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DEVELOPMENT OF A 10,000-AMPERE CELL FOR ELECTROREFINING TITANIUM

By F. P. Haver and D. H. Baker, Jr.

UNITED STATES DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
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DEVELOPMENT OF A 10,000-AMPERE CELL FOR ELECTROREFINING TITANIUM[1]

by

F. P. Haver[2] and D. H. Baker, Jr.[3]

SUMMARY

The Federal Bureau of Mines developed a 10,000-ampere cell to determine the economic feasibility of producing high-purity electrolytic titanium from mill scrap or offgrade sponge. Operating variables were investigated, matetial handling procedures were established, and the cost of electrorefining titanium was determined.

The prototype cell produced premium-grade metal (<100 Brinell hardness number (B.h.n.)) from very impure Kroll sponge at a processing cost of less than \$0.60 per pound. Refined metal was deposited at the cathode in the form of coarse (85 percent plus 34-mesh), hexagonal crystals of α titanium when the cell was operated at 850° C. A cathode current density of 1,000 amperes per square foot and a molten sodium chloride electrolyte containing approximately 5 percent by weight of soluble titanium were used.

In continuous operation, at the optimum number of ampere-hours, (40,000), the current efficiency averaged slightly less than 60 percent. It was possible to supply large enough amounts of electric current for electrolysis to maintain the temperature of the bath, thus reducing overall power consumption to less than 5 kilowatt-hours per pound of metal refined.

Labor was the highest cost per unit. It appeared to be largely dependent upon the number of ampere-hours used to refine each deposit. Dragout (salt contained in the deposit) was influenced by temperature, electrolyte composition, and current density. The best deposits contained approximately 20 percent (by weight) salt. The throwing power of the electrolyte proved to be excellent. Mechanical operation of the cell was satisfactory at all times.

INTRODUCTION

Many nonferrous metals today are refined electrolytically. An example is copper; the electrolytic grade has largely replaced the fire-refined grade in

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[1] Work on manuscript completed June 1960.

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commerce. The object of electrorefining usually is: (1) To produce a product with superior physical and chemical properties, (2) to recover precious metals present as impurities, and (3) to upgrade metal not meeting a buyer's specifications. Small-scale tests[4-6] at the Boulder City Metallurgy Research Laboratory showed that high-purity titanium could be electrorefined in fused alkali-halide salts from offgrade sponge or mill scrap. The metal to be refined was connected as an anode and titanium was recovered at the cathode in the form of coarse crystals essentially free of oxygen, nitrogen, carbon, iron, and other impurities.

Electrorefining of titanium may become economically feasible if sufficient demand is developed for a high-purity product. Metal with a Brinell hardness as low as 52 has been produced in laboratory work; however, metal with a Brinell hardness of 70 to 80 is more common in the output from small-scale operation. The degree of purification obtained using offgrade Kroll sponge as the anode material is indicated in table 1.

TABLE 1. - Analyses of titanium before and after electrorefining

Impurity	Analysis, percent	
	Feed, 149 B.h.n.	Product, 77 B.h.n.
Fe	0.065	0.011
Mg	.02	.003
Na	.005	.001
N	.012	.001
O	.106	.021
H	.005	.006
C	.026	.005
Cl	.09	.04
V	.07	.02
S	.007	.001

Figure 1 illustrates differences in the physical form of chemically reduced and electrorefined titanium. The sponge shown at the left had a bulk density of 50 pounds per cubic foot. Metal produced from this sponge (shown on the right) had a bulk density of 105 pounds per cubic foot.

An investigation of the commercial possibilities of the electrorefining process was sponsored by the General Services Administration. A 3-year program starting October 1, 1957, was set up covering the design, fabrication, and installation of a 10,000-ampere cell with power sources and necessary

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[4] Nettle, J. R., Baker, D. H., Jr., and Wartman, F. S., Electrorefining Titanium Metal: Bureau of Mines Rept. of Investigations 5315, 1957, 43 pp.

[5] Baker, D. H., Jr., and Nettle, J. R., Titanium Electrorefining: Cathode Studies and Deep Bath Deposition: Bureau of Mines Rept. of Investigations 5481, 1959, 11 pp.

[6] Leone, O. Q., Nettle, J. R., and Baker, D. H., Jr., Electrorefining Titanium Using an Internally Heated Cell: Bureau of Mines Rept. of Investigations 5494, 1959, 20 pp.

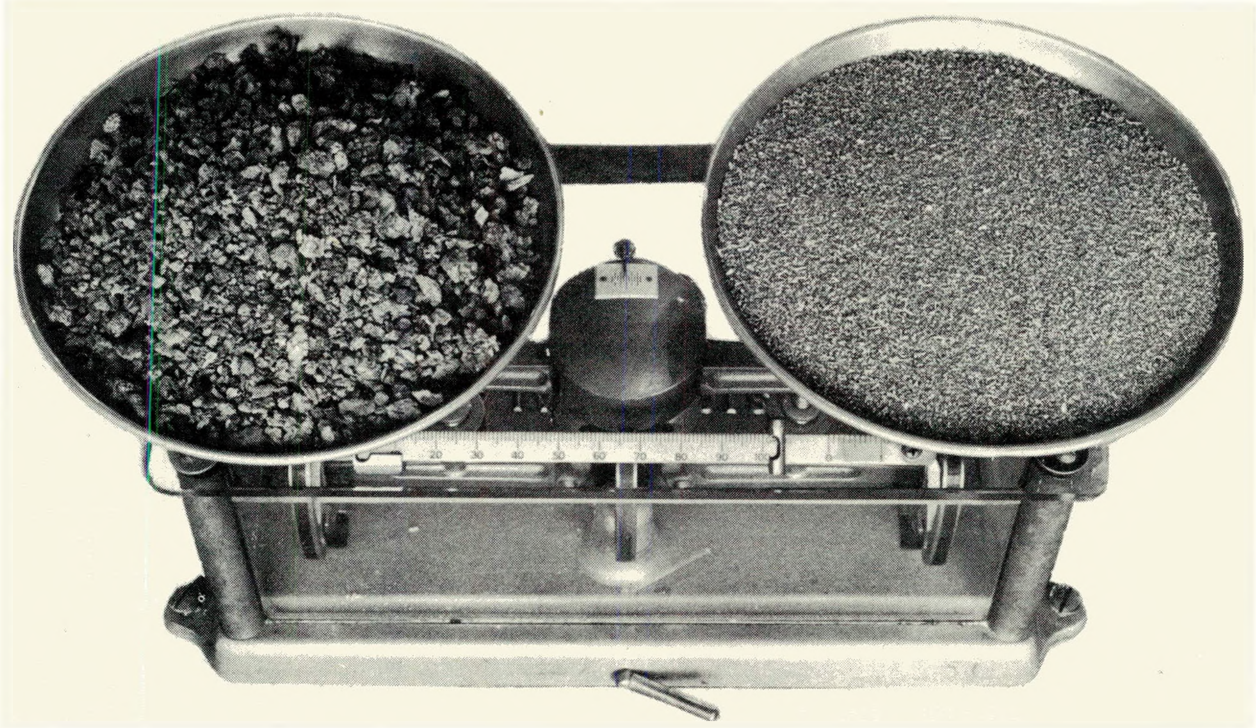

FIGURE 1. - Comparison of Equal Weights of Titanium Before and After Electrorefining.

auxiliary equipment. Operating variables were investigated, material handling procedures were developed, and the cost of refining titanium scrap was determined. The object of the program was to obtain data that could be used by industry to evaluate use of the process for the production of high-purity titanium from poor-quality Kroll sponge or industrial scrap.

ACKNOWLEDGEMENTS

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DESIGN AND OPERATION OF EQUIPMENT

A number of factors had to be considered in designing a 10,000-ampere cell for fused-salt electrolysis. These included materials of construction for the cell and electrodes, operating variables such as current density and temperature, and the properties of the metal to be made. The chemical stability of the electrolyte and the vapor pressure, melting point, electrical conductivity, and solvent power for the feed and product metal also had to be considered. Titanium, which is extremely reactive at elevated temperatures, presents many problems not encountered in the production of metals such as aluminum and magnesium. Because of its high melting point (1,668° C.), titanium must be deposited at a cathode in the form of heterogeneous crystals. A protective atmosphere, such as helium, must be maintained in the cell during electrolysis. Both of the above factors make development of a truly continuous process for the production of high-purity titanium difficult.

The prototype cell design was based on several empirical relationships established in small-scale laboratory work:

1. The electrolytic current should not exceed 4 amperes per pound of electrolyte.
2. The initial cathode current density should not be greater than 1,000 amperes per square foot.
3. The maximum size of deposit should be limited to 0.1 pound per square inch of cathode surface area.
4. The anode surface area should be at least twice that of the cathode.

Figure 2 shows the flowsheet selected for the production of high-purity titanium from scrap or offgrade sponge. A description of the equipment required in the process follows.

Electrolyte Chamber

Small-scale tests showed that low-carbon steel was a suitable material for constructing the cell and electrodes. It is easily fabricated, inexpensive, and not attacked by the electrolyte in the absence of air. At operating temperature (850° C.) its creep strength is very low, however, and care must be used in cell design to minimize stresses. Local overheating must also be avoided, since titanium reacts with iron at 1,050° C. to form a eutectic. Extreme care is necessary in welding cell components because the electrolyte ($NaCl-TiCl_2$) at 850° C. will penetrate the smallest pinhole or slag inclusion.

Figure 3 shows the electrolyte chamber for the 10,000-ampere cell. The vessel had an inside diameter of 48 inches and an overall length, including the shallow dish-shaped ends, of 9 feet 8-5/8 inches. It was fabricated from A-285, grade C flange-quality steel 20 percent clad on all external surfaces with type 310 stainless. Wall thickness was five-eighths of an inch except for the two 12-inch-diameter cathode nozzles and the two 10- by 30-inch anode nozzles which were made of ½-inch clad material. The 18- by 24-inch center nozzle, provided for an internal heater, was also fabricated from ½-inch clad plate. Interior surfaces were sand-blasted with metallic grit to remove any oxides. All welded areas were radiographed, and any visible defects were corrected.

