

For this theory there is no positive proof ; but it is plain that the hydrogen sulphide must reduce both copper chloride and selenous acid, that copper and selenium may combine in their nascent state, and that sulphur is precipitated, or that copper may combine with previously formed selenium sulphide, and that this also must be accompanied by sulphur precipitation.

The reaction appears one of the most interesting in inorganic chemistry and deserves further investigation.

BALTIMORE COPPER WORKS, July, 1897.

COMPOSITION AND FORMATION OF TANK RESIDUES IN ELECTROLYTIC COPPER REFINERIES.

BY EDWARD KELLER.

Received July 30, 1897.

THE production of electrolytic copper and its separation of other metals by means of the electric current, was first established on a commercial scale by James B. Elkington, of England. In two patents, No. 2,838, Nov. 3, 1865, and No. 3,120, Oct. 27, 1869, he laid down all the essential points of the processes which guide the operations at the present day.

The original object of the process was mainly the separation of the precious metals from the copper. The production of a pure copper from the crude metal is, however, now equally important. The process may be described briefly as follows: The crude copper is cast into anodes of generally six to eight square feet by one to one and one-half inches in thickness. These are suspended in tanks, alternating with thin sheets of pure copper, as cathodes, one to two inches apart. Of the cathodes there is one more in number than of the anodes. In the tanks the electrolyte, in which anodes and cathodes are submerged, is forced to circulate in order to maintain uniform density. This electrolyte is said to be generally a solution of three per cent. copper (as sulphate) with six per cent. of free sulphuric acid.

Each anode is connected with the conductor from the positive pole of the dynamo, each cathode with the negative. If the number of anodes in one tank be n , we have n branches of the electric current from the positive pole, and $n + 1$ from the negative. Anodes and cathodes being otherwise insulated, the current must pass from anode through the electrolyte to cathode,

dissolving the copper of the former and depositing it on the latter. The same current passes through a series of tanks, which may number many hundred.

The system described is called the "multiple." The "series" system is a later invention. It differs from the former, that in each tank there is at one end but one anode connected with the positive pole, and at the opposite end but one cathode with the negative. The space between is filled with rolled copper plates, set vertically, all a certain distance from each other. Electrolyte and circulation are the same as in the other system. When the electric current passes through this system, each surface of the individual plates facing the anode becomes a cathode surface, and that facing the cathode becomes an anode surface, so that the copper dissolved on the anode surface of each plate is deposited on the opposite, or cathode surface of the next plate.

Details of the series system, with illustrations, may be seen in the papers of United States patents No. 377,487, Feb. 7, 1888, and No. 459,838, Sept. 22, 1891, secured by Mr. Edward S. Hayden, of Waterbury, Conn.

The precious metals and part of the impurities of the dissolved anodes, in either system, fall to the bottom of the tanks, forming there a sediment or residue, frequently also called slimes, mud, etc.

It is the object of this paper to show how some of these latter products are composed and to what extent the various impurities in the anode copper take part in their formation.

In the following are given partial analyses (oxygen and hydrate water were not determined) of residues from copper derived from ores from Butte, Mont., as also the composition of the corresponding anode copper. The copper of I was made by the reverberatory, of II by the converter process:

Residues.		I.	Anode copper.
Ag....	53.894 per cent.	= 15718.7 ozs.	100.1 ozs.
Au....	0.2959 " "	= 86.3 "	
Cu....	11.010 " "		
Pb....	0.910 " "		0.0093 per cent.
Bi....	3.930 " "		0.0320 " "
Sb....	6.250 " "		0.0651 " "
As....	2.107 " "		0.0586 " "
Se....	0.394 " "		Se and Te.. 0.0098 " "

	Residues.	Anode copper.
Te	1.174 per cent.	
SO ₄ ..	5.268 " "	
H ₂ O ¹ ..	2.365 " "	

II.

	Residues.	Anode copper.
Ag....	55.150 per cent. = 16085.04 ozs.	100.47 ozs.
Au....	0.198 " " = 57.749 "	
Cu....	13.820 " "	
Pb....	2.070 " "	
Bi	0.340 " "	0.0035 per cent.
Sb	2.440 " "	0.0510 " "
As	1.090 " "	0.0180 " "
Se.....	0.718 " "	
Te	0.892 " "	
Fe	0.800 " "	
SO ₄ ...	10.680 " "	
H ₂ O...	2.604 " "	

The figures in I represent the average of nearly a one year's run ; in II a three months' run in the same refinery.

