of their reducing action. And, for this reason, in order to maintain the deposition of smooth, dense, coherent deposits, the organic addition-agent must be added in definite amounts, to electrolytes from time to time."

From the results of his investigations on inorganic addition-agents, he writes as follows: "The deposits formed in electrolytes, which contain alkali or alkaline earth salts, are generally denser, smoother and less crystalline than those which are formed in electrolytes which do not contain these salts. This is the case with nickel sulphate and nickel chloride electrolytes, which contain salts of sodium, potassium, or magnesium. The formation of smoother and less crystalline deposits from these electrolytes may be attributed to the reducing action of the sodium, potassium, or magnesium ion in the layer of electrolyte which surrounds the cathode. Ammonium salts act similar to the alkali salts, but to a less marked degree. These facts also seem to conform to the above advanced theory."

Not only have the organic and inorganic addition-agents been found to improve copper deposits, but the temperature. of the electrolyte has also been found to exert a marked beneficial influence. The investigations of Förster and Seidel[8] have shown that the deposits produced at 40° C. were uniformly crystalline and possessed great ductility, and those formed at 60° C. were less ductile and of coarser crystals. They have also shown that the deposits formed at higher temperatures were of greater tensile strength than those formed at lower temperatures.

There are found other literatures in regard to the addition-agents in electrolytes of lead, silver, and nickel. As these have nothing to do with the present investigation, they will not be here discussed.

[8] *Zeitschrift für Electrochemie,* 1899, Vol. 5, p. 508.

EXPERIMENTAL PART.

PREPARATION OF COPPER-ARSENIC AND COPPER-ANTIMONY ALLOYS.

For making the anodes, alloys of copper-arsenic, and of copper-antimony were first prepared. Ten pounds of granulated copper, covered with a layer of charcoal, were first melted in a Dixon graphite crucible (no. *20*) in a gas-fired furnace. When the copper was completely melted, it was thoroughly poled with sticks of wood. The crucible was then taken out of the furnace, and to the molten copper 1.5 pounds of metallic arsenic wrapped with copper foil was added. The crucible was again heated. The molten alloy was stirred with a graphite rod so as to secure uniform composition. It was granulated by pouring slowly at a vertical distance of six or seven feet into a large basin full of cold water; depth 2 feet. The copper-antimony alloy was made in the same way as above, except that 0.5 pounds of antimony was added in small chunks to 10 pounds of molten copper.

MAKING OF ANODES.

Twelve pounds of granulated refined copper covered with a layer of charcoal was first melted in a Dixon graphite crucible in a gas-fired furnace and poled to tough pitch as described in the case of making copper-arsenic alloy. Then 1.5 pounds of the copper-arsenic alloy and 2 pounds of copper-antimony alloy were mixed and added to the molten copper. Having been thoroughly stirred with a graphite rod it was cast into anodes in an iron mould, which had previously been warmed and painted with bone ash. The size of the anodes was $4\frac{1}{4}$ inches high, $2\frac{3}{4}$ inches wide, and $\frac{3}{8}$ inch thick

A small portion of the anode copper was granulated as before and taken for analysis for arsenic and antimony. The methods of determining these two metals are described in the following.

DETERMINATION OF ARSENIC AND ANTIMONY IN ANODE AND CATHODE COPPER.

Considerable time was given to the determination of arsenic and the separation of antimony from it by the distillation method, for which different procedures and various reducing agents were tried. It was found that most of the methods ordinarily used, particularly the reducing agents, did not give satisfactory results. The adopted standard method finally worked out and found to be successful and practical may be described as follows:

A sample of about 10 grams, in the case of anode copper, and from 30 to 100 grams, in the case of cathode copper, depending upon the amount of arsenic it contained, was weighed out and dissolved in a no. 6 breaker with concentrated nitric acid (45 c.c. for 10 gm. of copper). The breaker was covered with a watch glass and warmed on a hot plate in order to hasten the dissolution of copper. When the solution was complete, the beaker was removed from the hot plate and about 1 gm. of ferrous sulphate added. The beaker was again heated to expel the red fume. The solution was then diluted to 400 or 500 c.c. and warmed. The iron, arsenic, and antimony was precipitated with strong ammonium hydroxide. Sufficient excess was added to dissolve all the copper compounds. The precipitate was allowed to settle, decanted, filtered while still warm and finally washed with a hot solution of ammonia (10 water to 1 ammonium hydroxide, sp. gr. 0.9). The precipitate, together with the filter paper was transferred into a no. 1 beaker covered with a watch glass, and digested gently on the hot plate with 20 c.c. of concentrated nitric acid, until practically all the red fume was driven off. (Care should be taken not to heat the solution vigorously lest some of it would be lost by spattering.) After cooling the solution, 10 c.c. of concentrated sulphuric acid was added, and the beaker was re-heated on the hot plate till fume of sulphuric anhydride freely evolved. It was then allowed to cool and about 5 c.c. of a 10-per cent. solution of hypophosphorous acid, or 6 c.c. of a 20-per cent. solution of potassium hypophosphite was added (provided the solution did not contain more than 0.3 of a gram of arsenic). The solution was again heated on the hot plate until all the excess of the hypophosphorous acid, or potassium hypo-

phosphite was destroyed: this was indicated by the evolution of strong fume of sulphuric anhydride. (In order to be sure of destroying the excess of the reducing agent, let it fume for at least one half an hour.)

The content in the beaker, after cooling, was transferred into the distilling flask (D, Fig. 1), the beaker was then rinsed twice with only 10 c.c. of water. The distilling flask was gently heated to boiling, with a smoky flame, in order to expel any sulphurous-acid gas that might be present in the solution. Bumping of the solution sometimes occurred and was prevented by imparting a rotary motion to the solution. It was then allowed to cool. After cooling, any solution that was left in the beaker was rinsed into the distilling flask twice or three times with 30 c.c. of concentrated hydrochloric acid, making a total of not over 10 c.c. water and 40 c.c. concentrated HCl. The apparatus, as is shown in Fig. 1, was now connected and adjusted; the receiver R (a no. 4 beaker), containing about 250 c.c. of water, was placed in a bath of cold water, B, and under the condenser, C, the tip of which was immersed into the water to a depth of about $\frac{1}{8}$ inch. Ten c.c. of concentrated hydrochloric acid was poured into the funnel, F, and allowed to run slowly into the distilling flask, D, through the stop-cock, S, in order to drive off the air in the lower part of the stem of the funnel, which would disturb the regularity of the acid-feed. The stop-cock was closed and the funnel filled with 80 c.c. of concentrated hydrochloric acid. Now heat was applied, first with a smoky flame, and when the solution began to boil was gradually increased, until a proper flame was adjusted. The hydrochloric acid in the funnel, F, was now allowed to run into the flask, drop by drop, at such a rate that the liquid volume in the flask might be, during the entire distillation, maintained approximately constant. (The rate was, usually, about three drops per two seconds.) When the acid in the funnel, F, was nearly exhausted, the distillation was complete. The receiver, R, containing the distillate, was carefully removed and then the flame was turned off. The content in the distilling flask was left in place to cool and reserved for the determination of antimony.

The distillate was transferred into a no. 6 beaker and nearly neutralized with a strong (30 per cent.) solution of potassium hydroxide and the neutralization completed with a saturated solu-
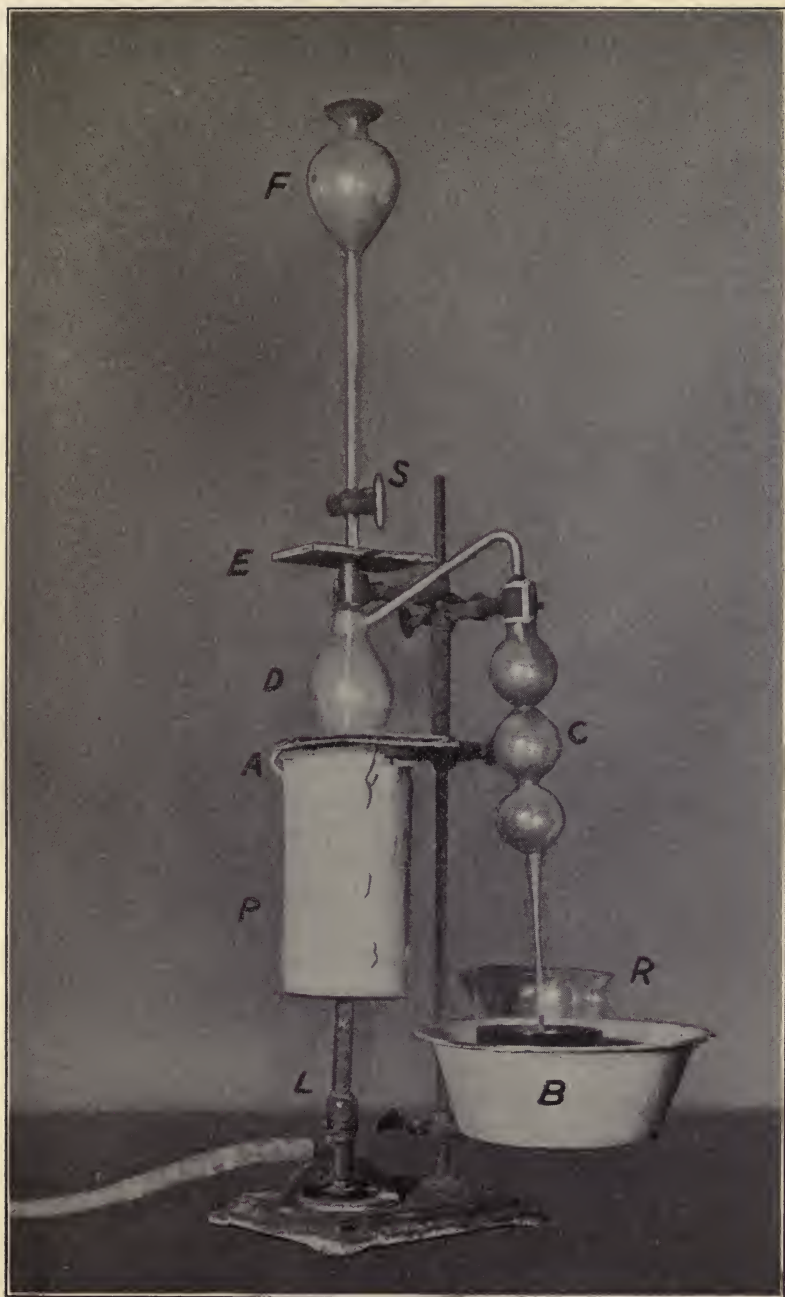
Fig. I.

tion of sodium bicarbonate, the addition of an excess of 70 to
80 c.c. being necessary. The neutralization was done by placing
the beaker in a bath of cold water, in order to keep the solution
cool while the neutralization was taking place. The neutralized
solution was then titrated with a standardized solution of iodine
(N/10). Starch solution was used as indicator.

PRECAUTIONS IN THE DISTILLATION METHOD OF ARSENIC.

The analysis of arsenic by the above method requires careful
manipulation. In order to do it successfully, it is of much im-
portance that the quantity of hypophosphorous acid, or potassium
hypophosphite, added for the reduction should be limited to as
small amount, as given in the above procedure; otherwise, it re-
duces not only the compounds of arsenic and antimony to their
metallic state, but also those of other metals, such as iron, copper,
etc. Over-reduction, according to A. E. Knorr,[9] would fail to
give satisfactory results, even though the metallic arsenic and anti-
mony would afterwards re-dissolve in the concentrated hydro-
chloric acid solution. It is also important that complete destruc-
tion of the excess of hypophosphorous acid, or potassium hypo-
phosphite, should be accomplished before the transference of the
reduced content (solid salts and solution) into the distilling flask
takes place. Any of either reducing agents remaining unde-
stroyed will interfere with the determination, and the result will
in all cases be low.

The advantages of having a continuous acid-feed, during the
entire distillation, are great and manifold. In the first place, the
temperature may be properly regulated, secondly, the strength of
the hydrochloric acid in the distilling flask may be maintained to
prevent the reversible action, which may be shown by the follow-
ing chemical equation:

$$As_2O_3 \text{ plus } 6HCl \rightleftharpoons 2AsCl_3 \text{ plus } 3H_2O.$$
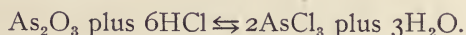
and, finally, a more rapid and effective distillation may result and,
therefore, much time may be saved.

In order to secure a steady flow of the acid-feed, a grooved
rectangular board of asbestos, E, is placed on the mouth of the

[9] Private communication.

distilling flask, so as to prevent the heating of the stop-cock, which would, otherwise, cause irregularity of the flow. Back-suction is the chief cause of failure. It is caused either by draught or by variation in the flame, which supplies insufficient heat. To prevent the former it becomes necessary to protect the flame from draught by suspending under the ring, *A*, an asbestos cylinder, *P*, 4½ inches high and of the same diameter of the ring (see Fig. 1). To prevent the latter, the flame should be carefully regulated from time to time. In this way, back-suction is less liable to occur and success may be insured. If the distillate is once sucked into the flask, re-distillation proves absolutely fruit-less, because arsenous chloride refuses to distill in such dilute solution.

TEST OF THE ABOVE METHODS.

The accuracy of the above method was tested according to the following procedure: A weighed sample of about 0.1 gm. of c.p. arsenous oxide was dissolved in 10 c.c. of sodium hydroxide. When the solution was complete 50 c.c. of concentrated nitric acid was added and then 20 c.c. of saturated bromine water, in order to oxidize the arsenic to the higher state. The solution, after an addition of about 1 gm. of ferrous sulphate, was heated to expel the excess of bromine, and, after adding 15 gm. cupric sulphate to the solution, it was diluted to about 300 c.c. and heated to boiling. The iron and arsenic was precipitated with concentrated ammonium hydroxide and the red precipitate was treated in the same way as above described (page 11).