Use of a cylindrical form with nozzles for cathode and anode openings gave maximum hoop strength, distributed the weight of the superstructure over a wide area, and allowed parts of the cell at elevated temperatures to be covered with a minimum of 9 inches of insulation. Carbon steel is not normally used for temperatures in excess of 540° C. Its short-time proportional

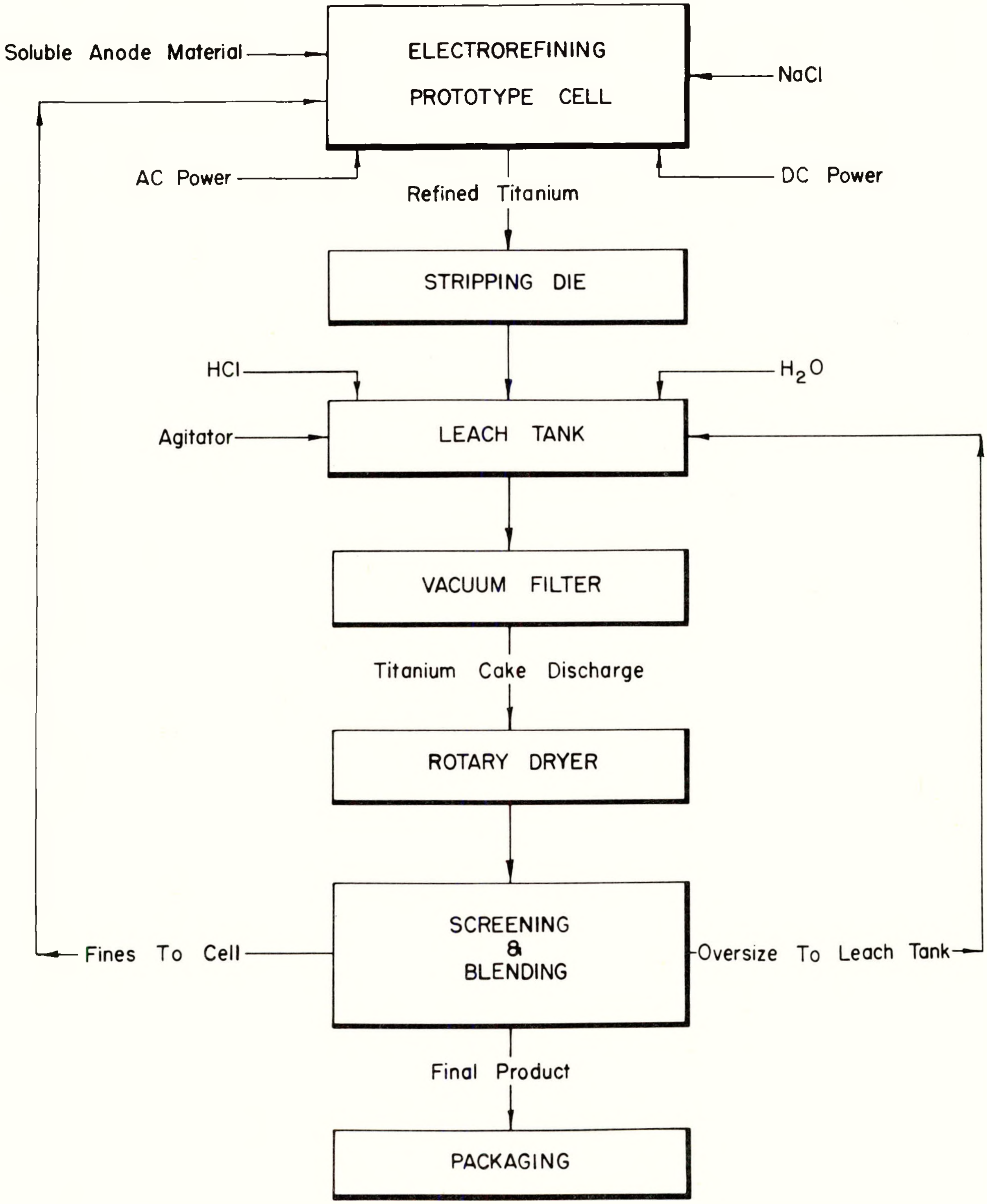

FIGURE 2. - Flowsheet Developed for Production of High-Purity Titanium From Scrap or Offgrade Sponge.

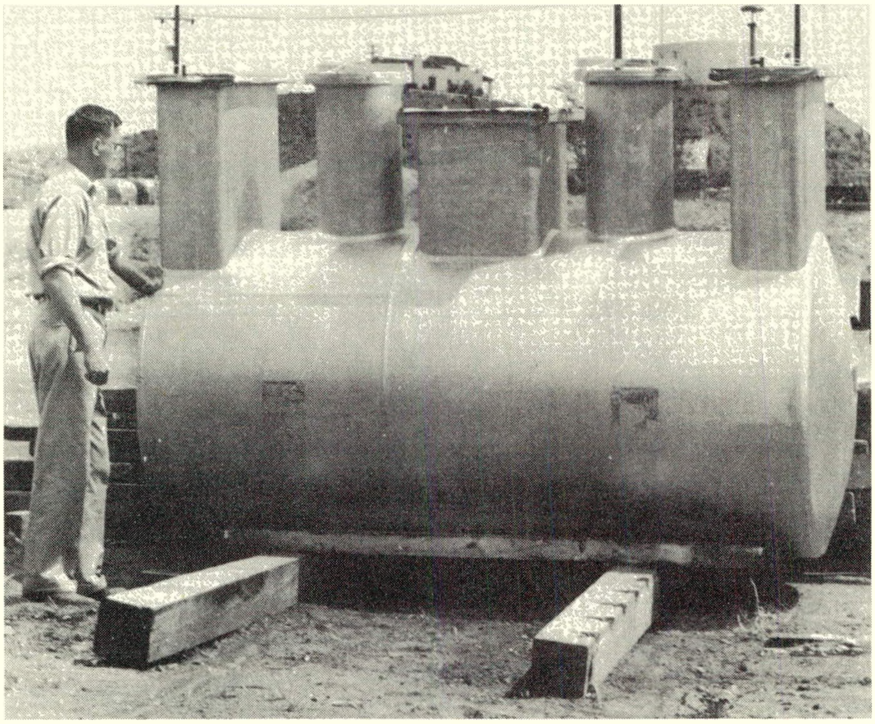

FIGURE 3. - Electrolyte Chamber.

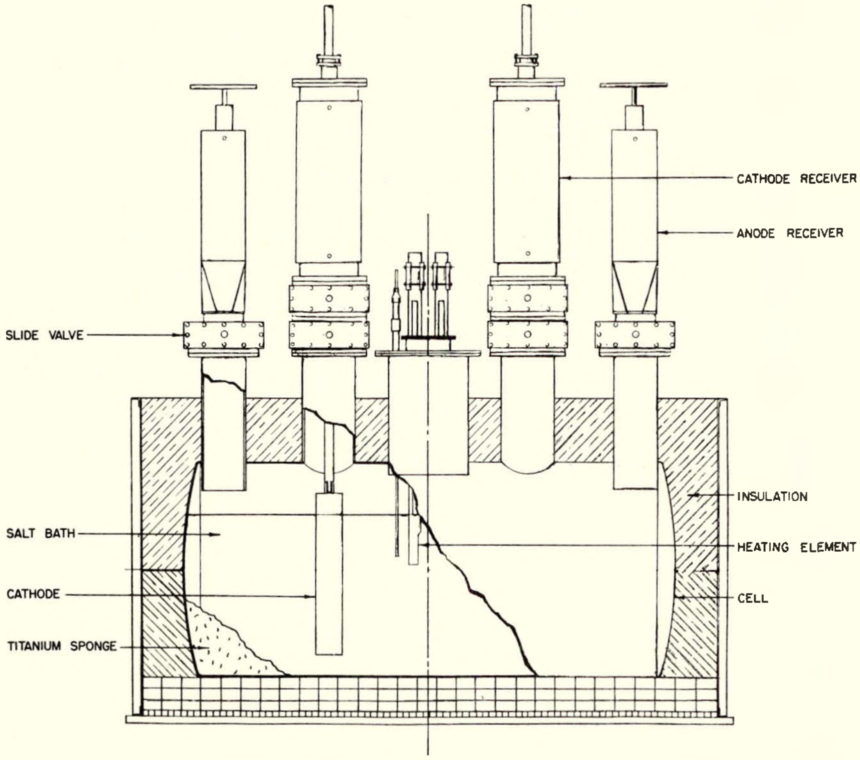

FIGURE 4. - Cross Section Through Longitudinal Axis of Cell.

limit approaches zero at 650° C. At higher temperatures, carbon steel will continue to creep regardless of the applied stress. To prevent deformation, it was necessary to use castable insulation to support the lower half of the electrolyte chamber. Weight of the superstructure was carried on cross braces. With this arrangement, the cell maintained its shape at 850° C.

The unit was placed in operation on December 15, 1958. On April 6, 1959, a brown stain appeared on the insulation covering one end of the cell. Power to the cell was immediately disconnected, and the top half of the insulation was removed. A small section of weld on one anode nozzle was found to be severely corroded just above the point where the nozzle joined the cylindrical part of the chamber. Only a minute perforation extended through the inner mild steel wall, but the type 310 cladding was badly attacked over a wide area in the vicinity of the hole. Cause of failure appeared to be a slag inclusion in the weld.

Mild steel will not react with the NaCl-$TiCl_2$ electrolyte in a helium atmosphere. Stainless steel, however, is subject to catastrophic corrosion on contact with the bath at 850° C. in the presence of air. The opening in the weld occurred approximately 12 inches above the level of the fused salt, and most of the damage was caused by reaction of NaCl vapor with the cladding. Repairs were made and the unit was again placed in operation on May 18, 1959. The cell operated satisfactorily until August 11, 1959, when it was noticed that consumption of helium, used to pressurize the cell, was abnormally high. The unit was again shut down, and the insulation was removed. This time a number of welds connecting anode and cathode nozzles to the electrolyte chamber had been attacked, as shown in figure 4. Damage was so great that no further repairs could be made and the unit was scrapped, (see figure 5).

The use of 20 percent cladding on the outside of the electrolytic chamber was probably responsible for the final failure. Cladding was used to protect the outer surface of the cell from oxidation. It performed well as long as the cell was vacuum and air tight. In the presence of salt left from the initial failure, however, the stainless steel formed a built-in couple which greatly accelerated corrosion. A spare electrolyte chamber was placed in operation on August 13, 1959. It was still in excellent condition when the operation was terminated on March 28, 1960. Service time was too short to permit an accurate estimation of pot life. However, some laboratory cells have now been in use for over 3 years with no sign of deterioration. Others have failed in a few days. Defective welds have been responsible for most of the trouble encountered at the Boulder City Laboratory.

Superstructure

The superstructure for the prototype cell consisted of cathode receivers, anode receivers, and slide valves arranged as shown in figure 4. A cross section of the cell through a cathode receiver is shown in figure 6. Cathodes were made from 36-inch lengths of 6-inch-o.d. seamless steel tubing having a ½-inch wall thickness. These were bolted to the bottom of 9-foot lengths of 1½-inch double extra-heavy hard-drawn copper tubing. The copper electrodes were water-cooled by two concentric stainless steel pipes placed inside the tubing.

When the cell was in operation, water flowed down the inner steel pipe and back to the top of the outer pipe through the opening between the walls. This was sufficient to keep the electrodes cool even when carrying full load (5,000 amperes). A low-melting fusible alloy of bismuth and lead was used to fill the space between the inner wall of the copper tubing and the outer wall of the cooling pipe. This alloy served as a heat-exchange medium and also stiffened the electrodes. As a safety precaution in the event of contact between cooling water and fused salt, the cell was provided with two 3-inch rupture disks rated at 50 pounds per square inch gage (315° C.). The disks were made of Inconel with a silver seal on the inner side and were furnished with type 347 stainless steel vacuum supports.

