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A QUALITATIVE EVALUATION OF SEVERAL ELECTROLYTES FOR ELECTROREFINING BISMUTH

BY P. M. GRUZENSKY AND W. J. CRAWFORD

United States Department of the Interior — January 1956

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by

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CONTENTS

TABLES

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Report of Investigations 5182

941-2

ILLUSTRATIONS

SUMMARY

Several experiments have been carried out in efforts to evaluate qualitatively a variety of electrolytes for refining bismuth. Most extensive work was done with the basic tartrate, hydrochloric acid, and hydrofluosilicic acid electrolytes. Deposits that are smooth and adherent can be obtained from these three electrolytes if low cathode current densities are employed. All three electrolytes were effective in purifying crude bismuth considerably, with additional purification indicated in each instance by a reelectrolysis step.

With the basic tartrate electrolyte best results were obtained when the electrolyte was at 40° C. and contained at least 100 grams of bismuth per liter. An apparent disadvantage was depletion of bismuth from this electrolyte, causing the deposits to become spongy and nonadherent.

The hydrochloric acid electrolyte had the greatest tendency to yield rough, dendritic deposits. Best deposits were obtained at cathode-current densities below 2 amperes per square decimeter. A small amount of glycerin helped to produce a smoother deposit, and adding sulfuric acid or methyl sulfuric acid retarded the deposition of impurities. Very good results were obtained in electrowinning bismuth from a bismuth trichloride-hydrochloric acid electrolyte.

Smooth and adherent deposits were obtained from a hydrofluosilicic acid electrolyte, with very good refining as regards lead and silver impurities; however, higher reagent costs and slow decomposition of the electrolyte have discouraged its use.

INTRODUCTION

Methods of recovering bismuth from ores and byproducts were underdeveloped for many years because of the limited uses for bismuth, the pharmaceutical industry being the chief consumer. In the past decade or so additional uses for bismuth, particularly in the metallurgical field, have brought about increased demand for the metal with the result that bismuth is being recovered from byproducts that were once discarded. In addition to such uses as low-melting alloys, solders, bearings, die setting, etc., some interest has been indicated in bismuth as a possible coolant for nuclear reactors. The advent of ductile bismuth and bismuth-alloy thermocouple wire has contributed greatly to temperature measurement, particularly in the below-zero range.

Virtually no ores in this country are mined primarily for their bismuth content, but bismuth is recovered as a byproduct from such sources as lead refining by the fluosilicate process, manufacture of white lead, tin refining, copper refining, and silver refining. This variety of sources for bismuth-bearing materials places bismuth metallurgy in a unique field, for treatment often depends on history. In view of the variety of source materials selection of a method for refining bismuth would have to consider the impurities present.

941-4

The work reported herein presupposed the starting material to be crude bismuth containing small amounts of lead, silver, antimony, and copper in varying percentages. This work was undertaken in an effort to evaluate some of the electrolytes for refining crude bismuth and to add to the available information pertaining to such processes.

The following key applies to all qualitative spectrographic analyses reported in the tables:

	Percent
A	= Over 10
B	= 5 to 10
C	= 1 to 5
D	= 0.1 to 1
E	= 0.01 to 0.1
F	= 0.001 to 0.01
G	= Less than 0.001
ND	= Not detected.

A plus or minus sign following the letter designation indicates the value to be near the upper or lower limit of the range, respectively. Only the analyses of the principal impurities are tabulated, and the bismuth content can be obtained by difference.

To select words for describing the nature of a deposit is difficult and usually a matter of personal opinion; however, an attempt has been made to do so, and remarks pertaining to the nature of the deposits are given in the tables, for what they may be worth.

EXPERIMENTAL PROCEDURE AND DISCUSSION OF RESULTS

Fluoboric Acid Electrolyte

Two experiments with a fluoboric acid electrolyte were carried out, both at a cathode current density of 0.5 ampere per square decimeter and 60° C. The electrolyte was prepared by dissolving 84.8 grams of boric acid in a minimum amount of distilled water and adding to 223 ml. of 50 percent hydrofluoric acid. Addition of 112 grams of bismuth trioxide to the fluoboric acid and dilution to 1 liter resulted in considerable precipitation. The solution was decanted and used as electrolyte. Impure bismuth anodes were used, containing approximately 7 percent lead, 4.5 percent antimony, 0.25 percent silver, and 0.18 percent arsenic. Qualitative spectrographic analyses of the cathode deposits indicated little or no purification. One gram of hydrazine hydrochloride was used as an addition agent in the second experiment, but the deposit in both instances was soft and nonadherent.

Methyl Sulfuric Acid Electrolyte

A solution containing 10 percent free methyl sulfuric acid and 4 percent bismuth as methyl sulfate was reported to be an excellent electrolyte for bismuth refining.[4] Methyl sulfuric acid was prepared by mixing stoichiometric amounts of methyl alcohol and sulfuric acid, with constant stirring and cooling. An attempt was made to prepare the specified electrolyte by adding the stoichiometric amount

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[4] Betts, A. G., Lead Refining by Electrolysis: John Wiley & Sons, New York, N. Y. 1908, p. 89.

941-5

of bismuth trioxide to a quantity of methyl sulfuric acid. This resulted in a voluminous white precipitate that required additional methyl sulfuric acid for dissolution, and so the final electrolyte was 4 percent bismuth as bismuth methyl sulfate and 96 percent free methyl sulfuric acid. Because of the poorly adherent deposit obtained and the difficulties involved in preparing the specified electrolyte further work with this electrolyte was discontinued.

Acetic Acid Electrolyte

In connection with the electrolytic determination of bismuth, Metzger and Beans[5] indicated that the addition of acetic acid to a bismuth nitrate solution prevented formation of peroxide at the anode and that a smooth, compact, and adherent cathode deposit could be obtained if boric acid was present in the electrolyte.

An electrolyte was prepared by dissolving 30 grams of bismuth nitrate in a liter of water containing 25 ml. of 70-percent nitric acid. The solution was made alkaline with sodium hydroxide, and acetic acid was added until the precipitated bismuth oxynitrate just redissolved; then 2 grams of boric acid was added. Electrolysis was carried out in a rectangular glass cell with two impure bismuth anodes, one at either end of the cell, and a copper sheet cathode in the center. The cell was 2-1/2 inches wide, 5 inches long, and 4 inches deep. A cathode current density of 0.5 ampere per square decimeter was used. A dendritic deposit was obtained at the cathode, and a white, crusty oxysalt coated the anode. An increase in the stirring rate of the electrolyte and an increase of the temperature from 30° to 60° C. did not affect the nature of the deposit.

Basic Tartrate Electrolyte

The use of a basic tartrate electrolyte was reported by Kny-Jones[6] in the electrolytic separation and determination of bismuth using a graded cathode potential.

Several preliminary experiments were conducted with such an electrolyte, and when it became apparent that a solid, adherent cathode deposit could be obtained and, furthermore, that at least a degree of electrolytic refining could be expected, a program was outlined to evaluate this electrolyte in more detail and to determine the most satisfactory conditions for operation. Experiments were undertaken to study the purity and nature of cathode deposits as a function of cathode current density, temperature, electrolyte composition, and anode composition. Data pertaining to these experiments are shown in table 6.

All experiments were carried out in rectangular glass cells. The first 16 runs employed a cell 4 inches wide, 7 inches long, and 4 inches high. The remainder of the runs employed cells that were 2-1/2 inches wide, 5 inches long, and 4 inches high. For experiments above room temperature, the cells were placed in a water bath, the temperature of which was regulated to ±2° C. Figure 1 is a photograph of the equipment used for most of the experiments reported. Bismuth anodes were cast in a rectangular, stainless-steel mold and varied in thickness up to one-half inch. Two anodes were placed at either end of the cell with a copper cathode in the center, spacing between electrodes being approximately 2 inches. A stirrer

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[5] Metzger, F. J., and Beans, H. T., The Electrolytic Determination of Bismuth: Jour. Am. Chem. Soc., vol. 30, 1908, p. 589.

[6] Kny-Jones, F. G., Electrolytic Determination and Separation of Bismuth: Analyst, vol. 66, 1941, p. 101.

