Bureau of Mines
Report of Investigations 5175

EXPERIMENTAL PRODUCTION OF HIGH-PURITY COBALT

BY K. K. KERSHNER, F. W. HOERTEL, AND J. C. STAHL

United States Department of the Interior — January 1956

EXPERIMENTAL PRODUCTION OF HIGH-PURITY COBALT

BY K. K. KERSHNER, F. W. HOERTEL, AND J. C. STAHL

* * * * * * * * * **Report of Investigations 5175**

MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Douglas McKay, Secretary
BUREAU OF MINES
Thos. H. Miller, Deputy Director

Work on manuscript completed May 1955. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is made: "Reprinted from Bureau of Mines Report of Investigations 5175."

January 1956

EXPERIMENTAL PRODUCTION OF HIGH-PURITY COBALT

by

K. K. Kershner,[1] F. W. Hoertel,[1] and J. C. Stahl[1]

CONTENTS

ILLUSTRATIONS

---

[1] Chemist, Bureau of Mines, Rolla, Mo.

SUMMARY

To meet an increasing demand for high-purity cobalt, the Bureau of Mines has conducted investigations for producing this metal. Cobalt having a purity of 99.95 percent or higher is needed to determine heats of formation, corrosion resistances, phase diagrams, and other basic properties of the element and its compounds. This grade of cobalt may be used for preparing radioactive metal.

As a result of its investigations a detailed procedure, which is of practical significance to the production of high-purity cobalt, has been developed by the Bureau for purifying cobalt solutions and for electrolytic deposition of the metal.

Cobalt metal, which had a purity of 99.99 percent with reference to metallic contaminations, was deposited electrolytically. Qualitative spectrographic analysis showed only traces of calcium, copper, iron, magnesium, nickel, and zinc.

Electrolytic cobalt was cast into ingot metal containing smaller proportions of trace impurities but a slight increase in iron.

More than 99 percent of nickel and copper contaminations in pentamine cobalt III chloride solutions was removed by chelation and passage through a column of cation exchange resin. Approximately 85 percent of the total cobalt was eluted from the resin with 10 percent sulfuric acid.

A purer grade of hydrated cobaltic oxide was obtained by pretreating cobalt sulfate solutions with sodium carbonate to remove copper and iron and by pulping the precipitated oxide in hydrochloric acid of pH 3 to remove nickel.

1,2-Cyclohexanedione dioxime was used to precipitate nickel selectively from cobalt sulfate solutions. Only minor amounts of cobalt were coprecipitated. Methods for partial recovery of 1,2-Cyclohexanedione dioxime, which is an expensive reagent, were developed.

Final traces of nickel and cooper were removed from cobalt solutions treated with 1,2-Cyclohexanedione dioxime by electrolysis with graded mercury cathode potential. Electrolytes having gram-per-liter concentrations of 90 to 95 cobalt, 0.001 to 0.002 nickel, 0.001 copper, and 0.001 to 0.002 iron were prepared for use in final deposition of high-purity cobalt plate.

Methods for analyzing purified products are listed.

INTRODUCTION

The Bureau of Mines is conducting research on recovering cobalt and nickel from important reserves of these metals in southeastern Missouri. A process has been developed[2] on a laboratory scale for hydrometallurgical treatment of complex sulfide ore concentrates, and pyrometallurgical investigations have been made[3] on ore concentrates and smelter mattes. One phase of this research deals with the production of high-purity cobalt.

An insistent demand for metals of greater and greater purity has been accentuated by expanding technologies of the past decade. Atomic energy requirements for reactors and controls, supersonic aircraft needs for heat resistance, and transistor demands for electronic devices have added tremendous impetus to the search for means of improving purity.

Cobalt is one of the most important of the strategic metals. Once considered as having little value, it is now recognized along with nickel as one of the most needed metals of the atomic era. Cobalt alloys have been fabricated to withstand the excessive temperatures encountered in jet engines, superchargers, and turbines. Cobalt contributes to the heat-resistant properties required by rockets and guided missiles. As a component of cutting tools it has revolutionized the speed of lathe work. Cobalt has importance in armor plate, cancer "needles," ceramics, electroplating, gun linings, magnets, and projectiles. For many of these uses its degree of purity is becoming an increasingly important factor. The Nation's industrial needs and the requirements for defense are steadily increasing domestic consumption of cobalt, a major portion of which is imported.

Experimental work by the Bureau of Mines at Rolla, Mo., for recovery of cobalt and nickel largely follows hydrometallurgical lines. Such hydrometallurgical processes are becoming increasingly important for production of metals, particularly the recovery of cobalt and nickel. Sherritt Gordon Mines, Ltd., has adopted an ammonia leach-hydrogen reduction process for recovering cobalt and nickel from Lynn Lake sulfide concentrates. Howe Sound Mining Co. near Salt Lake City, Utah, and National Lead Co. at Fredericktown, Mo., have built refineries to produce cobalt, nickel, and other metals by a chemical process developed largely by the Chemical Construction Co. Ore concentrate is leached under pressure with sulfuric acid and air or oxygen and metal powders precipitated from ammoniacal solution by compressed hydrogen reduction. These hydrometallurgical processes eliminate roasting, smelting, and electrolytic and fire refining.