Cathode receivers were made from 3-foot 8-inch lengths of schedule 40 12-inch steel pipe fitted with external water jackets. Cover plates for the

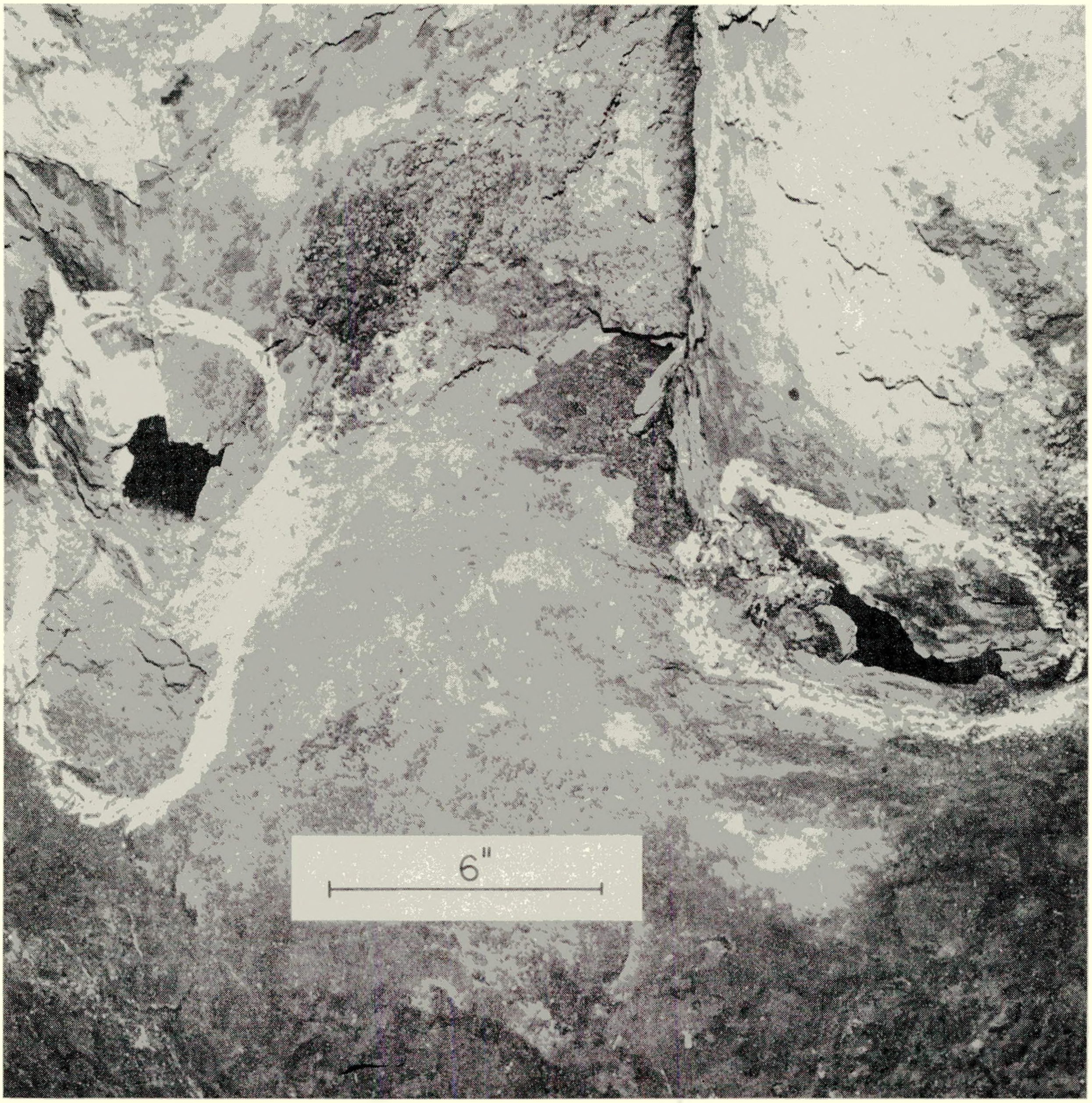

FIGURE 5. - Anode and Cathode Nozzles After Weld Failure.

receivers were insulated from the cell with plastic bushings. A rubber seal at the center of the cover plates kept air from entering the cell when the electrodes were raised or lowered. Similar seals were used on all other moving parts. To maintain a vacuum- and air-tight cell, it was necessary to keep such seals well lubricated with a heavy silicone grease. Flat gaskets were used between bolted sections. These were made of a fluorinated synthetic rubber (Viton) to keep water-cooling at a minimum.

Before the cell was placed in operation, the cathodes were positioned in the receivers and both the top and bottom slide valves shown in figure 6 were

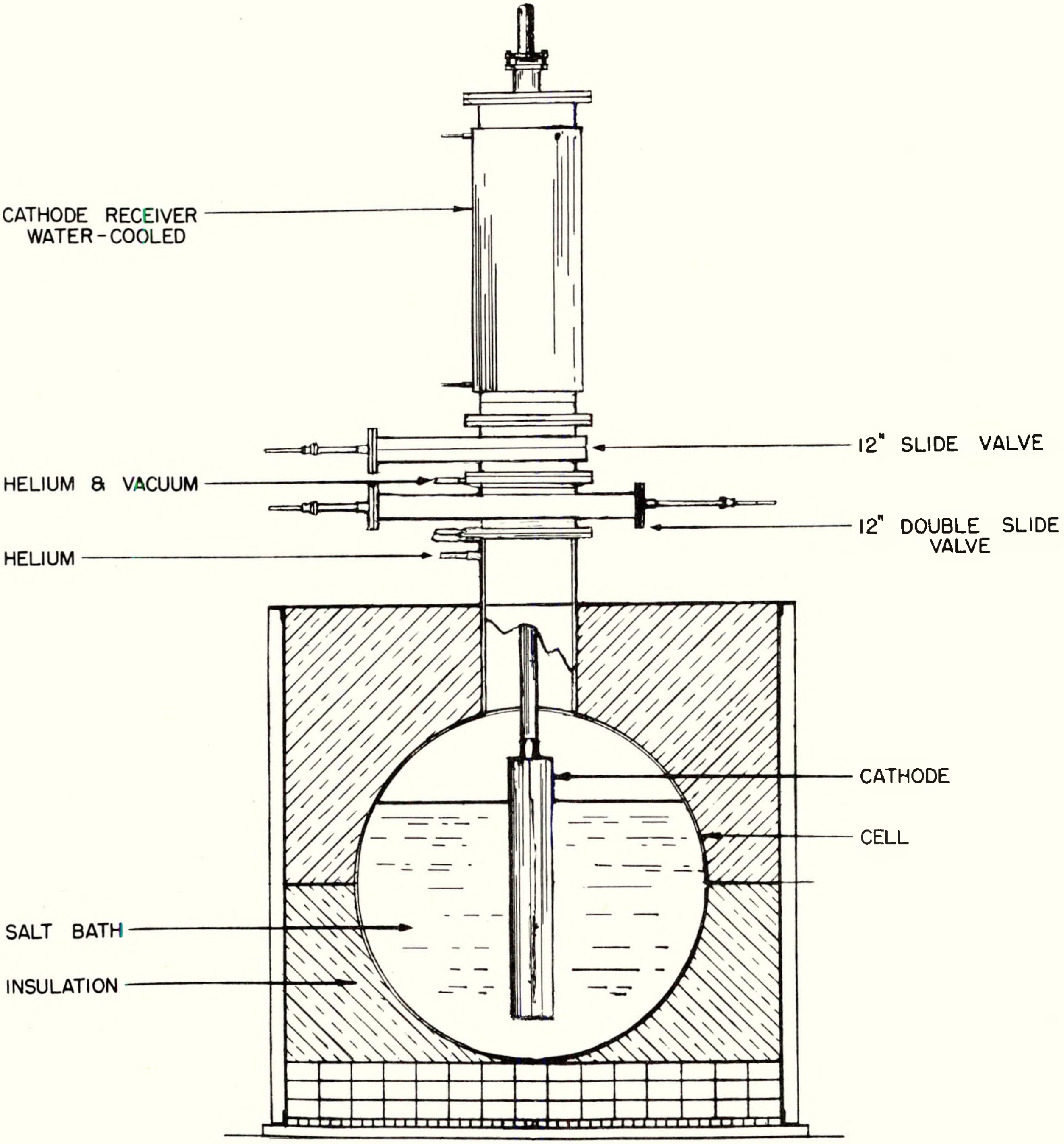

FIGURE 6. - Cross Section of Cell at a Cathode Receiver.

closed. The top valve contained a single, rectangular water-cooled slide, 14-5/8 inches wide by 15 inches long by 1¼ inch thick. When it was in place under the receiver, the rubber-gasketed top surface of this slide could be raised against a circular seat with cams to form a vacuum-tight seal. The component parts of this type of valve, which was developed at the Boulder City Metallurgy Research Laboratory, are shown in figure 7. The lower valve shown in figure 6 contained two water-cooled slides. One, 14-5/8 inches wide

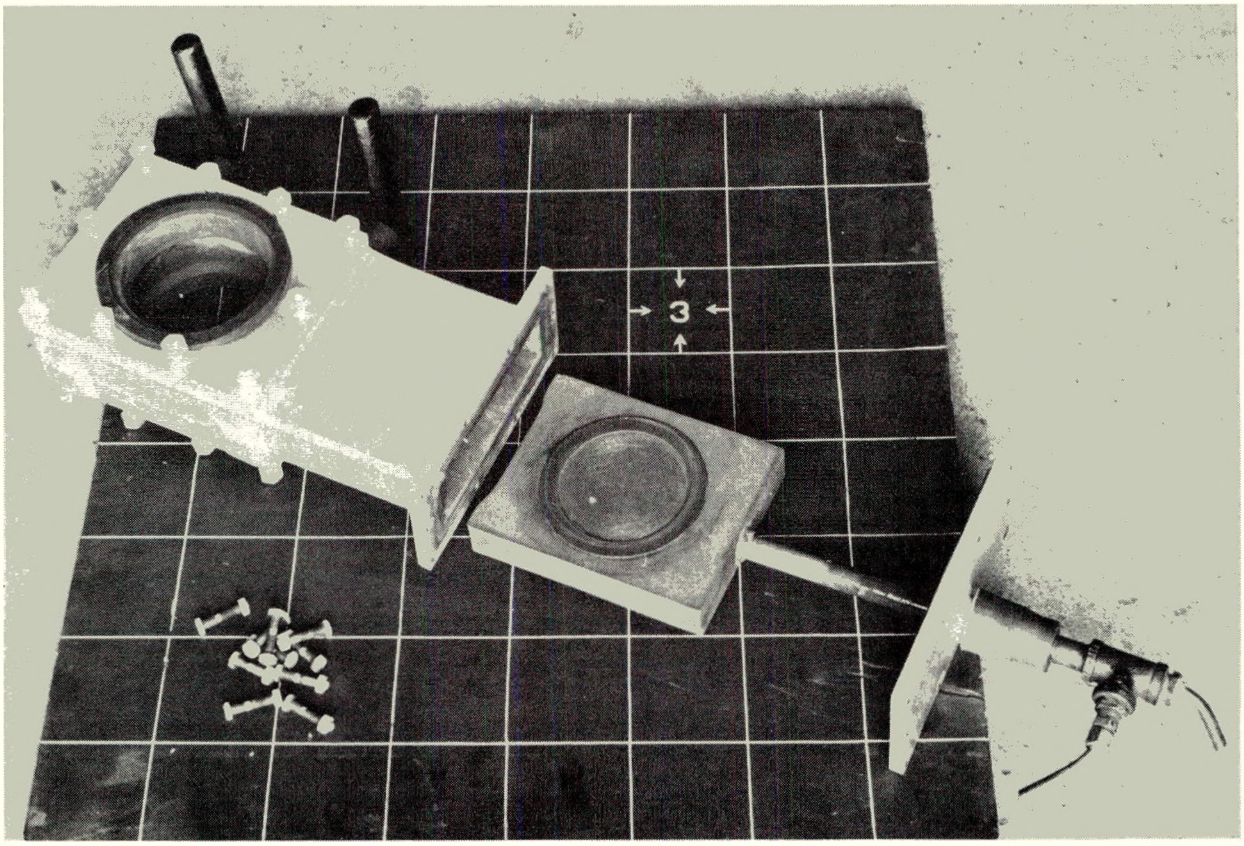

FIGURE 7. - Typical Slide Valve Disassembled to Show Parts.

by 7-3/4 inches long, was used only during deposition. It was operated from the rear of the cell. The front slide was the same as that used in the upper valve except for a 1-inch-radius half circle cut into its leading edge. A matching half circle was located in the back slide. Both half circles were lined with asbestos cement to prevent short-circuiting between the electrodes and the slides.