941-6

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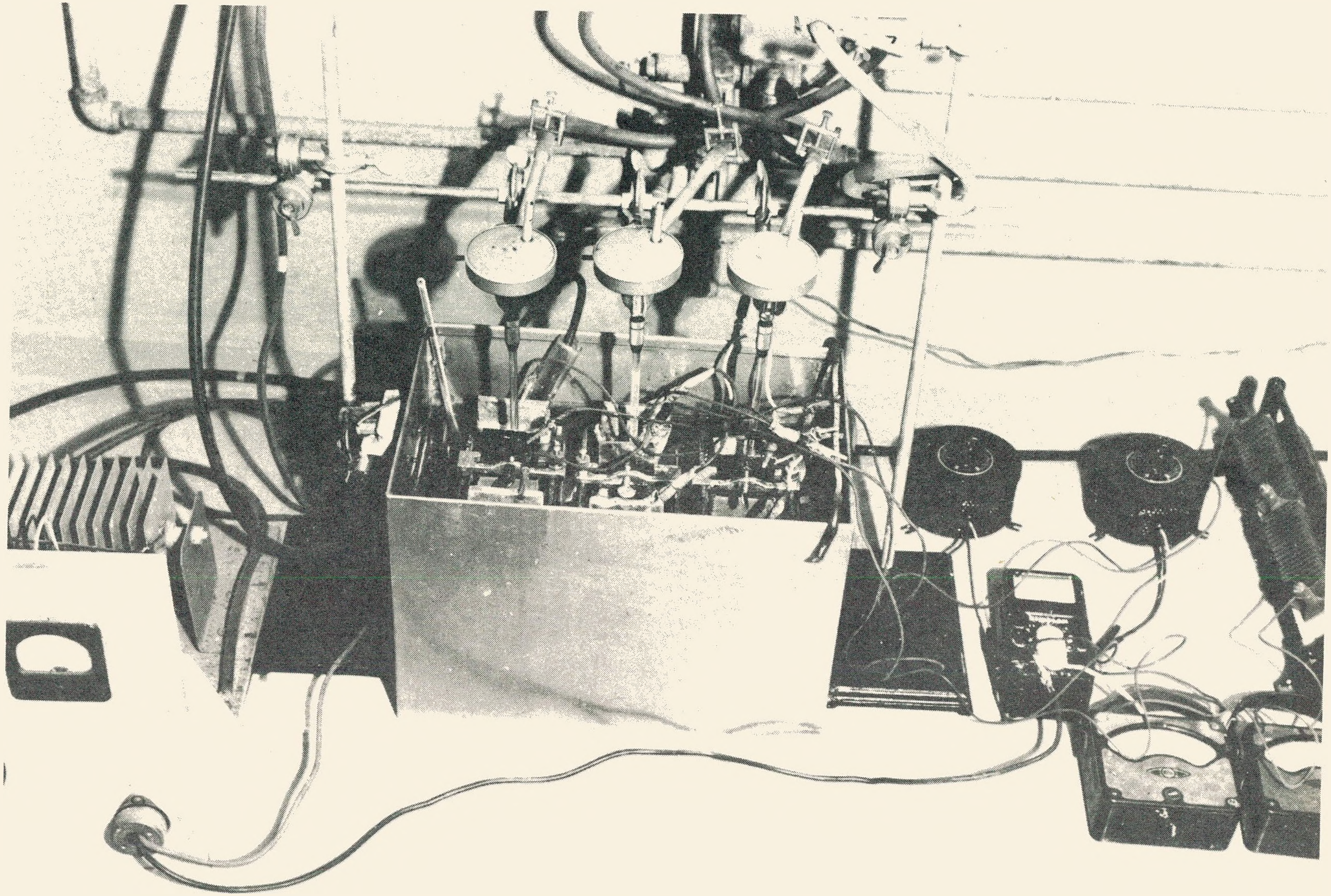

Figure 1. - Apparatus used for basic tartrate and hydrochloric acid experiments.

was used in each cell to circulate the electrolyte. Direct current was supplied by a selenium rectifier and controlled by a variable resistor in series with each cell. No attempt was made to determine current efficiency precisely, the primary objective being to develop conditions of operation that would yield a smooth, adherent deposit of greater purity than the anode material.

The electrolyte was prepared by dissolving a given quantity of bismuth trichloride or bismuth trioxide in enough hydrochloric acid to prevent hydrolysis, adding tartaric acid and finally sodium hydroxide. The tartaric acid and sodium hydroxide were dissolved in water before the additions were made. When the sodium hydroxide was added, a white precipitate formed, which redissolved as more sodium hydroxide was added. This procedure was adopted when it was discovered that reversing the order of addition of tartaric acid and sodium hydroxide produced a considerable quantity of insoluble material in the electrolyte. In some cases there was a slight darkening of the electrolyte, possibly indicating formation of colloidal bismuth.

Cathode current densities were investigated in the range of 0.25 to 2.0 amperes per square decimeter, most satisfactory results being obtained at the lower values. The effect of current density is illustrated by deposits 1 through 4, as shown in figure 2. The deposits as shown were made at room temperature and at 0.25, 0.5, 1.0, and 2.0 amperes per square decimeter of cathode area, respectively.

Results indicate that the variables investigated are interrelated, at least to a degree, particularly current density and temperature. The best deposits were obtained at a cathode current density of 0.25 ampere per square decimeter and room temperature, or at 0.5 ampere per square decimeter and 40° C. Higher temperatures indicated little or no advantage; in fact, additional problems were introduced, such as evaporation losses and cell failures, especially when the cells were left unattended overnight.

Concentration of bismuth in the electrolyte appeared to have an appreciable effect on the nature of the deposit. Plans to investigate the effect of electrolyte composition took on new meaning when the electrolyte during experiment 11 inadvertently evaporated to approximately half of the original volume, thus increasing the concentration, whereupon the deposit became smooth, shiny, and adherent. As indicated in the table, the smoothest and most adherent deposits were obtained with electrolytes containing 100 grams of bismuth per liter.

Anodes for some of the experiments were made by melting anode slimes obtained from lead refining at the Consolidated Mining & Smelting Co., Trail, British Columbia. This material was approximately 98 percent bismuth, and the chief impurities by qualitative spectrographic analysis were as follows: Lead, 1-2 percent; aluminum, iron, silicon, and zinc, all 0.1-1 percent; antimony, copper, and silver, all 0.001-0.01 percent. Anodes for some experiments were synthetically compounded and contained up to 10 percent lead, 1 or 2 percent antimony, less than 1 percent silver, and other impurities, such as copper and silicon, in trace amounts. The general trend of the analyses indicates that in nearly all of the experiments there is a notable reduction in percentage of the chief impurities as bismuth is transferred from the anode to the cathode deposit.

Commencing with experiment 41, the use of Dynel filter-cloth anode bags aided in retaining the anode mud and prevented it from being circulated throughout the electrolyte.

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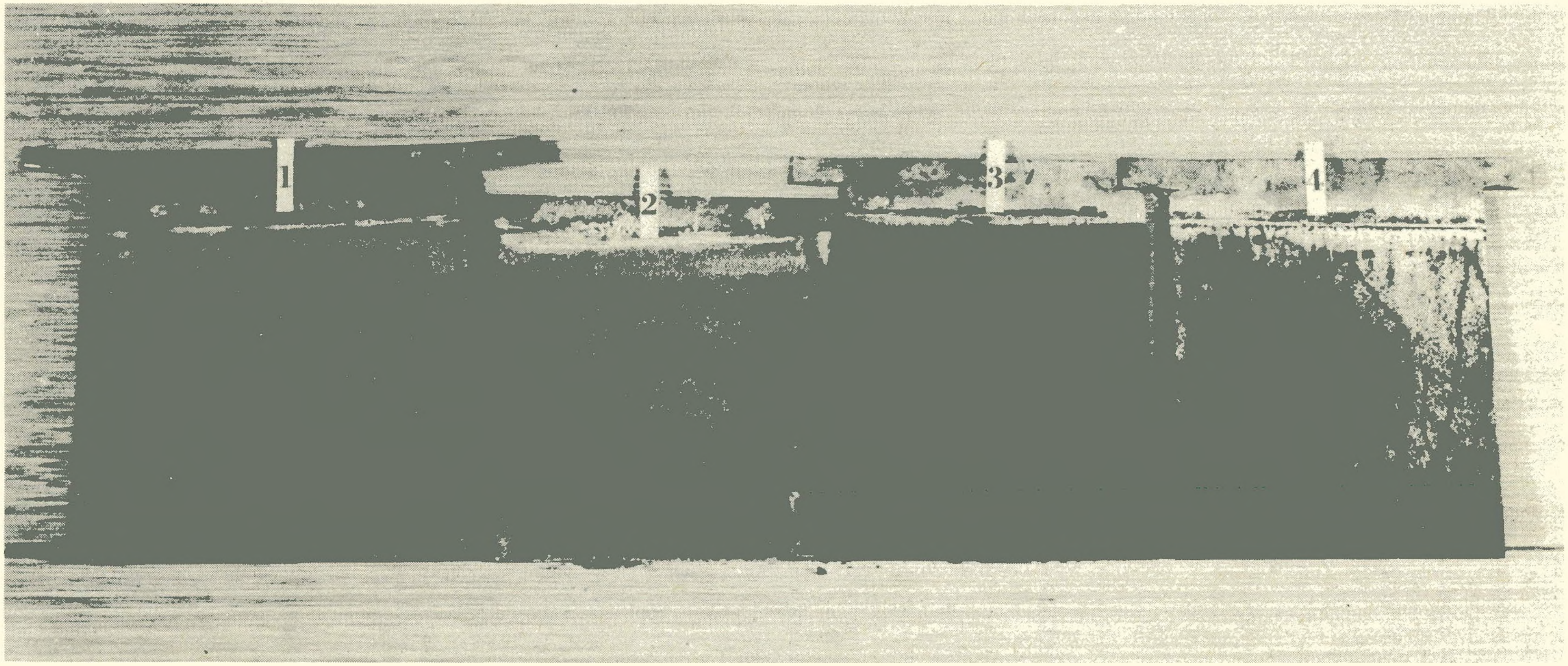

Figure 2. - Deposits obtained from basic tartrate electrolyte at cathode current densities of 0.25, 0.5, 1.0, and 2.0 amperes per square decimeter respectively.

It is interesting to note the qualitative spectrographic analyses of the anode mud obtained from the electrolytic runs starting with run 43. No analyses were obtained on the mud before this run. A definite concentration of impurities appears there, as indicated in table 1.