Important reserves of cobalt and nickel minerals occur in lead and copper sulfide ores of southeastern Missouri. It is estimated that the annual production of lead and copper sulfide ores in this region contains approximately 2,000,000 pounds of cobalt and 2,700,000 pounds of nickel. Known plans for future treatment of these ores indicate an annual production of 1,400,000 pounds of cobalt and 1,800,000 pounds of nickel. As the Nation depends largely on importation of cobalt and nickel, improved methods for increased recovery of these metals is very important.

Past Work on Production of Cobalt

Cobalt metal has been produced by different methods and in various degrees of purity since it was first prepared by Brandt[4] about the middle of the 18th century. Owing to a great similarity to nickel in chemical properties, it is difficult to

---

[2] Kenworthy, H., and Kershner, K. K., Metallurgical Investigations of Southeastern Missouri Cobalt-Nickel Resources: Bureau of Mines Rept. of Investigations 4999, 1953, 37 pp.

[3] Work cited in footnote 2 (p. 2).

[4] Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry: Longmans, Green & Co., Ltd., London, vol. 14, 1935, p. 421.

isolate cobalt in a state of high purity. Little cobalt metal was produced until a need for it arose in research on ferrous alloys during the early part of this century.

The Bureau of Mines has been conducting investigations on the various phases of the metallurgy of cobalt since 1940. In the course of this research, metallic cobalt has been obtained. F. K. Shelton[5] electrolyzed chemically pure materials to obtain cobalt having a purity of 98.97 percent with reference to nickel, lead, copper, zinc, and iron contaminations. From cobalt electrolytes obtained by purification of leach liquors he produced electrolytic cobalt with a purity of 98.51 to 99.00 percent with reference to the same contaminating elements. On a somewhat larger scale of production Shelton obtained electrolytic cobalt having a purity of approximately 96 percent. However, emphasis was not directed toward obtaining metal of unusual purity. While operating a small pilot plant on Howe Sound Co. ore concentrates from the Blackbird district, Lemhi County, Idaho, Shelton and coworkers[6][7] electrolyzed purified leach liquors to produce cobalt ranging in purity from 99.21 to 99.83 percent with reference to nickel, iron, and lead contaminants. A decrease in purity was caused mainly by a buildup of nickel in the electrolyte.

Oldach and Landau[8] prepared electrolytic cobalt of 99.85 percent purity with reference to nickel and iron as impurities. A cobalt sulfate electrolyte containing boric acid and sodium chloride was used with a rotating cathode of stainless steel. The anodes were commercial cobalt rondelles in contact with a platinum sheet.

Methods described in this report lead to the electrolytic deposition of cobalt having a purity of 99.99 percent with reference to metallic impurities.

ACKNOWLEDGMENTS

Appreciation is extended to the National Lead Co. and its production manager, H. A Krueger, at Fredericktown, Mo., for supplying concentrates that were used as a source of cobalt for these investigations.

PREPARATION OF HIGH-PURITY COBALT ELECTROLYTES

Hydrated cobaltic oxide was precipitated from chloride leach liquors resulting from extraction of cobalt and nickel[9] from complex sulfide ore concentrate obtained from the operations of the National Lead Co. at Fredericktown, Mo. The oxide was dissolved in sulfuric acid to produce solutions having gram-per-liter concentrations of 15 to 20 cobalt, 0.5 to 1.2 nickel, 0.01 to 0.10 copper, and 0.01 to 0.03 iron.

---

[5] Shelton, F. K., Metallurgical treatment of Cobalt Ores From the Goodsprings Mining District, Nevada: Bureau of Mines Rept. of Investigations 3836, 1946, p. 26.

[6] Shelton, F. K., Stahl, J. C., and Churchward, R. E., Electrowinning of Cobalt From Cobaltite Concentrates: Bureau of Mines Rept. of Investigations 4172, 1948, p. 55.

[7] Shelton, F. K., Churchward, R. E., Stahl, J. C., and Davis, C. W., Electrolytic Cobalt - A Commercially Feasible Process: Trans. Electrochem. Soc. vol. 91, 1947, pp. 115-131.

[8] Oldach, C. S., and Landau, R., Cobalt Electrolytically Refined: Metals and Alloys, vol. 17, 1943, pp. 967-968.

[9] Work cited in footnote 2 (p. 2).