In testing this method, both potassium hypophosphite and hypo-phosphorous acid were employed as reducing agents. In the case in which potassium hypophosphite was used, the amounts of arsenous oxide taken for analysis were 0.1004 gm. and 0.1014 gm., which corresponded to 0.076 gm. and 0.077 gm. of arsenic respectively, and the analyses gave 0.070 gm. and 0.072 gm. of arsenic. In the case where hypophosphorous acid was used, the amounts of arsenous oxide were 0.1027 gm. and 0.1014 gm. which corresponded to 0.078 gm. and 0.077 gm. arsenic while the analyses gave 0.070 gm. and 0.071 gm. of arsenic. The values in both cases approximated the calculated values of arsenic.

Reducing Agents, other than Hypophosphorous Acid and Potassium Hypophosphite.

As has already been said, many other methods of treating the iron precipitate, and in the use of various reducing agents, were employed for the distillation, but they were in no case satisfactory. Of these methods the first that may be mentioned, was that which practically got rid of all the copper in the ferric hydroxide precipitate, first, by dissolving the iron precipitate with 50 c.c. of hot dilute solution of hydrochloric acid (1 acid to 5 water) through the filter, and precipitating it with concentrated NH_4OH while hot. The re-precipitated precipitate was dissolved with 20 c.c. of concentrated hydrochloric acid through the filter, and filter paper was washed with the same amount and kind of acid. This was then transferred into the distilling flask which had previously contained 15 grams of ferrous sulphate, and distillation was made according to the method given by E. H. Miller,[10] which consisted of three intermittent distillations, using 50 c.c. concentrated hydrochloric acid each time. The results obtained varied and were always low and showed that ferrous sulphate did not appear in this case to be a satisfactory reducing agent. Besides, the distillation, with ferrous sulphate as reducing agent, was difficult to control, because, as the solution became concentrated, it often happened that violent bumping was inevitable, sometimes so violent as to cause the distilling flask to crack.

The combined reducing agents, composed of stannous chloride and ferrous sulphate, were next employed, and the object of using the former salt was to decrease the amount of the latter. The solution containing iron, arsenic and antimony was first reduced by adding, drop by drop, a saturated solution of stannous chloride in concentrated hydrochloric acid until it became colorless, and then transferred into the distilling flask containing 7 grams of ferrous sulphate crystals. The distillation was made as before. But this also proved unsatisfactory in that the results were low, varying from 15 per cent. to even 50 per cent.

The unsatisfactory results in this case were, perhaps, due to the excess and strong action of stannous chloride, which caused over-

[10] "Quantitative Analysis for Mining Engineers," E. H. Miller, ed. 1904, p. 110.

reduction of the compounds to their metallic state and these re-
duced metals remained undissolved even in a concentrated solu-
tion of hydrochloric acid, as black particles were observed in the
flask during and after the distillation. Another objection to the
use of stannous chloride was that it complicated the determina-
tion of antimony. A. E. Knorr[11] thinks that stannous chloride is
not a good reducing agent to use for the determination of arsenic,
because of the volatility of chloride of tin.

Both sodium thiosulphate and ferrous sulphate were also tried,
singly and combined. The iron precipitate with the filter paper,
in this case, was treated with 20 c.c. of concentrated nitric acid in
a 350 c.c. casserole covered with watch-glass. It was digested
and evaporated on a hot plate untill it became a pasty mass.
After addition of 3 grams of potassium bisulphate ($KHSO_4$)
and 10 c.c. of concentrated sulphuric acid, it was carefully heated
over a free flame until fume of sulphuric anhydride was strongly
given off. The solid mass, after being cooled, was taken up with
30 c.c. of concentrated hydrochloric acid and distilled as before,
using either 1 gram of sodium thiosulphate, or a mixture of 0.7
gram of sodium thiosulphate and 7 grams of ferrous sulphate
crystals. The low result obtained by this method might be due
partly to the loss of solution by spattering during evaporation to
dryness and partly to the interference of the sulphur dioxide
which was liberated by the decomposition of the sodium thio-
sulphate. A saturated solution of sodium thiosulphate, instead
of solid sodium thiosulphate, was also tried and the reduced solu-
tion in the distilling flask was boiled for a few minutes before
addition of the hydrochlorous acid, in order to expel any sulphur
dioxide that might be present. But this procedure also failed
to give satisfactory results, they being low, and varying from 20
per cent. to 60 per cent.

DETERMINATION OF ANTIMONY.

For the determination of antimony Miller's[12] method was
adopted. After the separation of arsenic by distillation, the con-
tent in the distilling flask was transferred into a no. 5 beaker and
diluted to about 400 c.c. The antimony, together with the copper,

[11] Private communication.
[12] "Quantitative Analysis for Mining Engineers," Miller, 1904, p. 106.

was precipitated in warm solution with a stream of hydrogen sulphide which continued to pass until the precipitate settled down and the solution became clear. The precipitate was separated first by decantation and then by filtration, and washed three times with hydrogen-sulphide water. It was placed with the filter paper in a no. 2 beaker and treated for an hour at room temperature, with 50 c.c. of potassium sulphide (10 per cent.) solution. The copper sulphide was filtered off, washed three or four times with hydrogen-sulphide water and discarded. To the filtrate now contained in a no. 5 beaker, 50 c.c. of dilute sulphuric acid (1 acid to 4 water) was added to precipitate the antimony. The yellow precipitate was filtered off and washed with hydrogen-sulphide water three times.

The antimony sulphide, together with the filter paper, was placed in no. 2 beaker, treated with 40 c.c. of concentrated hydrochloric acid and oxidized to the pentad state by adding, little by little, about one gram of potassium chlorate, and the solution was heated to expel the free chlorine. (During the heating, should the solution show a dark coloration, more potassium chloride should be added.)

After oxidation and the complete solution of the antimony sulphide, the filter paper was filtered off and washed three or four times with a hot dilute solution by hydrochloric acid (1 part acid to 3 parts water). The filtrate was evaporated to 50 c.c. so as to make the solution to contain a constant quantity of hydrochloric acid. Twenty c.c. of concentrated hydrochloric acid was added and the solution diluted from 600 to 700 c.c. After the addition of 3 grams of potassium iodide crystals, the solution was thoroughly stirred until the potassium iodide completely dissolved. It was then titrated at room temperature with a standardized (N/10) solution of sodium thiosulphate, starch solution being used as indicator.

As the liberation of all iodine does not take place instantaneously it is, therefore, necessary to titrate the solution slowly, that is, the thiosulphate solution should be run into the solution drop by drop until the blue color disappeared at least for one minute. Should, in any case, the blue color return, immediately more thiosulphate solution should be added.

PREPARATION OF ELECTOLYTES.

Two standard electrolytes were prepared for the electrolyses.

1. Electrolyte A, which contained 15 per cent. $CuSO_4 \cdot 5H_2O$ and 10 per cent. H_2SO_4, by weight.

2. Electrolyte B, which contained 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4 and 10 per cent. As in the form of H_3AsO_4, by weight.

For making electrolyte A, 160 grams of technical bluestone crystals from Eimer and Amend, New York, were weighed out and dissolved in about 700 c.c. of water. When solution was complete, 63 c.c. of concentrated sulphuric acid (100 grams H_2SO_4) were added to it, and the solution, when cooled, was diluted to exactly 1,000 c.c. The electrolyte was analyzed for copper and free sulphuric acid according to the following: For the copper determination, 10 c.c. of the electrolyte was drawn out by means of a pipette, transferred into a 250 c.c. calibrated flask and diluted to that volume. After stirring thoroughly, 50 c.c. of it was taken and diluted to 100 c.c. and concentrated ammonium hydroxide added in slight excess. The solution was boiled in order to expel the excess of ammonia, and then acetic acid added in slight excess. The solution was allowed to cool to ordinary temperature and titrated after an addition of 3 grams of potassium iodide with a standardized solution of sodium thiosulphate, starch solution being used as indicator. Two analyses gave 3.822 per cent. and 3.824 per cent. of copper, the average of which corresponded to 15.01 grams of $CuSO_4 \cdot 5H_2O$ per 100 c.c. of solution.

The method used for analyzing the free sulphuric acid in the electrolyte consisted in determining the total sulphate. This was conducted as follows: 50 c.c. of the above diluted solution was measured out and diluted to about 300 c.c. After an addition of a few drops of hydrochloric acid, the solution was brought to boiling, and 50 c.c. of barium chloride (20 grams $BaCl_2$ in 1,000 c.c.) was slowly added with constant stirring. When the barium sulphate settled down, it was filtered by decantation and washed with hot water three times. The precipitate was ignited in a porcelain crucible and weighed. The difference between the total sulphate and the sulphate as copper sulphate is the free sulphuric

acid. The electrolyte was found, by this method, to contain 9.92 grams of free sulphuric acid per 100 c.c. solution.

The preparation of electrolyte B, consisted in dissolving 100 grams of metallic arsenic in a sufficient quantity of concentrated nitric acid in a no. 5 beaker, much excess being avoided. After complete dissolution of arsenic, 63 c.c. of sulphuric acid was added and the solution was heated on a hot plate until the arsenic acid separated out and became a white pasty mass, which indicated complete expulsion of nitric acid. The arsenic acid was taken up with 200 to 300 c.c. of water; at the same time 160 grams of technical bluestone crystals were dissolved in about 300 c.c. of water, in another beaker. The two solutions were mixed and diluted exactly to 1,000 c.c. The arsenic in this electrolyte was determined as follows: 10 c.c. of the electrolyte was measured out and diluted exactly to 500 c.c. in a calibrated flask, from which 50 c.c. was drawn for analysis. It was evaporated to sulphuric fume with an addition of 8 c.c. of concentrated sulphuric acid. The reduction, distillation and titration were conducted in the same way as in the case of determining arsenic in cathode copper. The analyses showed that the electrolyte contained 10.01 and 9.91 grams arsenic in 100 c.c. of solution.

The electrolytes used for electrolysis were made to contain 1.5 per cent., 2 per cent., 3 per cent., 4 per cent., 6 per cent., and 8 per cent., of arsenic prepared from the above two standard electrolytes, by mixing as follows:

(a) For electrolyte containing 1.5 per cent. arsenic, 10 per cent. free H_2SO_4 and 15 per cent. $CuSO_4 \cdot 5H_2O$, 850 c.c. of electrolyte A was mixed with 150 c.c. of electrolyte B.

(b) For electrolyte containing 2 per cent. arsenic, 10 per cent. free H_2SO_4 and 15 per cent. $CuSO_4 \cdot 5H_2O$, 800 c.c. of electrolyte A was mixed with 200 c.c. of electrolyte B.

(c) For electrolyte containing 3 per cent. arsenic, 10 per cent. free H_2SO_4 and 15 per cent. $CuSO_4 \cdot 5H_2O$, 700 c.c. of electrolyte A was mixed with 300 c.c. of electrolyte B.

(d) For electrolyte containing 4 per cent. arsenic, 10 per cent. free H_2SO_4 and 15 per cent. $CuSO_4 \cdot 5H_2O$, 600 c.c. of electrolyte A was mixed with 400 c. c. of electrolyte B.

(e) For electrolyte containing 6 per cent. arsenic, 10 per cent. free H_2SO_4 and 15 per cent. $CuSO_4 \cdot 5H_2O$, 400 c.c. of electrolyte A was mixed with 600 c.c. of electrolyte B.

(f) For electrolyte containing 8 per cent. arsenic, 10 per cent. free H_2SO_4 and 15 per cent. $CuSO_4 \cdot 5H_2O$, 200 c.c. of electrolyte A was mixed with 800 c.c. of electrolyte B.

THE ELECTROLYSIS.

The electrolyses were conducted in no. 6 beakers (size $4\frac{1}{2}$ inches in diam. and $5\frac{3}{4}$ inches high) in each of which was immersed an anode and a cathode (size $4\frac{3}{8}$ inches long and $2\frac{3}{4}$ inches wide), the latter being plates cut from sheet copper, $\frac{1}{64}$ inch thick. The anodes were cast plates of copper $\frac{3}{8}$ inch thick. Before the cathodes were used they were straightened and cleaned by washing first with a little dilute nitric acid and then with water, which gave a clean bright surface. A horizontal mark was made on each, 4 inches from the bottom, so as to obtain the desired current density, and the surfaces were greased with a little vaseline. The anode and the cathode in each cell were suspended from glass rods (e, Fig. 2) at a distance of $1\frac{3}{4}$ inch and parallel to each other. The current density used in all experiments was 40 amperes per square foot.

THE APPARATUS.

The apparatus and its arrangement are shown in Fig. 2. This consists of two water-baths (W) which are used to keep the electrolyte at constant temperatures and in each of which were placed four cells (C) (no. 6 beakers). Each cell rests on two strips of wood, s, and the water-baths are supported at each end by an iron tripod (I). Under, and in the middle of each water-bath is placed a Bunsen burner (B) by which the desired temperatures of the two baths may be secured and adjusted. All the cells are connected in series. The electric current used for electrolysis is furnished by a storage battery of six cells, connected in series, measured by the ammeter (A), which permits readings to 0.05 ampere, and regulated by the rheostat (R).

CIRCULATION OF ELECTROLYTE.