In the formation of these residues the anodes contribute all their contents in silver, gold, selenium, and tellurium. From any one of these elements we are, therefore, enabled to compute their degree of concentration in the residues, and to figure the amount of partial deposition therein of the other elements.

Since silver constitutes by far the greatest quantity, and consequently its determination being the most accurate, it is best to proceed from it. We then have :

I.

	Residues. Ounces.	Anode copper. Ounces.	Concentration.
Ag	15718.7	100.1	157

II.

	Residues. Ounces.	Anode copper. Ounces.	Concentration.
Ag	16085.05	100.47	160

Dividing the percentages in residues of partially deposited elements by the figures for concentration, we obtain the percentages of the original quantity in the anodes deposited in the residues. The difference between this and the total contents in the anodes is the amount gone into solution in the electrolyte.

¹ The sample was dried at the temperature of boiling water and the remaining water determined at 25° C.

From the latter, practically all the copper dissolved from the anode is deposited on the cathode, carrying with it but a few per cent. of the impurities in solution.

Proceeding according to the above, we obtain the following :

I.

	Contents of anodes. Per cent.	Amount of original contents in anodes gone into residue and solution.	
		In residue. Per cent.	In solution. Per cent.
Cu.....	99.3	0.07	99.93
Bi.....	0.0320	78.22	21.78
Sb.....	0.0651	61.14	38.86
As.....	0.0586	22.90	77.10

II.

	Per cent.	Per cent.	Per cent.
Cu.....	99.4	0.086	99.914
Bi.....	0.0035	60.71	39.29
Sb.....	0.0510	29.90	70.10
As.....	0.0180	37.84	62.16

Lead is not considered in these figures, because lead-lined tanks and lead sulphate, carried by the commercial sulphuric acid employed, render the obtaining of correct results impossible.

There is little similarity between the compositions of I and II. In I the quantities of bismuth, antimony, and arsenic in the anodes are not very widely different. Bismuth shows the least solubility, arsenic the greatest. In II, where antimony greatly preponderates in the anodes, that element also shows the greatest solubility.

The ratio of selenium and tellurium in the two samples of residues may be worthy of notice. We have for I, 1 : 3 ; for II, 7 : 9. The current opinion, that selenium is merely a minor companion-element to tellurium in our western copper, seems thereby proven to be erroneous.

The ratio of the two elements in the anode copper is without doubt the same, and as they have never been separated from copper for quantitative determination individually, it can readily be shown by dividing their percentages in the residues by the figure of concentration what their quantities are in the corresponding anodes. We find :

IN ANODES.

	I. Per cent.	II. Per cent.
Se.....	0.00251	0.00449
Te.....	0.00748	0.00558
Total.....	0.00999	0.01007

The total of the two elements thus calculated, 0.0099 per cent., for I, corresponds closely with the actual amount, 0.0098 per cent., found in the anodes. For II no direct determination was made in the anodes.

BALTIMORE COPPER WORKS, July, 1897.

SOME PRODUCTS OF THE TUBERCULOSIS BACILLUS.

BY E. A. DE SCHWEINITZ AND MARION DORSET.

Received June 17, 1897.

TUBERCULIN, as is well known, is the extract of the tuberculosis bacilli, including the media upon which they are grown. From specially prepared artificial cultures of the tuberculosis germ, Kühne and independently one of us,¹ obtained a substance corresponding to a nucleo-albumin, which appears to be the fever-producing principle of the germ. However, many conditions in tuberculosis were not accounted for by this substance, and as Mafucci, Prudden and Hodenpeyl, Vissman, and others, had succeeded in producing tubercular nodules without necrosis by the intravenous injection of dead bacilli, it seemed as though it should be possible to isolate either from cultures or from bodies of the germs themselves, some substance which might be considered accountable for the coagulation necrosis of tissue which takes place, a necrosis which appears necessary for the progress of the disease. This problem was undertaken by my assistant, Dr. Dorset, and myself more than two years ago. After many fruitless attempts we succeeded in isolating from artificial cultures a crystalline substance, having a melting-point of 161°-164° C., readily soluble in ether, alcohol, and water, which separated from these solutions in needle-like or prismatic crystals, showing a slight yellow tint. They did not give the biuret reaction. The solution of this substance has an acid reaction to litmus, is acid in taste, and is optically inactive. The crystals give no precipitate with silver nitrate, platinic chloride, or barium hydroxide. The analy-

¹ DE SCHWEINITZ: Bulletin No. 7. Bureau of Animal Industry.