Contaminations were removed from these solutions by applying ion exchange resins, by selective precipitation, and by electrolysis. Analyses of impure and refined solutions were made by standard methods.[10 11 12 13 14]

EXPERIMENTAL PROCEDURES

Ion Exchange Resins

Pentammine cobalt III chloride solutions were prepared[15 16] by treating cobalt chloride solutions with ammonium hydroxide and sodium hydrochloric acid and maintained at this value while ionic contaminations were chelated by adding 9 mg. of tetrasodium ethylenediaminetetraacetate for each milligram of metallic impurity. A typical analysis of these solutions showed a gram-per-liter concentration of 4.49 cobalt, 0.14 nickel, 0.0018 copper, and 0.0006 iron. The chelated solutions were passed through columns of nuclear sulfonic cation exchange resins, Amberlite IR-120, in the hydrogen form. The valence of the cobalt III pentammine ion and its relatively high concentration compared to that of ionic contaminations favored its retention on the resin. After the resin was washed with water, 10 percent sulfuric acid was used for elution. Approximately 85 percent of the total cobalt was recovered with 0.10 to 0.01 percent each of nickel and copper in the original solution. Although this procedure offered considerable promise for removal of impurities, investigations were directed to cobaltous solutions to eliminate preparation of pentammine cobalt III chloride and its subsequent decomposition in order to obtain a cobaltous sulfate electrolyte.

Selective Precipitation

Nickel, copper, and iron were the chief impurities in cobalt solutions originating during extraction of cobalt from complex sulfide ore concentrates of southeastern Missouri.[17] To remove a portion of these contaminations, sodium orthophosphate and sodium carbonate were added to the solutions until slight precipitation occurred. The precipitates, which contained nickel, copper, iron, and minor amounts of cobalt, were separated by filtration. Hydrated cobaltic oxide was precipitated from the filtrates by adding 5 percent sodium hypochlorite; the pH of the solution was maintained at different values within the range of 4.0 to 6.3 by sodium hydroxide. Precipitates obtained under these conditions were pulped twice at 75° C. in

---

[10] Lundell, G., Bright, H., and Hoffman, J., Applied Inorganic Analysis: 2d ed., 1953, pp. 390, 408, 419, 447-448.

[11] Mitchell, A., and Mellon, M., Colorimetric Determination of Nickel With Dimethylglyoxime: Ind. Eng. Chem., anal. ed., vol. 17, 1945, pp. 380-382.

[12] Rollet, A., A New Colorimetric Determination for Nickel: Compt. redn., vol. 183, 1926, p. 212.

[13] Lingane, J., and Kerlinger, H., Polarographic Determination of Nickel and Cobalt With Dimethylglyoxime: Ind. Eng. Chem., anal. ed., vol. 13, 1941, pp. 77-80.

[14] Meites, L., Polarographic Determination of Iron in Nonferrous Alloys: Anal. Chem., vol. 24, 1952, pp. 1374-1376.

[15] Evans, U. R., Metals and Metallic Compounds: Longmans, Green & Co., Ltd., London, vol. 3, 1923, pp. 162-163.

[16] Harkins, W. D., Hall, R. E., and Roberts, W. A., Studies on Cobaltammines: Jour. Am. Chem. Soc. vol. 38, 1916, pp. 2643-2658.

[17] Kenworthy, H., and Kershner, K. K., Metallurgical Investigations of Southeastern Missouri Cobalt-Nickel Resources: Bureau of Mines Rept. of Investigations 4999, 1943, p. 13.

hydrochloric acid maintained at pH 3.0 to dissolve impurities coprecipitated as hydroxides or, in the case of nickel, as the sesquioxide or peroxide.[18] Only slight dissolution of hydrated cobaltic oxide occurred. In some tests the impurities were chelated by using 9 mg. of tetrasodium ethylenediaminetetraacetate for each milligram of contaminant before adding sodium hypochlorite and sodium hydroxide to precipitate hydrated cobaltic oxide. Solutions were prepared for analysis by dissolving hydrated cobaltic oxide prepared under these conditions.

This experimentation revealed that more than 90 percent of copper and iron and 5 to 10 percent each of cobalt and nickel were precipitated by adding normal sodium carbonate solution to pH 6.0 to 6.3. Chelation of contaminations before precipitation of hydrated cobaltic oxide was helpful only in separating copper when this contamination had not been removed by using sodium carbonate. Substantial amounts of nickel were removed by pulping hydrated cobaltic oxide in hydrochloric acid maintained at pH 3.0, but the concentration of this impurity was not lowered to a degree suitable for electrolytic deposition of high-purity cobalt. Wallis and West[19] pulped hydrated cobaltic oxide with sulfuric acid at 70° and pH 1.5 to 2.0 to dissolve nickel and a part of the cobalt. The pulped oxide contained less than 1 percent nickel. However, solutions prepared from this pulped oxide would also be unsuitable for electrolytes because of their nickel content.