The electrolyte in each cell was agitated during electrolysis by stirrer (g). Fig. 2 shows its arrangement and details. It con-

sists of the framework of which (F) are the two horizontal steel bars, and the ends of which are clamped to, and supported by a vertical iron rod (L). To each of the steel bars (F) are clamped four cylindrical collars (h), at such distance as to conveniently permit the stirrers to operate in the cells. The pulleys (p) ($\frac{7}{8}$ inch diam.), fastened to the stirring rods (f), rest on the collars (h). The upper part of the stirring rod (f) is of steel and the lower
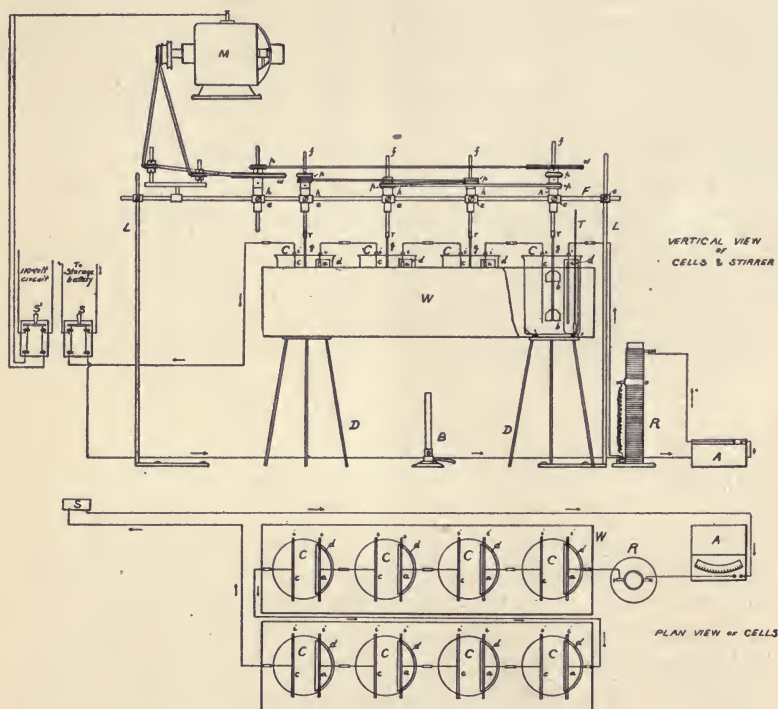

FIG. 2.

part (g) of glass rod, and these two parts are connected by means of a short piece of rubber tubing (r). Two "policemen" (b) attached to the glass rod, as are shown in Fig. 2, serve to give an effective circulation of the electrolyte in each cell. The stirrers are run by a half horse-power motor (M). The speed of the stirrers is about 120 revolutions per minute.

MODE OF OPERATION.

In these experiments the mode of operation is simple and may be stated as follows: After all the connections of the circuit had been made, and the electrodes had been properly placed and adjusted, the cells were filled with electrolyte until its surface reached the horizontal mark of the cathodes, which, as has already been said, were scratched for the purpose of obtaining the desired current density and which also served to keep the volume of the electrolyte constant. Water was then run into the two baths (W) until they became full. The stirrers were set in motion, and the baths (W) heated. When the desired temperatures of the electrolytes were attained, the electric current for electrolysis was turned on and kept constant by regulating the rheostat (R). The difference of potential between the anode and the cathode was read every two hours and sometimes every three hours with a voltmeter which permits reading to 0.01 of a volt. The temperatures of the electrolyte were measured with thermometers (T) immersed in the cells. At the end of the experiment the glass part of the stirrers was disconnected. The cathode copper was removed from the cells, washed and dried.

During electrolysis, it was observed that much water of the electrolyte was lost by evaporation. To make up this loss, water was added to the cells from time to time.

SAMPLE OF CATHODE COPPER FOR ANALYSIS.

In order to easily peel off the starting sheet, the edges of the cathode were first sawed off, and the deposited copper was sawed into strips from $\frac{1}{2}$ to $\frac{3}{4}$ inch wide, and from 3 to $3\frac{1}{2}$ inches long. These strips were used as samples for analysis, usually about 80 grams, unless the copper deposit shows dark surface and is brittle, indicating much impurities, in the latter case a sample of 40 grams was taken.

ELECTROLYTES, WHICH CONTAINED NO ADDITION-AGENT.

Experiment I.

Four runs were made on electrolytes which contained no "addition-agent." Electrolytes used for Experiment I. contained

15 per cent. cupric sulphate ($CuSO_4 \cdot 5H_2O$), 10 per cent. sul-
phuric acid: and cell 1, no arsenic; cell 2, 1 per cent. arsenic;
cell 3, 2 per cent. arsenic; and cell 4, 4 per cent. arsenic. The
electrolysis was conducted for 53 hours, in two series, each of
which consisted of four cells, C, as is shown in Fig. 2. The com-
position of the electrolytes in the two series was the same, but
the temperature of the electrolyte was 20° C. and 50° C.

It was observed during electrolysis that the potential difference
between the electrodes in the lower-temperature series was
gradually increased and that in the higher-temperature one only

to a small extent, and sometimes remained practically constant.
The increase of voltage was due to the fact that a sticky coating
of oxides of arsenic and antimony gradually formed on the sur-
face of the anode. But the coating formed at a higher temper-
ature was porous and offered little, or no, resistance and dropped
to the bottom of the cell when sufficiently thick. In order to
prevent the accumulation of the coating on the anodes in the
lower-temperature series, the surfaces were occasionally scraped.

It may be here mentioned that this experiment was attempted to run continuously, in other words, day and night; but it was soon realized that this could not be done, because two of the conditions could not be properly maintained during the night. In the first place, the coating of arsenic and antimony oxides which formed on the surface of the anodes in the lower-temperature series was so thick that it greatly increased the resistance, thus reducing the current density: and in the second place, the addition of water to the electrolytes to make up the loss by evaporation could not be readily accomplished. The result was that the hotter electrolytes became greatly concentrated. As the deviations of these conditions might have exerted a strong influence upon the physical and chemical properties of the deposit, analyses of the cathode copper for arsenic and antimony were not made, nor were these two elements determined in the electrolyte after the run.

In regard to the character of the deposits, a few words, however, may be said. It was observed that the deposits formed at 50° C. were, by far, better than those formed at 20° C. They were solid, coherent, and of bright color, though nodular crystals formed at the lower edge, especially in electrolytes containing higher percentage of arsenic. The deposits which formed at 20° C. in electrolytes containing 1 per cent., 2 per cent., and 4 per cent., were dark, brittle, and crystalline, and the crystals were easily broken off. The deposit formed at 20° C. in electrolyte which originally con-

TABLE I.

Time of Experiment 53 hours. Current Density 40 Amp. per square foot. Distance between Electrodes 1.75 inch. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$ and 10 per cent. H_2SO_4. Anode contained 1.15 per cent. As and 1.05 per cent. Sb.

No. of Cells.	Per Cent. of As in Electrolyte.	Temp. of Electrolyte deg. Cent.	Photo. I.
Series A.			A
1	0.0	20	1
2	2.0	20	2
3	4.0	20	3
4	4.0	20	4
Series B.			B
1	0.0	50	1
2	1.0	50	2
3	2.0	50	3
4	4.0	50	4

tained no arsenic, appeared bright. The deposits are shown in Photograph I. The upper row (A) are deposits formed at 20° C. and the lower row (B) are deposits formed at 50° C.

Experiment II.

This experiment was conducted in the same manner as the previous one, except that the electrolysis was carried on only during the day-time. The electrolytes used for this experiment contained 2 per cent., 4 per cent., 6 per cent., and 8 per cent. of arsenic with the usual proportion of cupric sulphate (15 per cent. $CuSO_4 \cdot 5H_2O$) and free sulphuric acid (10 per cent. H_2SO_4).
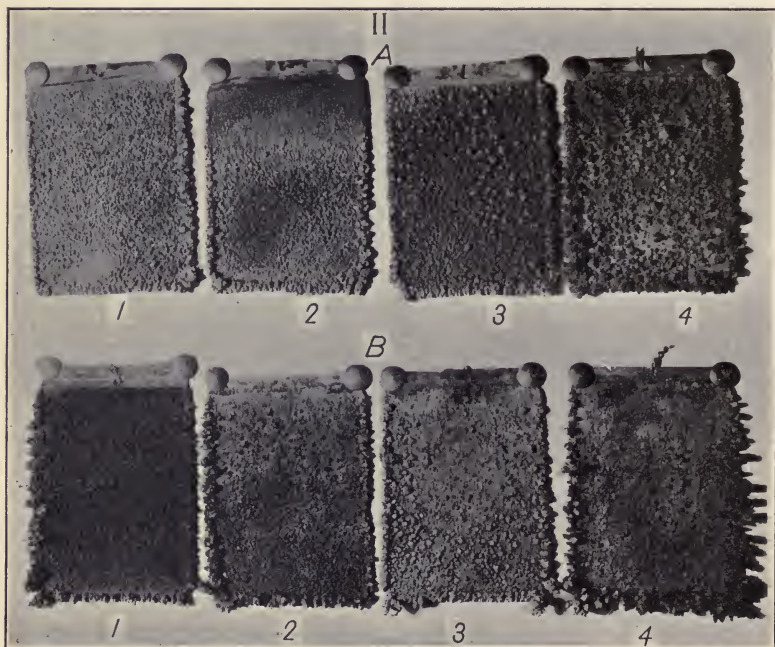
The temperatures of the two series were 35° C. and 60° C., and the time of the experiment was 42 hours.

The deposits formed at 35° C. and in electrolytes containing 2 per cent., 4 per cent., and 6 per cent. arsenic were bad and brittle and composed of coarse grains which were easily detached. Their surfaces became dark as soon as they were taken out of the

electrolytes and exposed to the air. The analysis shows that these deposits were high in arsenic and antimony (see no. 1, 2, and 3, Table II.). The deposit formed in electrolyte containing 8 per cent. arsenic and at the same temperature (35° C.) was much better. It was good, bright, and coherent, and ran low in arsenic and antimony (see no. 4, series A, Table II.). But it was observed that at the edges of this deposit dendritic nodules formed, and smaller nodules were scattered over the surface. This is clearly shown in series A, Photograph II. The deposits formed at 60° C. and in electrolytes which contained 2 per cent. and 4 per cent. arsenic were also bad, brittle, crystalline and incoherent. "Trees" were formed at the edges as shown in 1 and 2, series B, Photograph II. Their surfaces were dark and became darker when exposed to air. They ran much higher in arsenic and antimony than those formed at the lower temperature and in similar electrolytes. Those formed at 60° C. but in electrolytes containing 6 per cent. and 8 per cent. arsenic were, on the other hand, good, bright, solid and coherent, though larger "trees" were found at the edges, especially of the deposit formed in electrolytes containing 8 per cent. arsenic. 3 and 4, series B, Photograph II., show the "trees" of these deposits.

The analysis of the electrolytes after the run, as given in Table II., shows that they contained higher percentage of arsenic than before the run. This increase was, undoubtedly, due to the partial dissolution of the arsenic in the anode. The antimony, both in the cathode copper and in the electrolyte was also transferred from the anode by the current.

The potential difference between the electrodes should also be mentioned. It was observed that the potential difference in series A was higher on the first day than on the last day of the run, while that in series B was not so in every case. The potential difference in cells 1 and 2, series B, was higher on the last day than the first day of the run. This may be explained by the fact the formation of the porous layer of oxides of arsenic and antimony on the anode which, at the time when the voltage was read, did not drop off, and, therefore, offered resistance. In series A the anodes were scraped occasionally and readings were taken just after scraping. The diminution of potential difference may be due to the formation of nodular crystals, reducing the actual distance between the electrodes.

TABLE II.

Time of Experiment was 42 hours. Distance between Electrodes was 1.75 inch. Electrolytes contained 15 per cent. $CuSO_4 \cdot 5H_2O$ and 10 per cent. H_2SO_4. Anode contained 1.15 per cent. As and 1.05 per cent. Sb. Current Density was 40 Amp. per square foot.

No. of Cells.	Per Cent. of As in Electrolyte.	Temp. of Electrolyte in deg. Cent.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. II.
				% As.	% Sb.	% As.	% Sb.	
Series A.								A
1	2	35	0.58	0.199	0.253	2.22	0.004	1
2	4	35	0.57	0.217	0.391	4.32	0.002	2
3	6	35	0.53	0.314	0.361	6.15	0.003	3
4	8	35	0.59	0.036	0.014	8.15	0.004	4
Series B.								B
1	2	60	0.45	0.026	0.395	2.29	0.006	1
2	4	60	0.42	0.388	0.496	n.d.	n.d.	2
3	6	60	0.39	0.018	0.009	6.23	0.002	3
4	8	60	0.38	0.014	0.004	8.10	0.004	4

Experiment III.

In this experiment the cathodes were surrounded with diaphragms, and the object of using them was to prevent particles of impurity from depositing mechanically on the cathode. The diaphragm-frame was made of glass rod and was of semi-cylindrical shape (D, Fig. 2). The circular side and the bottom of the frame were closed with thin rubber dam, used by dentists, and the side, which is between the electrodes with linen cloth. The cloth, before used, was thoroughly washed with hot water, and the rubber dam was first treated with dilute sulphuric acid and, then, with water, in order to free any impurity that might have been present.

During the electrolysis one difficulty was encountered when the cathodes were surrounded with diaphragms. The latter, when soaked with electrolyte and in contact with the former, became cathodes, and thus copper was deposited on their sides and bottom, which soon bridged the electrodes and short-circuited the electric current. Moreover, rubber dam was found not a proper material to use because it decayed and became tender, and, because it increased the potential difference between the electrodes to a small extent.

The electrolysis was conducted at 60° C. and 30° C. and the

electrolytes used for both series contained 2 per cent. and 6 per cent. arsenic with the same proportion of cupric sulphate (15 per cent.) and free sulphuric acid (10 per cent.) as before.

As has already been stated, a sticky layer of oxides formed on the surface of the anode in the low-temperature series, and the formation of this caused the potential difference between the electrodes to be unusually high. To show whether or not this high potential difference had any effect on the deposition of arsenic and antimony on the cathode, the surface of two anodes (nos. 1 and 3, series A, Table III.) was occasionally scraped with a rubber "policeman" attached to a glass rod, while the surface of the other two anodes of series A (nos. 2 and 4, Table III.) was undisturbed.