TABLE 1. - Qualitative spectrographic analyses of anode mud, basic tartrate electrolyte[1/]

Experiment No.	Silver	Bismuth	Copper	Lead	Antimony	Silicon
43	A	A	A	A	A	D+
44	A	A	A	A	A	D
45	A	A	A	A	A	E+
46	A	A	A	A	B	C
47	A	A	B	A	C	D
48	D	A	D	B	D	E
49	A	A	C	A	C	E+
50	A	A	C	A	C	E
51	A	A	C	A	C	E
52	B	A	C	A	C	E
53	D+	A	D	B	D	E
54	D+	A	D	B	D	E
55	C	A	C	A	C	E+
56	C	A	D	A	C	E+
57	C	A	D	A	C	E+
58	D-	A	E+	A	D-	E
59	D-	A	E+	A	D-	E
60	D-	A	E+	A	D-	E
61	D-	A	D-	C+	C	E
62		A	G	C		E
63		A	G	C		E
64		A	G	C		E
65	D	A	D	C	C	E
66	D	A	D	B	D	E
67	D	A	D	B	D	E
68	F	A	E	D		E
69	D	A	D	B	D	E
70	E	A	E	C		E

[1/] See key on p. 2.

In an effort to gain additional information regarding the disposition of lead ions that may enter the electrolyte by lead dissolving anodically, experiments 62, 63, and 64 were carried out using pure bismuth anodes and electrolytes to which lead ions were added as lead chloride in amounts of 0.67, 1.35, and 2.69 grams of lead chloride per liter for the respective experiments. The maximum solubility of lead chloride per liter that could be obtained was 2.69 grams. Upon completion of the runs chemical analyses of the electrolytes indicated only a trace of lead, and qualitative spectrographic analysis of the cathode deposits indicated 0.1 to 1.0 percent lead. In view of these results it appears that, even though there is a degree of electrolyte refining with this electrolyte, some codeposition of lead could always be expected as long as some lead dissolves at the anode. To determine if the deposited metal could be purified further by reelectrolysis, the anodes for experiment 67 were made from several of the previous deposits. To carry this investigation even further, anodes for experiment 68 were made from the deposit obtained in experiment 67. A notable reduction of impurities by these two reelectrolyses was demonstrated.

941-10

As can be noted from the remarks in table 6, several deposits started out smooth, shiny, and adherent but after a time became powdery and nonadherent. In view of the poor deposits obtained when electrolytes were used that contained a relatively low concentration of bismuth, it was postulated that the poor deposits might be caused by depletion of bismuth from solution; in other words, cathode current efficiency was greater than anode current efficiency. A great deal can be learned by comparing the deposits obtained from experiments 55, 56, and 57, which are quite typical and are shown in figure 3. These experiments were carried out at 40° C., employing electrolytes that contained approximately 100 grams of bismuth ion per liter. The duration of each run was 103 hours, and cathode current densities for the respective runs were 0.5, 1.0, and 2.0 amperes per square decimeter. Upon completion of the runs analyses of the electrolytes for bismuth indicated 56.1, 34.5, and 8.7 grams of bismuth ion per liter, respectively. Deposit 55 was definitely metallic in nature. Deposit 56, though solid and adherent, had begun to turn dark and undoubtedly would have become powdery and nonadherent before long if electrolysis had continued. Deposit 57 was solid and adherent for approximately 36 hours, then become powdery and nonadherent.

The use of hydroxylamine hydrochloride and gelatin as addition agents in experiments 69 and 70 proved valueless.

Hydrochloric Acid Electrolyte

As early as 1907 the use of a hydrochloric acid-bismuth trichloride electrolyte for refining bismuth was reported.[7] At that time bismuth of 99.8-percent purity was obtained by the process, the chief impurity being silver. In succeeding years this electrolyte attracted the interests of several investigators, who reported varying degrees of success with its use. In 1945 Arend,[8] in reviewing the developments in bismuth recovery, indicated that electrolytic refining with a hydrochloric acid-bismuth trichloride electrolyte was being practiced in the British Empire and reported some definite advantages over purification by chlorination of impurities commonly found in crude bismuth. The method, as reported by Arend, utilized several improvements over the process as first reported, some of which have not been disclosed. The deposit was reported to be dendritic in nature, and periodically the cells were stopped and the dendrites broken off to prevent short circuiting.

Experimental work with this electrolyte was undertaken to determine the degree of electrolytic purification that could be expected and the conditions that would produce the most satisfactory deposits. Data pertaining to the runs made are shown in table 7.

Apparatus used for these experiments was the same as that described for work with the basic tartrate electrolyte and is shown in figure 1. Anodes for most of the experiments were synthetically compounded. Electrolytes were prepared by dissolving bismuth trichloride or bismuth trioxide in hydrochloric acid and adding other components, as indicated in table 7.

From a comparison of the qualitative spectrographic analyses of the deposits with the analyses of the anode material, it is evident that considerable electrolytic refining can be expected. This is substantiated further by the fact that anode impurities became concentrated in the anode mud, as shown in table 2.

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[7] Mohn, A., Electrolytic Refining of Bismuth: Electrochem. Met. Ind., vol. 5, 1907, p. 314.

[8] Arend, A. G., Developments in Bismuth Recovery: Ind. Chem., vol. 21, 1945, p. 199.

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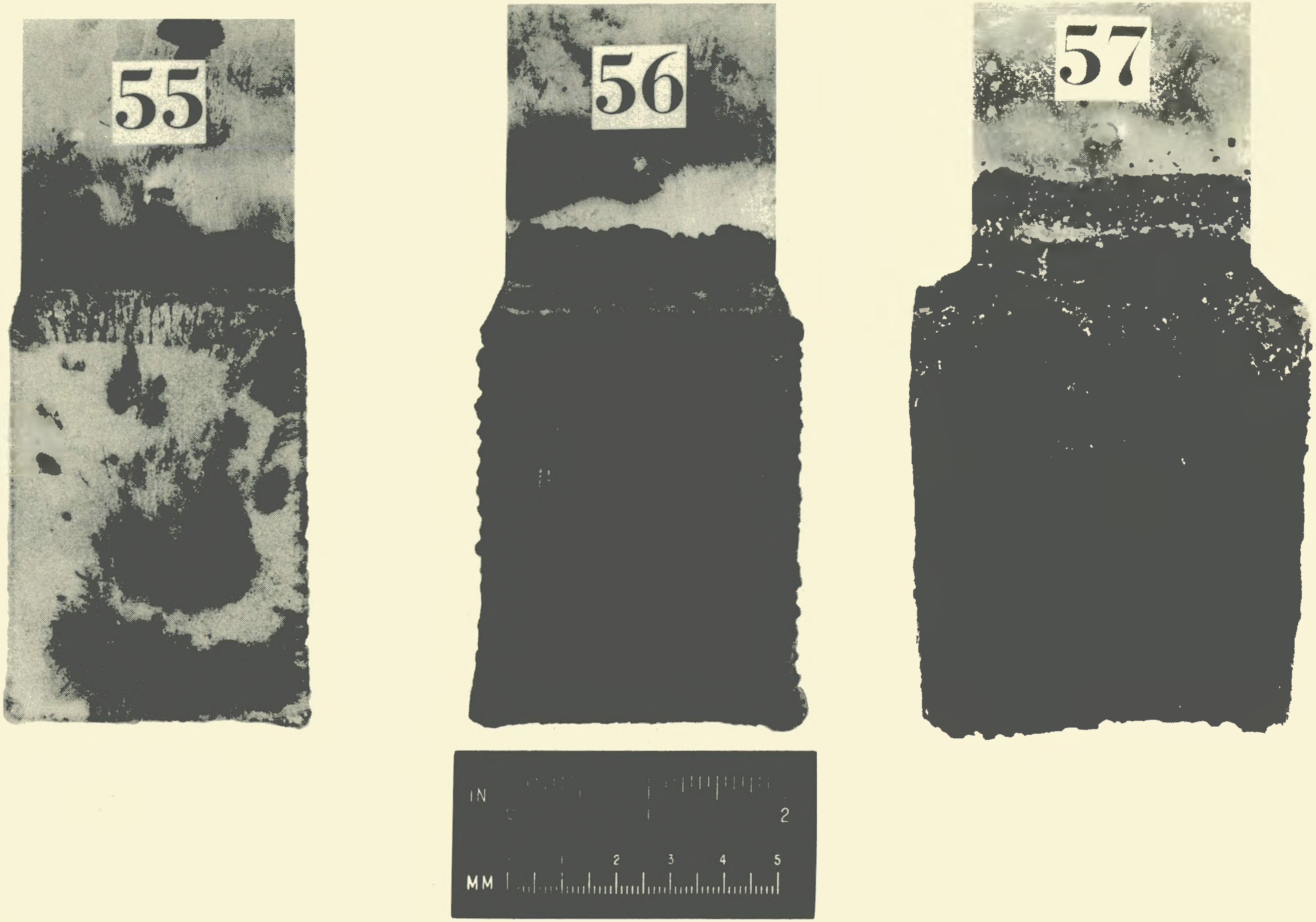

Figure 3. - Deposits obtained from basic tartrate electrolyte indicating correlation between nature of deposit and depletion of bismuth ion from electrolyte.