To start a run, cams on the top valve were unlocked and the slide was pulled out. The bottom valve remained closed, since no air could be allowed to enter the electrolyte chamber at any time. The receiver section was then evacuated and filled with helium three times. Argon may be used for purging equipment, but helium is preferred since it causes less sublimation from the bath. When helium pressure in the receiver equaled helium pressure in the electrolyte chamber, the bottom slide valve was opened and the cathode was lowered into the electrolyte. A 30-inch immersion was used in most work with the prototype cell. A connector at the top of the electrode mated with a similar connector on a bus bar from the rectifier when the proper immersion was reached. The two connectors were then bolted together to complete the electrical circuit. (The electrolyte chamber was permanently connected to the positive side of the rectifier by a copper bus bar.) The two slides of the bottom valve were butted together in the center of the receiver opening before electrolysis was started. The half circles in their leading edges joined to form a 2-inch opening surrounding the electrode. This confined sublimate to the lower section of the cell and prevented condensation of vapors on the inner water-cooled surfaces of the receivers.

When deposition was completed, power to the rectifier was disconnected, the connectors were unbolted, and the cathodes were raised high enough to clear the electrolyte. The deposits were allowed to drain for 15 minutes to remove as much salt as possible. The two slides on the lower valve were then pulled out, and the cathodes with their deposits were raised into the receivers to cool. The front slides on both valves were next pushed in and the cams were turned, sealing off both the receivers and the cell. After this, the receivers were unbolted at the connection between the top and bottom slide valves and placed to one side to allow the deposits to cool to room temperature. Spare receivers complete with slide valves, cathodes, and electrodes were bolted in their place on the cell, and the cycle was repeated.

Figure 8 shows a cross section of the cell through one of the anode receivers. The receivers for the prototype cell were large enough to contain a full week's supply of anode material. Titanium sponge or scrap was added to the receivers through the openings at the top with the lower slide valves closed. After replacing the cover plates, the anode receivers were evacuated and filled with helium three times. When the helium pressure in the receivers equaled the helium pressure in the electrolyte chamber, the slide valves were opened. Anode material could then be dropped into the electrolyte at will by raising the handles at the top of the receivers. These lifted a steel plug ground into a conical opening at the bottom of each receiver. In continuous operation, frequent small additions of anode material gave better results than occasional large drops. Salt additions were made to the cell as needed in the same manner.

One of the most important factors in the electrorefining of titanium is the ratio of anode to cathode surface area. When the anode surface area equals the cathode surface area, electrowinning rather than electrorefining will occur except at very low current densities. For optimum results, the anode surface area should be at least four times that of the cathode. The exact ratio required must be determined experimentally since it depends upon cell configuration and the type of anode material used. In refining off-grade Kroll sponge in the prototype cell, it was necessary to maintain a "heel" of approximately 800 pounds of anode material in the electrolyte chamber at all times to obtain satisfactory results.

A second very important factor in fused-salt electrorefining is anode contact. As noted above, anode material was dropped into the bottom of the cell through air-locks at each end. Continuity of the circuit depended entirely upon contact between anode material and the bottom of the cell which was, in turn, connected through a bus bar to the positive side of the rectifier. While this method of anode addition was convenient and inexpensive, it did have some disadvantages. As titanium was transferred to the cathodes, a fine sludge containing most of the impurities was left behind. This blanketed the remaining anode material, reducing its effective area. It also prevented good electrical contact between subsequent additions of anode material and the sides of the electrolyte chamber.

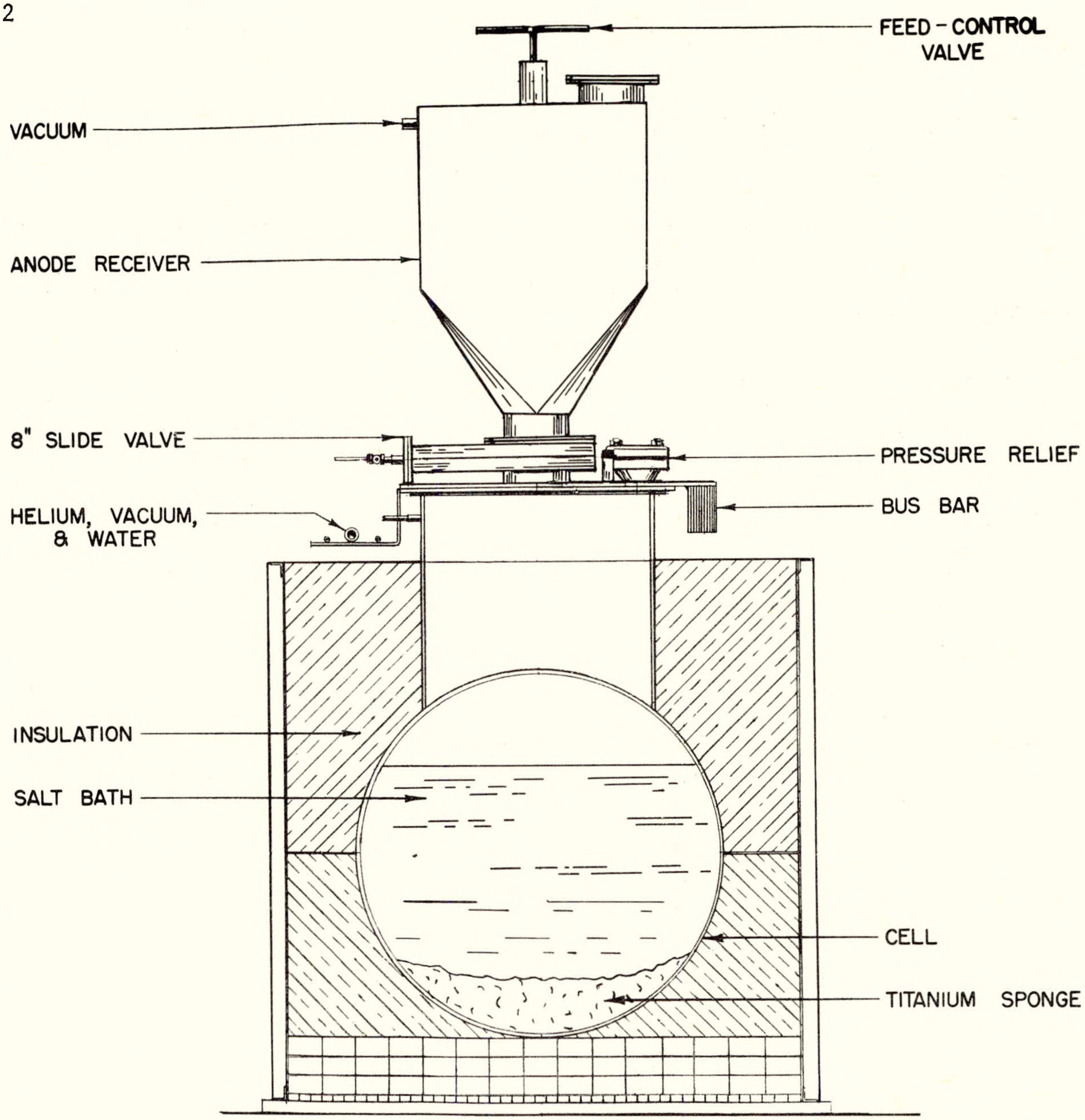

FIGURE 8. - Cross Section of Cell at an Anode Receiver.

In an extreme case, sludge may render a cell inoperative. In most cases, however, it merely causes a gradual rise in the resistance of the circuit. Smaller crystals are formed at the cathode, and some electrowinning from the bath may take place. To bring conditions back to normal, it is necessary to stir up the material at the bottom of the cell with a poke rod. An immediate, dramatic improvement in the appearance of the deposit usually occurs. The prototype cell was not equipped with poke rods at the ends. It was, therefore, necessary to remove the anode receivers periodically and replace them with a special receiver fitted with a long 3/4-inch steel rod having a spade tip. The point of the rod was driven into the loose material at the ends of the cell to reestablish anode contact. Changing receivers was time-consuming, and it is recommended that any future cell be equipped with permanent poke rods that can be used at any time.

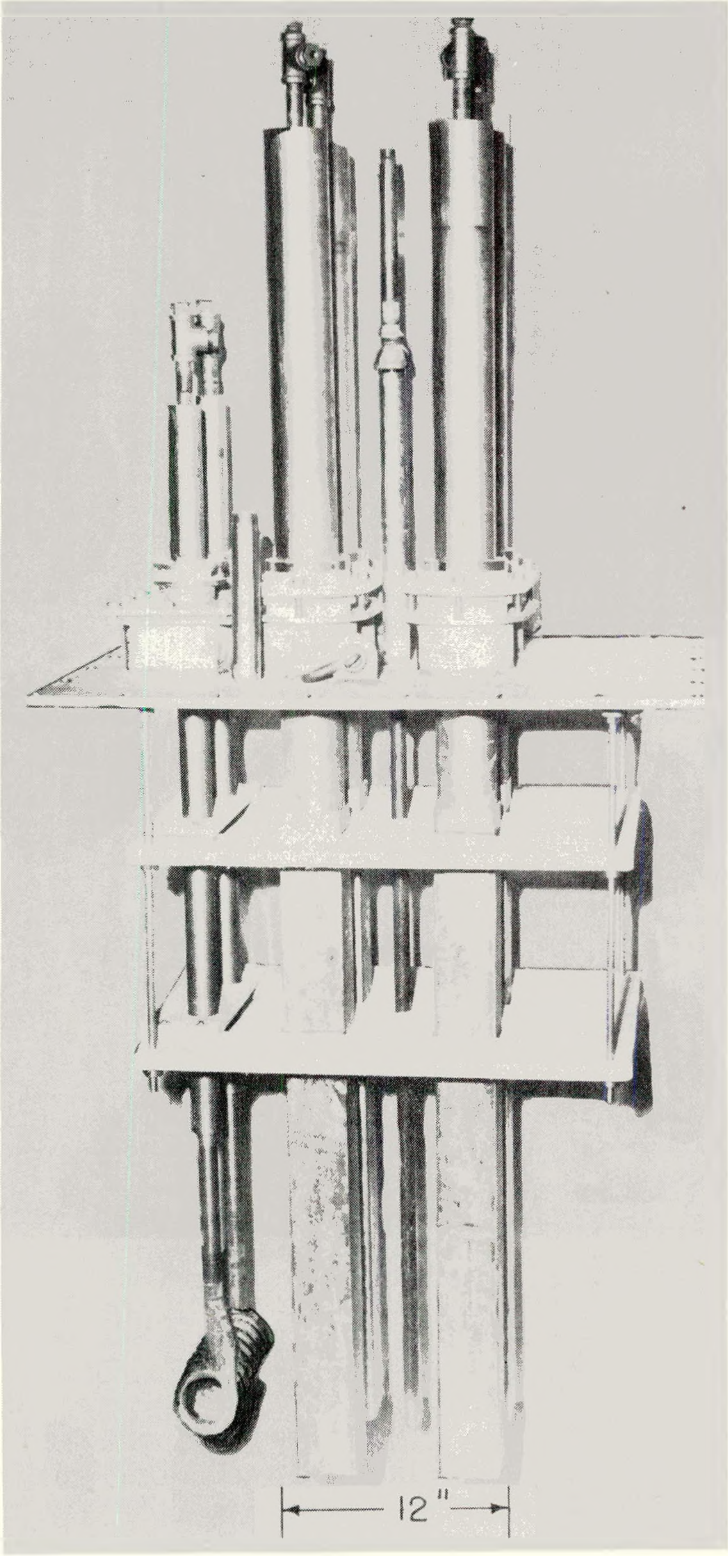

FIGURE 9. - Internal Heater With Its Starting Coil.