Table III. gives the results of this experiment and shows the averaged potential difference is much higher in the case where the anode surface was not scraped than that in the case where the anode surface was scraped. The amount of arsenic in the deposited copper is practically the same in both cases, while the amount of antimony appears little higher in the case where the anode surface was unscraped.
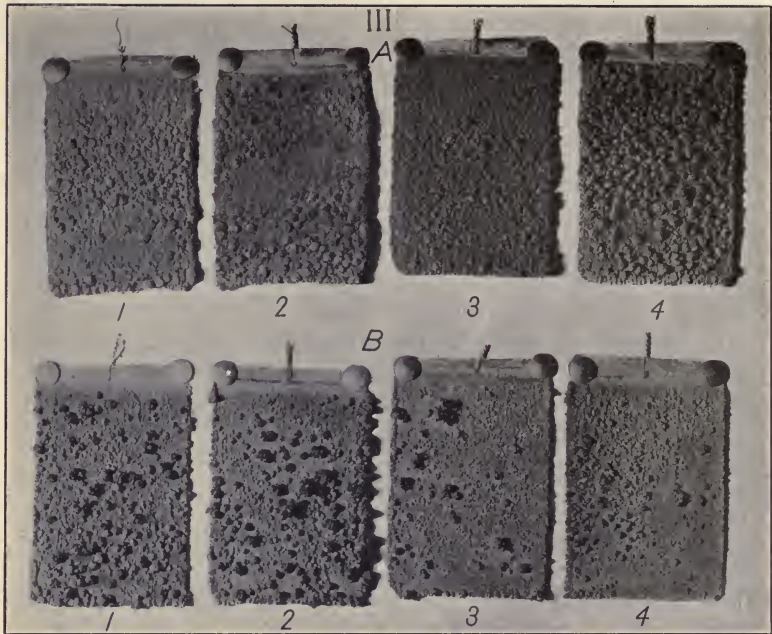
As to the physical properties, the deposits which formed at 30° C. were all bad, brittle and high in arsenic and antimony, as is shown in Table III., and composed of coarse, nodular and in-

TABLE III.

Time of Experiment 61 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$ and 10 per cent. H_2SO_4. Anode contained 1.15 per cent. As and 1.05 per cent Sb.

No. of Cells.	Per Cent. of As in Electrolyte.	Temp. of Electrolyte in deg. Cent.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. III.
				% As.	% Sb.	% As.	% Sb.	
Series A.								A
1	2	30	0.57	0.118	0.099	2.40	0.003	1
2	2	30	0.79	0.115	0.129	2.11	None	2
3	6	30	0.62	0.124	0.053	5.80	0.003	3
4	6	30	1.12	0.160	0.079	6.10	0.002	4
Series B.								B
1	2	60	0.49	0.186	0.268	2.28	0.004	1
2	2	60	0.44	0.171	0.228	2.21	0.002	2
3	6	60	0.44	0.025	0.001	6.28	0.002	3
4	6	60	0.46	0.031	0.001	6.30	0.004	4

coherent crystals. The deposits which formed at 60° C. and in
the electrolyte containing 2 per cent. arsenic were very bad.
They were dark, and became darker when exposed to the air.
The analysis shows that they contained much arsenic and anti-

mony. Those, on the other hand, which formed at the same
temperature but in electrolyte containing 6 per cent. arsenic, were
good, bright and dense, though a few nodular crystals formed on
the surface and at the edges of the deposits. Photograph III.,
B3 and B4, shows their character.

Experiment IV.

In this experiment, and in the rest of the experiments, muslin
diaphragms were used to surround the anodes, instead of the
cathodes. These diaphragms were found satisfactory; short-
circuiting was prevented and particles of impurities were col-
lected and, thus, prevented from collecting mechanically on the
cathode.

The electrolytes used were prepared to contain 1.5 per cent., 3 per cent., 6 per cent., and 8 per cent. arsenic, and the amount of cupric sulphate and free sulphuric acid was 15 per cent. and 10 per cent., respectively. The temperature of the electrolytes was 40° C. and 50° C. and the time of electrolysis was 104 hours. Table IV. gives the results of this experiment.

The deposits, no. 1, no. 2 and no. 3, series A, were all bad, rough, brittle, and crystalline. Of these deposits, no. 2 and no. 3
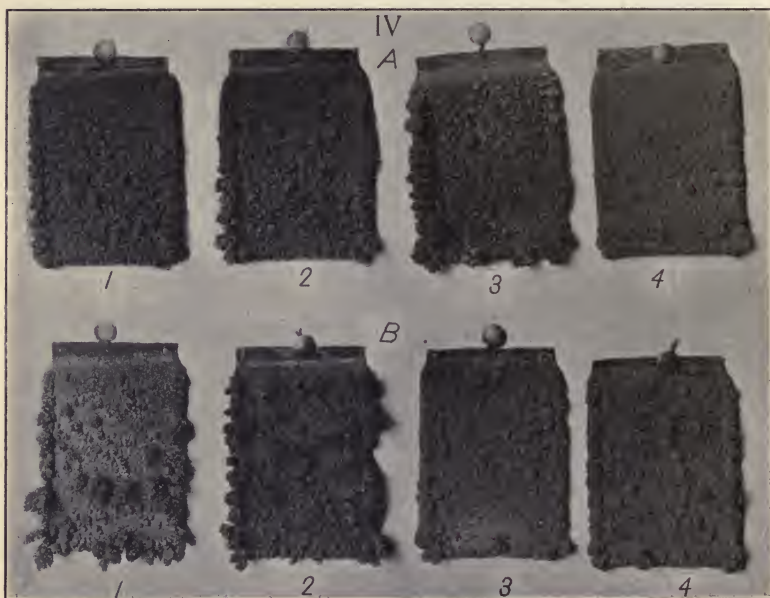
TABLE IV.

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$ and 10 per cent. H_2SO_4. Anode contained 0.75 per cent. As and 0.73 per cent. Sb.

No. of Cells.	Per Cent. of As in Electrolyte.	Temp. of Electrolyte in deg. Cent.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. IV.
				% As.	% Sb.	% As.	% Sb.	
Series A.								A
1	1.5	40	0.44	0.077	0.085	1.72	0.004	1
2	3.0	40	0.44	0.100	0.074	3.09	0.004	2
3	6.0	40	0.43	0.101	0.117	6.03	0.003	3
4	8.0	40	0.49	0.024	0.005	8.10	0.005	4
Series B.								B
1	1.5	50	0.40	0.063	0.175	1.65	Not detectable.	1
2	3.0	50	0.40	0.296	0.460	3.27	0.004	2
3	6.0	50	0.41	0.007	0.001	6.10	0.004	3
4	8.0	50	0.44	0.008	0.002	8.04	0.003	4

were worse; they were composed of crystals easily detached, and consisted of long dendritic "trees" which interfered with the operation of stirrers and tended to short-circuit the current. Their surfaces were dull and became dark on exposure to the atmosphere. The chemical analyses show that they contain much arsenic and antimony. Deposit no. 4, series A, was good, solid, bright, and absent of "trees," but consisted of a few small nodular crystals which scattered over the surface. It contained a very small amount of arsenic and antimony.

The deposits, no. 1 and no. 2, series B, which formed at 50° C. and in electrolytes containing 1.5 per cent. and 3 per cent. arsenic, respectively, were also bad and brittle, and both were composed of long dendritic "trees." It was observed that deposit no. 2

was much worse than no. 1, as it was very brittle and dark.   The
analysis shows that both deposits contained high percentage of
arsenic and antimony, but the percentage of these two impurities
contained in deposit no. 2 was by far higher than that in deposit
no. 1.   As to the deposits no. 3 and no. 4, series B, which formed
at the same temperature but in electrolytes containing 6 per cent.

and 8 per cent. arsenic, they were found to be good, solid, bright
and absent of "trees," though a few rounded nodules formed on
the surface.   They contained very low arsenic and antimony, as
shown in Table IV.   Photograph IV. shows the character of the
deposits.

ELECTROLYTES, WHICH CONTAINED INORGANIC "ADDITION-AGENTS."

This series of experiments was conducted with electrolytes of
the same composition as those used in Experiment IV., with the
exception that inorganic "addition-agent" was added.   The
temperature of electrolytes in series A was 40° C. and that in
series B was 50° C.

Experiment V.

In this experiment sodium chloride was used as "addition-agent," 0.1650 gram of this salt was weighed out and added to a liter of each electrolyte, in other words, the electrolytes contained 0.01 per cent. chlorine or 0.0065 per cent. sodium in the form of sodium chloride.

It may be pointed out here that when sodium chloride was added to the electrolyte it reacted with the cupric sulphate to form cupric chloride and sodium sulphate, as may be shown by the following equation.

$$2NaCl \text{ plus } CuSO_4 = CuCl_2 \text{ plus } Na_2SO_4.$$
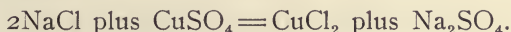
Thus, there were present in the electrolyte, in fact, two "addition-agents," instead of one, when sodium chloride was added.

The results of this experiment were very satisfactory and are shown in Table V.

TABLE V.

Time of Experiment was 104 hours. Distance between Electrodes was 1.75 inch. Current Density was 40 Amp. per square foot. Electrolytes contained 15 per cent. $CuSO_4 \cdot 5H_2O$ and 10 per cent. H_2SO_4 and 0.01 per cent. Cl as NaCl. Anode contained 0.87 per cent. As and 1.13 per cent. Sb.

| No. of Cells.	Per Cent. of As in Electrolyte.	Temp. of Electrolyte in deg. Cent.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. V.
				% As.	% Sb.	% As.	% Sb.	
Series A.								A
1	1.5	40	0.48	0.0012	0.0005	1.97	0.0056	1
2	3.0	40	0.56	0.0006	0.0005	3.39	0.0036	2
3	6.0	40	0.51	0.0019	0.0008	6.59	0.0056	3
4	8.0	40	0.54	0.0019	0.0007	8.51	0.0098	4
Series B.								B
1	1.5	50	0.47	0.0024	0.0003	1.90	0.0036	1
2	3.0	50	0.49	0.0012	0.0005	3.43	0.0097	2
3	6.0	50	0.47	0.0012	0.0005	6.70	0.0090	3
4	8.0	50	0.49	0.0006	0.0004	8.60	0.0058	4

The deposits from series A were very good, bright, solid, smooth, coherent and absolutely absent of "trees." The deposits from series B were similar to those from A, except that their surfaces were little brighter and the small crystals were a bit more pronounced. The analyses of these deposits show that the arsenic and antimony were very low in every case.

In addition to the chemical determination of the impurities in

the cathode copper, a physical bending test was also made. A
strip of the cathode copper, about ¾ inch wide, 3¾ inches long, was
taken for the test.   It was bent, with the under-side out and ham-
mered double; in no case did the strips crack at the bend.   This
bending test showed that the cathode copper was very ductile
and of high purity in all cases.

The addition of such a small amount of sodium chloride was
found to exert a remarkably favorable influence upon the deposited
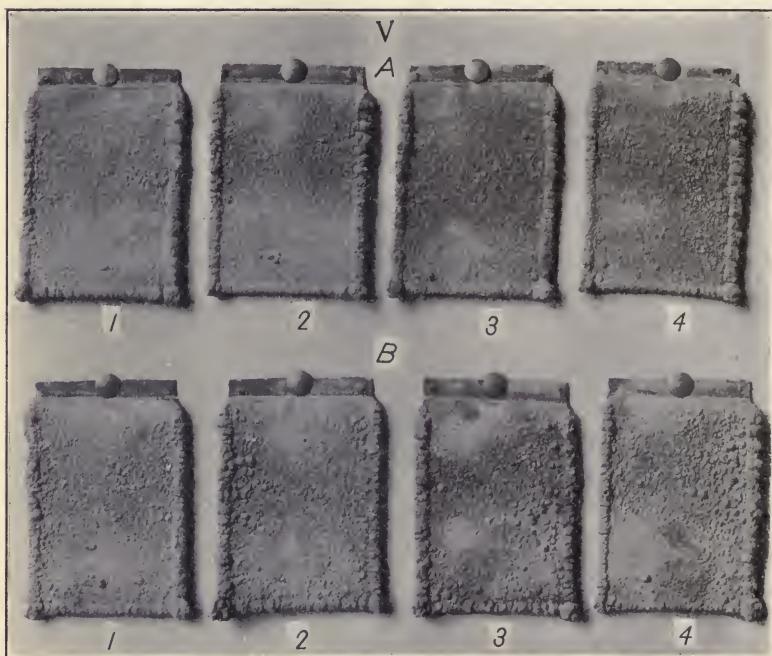
copper, for it not only improved the physical properties of the
deposits, but also overcame the formation of "sprouts," and pre-
vented the precipitation of arsenic and antimony with the cathode
copper. (Compare results given in Tables IV. and V.)   Photo-
graph V. shows the character of the deposits.

Experiment VI.

As has been found, that the presence of a small amount of
sodium chloride in the electrolytes exerts a marked beneficial in-

fluence upon the copper deposits, it becomes important to ascertain which of the two ions (Na ion and Cl ion) produces this good effect. To attain this object, hydrochloric acid, which has the Cl ion in common with sodium chloride, was first tried and used as "addition-agent" in this experiment. For this purpose, standard hydrochloric acid solution was prepared by diluting 10 c.c. of concentrated acid containing 37.5 per cent. HCl to 100 c.c. A measured volume of this solution was added to each electrolyte so that it contained the same amount of chlorine, per liter, as in the case of sodium chloride, that is, 0.01 per cent. chlorine.

It may be noted here that just as sodium chloride reacts with the cupric sulphate of the electrolyte, so hydrochloric acid reacts with it, to form cupric chloride. This reaction may be represented by the following equation:

$$2HCl \text{ plus } CuSO_4 = H_2SO_4 \text{ plus } CuCl_2.$$
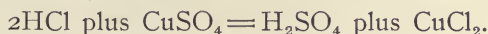
So, in reality, there exists in the electrolyte cupric chloride instead of hydrochloric acid, when the latter is added to the cupric sulphate electrolyte. The experimental data are given in Table VI.

TABLE VI.

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4, and 0.01 per cent. Cl as HCl. Anode contained 1.15 per cent. As and 1.12 per cent. Sb.