TABLE 2. - Qualitative spectrographic analyses of anode mud, hydrochloric acid electrolyte[1/]

Experiment No.	Silver	Bismuth	Copper	Lead	Antimony	Silicon
17a	A	A	D+	A	A	E+
18a	A	C	D-	A	C	E-
19a	A	A	C+	A		E-
20a	A	A	A	A	C	E-
21a	A	A	C+	A		E+
22a	A	A	C+	A	A	E
23a	A	A	B	A	A	D+
24a	A	A	C	A	A	E
25a	A	A	C+	A	A	E
26a	A	A	D	A	A	D-
27a	A	A	C	A	A	E
28a	A	A	D	A	C	E
29a	A	A	D+	A	C	E
30a	A	A	D	A	C	E
31a	A	A	D	A	C	E
35a	D-	A-	E	A	E	E
39a	D	C	D-	A	E-	F

[1/] See key on p. 2.

In some of the experiments small amounts of sulfuric acid or methyl sulfuric acid were added to the electrolyte to determine if codeposition of lead could be prevented. Presumably any lead dissolving at the anode should have been precipitated as lead sulfate; however, the results were not entirely satisfactory, for lead was detected in some of the deposits in the range of 0.01 - 0.1 percent.

Inasmuch as the presence of sodium chloride in a hydrochloric acid electrolyte has been reported to aid the production of a bright, metallic deposit,[9/] sodium chloride was added to the electrolytes in the first 10 experiments. No difference in the nature of the deposits was noted when the use of sodium chloride was discontinued. The appearance of sodium in the deposit analyses can undoubtedly be attributed to occlusion of sodium chloride in the deposits.

It should be pointed out that, starting with experiment 24 and following, the sampling technique was changed. The new technique consisted of melting the deposit, using sodium hydroxide as a flux, and then drilling the solidified metal in several places to obtain a representative sample. Before this sampling consisted of scraping portions of the deposit in several places. As a result, any impurities that may have been occluded in the deposit could have appeared in the sample.

Several addition agents were tried in an effort to determine if their presence would produce a smoother deposit. Resorcine, formaldehyde, glue, and various amounts of glycerin and methyl sulfuric acid were tried. Best results were obtained when approximately 5 drops of glycerin was used per liter of electrolyte.

Commencing with experiment 19a and in all experiments following, anode bags made of Dynel filter cloth were used to retain anode mud and prevent its circulation throughout the electrolyte.

[9/] Kern, E. F., and Jones, T. R., Addition Agents in Bismuth Electrolytes: Trans. Am. Electrochem. Soc., vol. 57, 1930, p. 255.

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Experiment 32a was carried out to determine if further purification could be effected by reelectrolysis of deposited metal. Anodes for this experiment were prepared by melting and casting the deposits obtained in experiments 17a, 18a, 20a, 21a, 22a, 23a, 25a, 26a, and 27a. Comparison of the analyses of the anode material and cathode deposit obtained in this run indicated that additional lead was removed from the deposited metal but no more silver or copper was removed.

Experiments 33a and 34a were carried out to determine if electrowinning bismuth from a bismuth trichloride-hydrochloric acid electrolyte would present any problems not encountered in electrorefining. An electrowinning process would have commercial interest if bismuth-containing ores or byproducts were oxidized, thus permitting hydrochloric acid leaching. Graphite anodes were used, and in experiment 34a bismuth trichloride was added to the electrolyte periodically to prevent depletion of bismuth ions. No new difficulties were apparent.

To determine the extent of deposition of impurities as a function of the duration of the run the cathode was withdrawn and a new cathode inserted every 24 hours in experiment 35a. Crude bismuth anodes were used, and the electrolyte contained 150 grams of bismuth trichloride per liter. Table 3 compares qualitative spectrographic analyses of the various deposits obtained from day to day. The deposits are pictured in figure 4; it is evident that for the first and second days the deposits were fairly smooth but after the third or fourth day the deposit was more irregular, with little change in its nature from the fourth to the ninth day. In stripping the deposits from the cathodes it was noted that the ease of stripping decreased from deposit 1 to deposit 9, the smoothest deposit appearing to be under greatest stress.

TABLE 3. - Qualitative spectrographic analyses of deposits obtained in experiment 35a[1]

Deposit No.	Lead	Antimony	Copper	Silver	Silicon
1	D-	F	F	F	E
2	D-	ND	F	F	E
3	E	ND	F	F	E
4	E	ND	F	F	E
5	E	ND	F	F	E
6	E	ND	F	F	E
7	E	ND	F	F	E
8	E	ND	F	F	E
9	E	ND	F	F	F

[1] See key on p. 2.

Experiment 39a, exploratory in nature, was aimed at determining the results of using an anode containing approximately 50 percent lead and 50 percent bismuth. The greatest portion of the deposit was nonadherent and powdery, with a small amount of underlying adherent deposit. Separate analyses of the adherent and nonadherent portions of the deposit indicated that the powdery material was much higher in lead content as well as in some other impurities.

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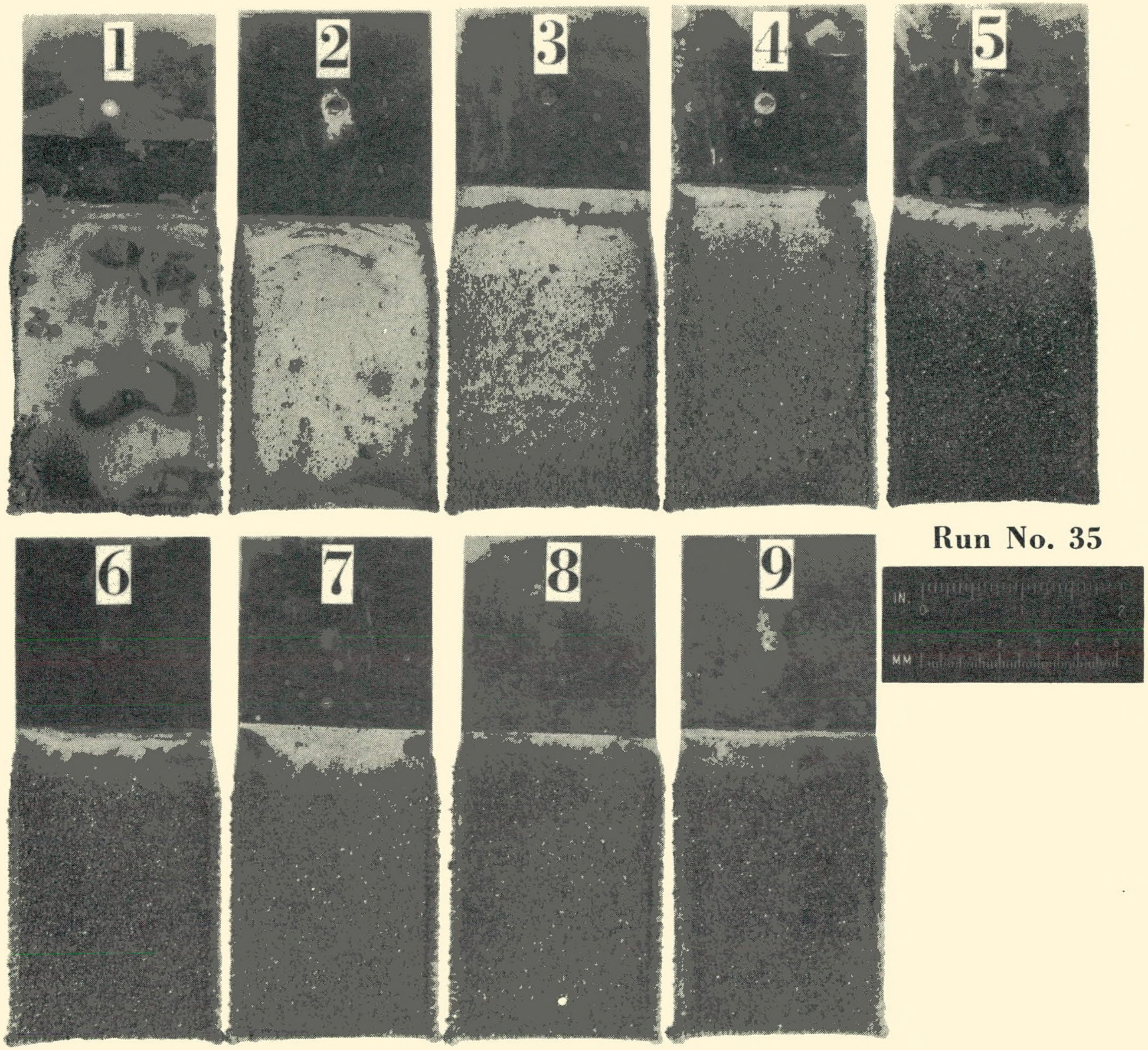

Figure 4. - Change in nature of deposit with duration of electrolysis, hydrochloric acid electrolyte.

Hydrofluosilicic Acid Electrolyte

A hydrofluosilicic acid electrolyte has been used for the electrolytic refining of bismuth on a commercial scale,[10] however, some investigators[11] have attempted to use it on a laboratory scale with little success.

Preliminary experiments with this electrolyte indicated that a more detailed evaluation would be justified. Data pertaining to the experiments made with a hydrofluosilicic acid electrolyte appear in table 8.

All experiments were carried out in rectangular, polyethylene cells 6 inches long, 3-1/2 inches wide, and 4 inches deep. Glass stirrers, which were used to circulate the electrolyte, were coated with plastic to prevent attack on the glass by the electrolyte. As in previous work, 2 anodes were used, 1 at either end of the cell, with a copper sheet cathode in the center. With the exception of experiments 16F and 17F anodes for all experiments were synthetically compounded and were approximately 90 percent bismuth, 9 percent lead, and 1 percent silver.