To remove more nickel from cobalt solutions and to eliminate precipitation and pulping of hydrated cobaltic oxide, a specific reagent was sought for selective precipitation of nickel. Dimethylglyoxime is a well-known reagent for this purpose[20,21] but has the disadvantage of limited solubility in aqueous solutions and of requiring the use of enough excess reagent to simultaneously complex cobalt ions.[22]

1,2-Cyclohexanedione dioxime, sometimes called nioxime, is used for quantitative estimation of nickel,[23] and tests were conducted to precipitate nickel selectively by its use.

Cobaltous sulfate solutions were treated with sodium carbonate at pH 5.0 to 6.0 to remove copper and iron, and 8 ml. aqueous nioxime solution, saturated at 25., was added for each 10 mg. of nickel, copper, and iron present. The solutions were kept at 90° to 95° for 1 hour, with occasional stirring, and then filtered to remove nickel precipitates. By this procedure solutions were produced that had

---

[18] Howell, O. R., Constitution of the Higher Oxide of Nickel: Trans. Jour. Chem. Soc., vol. 123, 1923, pp. 1772-17783.

[19] Wallis, A. E., and West, D. H., U. S. Patent 2,415,665, Feb. 11, 1947.

[20] Tschugaeff, L., Ztschr. anorg. Chem. vol. 46, 1905, p. 144.

[21] Kraut, K., Ztschr. anorg. Chem. vol. 19, 1906, p. 1793.

[22] Lundell, G. E., Bright, H. A., Hoffman, J. I., Applied Inorganic Analysis: John Wiley & Sons, Inc., New York, N. Y., 2d ed., 1953, p. 409.

[23] Voter, R. C., Banks, C. V., and Diehl, H., 1,2-Cyclohexanedione Dioxime. A reagent for Nickel: Anal. Chem., vol. 20, 1948, pp. 458-460.

gram-per-liter concentrations of 90 to 95 cobalt, 0.01 to 0.02 to 0.01 nickel, 0.001 copper, and 0.001 iron. Part of the 1,2-Cyclohexanedione dioxime, which is an expensive reagent, may be recovered.[24]

The nickel content was still too high for the solutions to serve satisfactorily as electrolytes for deposition of high-purity cobalt. Further removal of nickel was attempted by electrolysis with graded mercury cathode potential. However, selective reprecipitation of a major portion of the nickel was helpful as smaller quantities remained to contaminate the surface of the mercury cathode.

Electrolysis With Controlled Cathode Potential

The greater the difference between the cathode decomposition potentials of metallic ions, the easier it is to deposit metals selectively from an aqueous solution. The closer the individually required cathode potential is maintained during electrolysis, the greater is the selectivity of deposition. It is difficult to separate two metals completely when they have approximately the same decomposition potentials. Addition of complexing agents is sometimes helpful. Complex metal ions are formed, which have a wider range between decomposition potentials. Cobalt and nickel are two metals of this type. When pyridine is added to an aqueous solution of these metals, a definite shift occurs to more positive values. That of nickel is moved more than that of cobalt.

Nickel and copper contaminations were separated by electrolytic deposition from cobalt sulfate solutions. The electrolyte contained 0.2 mole pyridine per liter of solution. The pH was adjusted to 5.5 with sodium hydroxide, and precipitated iron was removed by filtration. Graded cathode potential was used with a mercury cathode, which had a surface area of 206 sq. cm. The interface was agitated to prevent concentration polarization. Platinum plates served as anodes, and electrolyses were conducted at 25°. The cathode potential was maintained at 0.78 volt measured against a saturated calomel cell and using a vacuum-tube voltmeter. For manual control of the cathode voltage an electrical circuit(figs. 1 and 2) like that of Lingane[25] was used, and for automatic control an apparatus (fig. 3) similar to the one described by Caldwell, Parker, and Diehl[26] was employed.

---

[24] The scarlet-red precipitate of the nickel derivative of 1,2-Cyclohexanedione dioxime was dissolved in hydrochloric acid of pH 1, and the stoichiometric amount of potassium ferrocyanide was added to precipitate nickel. The pH was raised to 3 with sodium hydroxide and the solution digested for an hour at 60°. The precipitate was removed by filtration. The filtrate contained the reagent. Recoveries of approximately 70 percent were obtained.

25 percent of 1,2-Cyclohexanedione dioxime was recovered by dissolving the scarlet-red precipitate in 95 percent ethanol acidified to pH 0.8 with hydrochloric acid and passing the solution through a column of cation exchange resin, Dowex 50, to remove nickel ions. The treated solution contained the reagent.

[25] Lingane, J. J., Systematic Polarographic Metals Analysis: Ind. Eng. Chem., anal. ed. vol. 16, No. 3, 1944, pp. 147-152.