No. of Cells.	Per Cent. of As in Electrolyte.	Temp. of Electrolyte in deg. Cent.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. VI.
				% As.	% Sb.	% As.	% Sb.	
Series A.								A
1	1.5	40	0.49	0.0022	0.0004	1.83	0.0070	1
2	3.0	40	0.47	0.0030	0.0004	3.24	0.0036	2
3	6.0	40	0.48	0.0074	0.0005	6.04	0.0080	3
4	8.0	40	0.49	0.0106	0.0004	8.06	0.0030	4
Series B.								B
1	1.5	50	0.45	0.0015	0.0009	2.09	0.0075	1
2	3.0	50	0.44	0.0014	0.0002	3.46	0.0083	2
3	6.0	50	0.44	0.0037	0.0007	6.25	0.0030	3
4	8.0	50	0.44	0.0023	0.0007	8.31	0.0030	4

The deposits formed at both temperatures (40° C. and 50° C.) were satisfactory. Those which formed at 40° C. were bright,

solid, smooth, slightly crystalline deposits, free of "trees," but nodular at their edges, whereas the deposits formed at 50° C. were similar in character, but brighter.   As to the result of bending test, the deposits obtained from the higher temperature appeared to be more ductile than those from the lower temperature, as they cracked less than those formed at 40° C.   When the test-strips of deposits no. 3 and no. 4, series A, were hammered double, they cracked at the outer side of the bend.

Chemical analyses show that the deposits formed at 40° C.
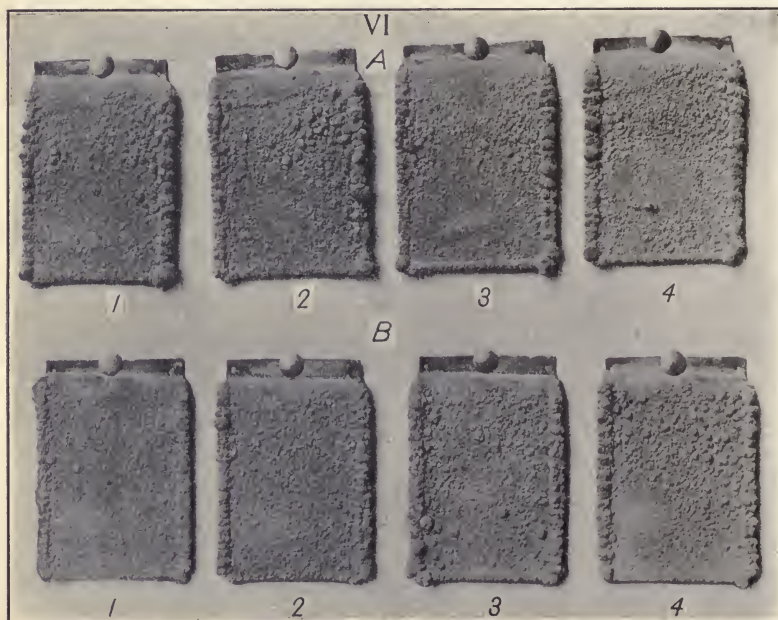
were higher in arsenic than those at 50° C. and that they were not so pure as those obtained in electrolytes containing sodium chloride.

The results of this experiment, therefore, indicate that the Cl ion does exert a beneficial influence upon the deposited copper and that hydrochloric acid is not so active an addition-agent as sodium chloride, as the presence of the latter gives cathode copper which is purer and more ductile.   Photograph VI. shows the character of the deposits.

Experiment VII.

As Cl ion was found to produce a good effect upon the deposited copper and to prevent, to a great extent, the deposition of arsenic and antimony, it now remains to find that the Na ion would produce the same effect. In order to accomplish this, sodium sulphate ($Na_2SO_4 \cdot 10H_2O$) was selected and a weighed amount of this salt added to each electrolyte, so that it contained 0.0065 per cent. sodium, which corresponded to the same amount of sodium as in the case of sodium chloride (Experiment V.).

Table VII. gives the results of this experiment and Photograph VII. shows the character of the deposits.

TABLE VII.

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4, and 0.0065 per cent. Na as Na_2SO_4. Anode contained 1.47 per cent. As and 1.12 per cent. Sb.

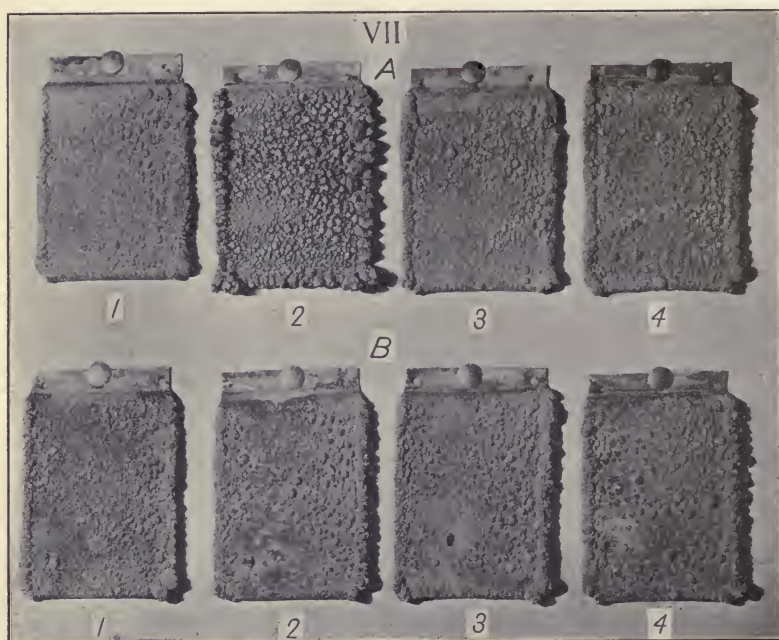| No. of Cells.	Per Cent. of As in Electrolyte.	Temp. of Electrolyte in deg. Cent.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. VII.
				% As.	% Sb.	% As.	% Sb.	
Series A.								A
1	1.5	40	0.51	0.0023	0.0006	1.86	0.0017	1
2	3.0	40	0.50	0.0975	0.1403	3.36	0.0090	2
3	6.0	40	0.51	0.0066	0.0016	6.16	0.0084	3
4	8.0	40	0.50	0.0061	0.0004	8.44	0.0060	4
Series B.								B
1	1.5	50	0.45	0.0011	0.0005	1.97	0.0045	1
2	3.0	50	0.46	0.0023	0.0003	3.32	0.0021	2
3	6.0	50	0.44	0.0018	0.0002	6.37	0.0073	3
4	8.0	50	0.46	0.0063	0.0004	8.45	0.0056	4

The deposits which formed at 40° C. and in electrolytes containing 1.5 per cent., 6 per cent., and 8 per cent. arsenic were found bright, solid, and absent of "trees," while the deposit which formed at the same temperature, but in electrolyte which contained 3 per cent. arsenic was very bad, exceedingly brittle and of dull color. It was composed not only of nodular crystals, but of dendritic "trees" formed especially at the edges, as clearly shown in No. 2, Photograph VII., A.

When the test-strips of deposits of series A were hammered double it was found that they were not very ductile, as deposits no. 3 and no. 4 were broken into two and deposit no. 1 almost into two.

The deposits which formed at 50° C. were all bright, and solid
and free of "trees," though a few small rounded nodules formed
on the surface.   The bending test showed that these deposits were
much tougher and more ductile than those which formed at 40°
C., for the test-strips did not even crack when they were hammered double.

As to the purity of the deposited copper, it will be observed in
Table VII. that the amount of arsenic and antimony in the cathodes of both series was in all cases low, except deposit no. 2,
series A, which was obtained at 40° C. and in electrolyte containing 3 per cent. arsenic.   It contained much arsenic and anti-

mony.   It should also be observed that the amount of impurities
contained in deposits which formed at 40° C. was notably higher
than that contained in those which formed at 50° C.

From what has been said, it will then be seen that the presence
of a *small* amount of sodium sulphate in the electrolytes had a
decidedly good effect, chemically and physically, upon the deposited copper ; provided that the electrolysis be conducted at 50° C.

At 40° C., however, its effect was somewhat decreased and it had practically no effect upon the deposited copper when the electrolyte contained 3 per cent. arsenic.

As to the relative effectiveness of the Na ion and the Cl ion, the former appeared to be less effective at the lower temperatures, whereas at the higher temperature the beneficial effect of the presence of either of the ions was appreciably the same.

Experiment VIII.

In this experiment a larger amount of sodium sulphate was employed than in Experiment VII. It was added to the electrolytes, with the object of ascertaining whether the larger amount would produce a greater effect upon the deposited copper. The amount added was 100 times that which was used in Experiment VII.; in other words, each of the electrolytes contained 0.65 per cent. sodium.

It should be mentioned here that during the electrolysis the potential difference, particularly in the lower temperature series, seemed to increase slightly, with the presence of this large amount of sodium sulphate.

The deposits which formed at both temperatures were satisfactory. They were bright, smooth, tough and solid, though a few small rounded nodules scattered on the surface. Deposit no. 2,
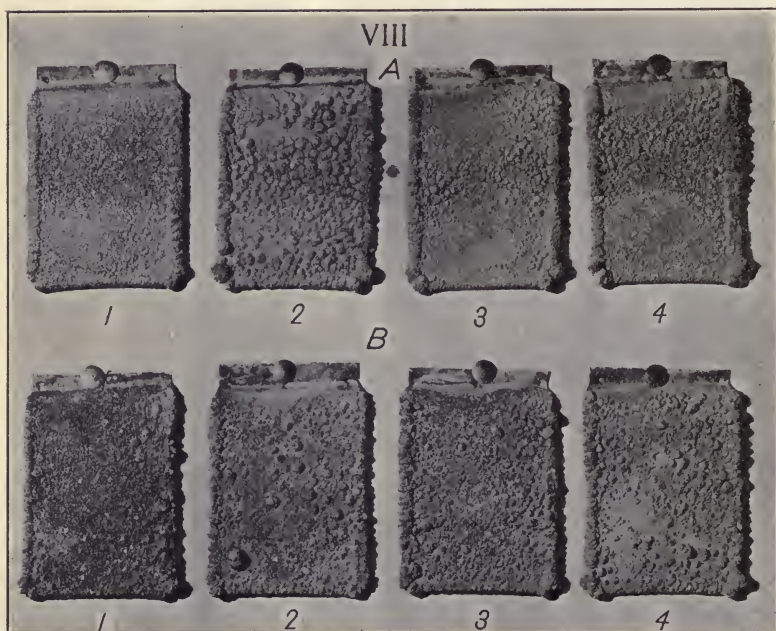
TABLE VIII.

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4, and 0.65 per cent. Na as Na_2SO_4. Anode contained 0.98 per cent. As and 0.75 per cent. Sb.

No. of Cells.	Per Cent. of As in Electrolyte.	Temp. of Electrolyte in deg. Cent.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. VIII.
				% As.	% Sb.	% As.	% Sb.	
Series A.								A
1	1.5	40	0.54	0.0020	0.0002	1.85	0.0040	1
2	3.0	40	0.52	0.0051	0.0028	3.16	0.0021	2
3	6.0	40	0.51	0.0086	0.0006	6.02	0.0016	3
4	8.0	40	0.54	0.0104	0.0002	8.20	0.0029	4
Series B.								B
1	1.5	50	0.44	0.0013	0.0004	1.85	0.0015	1
2	3.0	50	0.44	0.0018	0.0004	3.42	0.0058	2
3	6.0	50	0.45	0.0019	0.0006	6.34	0.0054	3
4	8.0	50	0.45	0.0023	0.0007	8.05	0.0032	4

series A, was the most nodular. The bending test showed that
they were ductile and that those formed at the higher tempera-
ture were more ductile than those formed at the lower tem-
perature.

The chemical analyses show that the deposits formed at 40° C.
contained higher percentage of arsenic than those which formed
at 50° C., while the percentages of antimony in both series were
low, except no. 2, series A, which contained a much greater per-
centage than the rest. The experimental data of this experiment

are given in Table VIII. and the character of the deposits is
shown in Photograph VIII.

Comparing the results with those obtained in Experiment VII.,
it is found that the larger amount of sodium sulphate added to
the electrolytes does not appear to have much improved the copper
deposits of either series, except the deposit which formed at 40°
C. and in electrolyte containing 3 per cent. arsenic, in which case
it hindered, to a great extent, the precipitation of arsenic and
antimony.

It is, therefore, obvious from the results of the two experiments (VII. and VIII.) that at 50° C. the presence of a small amount of sodium sulphate had a decidedly good effect on the deposited copper in all cases, whereas at 40° C. such a small amount had the same effect, but no effect in the case in which the electrolyte contained 3 per cent. arsenic, unless a sufficiently large amount was present. The higher temperature is, therefore, preferable, as it does not only cause the deposited copper to form more ductile, but also renders, in this case, the "addition-agent" more effective.

Experiment IX. A.

The electrolytes used in this experiment contained only 3 per cent. and 6 per cent. arsenic, as the electrolysis was conducted only at 50° C. The "addition-agents" tried were aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$) and aluminium chloride ($AlCl_3 \cdot 6H_2O$). In either case, the amount of salt added was such that the electrolyte contained 0.10 per cent. Al.

TABLE IX. A.