Electrolytes were prepared by dissolving bismuth trioxide, bismuth nitrate, or bismuth subnitrate in 30-percent hydrofluosilicic acid. In contrast to the work with other electrolytes for which fresh solutions were prepared for every experiment, the hydrofluosilicic acid electrolytes were used repeatedly for several runs. The following electrolytes were prepared and are designated by number in table 8.

1. 150 gm. of Bi_2O_3 per liter of 30 percent H_2SiF_6.
2. 231.8 gm. of $Bi(NO_3)_3.5H_2O$ per liter of 30 percent H_2SiF_6.
3. 145.9 gm. of $BiONO_3.H_2O$ per liter of 30 percent H_2SiF_6.
4. Same as 1.
5. Same as 1.

The electrolytes were rejuvenated by arbitrarily adding a small amount of freshly prepared electrolyte to the original electrolyte before commencing some of the runs. These additions are noted in the table under Electrolyte. Evaporation losses during the course of the experiments were made up with distilled water.

Little or no change was noted in the nature of the deposit when the temperature was increased from 22° to 40° C. Cathode current densities were investigated in the range of 0.5 to 2.5 amperes per square decimeter. As expected, the smoothest deposits were obtained at the lower current densities. Deposit 10-F, shown in figure 5, is typical of deposits that can be obtained from a bismuth trioxide-hydrofluosilicic acid electrolyte.

The accumulation of lead ions in the electrolyte is indicated by the chemical analyses of electrolytes 1 through 4, shown in table 4. No silver was detected in the electrolytes by chemical analysis.

It is interesting to note the qualitative spectrographic analyses of the anode mud from some of the experiments, as shown in table 5. Silver from the anodes accumulated almost entirely in the anode mud, whereas lead predominantly accumulated in the electrolyte.

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[10] Shiga, Kiyoshi, Cottrell Electrical Precipitation Processes in Japan: Eng. and Min. Jour., vol. 128, 1929, p. 86.

[11] Kern, E. F., and Jones, T. R., Addition Agents in Bismuth Electrolytes: Trans. Am. Electrochem. Soc., vol. 57, 1930, p. 255. Harbaugh, M., and Mathers, F. C., The Electrodeposition of Bismuth From Perchloric Acid Solutions: Trans. Electrochem. Soc., vol. 64, 1933, p. 293.

941-16

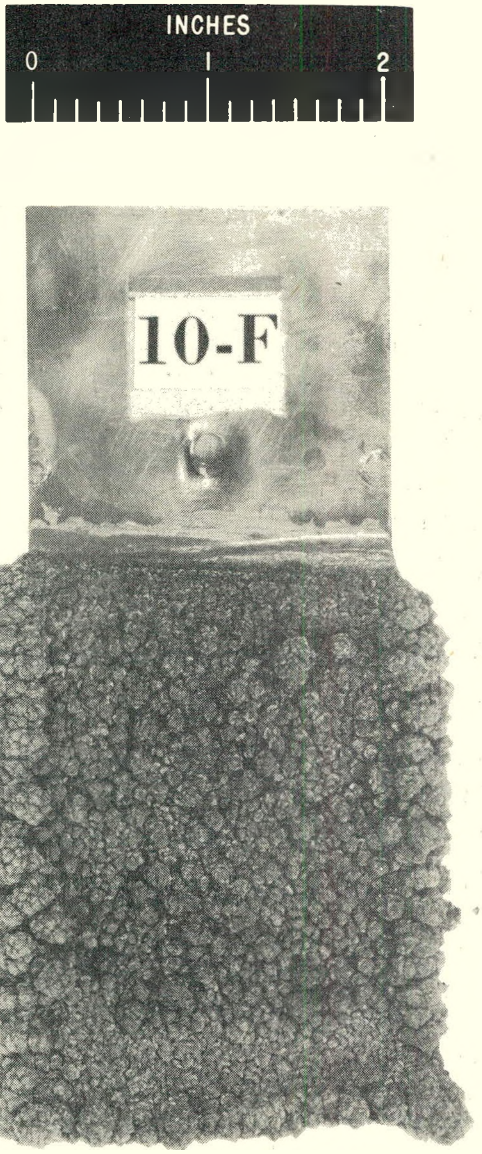

Figure 5. - Typical deposit obtained from bismuth trioxide-hydrofluosilicic acid electrolyte.

TABLE 4. - Chemical analyses of hydrofluosilicic acid electrolytes

Electrolyte No.	Use, hours	Lead per liter of electrolyte, grams
1	1,386	144
2	1,145	199
3	856	117
4	400	29

TABLE 5. - Qualitative spectrographic analyses of anode mud, hydrofluosilicic acid electrolyte[1]

Experiment No.	Silver	Bismuth	Copper	Lead	Antimony	Silicon
1 F	A	A	F	D-	E	
5 F	A	B	E	E	D-	D
6 F	A	A	C	E	D	D
8 F	A	A	E+	D	D	D-
9 F	A	A	E	D	D-	D+
10 F	A	A	D	C	D	D
11 F	A	A	E	C	C	D
12 F	A	A	E	C	E	D-
13 F	A	A	E	D	E	D
14 F	A	A	D	C		E
15 F	A	A	E	C	E	D
16 F	A	A	B	D		A
6 N	A	A	D	C	C	D-
7 N	A	A	C	D	D	D
8 N	A	A	E	D+	D	C-
9 N	A	A	E	C	D	D
10 N	A	A	F	C	E	D
11 N	A	A	D	C	D	C
1 SN	A	A	D	D	D	C-
2 SN	A	A	C	D	D	D
3 SN	A	A	E+	D	D-	D-
4 SN	A	A	E	C		D
5 SN	A	A	E	D	E	D
6 SN	A	A	E	C	D	D

1/ See key on p. 2.

To determine the extent of purification that could be achieved by reelectrolysis of deposited metal anodes for experiment 16 F were made from several previous deposits and contained 0.1 - 1.0 percent lead, 0.01 - 0.1 percent silver, 0.01 - 0.1 percent copper, and 0.001 - 0.01 percent silicon. A new electrolyte, 5, was prepared for this experiment, and, as indicated in table 6, qualitative spectrographic analysis of the deposit detected no lead, less than 0.001 percent silver, and 0.001 - 0.01 percent copper.

Experiment 17 F was exploratory, employing anodes of powdered anode mud obtained from lead refining contained in Dynel filter-cloth anode bags. Graphite rods were placed in the anode bags for connection to the power source. The high cell resistance and poorly adherent deposit obtained precluded any further efforts with such a process.

CONCLUSIONS

Preliminary work with perchloric acid, fluoboric acid, methyl sulfuric acid, and acetic acid as electrolytes offered little or no promise.

In the use of a basic tartrate electrolyte, good deposits were obtained at 40° C. and at cathode current densities below 2.0 amperes per square decimeter, with the lowest current densities producing the best deposits. The bismuth concentration should be at least 100 grams per liter for best results, although some good deposits were obtained with much lower concentrations. Anode current efficiency appears to be lower than cathode current efficiency, thus causing depletion of bismuth ions from the electrolyte. The rate of this depletion is not established and is undoubtedly influenced by other factors, such as current density. It has been shown that impurities present in the anode material become concentrated in the anode mud, smaller amounts being transferred to the cathode deposit. Lead that may be present in the electrolyte is readily deposited at the cathode. Reelectrolysis of deposited metal offers additional purification. Some difficulty may be experienced in preparing a basic tartrate electrolyte if due consideration is not given to the order of addition of reagents. Best results are obtained if bismuth trichloride or bismuth trioxide is dissolved in dilute hydrochloric and then solutions of tartaric acid and sodium hydroxide are added in that order.

The hydrochloric acid-bismuth trichloride electrolyte offers the advantage of lower cost, but smooth deposits are difficult to obtain unless the cathode current density is kept below 2.0 amperes per square decimeter. The use of a small amount of glycerin aids in producing a smoother deposit. Addition of sulfuric acid or methyl sulfuric acid to the electrolyte somewhat retards the deposition of impurities, especially silver and lead, although it does not prevent their deposition entirely. Reelectrolysis of deposited metal indicated further elimination of lead but not of silver or copper. Electrowinning of bismuth from a hydrochloric acid-bismuth trichloride electrolyte gives satisfactory results and would undoubtedly be of interest where bismuth-bearing material that was amenable to hydrochloric acid leaching might be available.

A hydrofluosilicic acid electrolyte is capable of producing satisfactory deposits, along with very good refining with respect to lead and silver impurities; however, there are some definite disadvantages. Hydrofluosilicic acid, even at room temperature, slowly decomposes to hydrogen fluoride and silicon tetrafluoride. Along with the reagent loss in this manner, a health hazard is created, and proper ventilation would be necessary. The high reagent cost has discouraged its consideration for refining purposes, and for large-scale use a method would have to be devised to remove lead that accumulates in the electrolyte. Silver was found to concentrate almost entirely in the anode mud. Reelectrolysis of deposited metal, using a fresh electrolyte, produced a deposit of excellent purity.