Internal Heater

Laboratory cells were externally heated using either silicon carbide rods or ribbon-type resistance elements. Heating in this manner, although acceptable on a small scale, was expensive, since radiant heat losses were difficult to limit or control. It also introduced design complications, particularly in insulating equipment. To overcome these faults, an internal heater (figs. 9 and 10) was devised for use in the prototype cell. It consisted of a startup coil (two 1½-inch-diameter steel rods 4 feet 10 inches long connected at the bottom by a ½-inch rod wound into a 4-inch helix) plus four main heating electrodes (5-foot lengths of 3-inch square steel bar). Radiation shields, made of silica foam, were used to prevent overheating of the cover plate. The top 18 inches of the 1½-inch-diameter rods and the top 24 inches of the 3-inch bars were also water-cooled to protect the packing glands.

When the cell was put into operation for the first time, the electrolyte chamber was filled to the top with granular sodium chloride. The above assembly was then bolted in place in the 18- by 24-inch center opening of the cell with the bottom of the electrodes immersed in the salt. Alternating current was applied to the starting coil to melt the salt in the vicinity of the main electrodes, allowing alternating current to pass between them. The

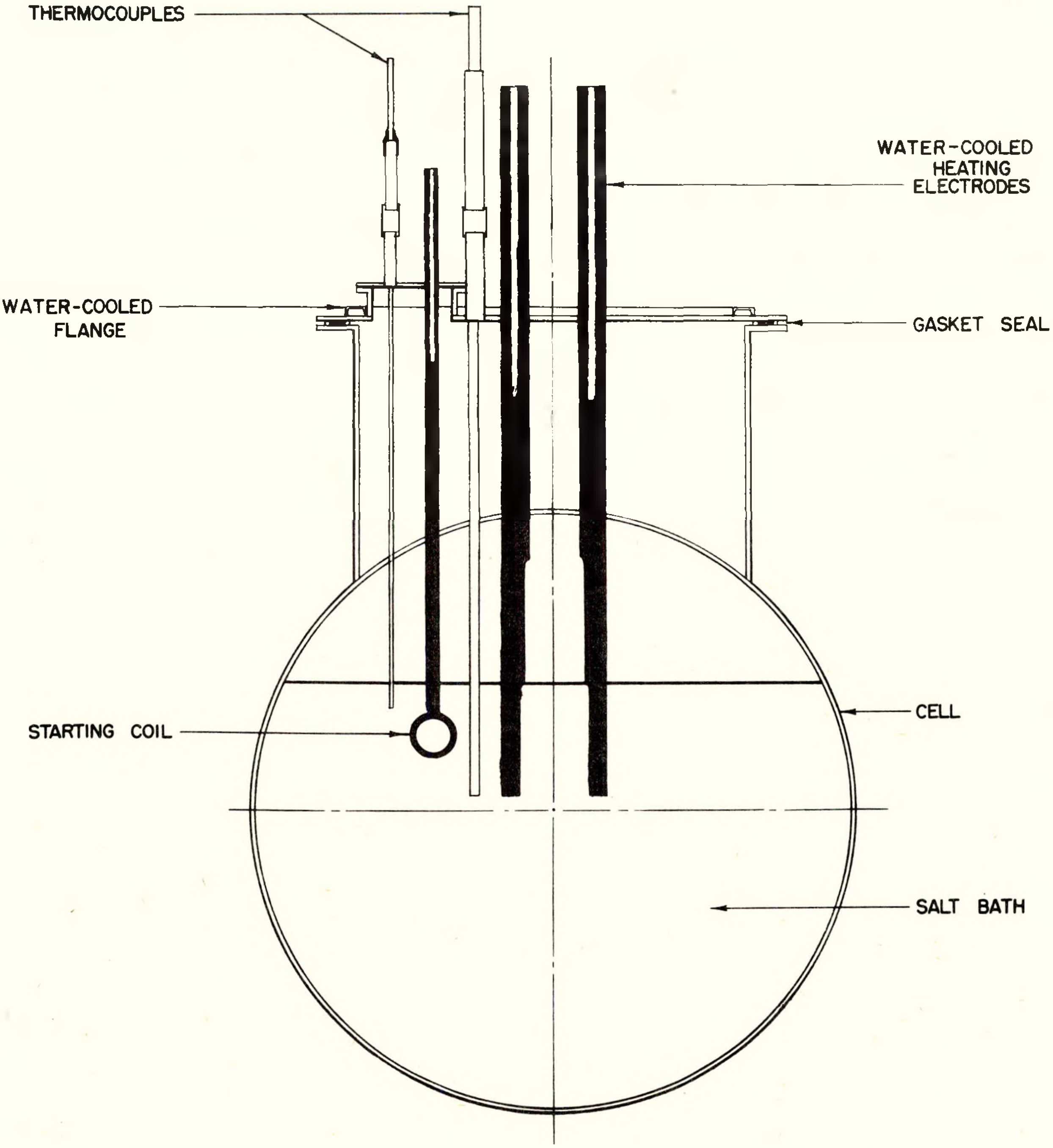

FIGURE 10. - Cross Section of Cell Through Internal Heater.

starting coil was disconnected and raised up out of the bath as soon as the main electrodes took over. Heat (I^2R) for melting the salt and holding the electrolyte at operating temperature was supplied by the resistance of the bath between the two sets of 3-inch electrodes connected in parallel. Automatic controls were used to maintain the temperature at the set point. The voltage of the system could be regulated by raising or lowering the electrodes.

Convection currents at the heater usually proved sufficient to keep the electrolyte well mixed. Operation of the internal heater was satisfactory throughout the test period.[7]

Electrical Components

Direct-current equipment was selected using the diagram shown in figure 11.[8] The rectifier consisted of a 150-kilowatt, three-phase, full-wave unit with sealed, water-cooled germanium diodes. It had a maximum d.c. rating of 10,000 amperes at 15 volts and a control range of 1½ to 15 volts. The unit was furnished complete with a low-voltage a.c. transformer, necessary switch gear, water-cooled heat exchanger, and controls which were arranged for stepless, remote operation.

Power for the internal heater was supplied by a low-voltage, single-phase, 100-kilovolt-ampere transformer having a maximum alternating current rating of 4,000 amperes at 25 volts and a control range of 5 to 25 volts. Switch gear and controls were furnished for stepless, remote operation. All operating controls were placed on the central control panel shown in figure 12. (This photograph also shows one side of the 10,000-ampere cell ready for operation.) Instruments on the panel board included a temperature recorder, two temperature indicators, two over-temperature controls, and a recording ammeter.

Processing Units

Cathode deposits must be stripped, crushed, leached, washed, dried, and screened. The above operations can be highly automated to obtain a product superior to that from the Kroll process, both physically and chemically. Equipment for the leaching, washing, drying, and screening steps is shown in figure 13. Its size was chosen to be such that it could handle a full day's production from the prototype cell in one shift.

Deposits cooled to room temperature in a helium atmosphere were stripped by drawing the cathodes through a split cutting die (fig. 14). No disassembly was necessary for this operation. The deposits, after removal from the cathodes, were passed through a set of saw-tooth rolls to break down any large masses of crystals. The crushing rollers, which intermeshed, were 8-inches in diameter and 18 inches long. They were driven at 10 revolutions per minute by a 5 horsepower motor. When 500 pounds of product had accumulated, the mixture of refined metal and salt was leached for 1 hour in a 5-percent (by volume) solution of concentrated hydrochloric acid in water. Leaching was done in a 200-gallon glass-lined tank equipped with a high-speed propeller-type agitator (3 horsepower, 1,750 revolutions per minute). To obtain high-purity metal (Brinell hardness <100), it is not only necessary to remove all traces of chlorides, but also to effectively separate fines from the coarser fractions of the deposits. Fines are always relatively impure and increase the hardness of the titanium produced if included in the final product. The

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[7] Work cited in footnote 4, p. 2.

[8] Gutzwiller, W. E., How to Pick the Right Rectifier: Chem. Eng., vol. 66, No. 21, 1959, pp. 189-192.

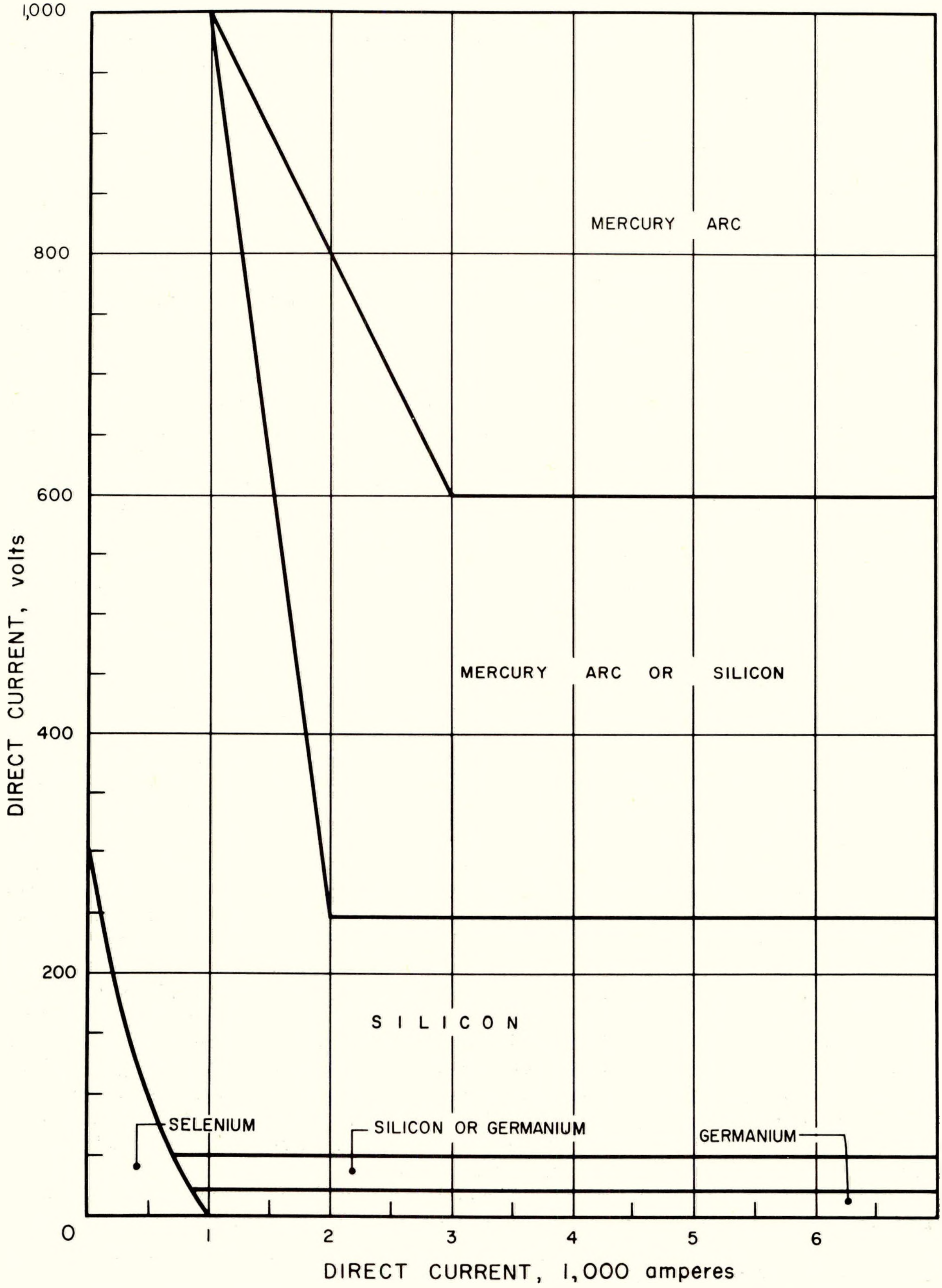

FIGURE 11. - Proper Choice of Rectifier According to Load Requirements.