[26] Caldwell, C. W., Parker, R. C., and Diehl, H., Apparatus for Automatic Control of Electrodeposition With Graded Cathode Potential: Ind. Eng. Chem., anal. ed., vol. 16, 1944, p. 532.

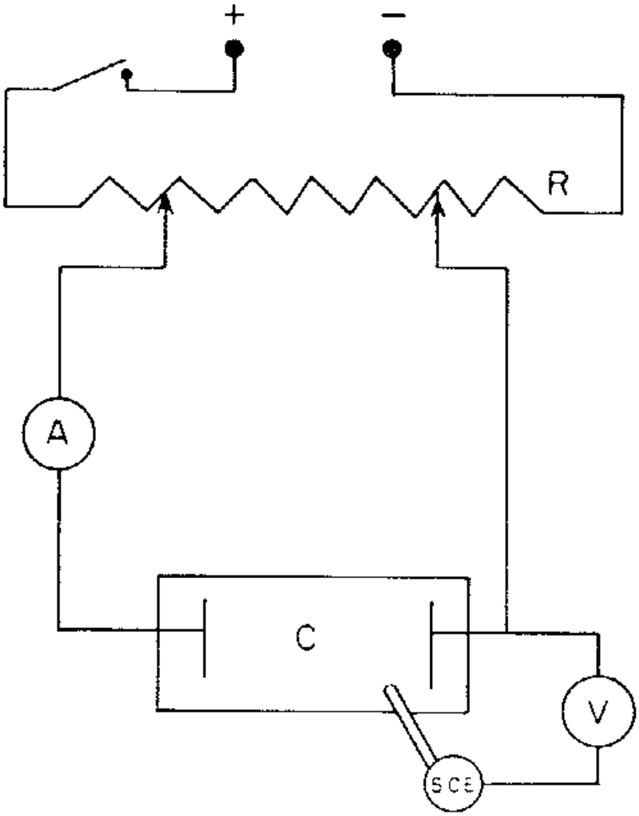

Figure 1. - Electrical circuit for controlled cathode potential separation.