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$ and 10 per cent. H_2SO_4. Temperature of Electrolyte 50° C. Anode contained 0.97 per cent. As and 0.89 per cent. Sb.
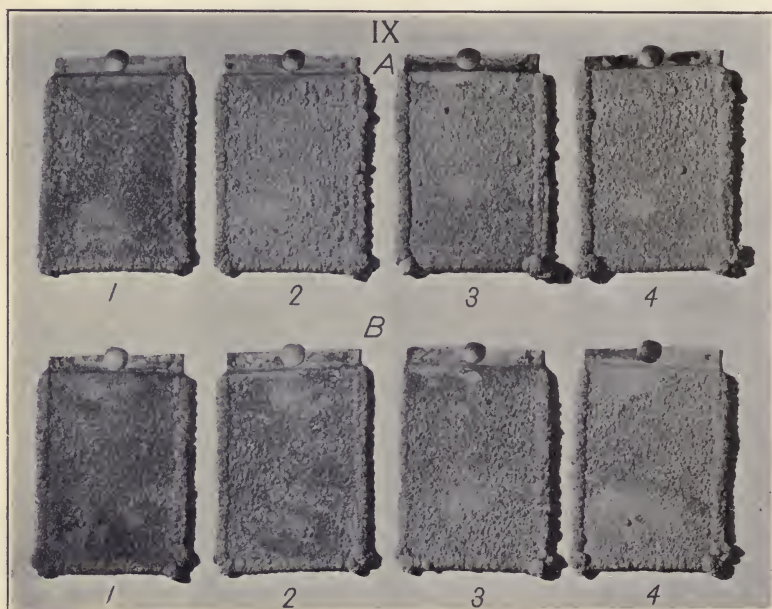
No. of Cells.	Per Cent. of As in Electrolyte.	Addition-Agent.		Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. IX. A.
		$Al_2(SO_4)_3$ % in Al.	$AlCl_3$ % in Al.		% As.	% Sb.	% As.	% Sb.	
1	3.0	0.10	——	0.47	0.0028	0.0003	3.44	0.0061	1
2	6.0	0.10	——	0.47	0.0050	0.0003	6.48	0.0095	2
*3	3.0	——	0.10	0.45	0.0030	0.0004	3.08	0.0081	3
*4	6.0	——	0.10	0.43	0.0087	0.0004	5.92	0.0041	4

* The bad copper first deposited was filed off before the samples were taken for analysis.

It should be mentioned here that at the beginning of the electrolysis, a peculiar effect was observed in the case in which aluminium chloride was used. A white layer, which appeared to be oxide of arsenic formed on the cathode surface, as soon as electrolysis began, and in the course of a few hours became dark-red. During the formation of this layer the potential difference was

high, reading from 0.58 to 0.60 volt. After a period of fifteen hours the deposited copper, however, began to improve, giving a bright surface. This action of aluminium chloride is difficult to explain at present, unless it precipitated arsenic from solution at the first period of the run. A satisfactory explanation may be had with further investigations. But, suffice it to say that the strange effect might be due to the presence of an excessive amount of aluminium chloride in the electrolyte ; these electrolytes, at the end of the run, contained less arsenic than those to which aluminium sulphate was added.

The two deposits from electrolytes containing aluminium chlo-

ride were found each to consist of two layers. The layer first deposited was bad, brittle and incoherent, while the other layer, on the contrary, was bright, smooth, and quite coherent. The analytical results of no. 3 and no. 4, Table IX. A, show that both of these layers were low in arsenic and antimony. The character of these two deposits are shown in Photograph IX. A, marked 3 and 4.

With aluminium sulphate in the electrolytes no such action as

that of aluminium chloride was observed.   The presence of alumi-nium sulphate rendered the deposited copper bright, solid and coherent, and prevented the deposition of arsenic and antimony, as is clearly shown in Table IX. A, no. 1 and no. 2.   The deposits also possessed great ductility, which the test-strips indicated, when they were hammered double.

Experiment IX. B.

With a view to determining the relative effect of a larger or a smaller amount of sodium chloride upon copper deposits, this experiment was performed with electrolytes of the same compo-sition as was used in Experiment IX. A, but with the addition of two different amounts of sodium chloride.   In the one case the amount of salt added was such that the electrolyte contained 0.05 per cent. Cl, and in the other case the electrolyte was made to contain twice as much, that is to say, 0.10 per cent. Cl.

The deposits from both cases were similar in character, but those from electrolytes containing less sodium chloride appeared to be little better, particularly in color.   All the deposits were bright, solid, smooth and free of nodules, but they, as compared with those obtained from electrolytes which contained only 0.01 per cent. Cl (Experiment V.) seemed to be a little inferior in physical properties, that is, less bright, less smooth and less ductile.

The result of bending test showed that the deposits from elec-trolytes containing 0.05 per cent. Cl were more ductile than those

TABLE IX. B.

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$ and 10 per cent. H_2SO_4. Temperature of Electrolyte 50° C. Anode contained 0.97 per cent. As and 0.89 per cent. Sb.

No. of Cells.	Per Cent. of As in Electrolyte.	Addition-Agent NaCl.		Average E.M.F. in Volt.	Impurities in De-posited Copper.		Impurities in Elect. after Run.		Photo. IX. B.
		% in Cl.	——		% As.	% Sb.	% As.	% Sb.	
1	3.0	0.10	——	0.43	0.0022	0.0004	3.50	0.0078	1
2	6.0	0.10	——	0.42	0.0048	0.0007	6.48	0.0064	2
3	3.0	0.05	——	0.41	0.0020	0.0008	3.41	0.0223	3
4	6.0	0.05	——	0.41	0.0018	0.0003	6.41	0.0190	4

which formed in electrolytes containing 0.10 per cent., as the test-strips of the latter cracked almost in two, while those of the former did not crack, when they were hammered double.

The purity of the deposits was in all cases high, but was not so high as those from electrolytes which contained 0.01 per cent. Cl as sodium chloride, when the electrolysis was conducted under similar conditions. The results of this experiment are expressed in Table IX. B, and the character of the deposits are shown in Photograph IX. B.

From the results of this experiment and those of Experiment V., series B, it will be seen that the presence of a greater amount of sodium chloride in the electrolyte proved to be less beneficial on the deposited copper. Therefore, when sodium chloride is used to improve the character of the deposits and to prevent the deposition of arsenic and antimony, the amount added to the electrolyte seems to be better limited to not more than 0.01 per cent. Cl.

ELECTROLYTES WHICH CONTAINED ORGANIC "ADDITION-AGENTS."

In this series of experiments, the organic "addition-agents" tried were gelatine, tannin and peptone (E. & A. from meat) and the electrolyses were conducted with electrolytes of the following composition:

(*a*) Electrolyte containing 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4 plus 3 per cent. arsenic and 0.01 per cent. organic addition-agent.

(*b*) Electrolyte containing 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4 plus 6 per cent. arsenic and 0.01 per cent. organic addition-agent.

(*c*) Electrolyte containing 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4 plus 3 per cent. arsenic and 0.02 per cent. organic addition-agent.

(*d*) Electrolyte containing 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4 plus 6 per cent. arsenic and 0.02 per cent. organic addition-agent.

The gelatine and tannin were each prepared by dissolving 5 grams in a small quantity of boiling water. The solution was then diluted to 200 c.c. which contained 2.5 per cent. of the reagent. The solution of peptone was prepared in the same way,

but dissolved in a larger quantity of water (about 350 c.c.) and diluted to 400 c.c, for peptone is not so soluble as the other two organic substances.   The solution contained 1.25 per cent. peptone.

Experiment X.

In this experiment gelatine and tannin were used as "addition-agents," and the amount added in each case was such that the electrolytes contained one part, by weight, of the "addition-agent" to 10,000 parts of electrolyte, and one part to 5,000 parts, that is to say, the electrolytes contained 0.01 per cent. and 0.02 per cent. of the organic "addition-agent."

With the presence of gelatine in the electrolyte it was observed that during the first few hours of electrolysis the gelatine had strange effect upon the deposited copper, as small "trees" which are shown in C, Photograph X., were formed in every case all over the cathode surface and particularly at the edges.   With the higher proportion of gelatine in the electrolytes, the more and larger the "trees," some of which grew as long as half an inch at the end of fifteen hours' electrolysis.   At this period the cathodes were withdrawn and the "trees" knocked off.   The cathodes were again placed in the original position, but with the reverse sides front, in order to ascertain whether the gelatine had the same effect after fifteen hours' electrolysis.   It was, however, surprising to find that it behaved entirely differently.   The copper deposited from this time on was observed to be perfectly smooth, and neither "trees" nor nodules were formed on the cathode surface.

Another fact that was also observed during the electrolysis was that the presence of gelatine caused the potential difference much higher, an average of about 0.04 to 0.08 volt, and, as the electrolysis continued, it gradually diminished.

From the two facts mentioned above, it appears that gelatine, as the result of electrolysis, undergoes a chemical change and the product, or products, thus formed, must have produced such a beneficial influence as not only to prevent the formation of "trees" and the deposition of arsenic and antimony, but also to cause the deposited copper to form smooth, and tough.

With tannin in the electrolyte, the copper deposited was observed to be perfectly smooth throughout the run, and after fifteen hours' electrolysis the cathodes were turned reverse side front, in

the same manner as in the case of those in the electrolytes containing gelatine. This was done in order to show whether tannin would produce different effect on the deposited copper after a period of electrolysis. The presence of tannin in the electrolytes did not raise the potential difference to any extent, and it was in every case lower than the electrolytes which contained gelatine.

After forty-two hours' run, the deposited copper formed in electrolytes containing tannin, in each case, was observed to become sprangling and the crystals appeared to have sharp edges, which might be due to the "addition-agent" having been consumed. At this period a further addition of tannin was, therefore, made and the amount added to each cell was the same as originally present. But this addition did not seem to cause any apparent improvement of the deposits.

The results of this experiment are recorded in Table X.

TABLE X.

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$ and 10 per cent. H_2SO_4. Temperature of Electrolyte 50° C. Anode contained 1.06 per cent. As and 1.01 per cent. Sb.

No. of Cells.	Per Cent. of As in Electrolyte.	Addition-Agent.		Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. X.
		% Gelatine.	% Tannin.		% As.	% Sb.	% As.	% Sb.	
Series A.									A
1	3.0	0.01	——	0.48	0.0013	0.0003	3.19	0.0023	1
2	6.0	0.01	——	0.48	0.0018	0.0003	6.11	0.0023	2
3	3.0	0.02	——	0.48	0.0009	0.0003	3.17	0.0019	3
4	6.0	0.02	——	0.50	0.0020	0.0007	5.97	0.0062	4
Series B.									B
1	3.0	——	0.01	0.46	0.0020	0.0002	3.12	0.0023	1
2	6.0	——	0.01	0.45	0.0015	0.0003	6.18	0.0033	2
3	3.0	——	0.02	0.41	0.0012	0.0002	3.25	0.0039	3
4	6.0	——	0.02	0.45	0.0017	0.0002	6.16	0.0042	4

The deposits, series A, which formed in electrolytes containing gelatine were very bright and solid, perfectly smooth and coherent, and composed of very fine grains. They also possessed very high ductility, as the test-strips did not crack nor show even signs of cracking when doubled and hammered flat.

The physical and mechanical properties of the deposits, series B, which formed in the presence of tannin were similar to those of series A, except that the grains of the deposits were coarse and more pronounced. They possessed very high ductility, similar to deposits from electrolytes which contained gelatine. Photograph X. shows the character of the deposits of these two series.

The purity of the deposited copper from both series was, in
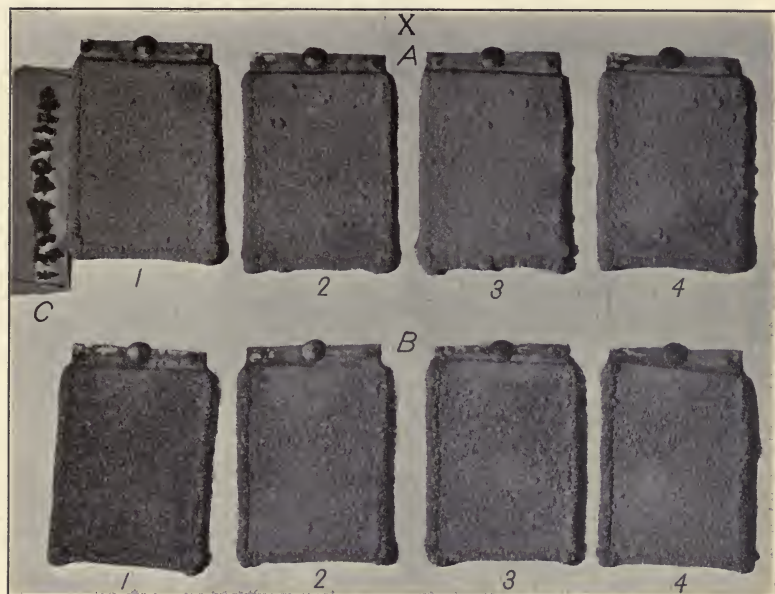
every case, extraordinarily high. The analyses show that they contained, in no case, more than 0.002 per cent. arsenic and 0.0007 per cent. antimony.

From what has been said regarding the physical and chemical properties of the deposits obtained from both series, it will be seen that the presence of gelatine in the electrolytes, though, at start, it caused the formation of small "trees," produced a remarkably beneficial effect upon the deposited copper and that the effect of tannin was very much the same. Both of these organic "addition-agents" rendered the deposits smooth, very ductile, and finely crystalline, and were very effective in preventing the deposition of arsenic and antimony. Of these two

organic substances, tannin seemed to be the more preferable.   No
"trees" formed at the start of the electrolysis.

Experiment XI. A.

Peptone (from meat) was employed in this experiment as
"addition-agent," the amount of which added, at the start, to
the electrolytes was in the same proportion as gelatine and tannin
in the preceding experiment, that is, one part, by weight, of pep-
tone in 10,000 parts, and 5,000 parts of each electrolyte.