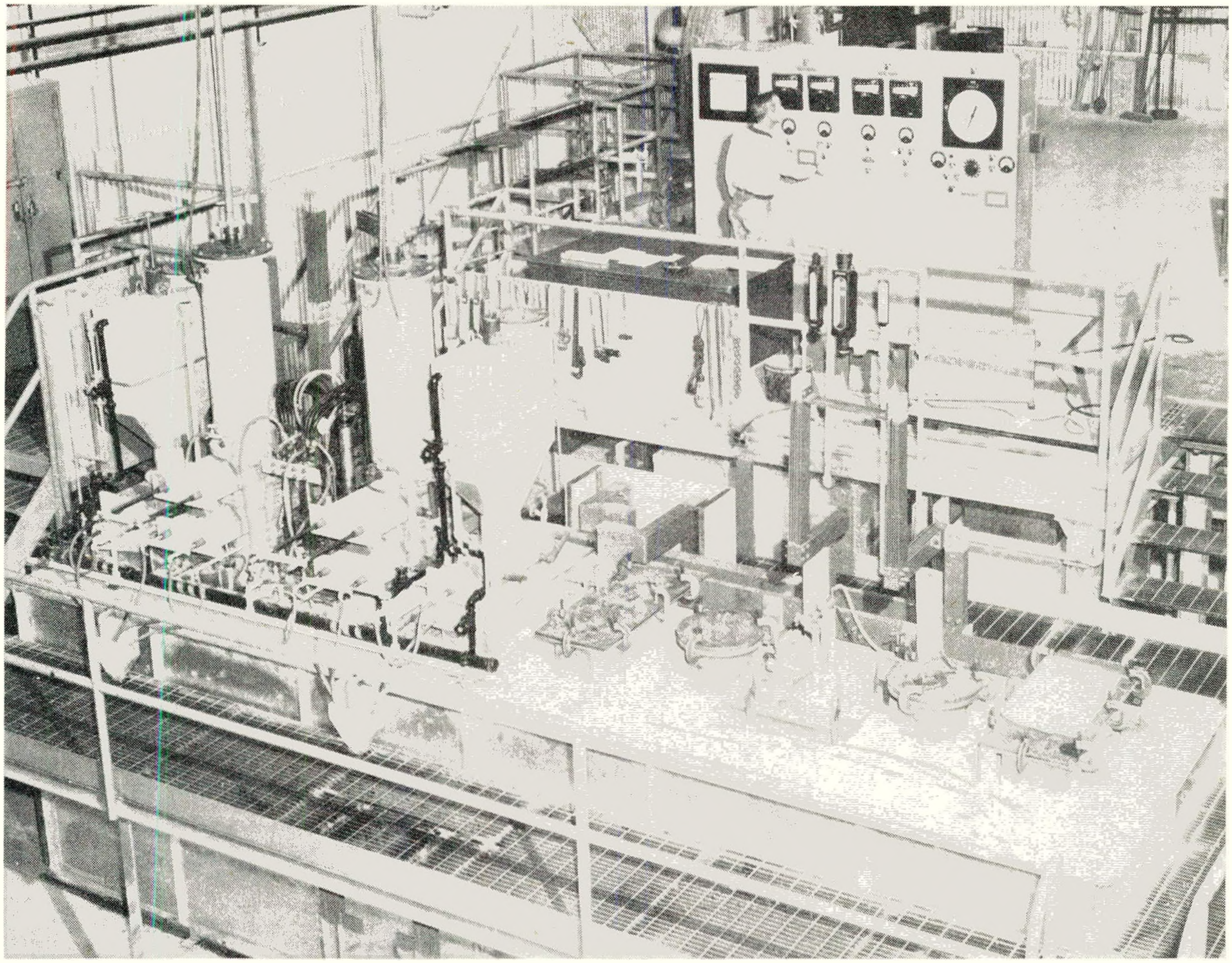

FIGURE 12. - View of Cell With One Side Ready for Operation.

typical relationship between crystal size and hardness is shown by the following analysis of a deposit from the prototype cell.

TABLE 2. - Screen analysis of deposit from 10,000-ampere cell

Screen size of leached metal	Distribution, percent	Hardness, B.h.n.
+8...........	6.4	70
-8 +34.........	80.2	74
-34 +48.........	10.5	132
-48 +120........	1.4	221
-120.............	1.5	-

The largest crystals are normally the softest. In some cases, however, the plus 8-mesh fraction may be harder than the minus-8- plus-34-mesh because of "cap" or "contact material," which, when present, appears in the largest screen size. "Cap" is a skin of metallic titanium that grows out from the cathode across the surface of the bath during electrolysis. "Contact material"

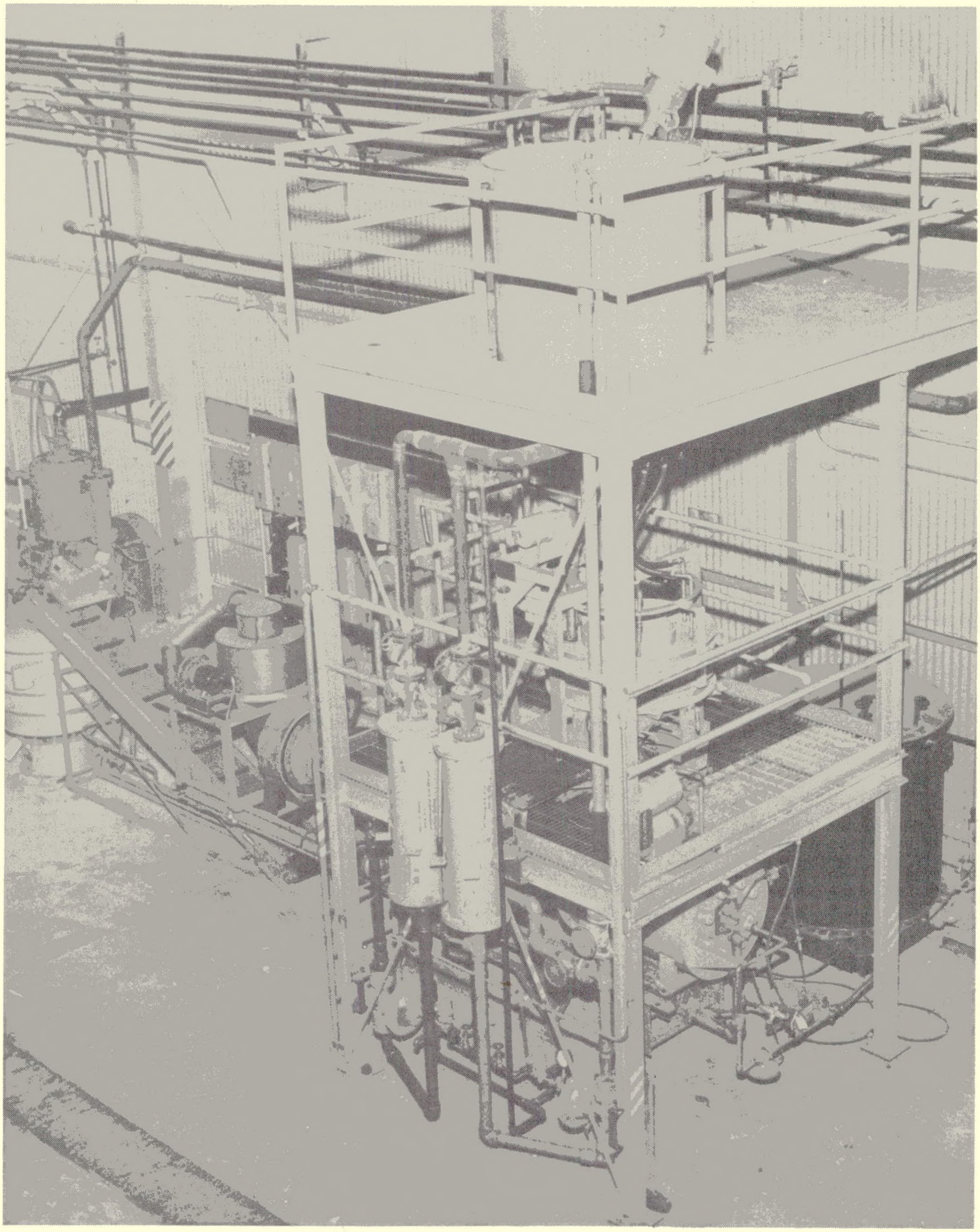

FIGURE 13. - Process Equipment Used for Leaching, Washing, Drying, and Screening.

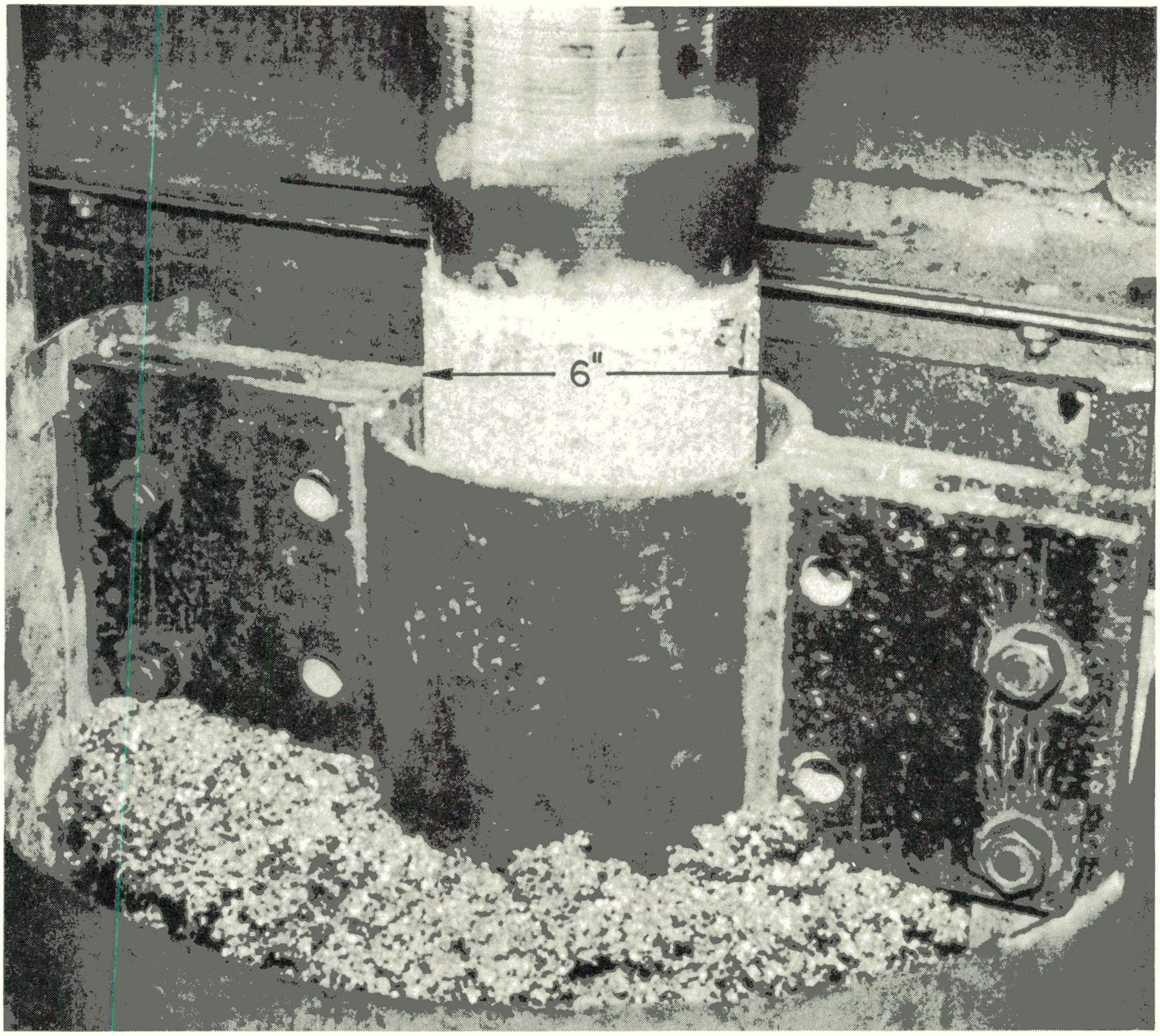

FIGURE 14. - Method of Removing Deposits From Cathodes.

is anode metal picked up from the bottom of the cell on dendrites extending from the cathode to the anode. Both are sometimes encountered in deposits.