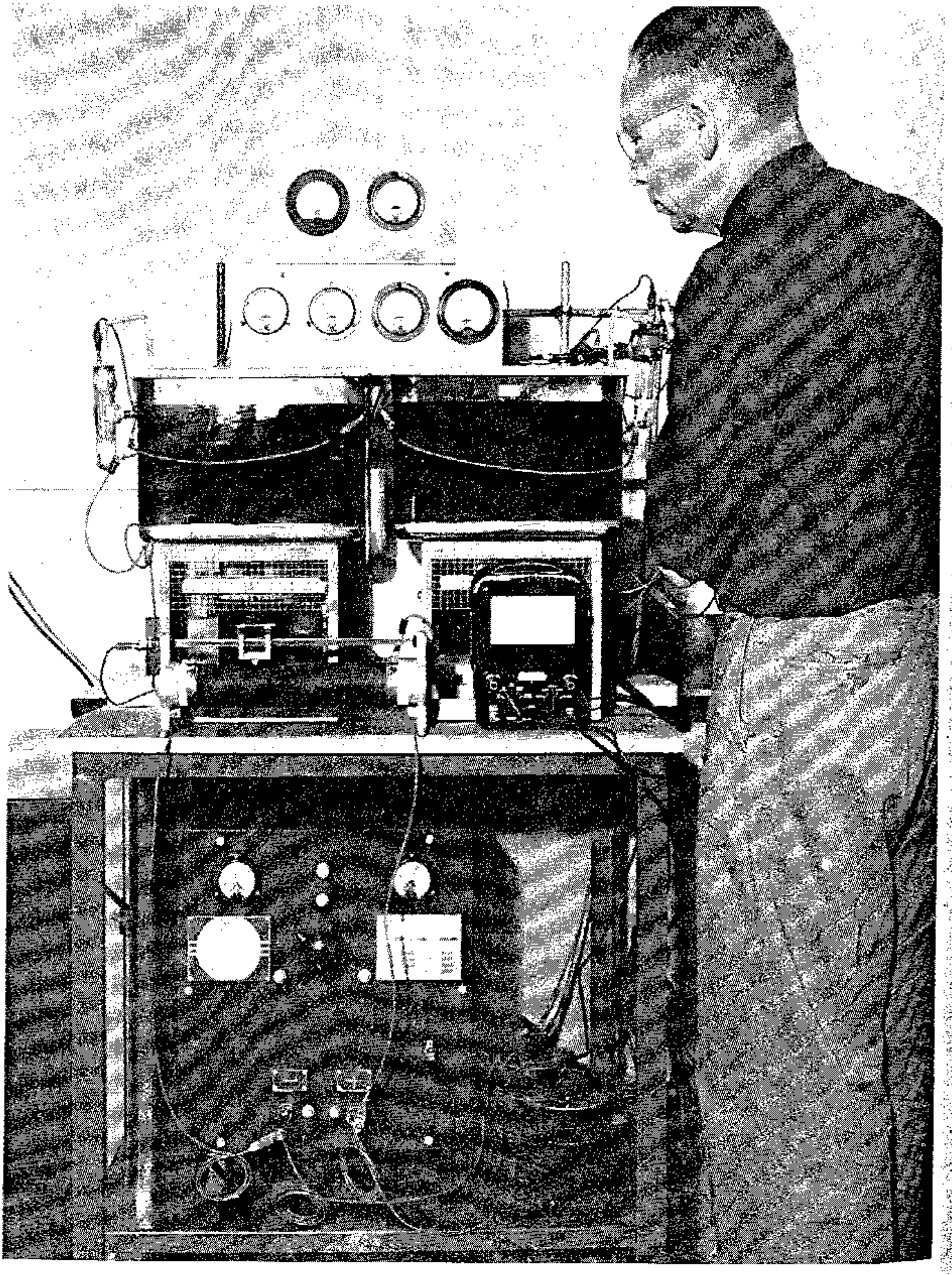

Figure 2. - Apparatus used in manually controlled cathode potential separation.

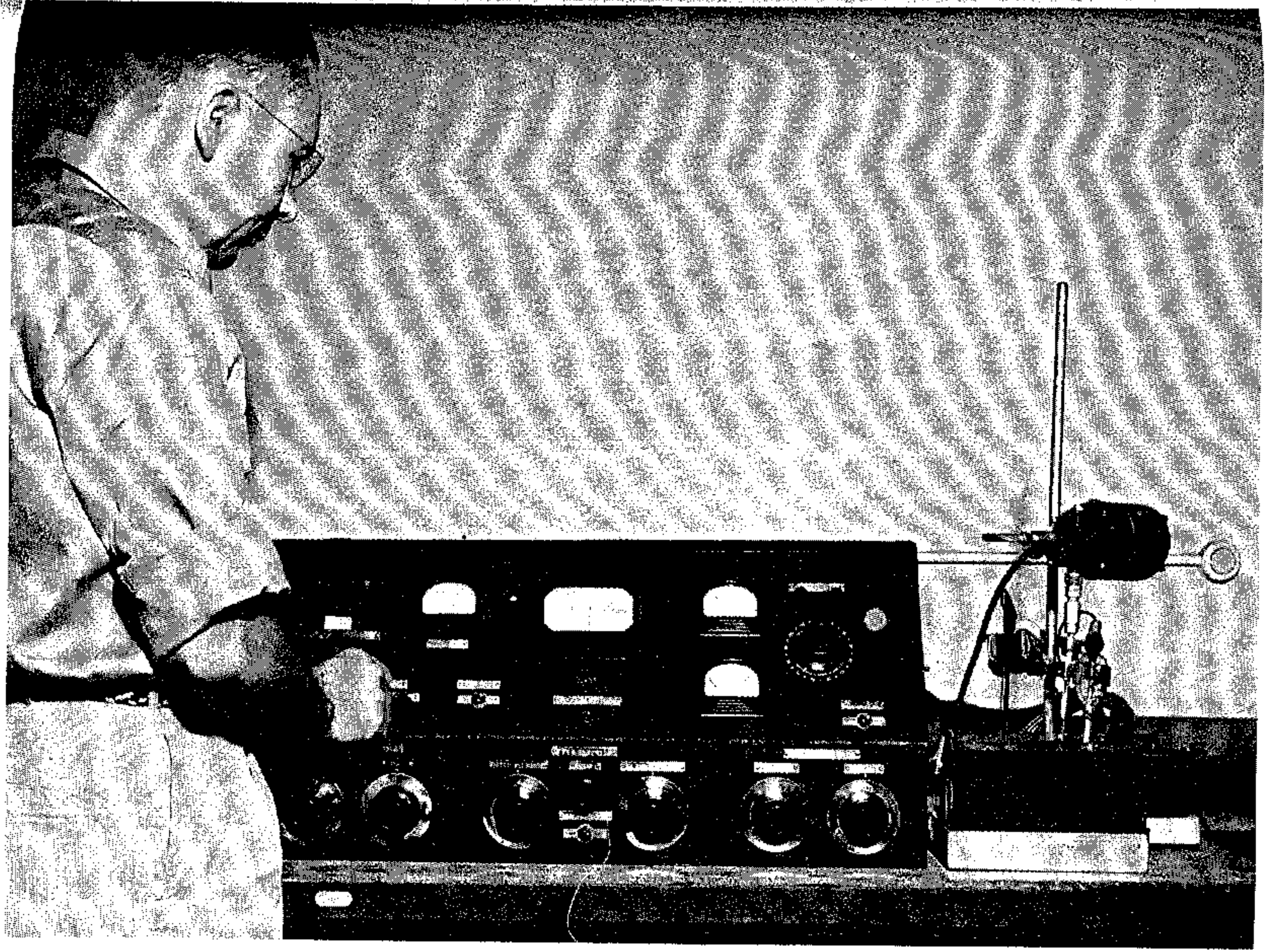

Figure 3. - Apparatus used in automatic cathode potential control.