941-19

TABLE 6. - Experiments with basic tartrate electrolyte

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.[2]	Electrolyte composition	Qualitative spectrographic analyses[1]		Description of deposit and remarks
					Anode	Cathode deposit	
1	244	22	0.25	12.8 gm. $BiCl_3$, 12 gm. $H_2C_4H_4O_6$, 40.6 gm. NaOH per liter.	Pb=D Cu=E Ag=E Si=F-	Pb=E Cu=E Ag=E Si=F	Evenly formed, fine-grained deposit; light colored and very adherent.
2	65	22	.5	do.	Pb=E Cu=E Ag=E Si=F	Pb=F Cu=E Ag=E Si=F Na=D	Somewhat powdery.
3	2.5	22	1.0	do.	Pb=D Cu=E Ag=E Si=F-	Pb=ND Cu=E Ag=E Si=F Na=D+	Dark, soft, and non-adherent.
4	2.5	22	2.0	do.	Pb=E Cu=E Ag=E Si=F	Pb=ND Cu=E Ag=E Si=F Na=D+	Do.
5	120	40	.25	do.	Pb=D Cu=E Ag=E Si=F	Pb=ND Cu=E- Ag=E- Si=F	Dense and adherent for first 24 hr., then pasty black mud formed on cathode.
6	120	40	.5	do.	Pb=D Cu=E Ag=E Si=F	Pb=ND Cu=E- Ag=E- Si=F	Do.
7	4.6	40	1.0	do.	Pb=D Cu=E Ag=E Si=F	Pb=ND Cu=E- Ag=F Si=E-	Black, powdery, non-adherent.
8	4.6	40	2.0	do.	Pb=D Cu=E Ag=E Si=F	Pb=ND Cu=E- Ag=F Si=F	Do.
9	91	75	.25	do.	Pb=E Cu=F Ag=F Si=F-	Pb=ND Cu=E+ Ag=G Si=E	Soft, nonadherent.

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[1] See key at end of table.

TABLE 6. - Experiments with basic tartrate electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses[1]		Description of deposit and remarks
					Anode	Cathode deposit	
11	32	75	0.5	12.8 gm. $BiCl_3$, 12 gm. $H_2C_4H_4O_6$, 40.6 gm. NaOH per liter.	Pb=E Cu=F Ag=F Si=F-	Pb=ND Cu=E Ag=E Si=E-	Powdery and nonadherent at first; became bright, metallic, and adherent when electrolyte inadvertently evaporated to approximately half of the original volume.
12	20	75	1.0	do.	Pb=E Cu=F Ag=F Si=F-	Pb=F Cu=E Ag=F Si=E Na=C	Bright and adherent at beginning of experiment, but soon turned black and powdery.
14	122	22	.25	25.7 gm. $BiCl_3$, 24 gm. $H_2C_4H_4O_6$, 81 gm. NaOH per liter.	Pb=E Cu=F Ag=F Si=F-	Pb=ND Cu=E Ag=E Si=E-	Adherent, coarsely crystalline.
15	120	40	.5	do.	Pb=E Cu=F Ag=F Si=F-	Pb=F- Cu=E Ag=F Si=F	Fairly bright, adherent, coarsely crystalline.
16	70	40	.5	do.	Pb=A Cu=F Ag=E Si=F Sb=D	Pb=ND Cu=E- Ag=F Si=F Sb=ND	Metallic for 36 hr., then became powdery and nonadherent.
38	298	40	1.0	150 gm. $BiCl_3$, 175 gm. NaOH, 212 gm. $H_2C_4H_4O_6$ per liter.	Pb=C Cu=C Sb=C Ag=D Si=E	Pb=D Cu=E Sb=ND Ag=F Si=F	Dense, adherent, some anode mud occluded in deposit.
40	75	40	1.0	150 gm. $BiCl_3$, 200 gm. NaOH, 212 gm. $H_2C_4H_4O_6$ per liter.	Pb=C Cu=C Sb=C Ag=D Si=E	Pb=B Cu=D Sb=ND Ag=F Si=E	Rough, nodular, and adherent, quite dark. Animal parchment-paper anode bags used, which deteriorated rapidly.

[1] See key at end of table.

TABLE 6. - Experiments with basic tartrate electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses[1/]		Description of deposit and remarks
					Anode	Cathode deposit	
41	161	40	1.0	112 gm. Bi_2O_3, 200 gm. NaOH, 208 gm. $H_2C_4H_4O_6$ per liter.	Pb=C Cu=C Sb=C Ag=D Si=E	Pb=D Cu=D Sb=ND Ag=F Si=E+	Bright, metallic-looking adherent. Deposited in odd, swirly pattern. Starting with this experiment, Dynel filter-cloth anode bags were used and continued with all following experiments in this table.
43	100	22	.5	25 gm. $BiCl_3$, 25 gm. $H_2C_4H_4O_6$, 100 gm. NaOH 50 ml. 37% HCl per liter.	Pb=B Sb=D- Cu=D Ag=D Si=E	Pb=C- Sb=ND Cu=E- Ag=F- Si=F-	Dark, soft, poorly adherent.
44	100	22	1.0	do.	do.	Pb=C- Sb=ND Cu=E- Ag=F- Si=F-	Do.
45	100	22	2.0	do.	do.	Pb=C- Sb=ND Cu=E Ag=F+ Si=F	Do.
46	97	40	.5	do.	do.	Pb=D+ Sb=ND Cu=E Ag=F Si=F	Dense, metallic, and adherent for approximately 48 hr., then soft, dark, and nonadherent.
47	97	40	1.0	do.	do.	Pb=D+ Sb=ND Cu=E Ag=F+ Si=F	Dark and nonadherent.
48	44	40	2.0	do.	do.	Pb=C Sb=ND Cu=E Ag=E Si=F	Do.

1/ See key at end of table.

941-22

TABLE 6. - Experiments with basic tartrate electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses[1]		Description of deposit and remarks
					Anode	Cathode deposit	
49	96	22	0.5	50 gm. $BiCl_3$, 50 gm. $H_2C_4H_4O_6$, 200 gm. NaOH, 100 ml. 37% HCl per liter.	Pb=B Sb=D- Cu=D Ag=D Si=E	Pb=C- Sb=ND Cu=E Ag=F Si=F	Smooth and adherent for first 24 hr., then became dark and nonadherent.
50	96	22	1.0	do.	Pb=B Sb=D- Cu=D Ag=D Si=E	Pb=C- Sb=ND Cu=E Ag=F Si=F	Do.
51	96	22	2.0	do.	Pb=B Sb=D- Cu=D Ag=D Si=E	Pb=C- Sb=ND Cu=E Ag=F+ Si=F	Bright and adherent for first few hours, then became dark and nonadherent.
52	96	40	.5	do.	do.	Pb=C Sb=ND Cu=E Ag=F- Si=E+	Bright, metallic, and adherent for approximately 24 hr., then became dark, crumbly, and nonadherent.
53	96	40	1.0	do.	do.	Pb=C Sb=ND Cu=E Ag=F- Si=E+	Dark and nonadherent.
54	96	40	2.0	do.	do.	Pb=C Sb=ND Cu=E Ag=F- Si=E	Do.
55	103	40	.5	150 gm. $BiCl_3$, 150 gm. $H_2C_4H_4O_6$, 250 gm. NaOH, 100 ml. 37% HCl per liter.	Pb=B Sb=D- Cu=D Ag=D Si=E	Pb=E Sb=ND Cu=E Ag=G Si=E+	Metallic looking, dense, and adherent.
56	103	40	1.0	do.	Pb=B Sb=D- Cu=D Ag=D Si=E	Pb=D Sb=ND Cu=E Ag=G Si=E+	Dull looking, dense, and adherent.

[1] See key at end of table.

941-23

TABLE 6. - Experiments with basic tartrate electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses[1]		Description of deposit and remarks
					Anode	Cathode deposit	
57	103	40	2.0	150 gm. $BiCl_3$, 150 gm. $H_2C_4H_4O_6$, 250 gm. HaOH, 100 ml. 37% HCl per liter.	Pb=B Sb=D- Cu=D Ag=D Si=E	Pb=C Sb=ND Cu=E Ag=G Si=E+	Metallic and adherent for approximately 36 hr., then became soft and spongy.
58	101	22	.5	do.	do.	Pb=D+ Sb=ND Cu=F Ag=ND Si=F	Dull looking, dense, and adherent.
59	101	22	1.0	do.	do.	Pb=C Sb=ND Cu=F Ag=ND Si=F	Coarse, dense, and adherent.
60	101	22	2.0	do.	do.	Pb=C Sb=ND Cu=F Ag=ND Si=F	Coarse, metallic, and adherent for 30 hr. Thereafter, gas bubbles were evolved from cathode, and deposit became dark and spongy.
61	143	22	.5	do.	Pb=D+ Sb=D+ Cu=D Ag=D- Si=E	Pb=D Sb=ND Cu=E Ag=ND Si=F	Dense, smooth, metallic deposit.
62	143	22	.5	150 gm. $BiCl_3$, 100 ml. 37% HCl, 150 gm. $H_2C_4H_4O_6$, 250 gm. NaOH, 0.67 gm. $PbCl_2$ per liter.	Pb=E Cu=G Ag=G Si=E	Pb=D Cu=G Si=F-	Adherent, dull, nodular deposit.
63	143	22	.5	Same as 62 except that 1.35 gm. of $PbCl_2$ added per liter.	do.	Pb=D Cu=G Si=F-	Do.

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[1] See key at end of table.