In small-scale tests, deposits were leached with a 5-percent (by volume) solution of concentrated hydrochloric acid in water using a water-jacketed glass-lined tank equipped with a portable mixer. This removed the salt from the deposits but did not break down masses of intergrown crystals to any extent. To separate the various crystal sizes, it was necessary to "chop" the leached deposits in a mechanical agitator such as an electric blender. This is, of course, not feasible on a commercial scale. Since no known standard piece of equipment would do a comparable job, it was necessary to order a special agitator for the prototype cell, designed to put a large amount of horsepower into a small volume of solution. Results with this mixer were comparable to those obtained in small-scale tests.

After being leached, the slurry passed into a 3-foot-diameter rotary, horizontal, gravity-fed, vacuum filter. This type of filter was selected because of its high washing efficiency and its ability to handle large, heavy crystals. It was constructed of cast iron coated with epoxy resin and trimmed with Hastelloy C. Auxiliary equipment included two polyvinylchloride-lined diaphragm slurry pumps, two epoxy-coated steel vacuum receivers, a rubber-lined scrubber condenser, and a wet vacuum pump. The titanium crystals were washed with both raw and deionized water after removal of the leach liquor. The final washing had to be thorough enough to remove all traces of chloride ion ($AgNO_3$ test). Deionized water was supplied by a single-stage mixed-bed deionizer, 14 inches in diameter by 84 inches high, having a capacity of 10 gallons per minute. The filter operated well, although plugging of the discharge line from the leach tank and blinding of the filter cloth occurred at times.

The filter discharged into a single-shell, direct-fired, parallel-flow, gravity-fed, rotary dryer, which was 18 inches in diameter by 16 feet 6 inches long. This dryer was provided with combustion controls and a dust collector. Natural gas was used for heating. All of the processing equipment, unless otherwise noted, was constructed of stainless steel. The dryer did not prove satisfactory for handling titanium even though the discharge temperature was kept below 80° C. Fines collected in the cyclone frequently caught fire. The dryer product was also harder than expected. To determine the relative merits of different kinds of dryers, a large sample of offgrade refined metal was split into three equal parts. One part was run through the rotary dryer using a discharge temperature of 80° C., one part was placed in a vacuum dryer held at 65° C., and the third portion was stored overnight in a "dry room" where the relative humidity was maintained at less than one-half percent. Table 3 shows the hardness of each of the portions.

TABLE 3. - Effect of drying operation on hardness of leached metal

Screen size of leached deposit, Tyler	Water removed in rotary dryer, B.h.n.	Water removed in vacuum dryer, B.h.n.	Water removed in "dry room", B.h.n.
+8	114	102	105
-8 +34	158	123	137

The data indicate that a direct-fired dryer should not be used for processing titanium metal of this type. Instead, it should be handled in either a double-shell, indirect-fired, rotary dryer, a low-humidity chamber, or, preferably, a vacuum dryer.

Metal from the rotary dryer, with the exception of fines caught in the off-gas cyclone, discharged onto a conveyor belt feeding a 30-inch-diameter, three-deck, vibrating-screen separator. The necessity of a screening operation is apparent from an examination of the data in table 2. The separator was provided with 8- , 34- , and 84-mesh (Tyler) stainless steel screens. If the plus 8-mesh fraction was contaminated with "cap" or "contact material", it was returned to the cell as anode metal. Otherwise, it was combined with the plus 34-mesh size representing the end product of the process. All metal below 34-mesh was recycled.

Electrolytic conditions were fixed to produce as much refined metal in the minus 8- plus 34-mesh size range as possible. Very large, pure crystals could be obtained by deposition at low current densities for prolonged periods of time. In tests made with the prototype cell, however, current densities were held as high as possible to reduce the cost of operation. Deposits made up of crystals in the minus 8- plus 34-mesh size, moreover, were easier to strip, leach, wash, dry, and composite. A uniform product was obtained, well suited to commercial operation.

CAPITAL COSTS

No attempt has been made to include amortization in the cost data shown in a latter section of this report. As a guide to capital costs, however, prices of the major items (f.o.b. Boulder City, Nev.) required for the project are listed below.

TABLE 4. - Cost of equipment required for production of high-purity titanium[1]

Item	Description	Cost
Electrolytic tanks	2 stainless clad vessels--4 ft. 0 in. by 9 ft. 8-5/8 in. long	[2] $15,824
D.c. equipment	1 150-kw. 3-phase full-wave germanium rectifier	18,225
A.c. equipment	2 100-kv.-a. single-phase supply transformers for internal heaters	[3] 12,390
Control board	1 panel with instrumentation for operation of electrical equipment	1,995
Insulation	16,000 lb. of light-weight castable insulation suitable for use at 1,800° F.	1,651.20
Crusher	1 set saw-tooth rolls with 5-hp. drive	1,510
Filter	1 3 ft.-diameter, rotary, horizontal vacuum filter with 2 diaphragm slurry pumps, 2 filtrate receivers, 1 scrubber, and 1 wet vacuum pump	9,770
Dryer	1 single-shell, direct-fired, parallel-flow rotary dryer with dust collector and combustion controls	7,155
Screen	1 30-inch-diameter 3-deck vibrating-screen separator	2,802.73
Water softener	1 single-stage ultra de-ionizer with ion-exchange resins	1,925

[1] Items costing less than $1,000 and equipment fabricated at the Boulder City Laboratory have not been included in this table.

[2] Similar vessels of unclad 1-inch mild steel plate, costing $11,876 would probably have been more satisfactory.

[3] Only one was required in actual operation.

STARTUP PROCEDURE

When fabriation of equipment had been completed, two electrolyte chambers were positioned inside a supporting shell (see figure 12) made from ¼-inch steel plate. A temporary "A" frame was used to hold them in place until the space between the chambers and the shell could be filled with insulation. The outer surfaces of these vessels were oiled, and castable insulation was rammed around the lower half of each as shown in figure 15. Forms were used to prevent mortar entering the spaces provided for expansion at the ends of the cell. After the castable insulation had set, the "A" frame was removed, and the shell was filled to the top with loose insulation. This was, in turn, topped with a thin layer of castable insulation to provide a working surface. The 10,000-ampere rectifier, the supply transformers for the internal heating elements, and the central control panel were installed at the same time. Platforms were then erected around the cell, and the superstructure, bus bars, and pipe were put in place.

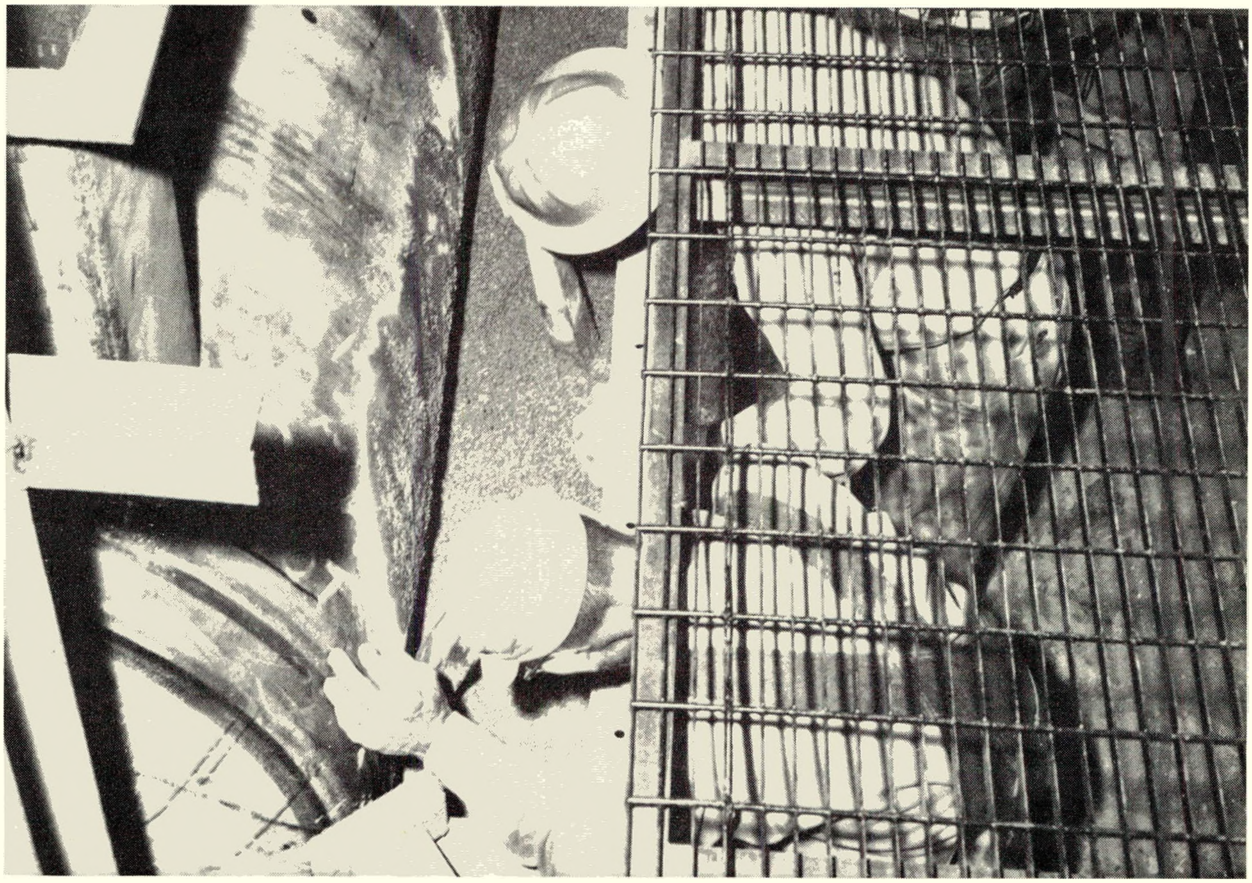

FIGURE 15. - Placing of Insulation Around the Electrolyte Chamber.

Only one-half of the prototype cell was prepared for operation. Either side could handle the full 10,000-ampere output of the rectifier. The second unit was kept on standby in case the first should have to be removed from service. Before heating elements were installed, both anode material and salt were added to the cell through the large center opening in the electrolyte chamber. A total of 800 pounds of offgrade Kroll sponge was spread uniformly across the bottom, covering it to a depth of 7 inches. The sponge consisted of minus 35-mesh fines (Brinell hardness 211) produced at the Boulder City Laboratory during the development of the Kroll process. Table 5 shows its average chemical analysis.

TABLE 5. - Analysis of anode material used for initial cell operation

Impurity	Percent	Impurity	Percent
Fe......	0.086	H.......	0.01
Mg......	.35	C.......	.032
Na......	.001	Cl......	.08
N.......	.016	V.......	.005
O.......	.27	S.......	.004

After the anode material was in place, 8,000 pounds of vacuum-refined, granular sodium chloride was added to the cell, filling it to the top. The salt, which had a minimum NaCl content of 99.96 percent, was used as it was received with no treatment of any kind. The heating elements were bolted in place and the entire assembly was pressurized (5 pounds per square inch gage) with Freon 12 and checked for leaks using a "halide" torch. This method of detection depends upon changes in the color of a propane flame. It is ideal for quick location of fair-sized leaks. A large number of small leaks was found in various joints and welds, mostly in piping. After these had been repaired, the cell was evacuated to remove most of the Freon and air. The vacuum (27 inches mercury) held well overnight, indicating that the cell was ready for operation.