A series of tests was made under the conditions described. Sulfate solutions having gram-per-liter concentrations of 50 to 100 cobalt, 0.05 to 0.50 nickel, 0.001 to 0.01 copper, and a maximum of 0.001 iron served as electrolytes. In each test 2,000 ml. of electrolyte was used. A purity of 99.99 percent with reference to nickel and copper was obtained for cobalt in solution. Electrolysis for 8 hours was required for solutions containing 0.05 to 0.10 grams per liter nickel, and 24 to 32 hours was required for a content of 0.5 gram per liter. The time needed for purification was affected by the electrolyzing-current value, which was controlled by such variable factors as the surface conditions of the cathode, the chemical composition and concentration of the electrolyte, and the selected cathode potential. The cobalt concentration of the electrolyte did not materially affect the time necessary for deposition of impurities. Cobalt loss due to cathodic deposition and anodic oxidation averaged about 5 percent of the total cobalt in the electrolyte, that due to anodic oxidation was regained by filtration of the electrolyte; and that caused by cathodic deposition was recovered during purification of the mercury. Amalgamated impurities gradually increased in the cathode, but only slight adjustment in primary voltage was necessary to maintain a given cathode potential. However, the mercury was cleaned occasionally by electrolytic or air-oxidation methods.

Recommended Procedure for Purifying Cobalt Solutions

Consideration of the described experimental work led to the purification procedure outlined as follows:

1. Add solid sodium carbonate in small quantities to the agitated impure solution to pH 3.5 and continue with normal sodium carbonate solution until precipitation of cobalt barely begins.

2. Filter off precipitated carbonates consisting mainly of iron and copper, some nickel, and a small quantity of cobalt.

3. Add 8 ml. aqueous solution of 1,2-Cyclohexanedione dioxime, saturated at 25°, for each 10 mg. of nickel, copper, and iron in the filtrate. Heat the solution to 90° to 95° and let stand for 1 hour, with occasional stirring.

4. Filter off nickel-containing precipitate.

5. Adjust pH of filtrate to 5.5 with sulfuric acid or sodium carbonate, add 0.2 mole of pyridine per liter of solution, and electrolyze with graded mercury cathode potential of 0.78 volt. The duration of the electrolysis varies with the nickel content, but 8 to 10 hours is usually satisfactory.

6. Filter electrolyte.

7. Add sodium hydroxide to filtrate to precipitate cobalt hydroxide.

8. Filter and wash precipitate with hot distilled water until washings no longer have an odor of pyridine. It is necessary to remove the complexing agent as it interferes later with cobalt deposition.

9. Dissolve washed precipitate in dilute sulfuric acid to form a solution containing 90 to 100 grams of cobalt per liter.

DEPOSITION OF HIGH-PURITY COBALT

Cobalt was electrodeposited from cobalt sulfate solutions prepared by the recommended procedure. The electrolyte was circulated through the cell (fig. 4) at a rate of 1 to 2 liters per hour. A pH of 1.2 to 1.6 was maintained by adding pyridine-free cobalt hydroxide. The electrolyte was reprocessed occasionally by the given procedure to prevent accumulation of contaminations. A 4-liter beaker with an outlet tube served as a cell. The cell and overflow collector were inclosed in a Lucite box to prevent contamination from atmospheric dust. Electrolyses were conducted at 50° to 55° with 3 platinum anodes and 2 titanium cathodes. Electrode surface areas were approximately the same. A cathode current density of about 6 amperes per square decimeter was used. Absence of impurities[27] permitted the deposition of dense, bright, metallic cobalt, which could be stripped from the titanium cathodes. Polarographic analyses of the deposited metal showed 0.001 to 0.002 percent nickel, 0.001 to 0.003 percent iron, and a maximum of 0.001 percent copper. About 0.005 percent of sulfur was detected. Spectrographic analyses indicated traces of calcium, copper, iron, magnesium, nickel, and zinc.

ELECTROLYTIC COBALT

Production of Ingot Cobalt

Several ingots of high-purity cobalt have been produced by vacuum melting of cathodes.