941-24

TABLE 6. - Experiments with basic tartrate electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses[1/]		Description of deposit and remarks
					Anode	Cathode deposit	
64	143	22	0.5	Same as 62 except that 2.69 gm. $PbCl_2$ added per liter.	Pb=E Cu=G Ag=G Si=E	Pb=D Cu=G Si=F-	Adherent, dull, nodular deposit.
65	323	22	1.0	150 gm. $BiCl_3$, 100 ml. 37% HCl, 150 gm. $H_2C_4H_4O_6$, 250 gm. NaOH per liter.	Pb=D+ Sb=D+ Cu=D Ag=D- Si=E	Pb=C Cu=E Si=F Ag=F	Dense, smooth, metallic deposit for 300 hr.; further deposition resulted in dark, crumbly deposit.
66	100.5	22	1.0	do.	Pb=B Sb=D- Cu=D Ag=D Si=E	Pb=C Sb=ND Cu=E Ag=F Si=F	Dense, adherent, metallic.
67	295	22	1.0	do.	Pb=C Sb=ND Cu=E- Ag=E Si=E	Pb=C- Sb=ND Cu=E Ag=F Si=F	Dense, adherent, metallic at beginning; became dendritic and black, nonadherent.
68	164	22	1.0	112 gm. Bi_2O_3, 200 ml. 37% HCl, 150 gm. $H_2C_4H_4O_6$, 200 gm. NaOH per liter.	Pb=C- Cu=E Ag=F Si=F	Pb=D Cu=F Ag=G Si=G	Do.
69	121	22	1.0	112 gm. Bi_2O_3, 200 ml. 37% HCl, 150 gm. $H_2C_4H_4O_6$, 200 gm. NaOH, 5 gm. $NH_2OH\cdot HCl$ per liter.	Pb=B Sb=D- Cu=D Ag=D Si=E	Pb=C Sb=ND Cu=F Ag=G Si=G	Black, nonadherent, porous, nonmetallic in appearance.
70	121	22	1.0	112 gm. Bi_2O_3, 200 ml. 37% HCl, 150 gm. $H_2C_4H_4O_6$, 200 gm. NaOH, 5 gm. $NH_2OH\cdot HCl$, 2 gm. gelatin per liter.	Pb=D Sb=ND Cu=F Ag=E Si=E	Pb=C Sb=ND Cu=F Ag=G Si=ND	Dark, nonadherent, dendritic. Metal has deposited in nodules.

[1/] Key for qualitative spectrographic analyses

Percent	Percent	Percent	Percent
A = Over 10	C = 1 to 5	E = 0.01 to 0.1	G = Less than 0.001
B = 5 to 10	D = 0.1 to 1	F = 0.001 to 0.01	ND = Not detected.

A plus or minus sign following the letter designation indicates the value to be near the upper or lower limit of the range, respectively.

941-25

TABLE 7. - Experiments with hydrochloric acid electrolyte

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses 1/		Description of deposit and remarks
					Anode	Cathode deposit	
3	1.2	22	1.5	106 gm. $BiCl_3$, 100 gm. NaCl, 50 gm. HCl, 20 gm. H_2SO_4 per liter.	Pb=10% Sb= 5%	Pb=ND Sb=ND Na=D Si=E Cu=E	Dendritic deposit, with underlying smooth deposit.
4	6.5	22	1.0	Same as 3, but 0.1 gm. of resorcine added	do.	Pb=E Sb=D Na=D Cu=E Si=E-	Do.
5	4.7	22	1.0	78.3 gm. Bi_2O_3, 100 gm. NaCl, 50 gm. HCl, 20 gm. H_2SO_4, 2 ml. HCHO per liter.	do.	Pb=F Sb=ND Cu=F- Si=F	Do.
6	4.0	60	1.0	Same as 5, except 1 ml. of glycerin added instead of HCHO as addition agent.	do.	Pb=E Sb=E- Cu=E Si=E- Na=D	Light colored, silvery, and rough.
7	2.0	60	1.0	Same as 6, except 2 ml. glycerin added.	do.	Pb=E Sb=ND Cu=D Sn=D- Na=C	Spongy deposit.
8	3.5	60	1.0	78.3 gm. Bi_2O_3, 100 gm. NaCl, 50 gm. HCl, 20 gm. H_2SO_4, 23 drops of glycerin per liter.	do.	Pb=E Sb=F Cu=E Si=E-	Smooth first hour, then became rough with dendrites.
9	2.6	60	1.0	Same as 8, but no addition agent.	do.	Pb=E- Sb=ND Cu=E Si=E	Some improvement in smoothness over previous deposit.
10	2.7	60	1.0	Same as 8, but 10 drops of glycerin.	do.	Pb=E Sb=E- Cu=E Si=E	Do.

1/ See key at end of table.

941-26

TABLE 7. - Experiments with hydrochloric acid electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses[1]		Description of deposit and remarks
					Anode	Cathode deposit	
11	6.9	60	1.0	Same as 8, but 5 drops of glycerin.	Pb=10% Sb= 5%	Pb=E- Sb=F Cu=E Si=E-	Smoothest deposit obtained thus far.
12	3	60	1.0	Same as 8, but 2 drops of glycerin	do.	Sb=ND Pb=E- Cu=E Si=E- Na=E	Rough, dendritic deposit.
38	55	40	1.0	223 gm. Bi_2O_3, 465 ml. 37% HCl per liter.	Pure bismuth Cu=E Si=F	Pb=ND Sb=ND Si=F Cu=G	Dendritic deposit; cell shorted out.
17a	175	22	.25	150 gm. $BiCl_3$, 233 ml. 37% HCl per liter.	Pb=5% Sb=2% Cu=2% Ag=1%	Pb=ND Sb=C Ag=E Cu=G Si=E-	Coarse, shiny, and adherent.
18a	175	22	.5	do.	do.	Pb=D Sb=D Cu=F Ag=E Si=E-	Do.
19a	42	22	2.0	do.	do.	Pb=E Sb=C Cu=F Ag=F Si=F	Voluminous, black, powdery deposit. The use of Dynel filter-cloth anode bags started with this run and continued throughout following runs.
20a	95	22	1.0	do.	do.	Pb=E Sb=D Cu=F Ag=F Si=F	Coarse, dense, and adherent.
21a	119	40	.25	do.	Pb=B Sb=C Cu=D+ Ag=D Si=E-	Pb=F Sb=E Cu=F Ag=F Si-D-	Dark, but smooth and adherent.

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[1] See key at end of table.

TABLE 7. - Experiments with hydrochloric acid electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses[1]		Description of deposit and remarks
					Anode	Cathode deposit	
22a	167	40	0.5	150 gm. $BiCl_3$, 233 ml. 37% HCl per liter.	Pb=B Sb=C Cu=D+ Ag=D Si=E	Pb=D Sb=D Cu=F Ag=G Si=D-	Dark, rough, and adherent.
23a	91	40	1.0	do.	do.	Pb=C Sb=E Cu=G Ag=E Si=E	Solid, adherent, pronounced dendrite growth at bottom where cathode touched bottom of cell.
24a	91	40	2.0	do.	do.	Pb=D+ Sb=ND Cu=E- Ag=E Si=ND	Adherent, dense, and somewhat dendritic.
25a	42	40	3.0	150 gm. $BiCl_3$, 147 ml. 37% HCl, 20 ml. 98% H_2SO_4, 0.2 gm. glue per liter.	do.	Pb=ND Sb=ND Ag=E Cu=F Si=ND	Very dendritic.
26a	40	40	4.0	Same as 25a, except no glue.	do.	Pb=E Sb=C Ag=E+ Cu=F Si=ND	Do.
27a	19	40	5.0	Same as 25a.	Pb=B+ Sb=C Ag=C Cu=C Si=E	Pb=ND Sb=ND Ag=E Cu=F Si=ND	Do.
28a	3.4	40	10.0	150 gm. $BiCl_3$, 147 ml. 37% HCl, 20 ml. 98 % H_2SO_4, 10 ml. methyl sulfuric acid per liter.	Pb=B+ Sb=C Ag=C Cu=C Si=E	Pb=ND Sb=ND Ag=E Cu=F Si=F	Do.

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[1] See key at end of table.

941-28

TABLE 7. - Experiments with hydrochloric acid electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses[1] Anode	Qualitative spectrographic analyses[1] Cathode deposit	Description of deposit and remarks
29a	2.4	40	10.0	150 gm. $BiCl_3$, 147 ml. 37% HCl, 20 ml. 98% H_2SO_4, 5 ml. methyl sulfuric acid per liter.	Pb=B+ Sb=C Ag=C Cu=C Si=E	Pb=ND Sb=ND Ag=E Cu=F Si=F	Very dendritic.
30a	3	40	10.0	Same as 29a, except 2 ml. of methyl sulfuric acid.	do.	Pb=F Ag=E Sb=ND Cu=F Si=F	Do.
31a	3	40	10.0	Same as 29a, except 1 ml. of methyl sulfuric acid.	do.	Pb=F Sb=ND Ag=E Cu=F Si=F	Do.
32a	114	40	1.0	150 gm. $BiCl_3$, 233 ml. 37% HCl per liter.	Pb=D- Ag=E- Cu=F Sb=ND	Pb=ND Ag=E Cu=F Si=F	Adherent and rough. This was a reelectrolysis run. Anodes were made from deposits of experiments 17a, 18a, 20a, 21a, 22a, 23a, 25a, 26a, 27a.
33a	11	40	1.0	do.	Graphite anode	Pb=ND Cu=F Ag=F Si=F	Adherent deposit. This was an electrowinning run.
34a	112	22	2.0	300 gm. $BiCl_3$, 155 gm. HCl per liter.	Graphite anode	Pb=ND Cu=F- Sb=ND Ag=F Si=F-	Rough and adherent $BiCl_3$ added to electrolyte periodically during course of experiment.
35a	216	40	1.0	150 gm. $BiCl_3$, 200 ml. 37% HCl, 20 ml. 98% H_2SO_4 per liter.	Pb=C+ Sb=D- Cu=E Ag=F Si=F	Pb=E Sb=ND Cu=F Ag=F Si=E (Average)	Cathode changed every 24 hr. for 9 days; see fig. 4.