It may be stated here that the presence of peptone produced
a strange and bad influence on the deposited copper.   Small
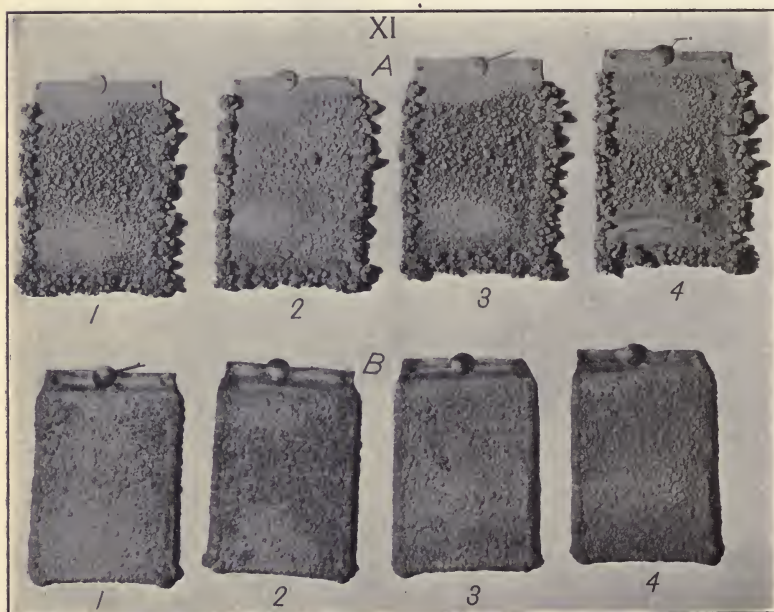
"trees" formed at the beginning of the run, which looked like
those formed at the start in electrolytes containing gelatine, but
more of dull color.   After an interval of fifteen hours from the
beginning of the electrolysis, the cathodes were withdrawn and,
after the "trees" at the edges were knocked off, again placed
in the original position but with the reverse sides front, in order
to ascertain whether the peptone, as in the case of gelatine, would

behave differently.   A further addition of the peptone was made at this time—same amount as originally present in each cell. During the three hours after this addition, the surface of the cathodes seemed to be smooth and spangling, but soon the same kind of "trees" began to appear, continued to grow, and became large and long at the end of the run, as shown in Photograph XI. A.

Another fact that was observed during the electrolyses is that the potential differences between the electrodes in each case dropped greatly, but gradually, and whenever an addition of peptone was made the potential difference was increased from 0.06 to 0.08 volt.   This shows that the drop of voltage was an indication of the consumption of the organic "addition-agent." In order,·then, to maintain a certain amount of peptone present in the electrolytes, it became necessary to add a certain amount at such intervals as the drop of voltage was observed.   Two further additions were made, and the amount added each time to the cells was in the proportion of one part, by weight, of original "addition-agent" to 5,000 parts of electrolyte.

The results of this experiment are recorded in Table XI. A,

TABLE XI. *A.*

Time of Experiment 104 hours.   Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot.   Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4.   Temperature of Electrolyte 50° C. Anode contained 0.96 per cent As and 0.96 per cent. Sb.

No. of Cells.	Per Cent. of As in Electrolyte.	Per Cent. of Peptone in Electrolyte.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. XI. A.
				% As.	% Sb.	% As.	% Sb.	
1	3.0	0.01	0.38	0.0478	0.0035	3.31	0.0026	1
2	6.0	0.01	0.40	0.0521	0.0029	6.10	0.0026	2
3	3.0	0.02	0.39	0.0552	0.0057	3.12	0.0016	3
4	6.0	0.02	0.39	0.0437	0.0025	6.21	0.0032	4

and the character of the deposits are shown in Photograph XI. A.

All the deposits from this experiment were not at all satisfactory: they were exceedingly brittle and their color was dark; they were also composed of coarse crystals loosely adhered and dendritic "trees," easily detached.   The latter interfered with the electrolysis and greatly decreased the resistance of the elec-

trolyte between the electrodes, thus causing the average potential difference to become low, as shown in Table XI. A.

As to the amount of impurities in the deposits, they all ran high, both in arsenic and in antimony, which impaired the physical properties of the deposited copper.

According to the results of this experiment, peptone alone is not at all a satisfactory "addition-agent" and is, therefore, not suitable to use in electrolytic refining. With a cupric sulphate electrolyte it causes not only the injurious impurities to deposit with the copper, but also the copper is deposited as individual crystals and dendrites, which is a very brittle mass.

ELECTROLYTES WHICH CONTAINED ORGANIC AND INORGANIC "ADDITION-AGENTS."

In this series of experiments, the composition of electrolytes was the same as the composition of those which contained an organic "addition-agent," but with the presence of an inorganic "addition-agent."

Experiment XI. B.

In the same way and with the same amounts of peptone added to the electrolytes at the same different intervals of time, this experiment was performed, as Experiment XI. A, but with an amount of sodium chloride added, to give the presence of 0.01 per cent. Cl. The results are given in Table XI. B, and the character of the deposit is shown in Photograph XI. B.

TABLE XI. B.

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4, and 0.01 per cent. Cl as NaCl. Temperature of Electrolyte 50° C. Anode contained 0.96 per cent. As and 0.96 per cent. Sb.

No. of Cells.	Per Cent. of As in Electrolyte.	Per Cent. of Peptone in Electrolyte.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. XI. B.
				% As.	% Sb.	% As.	% Sb.	
1	3.0	0.01	0.48	0.0011	0.0002	3.24	0.0026	1
2	6.0	0.01	0.49	0.0020	0.0001	6.10	0.0022	2
3	3.0	0.02	0.47	0.0008	0.0002	3.36	0.0013	3
4	6.0	0.02	0.49	0.0017	0.0001	6.18	0.0008	4

It is rather surprising to see that the deposits obtained from electrolytes containing the combined "addition-agents" of peptone and sodium chloride were very satisfactory, while those obtained from electrolytes containing peptone alone were, as has been previously mentioned, very rough and impure. A comparison of the deposits shown in Photograph XI. A and XI. B will show the difference in their character. With the sodium chloride and peptone the deposits were very good as regards their physical and chemical properties: they were hard, bright, smooth and finely crystalline. As to their ductility, they were found to be less ductile than those obtained from electrolytes which contained the same amount of sodium chloride alone, as "addition-agent," as the test-strips were broken in two pieces, except no. 3, which cracked almost in two, when they were bent double. The chemical analyses show that their purity was exceptionally high in all cases, and that none of them contained more than 0.002 per cent. arsenic and 0.0002 per cent. antimony.

Thus it is evident that the presence of a small amount of sodium chloride counteracted the bad or injurious effect of peptone, and that the combined action of these two "addition-agents" was beneficial, since it rendered the deposits to become smooth, solid and pure. Moreover, peptone with the presence of sodium chloride seemed to increase the hardness of the deposits, and, as evidence, there may be cited the fact that the copper deposited at the beginning of the electrolysis was so hard that it caused the starting-sheets to bend inward, top and bottom.

Experiment XII.

This experiment was conducted, as usual, in two series, A and B. The combined "addition-agents" for the former series were gelatine and sodium chloride, and those for the latter series were tannin and sodium chloride. The electrolytes for both series were to contain, at the start, the same proportion of organic "addition-agents" as in Experiment X., that is, one part by weight, in 10,000 parts (0.01 per cent.) and one part in 5,000 parts (0.02 per cent.) of electrolyte, and 0.01 per cent. Cl, as sodium chloride. The composition of the electrolytes and the results obtained are recorded in Table XII., and the character of the deposits is shown in Photograph XII.

TABLE XII.

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4, and 0.01 per cent. Cl as NaCl. Temperature of Electrolyte 50° C. Anode contained 1.17 per cent. As and 1.32 per cent. Sb.

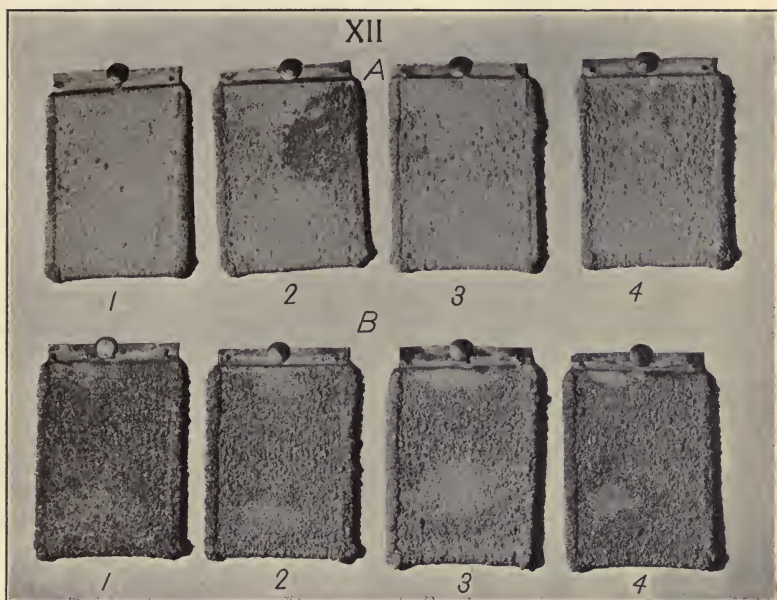| No. of Cells.	Per Cent. of As in Electrolyte.	Addition-Agent.		Average E.M.F. in Volt.	Impurities in Deposited Copper.		Impurities in Elect. after Run.		Photo. XII.
		% Gelatine.	% Tannin.		% As.	% Sb.	% As.	% Sb.	
Series A.									A
1	3.0	0.01	——	0.48	0.0008	0.0002	3.38	0.0054	1
2	6.0	0.01	——	0.47	0.0015	0.0003	6.51	0.0043	2
3	3.0	0.02	——	0.46	0.0007	0.0003	3.32	0.0054	3
4	6.0	0.02	——	0.50	0.0009	0.0003	6.28	0.0023	4
Series B.									B
1	3.0	——	0.01	0.43	0.0014	0.0002	3.91	0.0016	1
2	6.0	——	0.01	0.44	0.0024	0.0002	6.47	0.0013	2
3	3.0	——	0.02	0.44	0.0011	0.0003	3.38	0.0019	3
4	6.0	——	0.02	0.43	0.0026	0.0002	6.49	0.0033	4

The deposits from series A, that is, from electrolytes which contained the combined "addition-agents" of gelatine and sodium chloride, were, in every case, very satisfactory and similar to those obtained from electrolytes containing gelatine alone as "addition-agent." They were very bright, exceedingly solid, perfectly smooth and finely crystalline, and the results of bending tests showed that they possessed high ductility, as the test-strips, when beaten double, did not even show signs of cracking.

Their chemical properties also proved just as satisfactory as their physical properties. The analyses show that the amount of impurities in the deposited copper was, in each case, exceedingly small, running from 0.0007 per cent. to 0.0015 per cent. arsenic, and from 0.0002 per cent. to 0.0003 per cent. antimony, which is far below the required limit for the best commercial copper.

Here the fact, as has been pointed out in Experiment X., may be recalled that small dendritic "trees" were formed at the beginning of the electrolysis, when gelatine was alone present in the electrolytes. But it was found in this experiment, with sodium chloride present, that no such "trees" were formed, and, on the other hand, the copper first deposited was rendered perfectly

smooth. This brings out the fact that the presence of sodium chloride hindered the formation of dendritic "trees," which would have been formed, if the sodium chloride were absent and gelatine alone present in the electrolytes. From this it will be seen that an addition of a small amount of sodium chloride to the electrolytes is quite necessary and important, if gelatine is used to improve the copper deposits.

The potential difference was observed to be high with the pres-

ence of gelatine in the electrolytes: but as electrolysis continued it gradually dropped, as in the previous experiment. After 80 hours' electrolysis, a second addition of the organic "addition-agents" was made in both series, A and B, and the amounts added in both cases were the same as originally present.

The deposits from series B, that is, from electrolytes which contained tannin and sodium chloride, were also satisfactory, but to a slightly less degree than those obtained from the above case, as they consisted of coarse but coherent grains with sharp edges. Their physical properties, however, were similar to those of series B, Experiment X., that is, those from electrolytes which

contained, as "addition-agent," only tannin. With sodium chloride present, their ductility was more or less diminished, for test-strips from all deposits except no. 3, series B, were broken, when they were hammered double.

Though the presence of sodium chloride with tannin in the electrolytes decreased the ductility of the deposits, it did not seem to affect their chemical property to any appreciable extent, as the chemical analyses show that they were all very low in arsenic and antimony. The potential difference was lower than that of series A, and remained practically constant throughout the run.

From what has been said in regard to series B, it will be seen that an addition of sodium chloride does not seem necessary, when tannin is used, for tannin alone appears to improve the physical properties of the deposits more effectively than when sodium chloride is also an associate.

Experiment XIII. A.

In this experiment the combined "addition-agents" used were peptone and hydrochloric acid, and gelatine and hydrochloric acid. The object of using hydrochloric acid was to ascertain the effect of Cl ion in the presence of either of the organic substances mentioned above. The electrolysis was conducted in four cells, two for each of the combined "addition-agents." The electrolytes were, in each case, to contain, at the start, one part, by weight, of the original "addition-agent" in 5,000 parts of the electrolyte (0.02 per cent.) and 0.01 per cent. Cl, as hydrochloric acid, the preparation of which was made in the same manner as in Experiment VI. The composition of the electrolytes and the results obtained are expressed in Table XIII. A. and the character of the deposits is shown in Photograph XIII. A. Deposits no. 1 and no. 2 were obtained from electrolytes containing peptone and hydrochloric, and deposits no. 3 and 4 from electrolytes containing gelatine and hydrochloric acid.

During the electrolysis it was observed that the potential difference in each case was high and about the same as that of Experiment XI. B and Experiment XII., when gelatine and sodium chloride were used. And in the same way, the potential difference gradually dropped, as electrolysis proceeded. This drop of voltage, it is believed, ascertained the consumption of the

TABLE XIII. *A.*

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4$, 10 per cent. H_2SO_4, and 0.01 per cent. Cl as HCl. Temperature of Electrolyte 50° C. Anode contained 1.30 per cent. As and 1.27 per cent. Sb.