The cobalt was melted in a magnesium oxide crucible, using a vacuum-induction furnace. A rather complex melting procedure was followed to reduce the gas content of the solidified ingot to a minimum. Adsorbed gases in the charge and crucible were first reduced by heating them slowly to 800° C. and maintaining this temperature while the furnace was evacuated to a pressure of approximately 30 microns. The charge was then melted and raised to 1,560°-1,575° C. After a brief period at this temperature, the crucible was lowered very slowly from the heating zone of the furnace to promote directional solidification from the bottom to the surface of the melt. Thus, a very large proportion of any gases dissolved in the metal was removed. After complete solidification of the melt, the crucible was returned to the heating zone where the charge was remelted and again held at a temperature high enough to insure complete melting. Helium was then introduced to increase the gas pressure over the melt to 200 mm. of mercury, and the charge was gradually lowered from the heating section of the furnace. Directional solidification in this final operation served to concentrate shrinkage in the top portion of the ingot, leaving the bulk of the metal as a solid, essentially gas free mass.

27/ Churchward, R. E., Shelton, F. K., and Knickerbocker, R. G., A Study of Impurities in Cobalt Electrowinning: Tans. Electrochem. Soc. vol. 85, 1944, pp. 193-212.

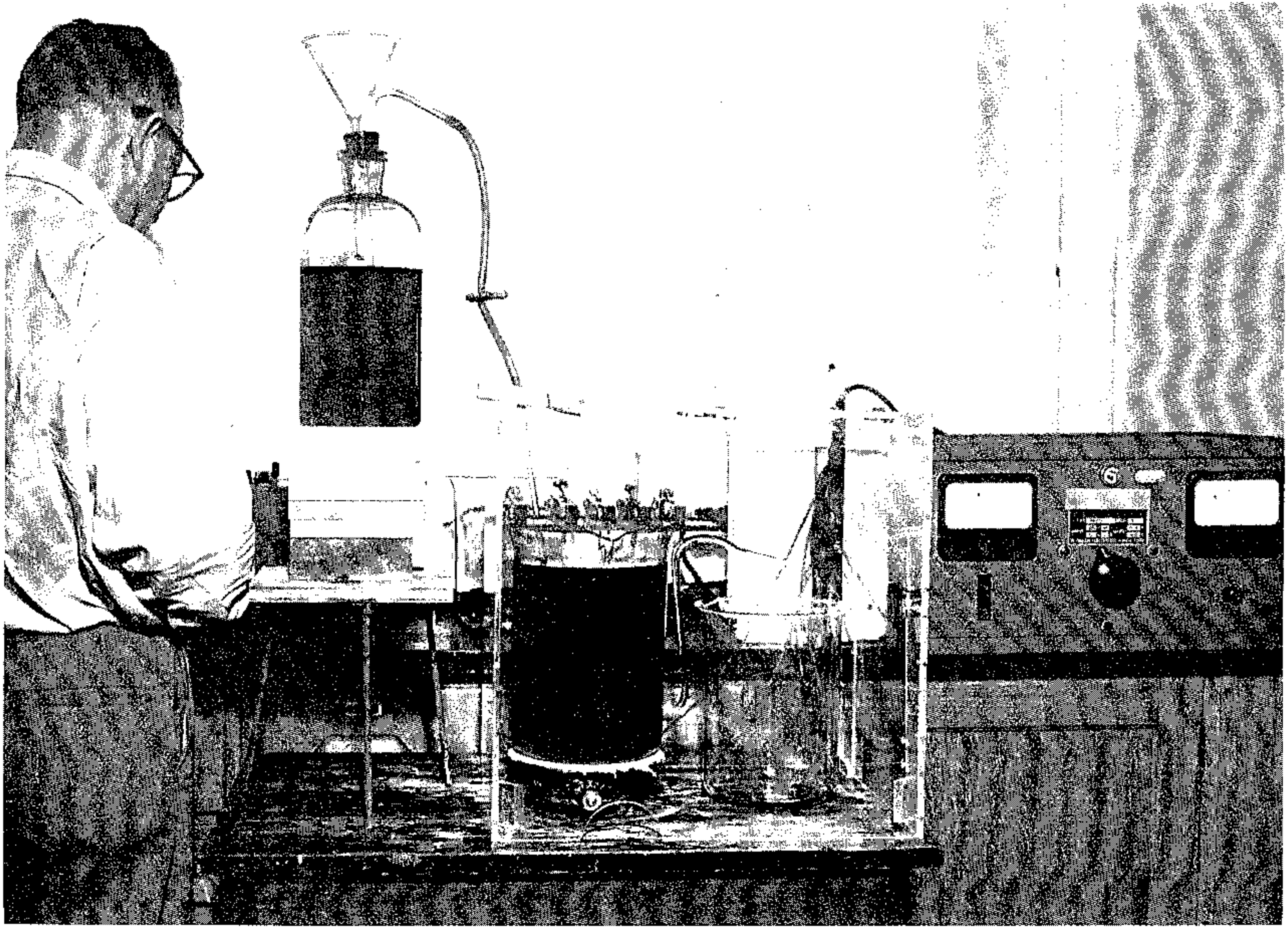

Figure 4. - Electrolytic deposition of high-purity cobalt.

INT.-BU.OF MINES,PGH.,PA. 7060