[1] See key at end of table.

TABLE 7. - Experiments with hydrochloric acid electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte composition	Qualitative spectrographic analyses[1/]		Description of deposit and remarks
					Anode	Cathode deposit	
36a	196	40	1.0	150 gm. $BiCl_3$, 200 ml. 37% HCl, 20 ml. 98% H_2SO_4 per liter.	Pb=C+ Sb=D- Cu=E Ag=F Si=F	Ag=E Pb=ND Cu=F Sb=ND Si=F	Rough and adherent.
37a	116	40	1.0	Same as 35a, plus 5 ml. of methyl sulfuric acid per liter.	do.	Ag=E Pb=ND Sb=F Cu=F Si=E	Do.
39a	145	40	1.0	Same as 35a.	Anode was approximately 50% Pb 50% Bi Ag=D Sb=D- Cu=E Si=F-	Powdery Solid Pb=A Pb=D Sb=D- Sb=D- Ag=D- Ag=E Cu=B Cu=E Si=E Si=F	Mostly powdery and nonadherent, some solid underlying deposit.

1/ Key for qualitative spectrographic analyses

Percent
A = Over 10
B = 5 to 10
C = 1 to 5
D = 0.1 to 1

Percent
E = 0.01 to 0.1
F = 0.001 to 0.01
G = Less than 0.001
ND = Not detected

A plus or minus sign following the letter designation indicates the value to be near the upper or lower limit of the range, respectively.

941-30

TABLE 8. - Experiments with hydrofluosilicic acid electrolyte

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte	Qualitative spectrographic analyses, cathode deposit 1/	Description of deposit and remarks
1 F	360	22	0.5	No. 1	Pb=ND Ag=F Cu=F Si=F	Adherent, dense, and metallic looking.
2 F	24	22	5.0	No. 1	Pb=ND Ag=F Cu=E Si=G	Metallic and adherent, some large dendrites.
3 F	72	22	2.5	No. 1	Pb=F Sb=ND Ag=E Cu=E Si=E	Metallic and adherent, quite dendritic.
4 F	217	22	1.0	No. 1	Pb=F Ag=F Cu=F Si=E Sb=ND	Coarsely crystalline, dense, and adherent.
5 F	120	22	1.5	No. 1	Pb=D- Ag=E- Si=G Cu=F	Dark, coarsely crystalline, dense, and adherent.
6 F	72	22	2.0	No. 1 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.5 gm. of Bi_2O_3.	Pb=D Ag=E- Si=G Cu=E	Dark, dense, adherent, and somewhat dendritic.
7 F	120	22	2.5	No. 1 "rejuvenated" with 75 ml. of 30% H_2SiF_6 containing 11.2 gm. of Bi_2O_3.	Ag=E+ Pb=E+ Cu=E Si=F	Dark, dense, adherent, and somewhat dendritic, with localized powdery, nonadherent spots.
8 F	400	40	.5	No. 4	Pb=ND Ag=F Cu=F Si=F	Dense and adherent, fairly smooth and uniform.

1/ See key at end of table.

941-31

TABLE 8. - Experiments with hydrofluosilicic acid electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte	Qualitative spectrographic analyses, cathode deposit1/	Description of deposit and remarks
9 F	400	40	0.5	No. 1 "rejuvenated" with 125 ml. of 27% H_2SiF_6 containing 18.7 gm. of Bi_2O_3.	Pb=D Cu=D Ag=E Si=F	Solid and adherent at beginning of run, followed by progressive deterioration to nonadherent, black, spongy mass.
10 F	202	40	1.0	No. 4 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.5 gm. of Bi_2O_3.	Pb=D Ag=F Si=F Cu=E	Coarsely crystalline, dense, and adherent.
11 F	202	40	1.0	No. 1 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.5 gm. of Bi_2O_3.	Pb=D Ag=F Cu=F Si=F	Do.
12 F	120	40	1.5	No. 4 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.5 gm. of Bi_2O_3.	Pb=D Ag=F Cu=F Si=F	Do.
13 F	120	40	1.5	No. 1 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.5 gm. of Bi_2O_3.	Pb=D Cu=F Ag=G Si=ND	Black, spongy, poorly adherent.
14 F	100	40	2.0	No. 4 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.5 gm. of Bi_2O_3.	Pb=D Ag=E Cu=F Si=ND	Dark, dense, adherent, somewhat dendritic.
15 F	100	40	2.0	No. 1 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.5 gm. of Bi_2O_3.	Pb=A Ag=D Cu=E Sb=E Si=E	Spongy and totally nonadherent.
16 F	100	40	2.0	No. 5	Pb=ND Ag=G Cu=F Si=ND	Reelectrolysis of previous deposits; somewhat rough, but adherent and metallic.

1/ See key at end of table.

TABLE 8. - Experiments with hydrofluosilicic acid electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte	Qualitative spectrographic analyses, cathode deposit[1]	Description of deposit and remarks
17 F	100	40	2.0	No. 5	Pb=D Ag=G Cu=E Si=ND	Black and spongy, high cell resistance.
1 N	24	22	1.0	No. 2	Ag=D Pb=E Cu=F- Si=E	Mostly dendritic; considerable anodic gas evolution, presumably NO_2.
2 N	24	22	2.5	No. 2	Pb=D- Ag=D+ Sn=D- Si=E- Cu=G	Poorly adherent and dendritic.
3 N	44	22	1.5	No. 2	Pb=E Ag=D Sn=D- Si=E- Cu=G	Very dendritic.
4 N	72	22	2.0	No. 2	Pb=D Ag=D- Cu=G Si=G	Poorly adherent and dendritic; white oxysalt deposited on anode.
5 N	122	22	2.5	No. 2 "rejuvenated" with 100 ml. of 27% H_2SiF_6.	Pb=E Ag=E+ Si=F Cu=F-	Partly adherent, rough and dendritic.
6 N	96	22	2.0	No. 2	Pb=D Ag=E Si=F Cu=E	Do.
7 N	360	22	.5	No. 2	Pb=D Ag=E Cu=F Si=E	Uniform, metallic-looking, and adherent.

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[1] See key at end of table.

TABLE 8. - Experiments with hydrofluosilicic acid electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte	Qualitative spectrographic analyses, cathode deposit 1/	Description of deposit and remarks
8 N	400	40	0.5	No. 2 "rejuvenated" with 125 ml. of 27% H_2SiF_6 containing 28.9 gm. of $Bi(NO_3)_3 \cdot 5H_2O$.	Pb=E Ag=F Cu=F Si=E	Adherent at beginning of run, followed by progressive deterioration to nonadherent, black, spongy mass.
9 N	202	40	1.0	No. 2 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 11.6 gm. of $Bi(NO_3)_3 \cdot 5H_2O$.	Pb=D Ag=E- Cu=G Si=ND	Coarsely crystalline, metallic-looking, some dentrites on edges.
10 N	120	40	1.5	No. 2 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 11.6 gm. of $Bi(NO_3)_3 \cdot 5H_2O$.	Pb=D Ag=D- Cu=G Si=F	Very dendritic.
11 N	100	40	2.0	No. 2 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 11.6 gm. of $Bi(NO_3)_3 \cdot 5H_2O$.	Pb=D Ag=F Cu=F Si=ND	Coarsely crystalline, adherent.
1 SN	96	22	2.0	No. 3	Pb=D Ag=D- Cu=F Si=F	Rough and dendritic, but adherent.
2 SN	360	22	.5	No. 3	Pb=E Ag=F Si=E Cu=F	Uniform, metallic-looking, dense, and adherent.
3 SN	400	40	.5	No. 3 "rejuvenated" with 125 ml. of 27% H_2SiF_6 containing 18.1 gm. of $BiONO_3 \cdot H_2O$.	Pb=D Ag=F Cu=F Si=F	Dark, adherent, dense.

1/ See key at end of table.

941-34

TABLE 8. - Experiments with hydrofluosilicic acid electrolyte (Con.)

Experiment No.	Duration, hours	Temp., ° C.	Cathode current density, amp./dm.^{2}	Electrolyte	Qualitative spectrographic analyses, cathode deposit[1]	Description of deposit and remarks
4 SN	202	40	1.0	No. 3 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.3 gm. of $BiONO_3 \cdot H_2O$.	Pb=D Ag=F Cu=F Si=F	Coarsely crystalline, dense, adherent.
5 SN	120	40	1.5	No. 3 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.3 gm. of $BiONO_3 \cdot H_2O$.	Pb=D Ag=G Cu=F Si=F	Black, poorly adherent.
6 SN	100	40	2.0	No. 3 "rejuvenated" with 50 ml. of 27% H_2SiF_6 containing 7.3 gm. of $BiONO_3 \cdot H_2O$.	Pb=D Ag=G Cu=F Si=ND	Black, powdery, totally non-adherent.

[1] Key for qualitative spectrographic analyses

Percent	Percent
A = Over 10	E = 0.01 to 0.1
B = 5 to 10	F = 0.001 to 0.01
C = 1 to 5	G = Less than 0.001
D = 0.1 to 1	ND = Not detected

A plus or minus sign following the letter designation indicates the value to be near the upper or lower limit of the range, respectively.

941-35