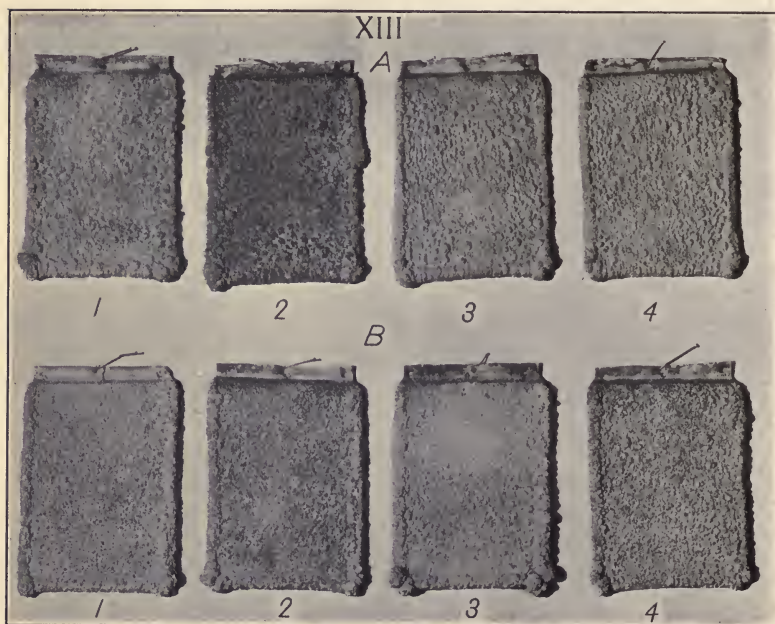| No. of Cells.	Per Cent. of As in Electrolyte.	Per Cent. of Gelatine.	Per Cent. of Peptone.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Photo. XIII. A.
					% As.	% Sb.	
1	3.0	——	0.02	0.52	0.0028	0.0003	1
2	6.0	——	0.02	0.49	0.0030	0.0004	2
3	3.0	0.02	——	0.48	0.0016	0.0003	3
4	6.0	0.02	——	0.49	0.0022	0.0002	4

original substance. Three further additions of the organic "addition-agents" were made in each case during the run, at such intervals as deemed necessary, in order to make up the deficiency.

With peptone and hydrochloric acid in the electrolytes it was observed that the copper first deposited was perfectly smooth and so hard, as in the case where sodium chloride and peptone were present, that the starting-sheets were caused to bend slightly inward, top and bottom. But, in the course of about 15 hours, small rounded nodules began to form, thinly scattered on the surface of the cathodes. As the electrolysis continued, the bright color of the deposits gradually, but slightly, changed, and began to appear more and more dull. Toward the end of the run the surface of both deposits became quite dull. In the case in which gelatine and hydrochloric acid were added to the electrolytes, no such action was observed and, on the contrary, the deposits were brighter and more smooth throughout the electrolysis.

Deposits no. 1 and no. 2, as shown in Photograph XIII. A., that is, deposits from electrolytes which contained as "addition-agents" peptone and hydrochloric acid, were exceedingly hard, coherent, but rough, and of dull color. They were composed of fine grains, but large rounded nodules scattered over their surface. The bending test showed that the ductility of these two deposits was inferior to that of those deposits which were obtained from electrolytes containing peptone and sodium chloride, as the test-strips were broken, when they were slightly bent. The impurities in the deposits were low.

Deposits no. 3 and no. 4, that is, deposits from electrolytes containing gelatine and hydrochloric acid as "addition-agents" were, however, satisfactory; they were bright, and fairly smooth, solid and coherent. The bending test showed their ductility to be very low, about the same as that of no. 1 and no. 2 of this experiment. The purity of the deposits was high, as shown in Table XIII. A.

The results of this experiment show that the combined "addi-

tion-agents" of peptone and hydrochloric acid had a somewhat similar behavior as combined peptone and sodium chloride, but proved less satisfactory and less effective.

The combined "addition-agents" of gelatine and hydrochloric acid were very effective in improving the physical properties of the deposits, and preventing the deposition of the impurities, but were not so effective as the combined gelatine and sodium chloride, which proved the most satisfactory and suitable of all the combined "addition-agents" which were employed in these experiments.

Experiment XIII. B.

In order to see if the addition of sodium salts which consists of an oxidizing acid radical, to the electrolytes would produce any bad effect upon the copper deposit, this experiment was performed with electrolytes containing 1.5 per cent. arsenic, as arsenic acid and the same proportions of cupric sulphate and sulphuric acid as in the previous experiments. The sodium salts tried were sodium chloride, sodium nitrate, sodium chlorate, and sodium borate. The amount of salt added to the electrolyte was such that it contained, in each case, 0.01 per cent. sodium. The results are given in Table XIII. B. and the character of the deposits is shown in Photograph XIII. B.

With sodium chloride in the electrolyte, the deposit was

TABLE XIII. *B.*

Time of Experiment 104 hours. Distance between Electrodes 1.75 inch. Current Density 40 Amp. per square foot. Electrolyte contained 15 per cent. $CuSO_4 \cdot 5H_2O$, 10 per cent. H_2SO_4, and 1.5 per cent. As as H_3AsO_4. Temperature of Electrolyte 50° C. Anode contained 1.30 per cent. As and 1.27 per cent. Sb.

No. of Cells.	Addition-Agents.	Average E.M.F. in Volt.	Impurities in Deposited Copper.		Photo. XIII. B.
			% As.	% Sb.	
1	0.01 per cent. Na as NaCl	0.40	0.0009	0.0002	1
2	0.01 per cent. Na as NaNO₃	0.42	0.0018	0.0002	2
3	0.01 per cent. Na. as NaClO₃	0.41	0.0019	0.0004	3
4	0.01 per cent. Na as Na₂B₄O₇	0.45	0.0010	0.0002	4

lustrous, perfectly smooth, solid and coherent, and was composed of crystals with sharp edges, while the deposits formed from electrolytes containing sodium nitrate, sodium chlorate, or sodium borate were also satisfactory and similar to one another in character. They were bright, solid, smooth, coherent, and finely crystalline, though at the lower corners of deposit no. 3 were formed a few large nodular crystals. As to the ductility of these four deposits, those obtained from electrolytes containing sodium nitrate, sodium chlorate, or sodium borate, were ductile, as the test-strips, when beaten double, did not break. The test-strip of the deposit from the electrolyte containing sodium chloride broke, when it was hammered double, and its fracture appeared

fibrous. The purity of all the deposits was exceptionally high, as may be observed in Table XIII. B.

During the electrolysis, the potential difference in the case of sodium borate was noted to be little higher than that of the rest.

According to the results obtained from this experiment, the sodium salts consisting of an oxidizing acid radical, such as those mentioned above do not appear to exert any injurious influence upon the deposited copper, when present in small amounts. On the other hand, they show themselves to be beneficial "addition-agents," instead of detrimental, as it was found that they improved, to a considerable extent, the chemical as well as the physical properties of the deposited copper.

Conclusions.

The experiments, as performed, may be grouped under four main headings: (1) Impure electrolytes, which contained no "addition-agent." (2) Impure electrolytes, which contained inorganic "addition-agents." (3) Impure electrolytes, which contained organic "addition-agents." (4) Impure electolytes, which contained organic and inorganic "addition-agents."

With electrolytes, which contained no "addition-agent," much arsenic and antimony was deposited with the copper, even when the electrolytes contain 1.5 per cent. arsenic. With electrolytes containing 2 per cent. and 3 per cent. arsenic, a still greater amount of these two impurities were deposited with the copper, and large dendritic "trees" also formed on the surface of the deposits. These impurities rendered the copper dull colored and brittle.

At temperatures between 50° C. and 60° C., and with electrolytes containing over 6 per cent. arsenic, the arsenic acid appeared to act as an "addition-agent," as it prevented, to some extent, the deposition of the impurities (arsenic and antimony) with the copper, and also retarded the formation of dendritic "trees." At temperature of 40° C. and below, however, this action of arsenic as "addition-agent" in the electrolyte did not appear to take place in the electrolyte containing under 6 per cent. arsenic, whereas in the electrolyte containing 8 per cent. arsenic, the deposited copper was purer, brighter, more solid and coherent,

and less brittle. This shows that the good effect of arsenic acid depends not only upon the temperature of the electrolyte, but also upon the amount which is present in the electrolyte. This phenomenon cannot be explained from the data obtained in these experiments, but it may be attributed as the result of hydrolization, which converts the arsenic sulphate $(As_2(SO_4)_3)$ into arsenous acid (H_3AsO_3) and sulphuric acid (H_2SO_4).

Reaction: $As_2(SO_4)$ plus $6H_2O$ $2H_3AsO_3$ plus $3H_2SO_4$
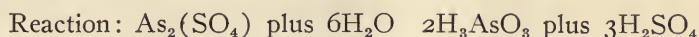
Temperature and the amount of arsenic in solution both appearing in this case to be functions of the reaction. As the arsenic is in the form of an acid radical, it would not be precipitated on the cathode, but would act as a reducing agent in the electrolyte, and, thereby, give results similar to those of the ordinary "addition-agents."

Hydrochloric acid, sodium sulphate, aluminium chloride and sodium chloride, all, when present in small amounts, have a distinct action upon the improvement of the deposited copper, both chemically and physically. They cause the deposits to become more or less smooth, dense, pure and free from "trees." Of these inorganic "addition-agents," the best and most effective is sodium chloride; hydrochloric acid to a slightly less degree. The effect of sodium sulphate is still less; it produces little or no effect if present in too small amounts, especially at temperature of 40° C. and when the electrolyte contains 3 per cent. arsenic. Aluminium chloride, though it improves the copper deposits to some extent, does not seem to be a suitable "addition-agent," while aluminium sulphate is, on the other hand, a satisfactory one; it causing the copper to deposit low in impurities and more ductile.

From the results of the trial of the inorganic "addition-agents" it appears to be true that the salts of those metals, which stand by far higher in the E.M.F. series than copper, are generally satisfactory "addition-agents." They possess the property of preventing, to a considerable extent, the deposition of arsenic and antimony, and the formation of "trees." The latter action of inorganic "addition-agents" is difficult to explain, but, according to Edward F. Kern,[13] it is due to the reducing effect of these metals

[13] *T. Am. El. Chem. S.,* 1909, Vol. 15, p. 473.

(in ionic state). The higher that the metal of the "addition-agent" stands in the E.M.F. series, the purer, smoother, and less brittle the deposit appears.

Temperature plays an important part in the electrolysis of copper. With higher temperature, the ductility of the copper seems to be increased, and the potential between the electrodes decreases. In the case of sodium sulphate as "addition-agent," with higher temperature it becomes more effective.

In the case of organic "addition-agents," both gelatine and tannin produce a remarkably beneficial effect upon the copper deposits and are satisfactory "addition-agents." The presence of gelatine at the beginning of the electrolysis has the effect of causing the formation of small fern-like "trees," but after operating for a period of time the deposits are smooth and ductile. Peptone, unlike gelatine, exerts a detrimental influence on the deposits and, therefore, is an unsatisfactory "addition-agent."

To explain the good and bad action of the organic "addition-agents," mentioned above, is of no easy matter, as their chemical structure, except tannin, is not yet fully and definitely known. It may, however, be of value to cite their properties. Tannin, $C_{12}H_3(OH)_3(COOH)_2$, possesses characteristic acid properties and contains three hydroxyls per molecule. Gelatine, whose chemical structure is not yet fully known, is also essentially acid in character, as it possesses, when pure, an acid reaction and dissociates carbonates.

"Peptone[14] is of two kinds, which differ from each other in one molecule of H_2O. Their chemical composition may be shown as follows: $C_{22}H_{34}N_6O_9$ and $C_{22}H_{36}N_6O_{10}$, the former is called A-peptone and the latter B-peptone. Peptones are pronounced acids, which redden litmus paper and which form salts with carbonates after having expelled the carbonic acid gas; adopting the simplest formula, peptones are monobasic acids, but such a simple formula has to be multiplied."

The deposits of copper obtained from electrolytes containing the combined "addition-agents" are all satisfactory, particularly when the combination of gelatine and sodium chloride is used. The striking effect of the inorganic substances, when present with the organic, is that it counteracts the bad effect of the latter. Of

[14] "Chemistry of Proteids," Mann, p. 188.

the two inorganic compounds (sodium chloride and hydrochloric acid) that were used for the combined "addition-agents," sodium chloride is in every case better, more satisfactory, and more effective in producing good copper. This shows that the better effect is due to the presence of sodium ion in the electrolyte. As evidence, a particular case may be cited, that is, a case in which peptone and sodium chloride, and peptone and hydrochloric acid were used as combined "addition-agents." The copper deposits obtained in the former case were found better, both in physical character and in purity.

In considering what has been said above, the questions may now arise: What causes the organic compounds to behave so differently in the electrolytes when an addition of a small amount of either sodium chloride or hydrochloric acid is made? Does the presence of either of these two inorganic compounds cause the organic ones to undergo a chemical change? These questions cannot be answered without special investigations and are not within the scope of the present research.

With the results that have been obtained, and with the effects of various "addition-agents" that have been tried, this may be said: the combined "addition-agent" of gelatine and sodium chloride, when present in a small amount, proves to be the most suitable and most satisfactory "addition-agent" for copper sulphate electrolytes containing, especially, a high proportion of arsenic, as the deposited copper possesses the greatest ductility and the highest purity.

VITA.

Ching Yu Wen was born on the 16th day of December, 1881, in the city of Canton, Kwangtung Province, China. He studied the English and the Chinese languages in Pei Yang University, Tientsin, and there prepared himself for entrance to the American institutions of learning. In the year 1904, he entered the Massachusetts Institute of Technology, to study metallurgical engineering under Professors Robert H. Richards and Heinrich O. Hofman, and was graduated in 1908. In 1909 the degree of Master of Science was conferred upon him by the same institution. Conjointly with Professor H. O. Hofman, he published an article on the "Heat of Formation of Some Ferro-Calcic Silicates" in the *Transactions of the American Institute of Mining Engineers*, July, 1910. He entered Columbia University in September, 1909, and studied metallurgy in the School of Mines.