A constant purge with argon was then started to remove traces of air from the cell and sweep out moisture given up by the salt during fusion. Cooling water to the electrodes, slide valves and heating elements was turned on. The heating elements were energized for the first time on December 15, 1958. A slow initial heating rate was used to dry out the large mass of insulation and to relieve stresses in welded joints (the electrolyte chambers had been sand-blasted but not stress-relieved during fabrication). After 6 hours enough salt had melted to allow the main electrodes to take over. The starting coil was disconnected and the power input to the heater was held at between 2,000 and 2,500 amperes overnight. The voltage dropped steadily (from 19 to 10 volts) during this period as the pool of molten salt within the cell increased in size.

On December 16, 1958, the power input was raised to 3,000 amperes (at 11 volts). This represented only about 30 percent of transformer capacity (100 kilovolt-amperes). Since a faster rate of heating was desirable, all four electrodes were raised on December 17 to increase the drop across the bath to 17 volts. Following this change, the temperature increased much more rapidly but did not reach 850° C. until December 19, 100 hours after energizing the starting coil. Power to the internal heater was disconnected on this date, and the cell was allowed to cool to room temperature.

On January 5, 1959, the heater assembly was removed and the inside of the cell was inspected. It was found that the sodium chloride has melted cleanly with no discoloration or crust formation. Very little sublimate was present, and the inner walls of the cell showed no sign of corrosion. The space created in the cell by fusion of the initial charge was then packed with 2,287 pounds of "master mix" (a mixture of NaCl and $TiCl_2$ containing about 19 percent soluble titanium). To minimize hydrolysis, the "master mix" was not crushed but merely broken up into pieces small enough to pass through the large center opening of the cell.

"Master mix"[9] is a difficult material to handle even under the best of conditions. It is prepared at the Boulder City Laboratory by reacting stoichiometrically determined amounts of $TiCl_4$ and sodium (at 650° C.) to produce the $2NaCl\text{-}TiCl_2$ eutectic that melts at 605° C. Actually, a mixture with more or less $TiCl_3$, depending upon the care used in preparation, is obtained. That used in the prototype cell contained 18.5 percent soluble titanium and had an average effective valence (A.E.V.) of 2.4. It was almost black in color with a "woody" structure. Pieces broke down into long, sharp needles which were extremely hygroscopic, dissolving in their own water of hydration if allowed to stand in contact with moist air. Full safety equipment had to be worn when adding the "master mix" to the prototype cell, since it burned the skin on contact and caused nasal irritation. Sublimate formed in the cell during operation also was irritating. It is recommended that operators wear respirators whenever they are exposed to any fumes or dust containing titanium chlorides.

The internal heater was reinstalled on January 9, 1959, and approximately 450 pounds of sodium chloride was packed around the starting coil. Thermocouples at the ends of the cell showed that the bath was again up to temperature on January 14. The first metal was refined on January 19. A number of deposits must always be made at a low current density (500 amperes per square foot) before a new cell will produce satisfactory metal. The number required depends upon the purity of sodium chloride and "master mix" used in making up the electrolyte. During the conditioning period, cathode deposits consist of very hard, finely divided crystals. Drainage is poor, current efficiency is low, and the soluble titanium content of the electrolyte gradually increases as the average effective valence approaches 2.0. No improvement is noted until impurities, especially combined oxygen, have been removed from the electrolyte. While the constituents used in making up the electrolyte for the prototype cell were reasonable pure, they did contain small amounts of $TiCl_3$, Na_2SO_4, and other compounds that will combine with metal deposited at the cathode. Any moisture present also forms oxychlorides, as shown in equation (1).

$$TiCl_2 + H_2O \rightarrow TiOCl_2 + H_2\uparrow \qquad (1)$$

The initial deposit consisted of small bright crystals covered with a heavy layer of black salt. The bath itself had a dark, opaque color although its composition (soluble titanium = 3.84 percent, A.E.V. = 2.33) was as expected. Metal from the next three deposits was extremely hard and gave off

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[9] Homme, V. E., Wong, M. M., and Baker, D. H., Jr., Sodium Reduction of Titanic Chloride: Bureau of Mines Rept. of Investigations 5398, 1958, 29 pp.

a large quantity of hydrogen sulfide when leached. After this, however, both crystal size and Brinell hardness of refined metal began to improve. The color of the electrolyte also changed to a clear bluish-green hue. At the same time the soluble titanium content rose to 4.04 percent and the A.E.V. decreased to 2.14.

Results obtained during initial cell operation are shown in table 6.

TABLE 6. - Results obtained during conditioning of electrolyte

Deposit	Cumulative a.-hr.	Crystal size, +34-mesh, pct.	-8- +34-mesh, B.h.n.	Current efficiency, pct.	Salt dragout, pct. of deposit
5......	48,700	14.5	235	38.9	71.6
6......	64,100	26.0	231	39.3	67.8
7......	77,300	73.4	163	55.0	57.3
8......	91,700	69.2	121	55.0	59.5
9......	111,700	72.1	105	67.3	44.2
10......	131,700	64.2	96	61.6	46.0
11......	151,700	67.0	93	64.0	51.1

Since the deposit from test 11 indicated that the electrolyte was fairly well conditioned, it was decided to start a series of runs to determine the effect of different variables on cell operation.

OPERATING VARIABLES

Before the prototype cell could be operated on a continuous basis to obtain cost data, it was necessary to determine optimum electrolytic conditions. Obvious variables were electrolyte composition, temperature, time of deposition, ratio of anode to cathode area, and current density.

The optimum electrolyte composition (87.5 percent NaCl--12.5 percent $TiCl_2$) had been fairly well established in previous small-scale tests. In spite of its high melting point (801° C.), sodium chloride makes an excellent base for fused-salt electrolytes. It has good thermal stability, is not hygroscopic, and offers a wide potential span between anodic and cathodic decomposition limits. A definite relationship exists between the amount of soluble titanium present in an electrolyte and the maximum cathode current density that will produce high-purity metal. This is shown in figure 16. Electrolytes containing less than 5 percent soluble titanium had lower maximum allowable cathode current densities. On the other hand, higher concentration of soluble titanium did not appreciably increase the allowable density. The greater loss of titanium caused by salt adhering to the deposits also made higher concentrations less attractive. In work with the prototype cell, the soluble titanium content of the electrolyte was, therefore, held between 4 and 5 percent.

In small scale tests, chemically pure sodium chloride costing $0.21 per pound was used to prepare the electrolyte. The use of this type of salt could be expensive in operations on a commercial scale, since considerable salt is

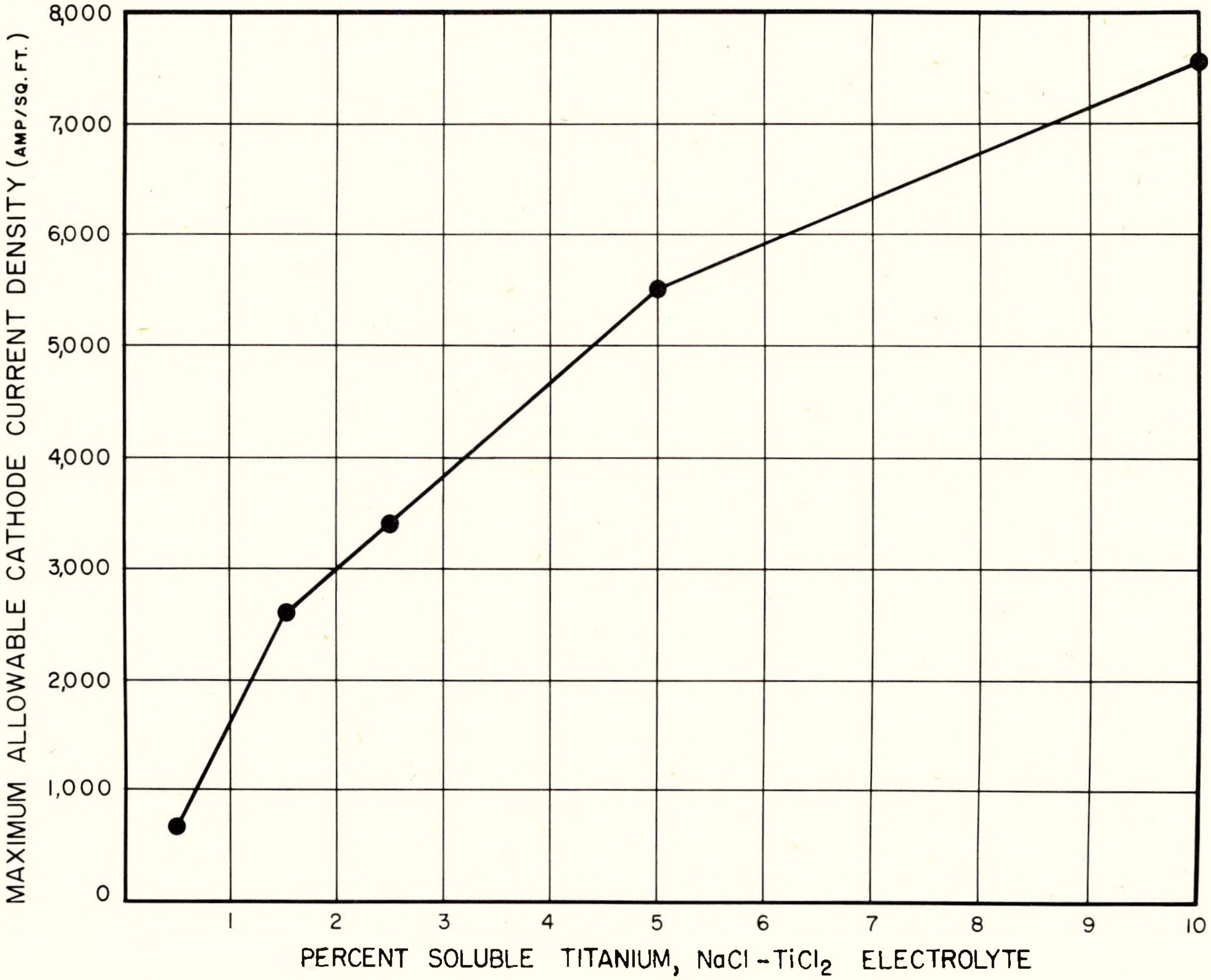

FIGURE 16. - Effect of Soluble Titanium Content of the Electrolyte on Maximum Allowable Cathode Current Density.

removed with the cathode deposits in the electrorefining of titanium. Attempts to use less expensive forms of sodium chloride such as rock salt had not been successful heretofore, since the contained oxygen-bearing radicals (mainly sulfates) tended to oxidize the deposits. It was therefore decided to try vacuum-refined salt having a minimum purity of 99.96 percent, which was available at only $0.02 per pound delivered in Boulder City. Results were comparable in every respect to those obtained with the more expensive reagent grade of salt. Vacuum-refined salt was used as it was received to prepare the electrolyte for the prototype cell.

The temperature of the cell is limited by the freezing point of the electrolyte and the structural strength of the mild steel used in equipment. Fig-17[10] shows a phase diagram for the NaCl-$TiCl_2$ system. According to this

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[10] Komarek, K., and Herasymenko, P., Equilibrium Between Titanium Metal and Solutions of Titanium Dichloride in Fused Sodium Chloride: Jour. of Electrochem. Soc., vol. 105, No. 4, 1958, pp. 216-219.

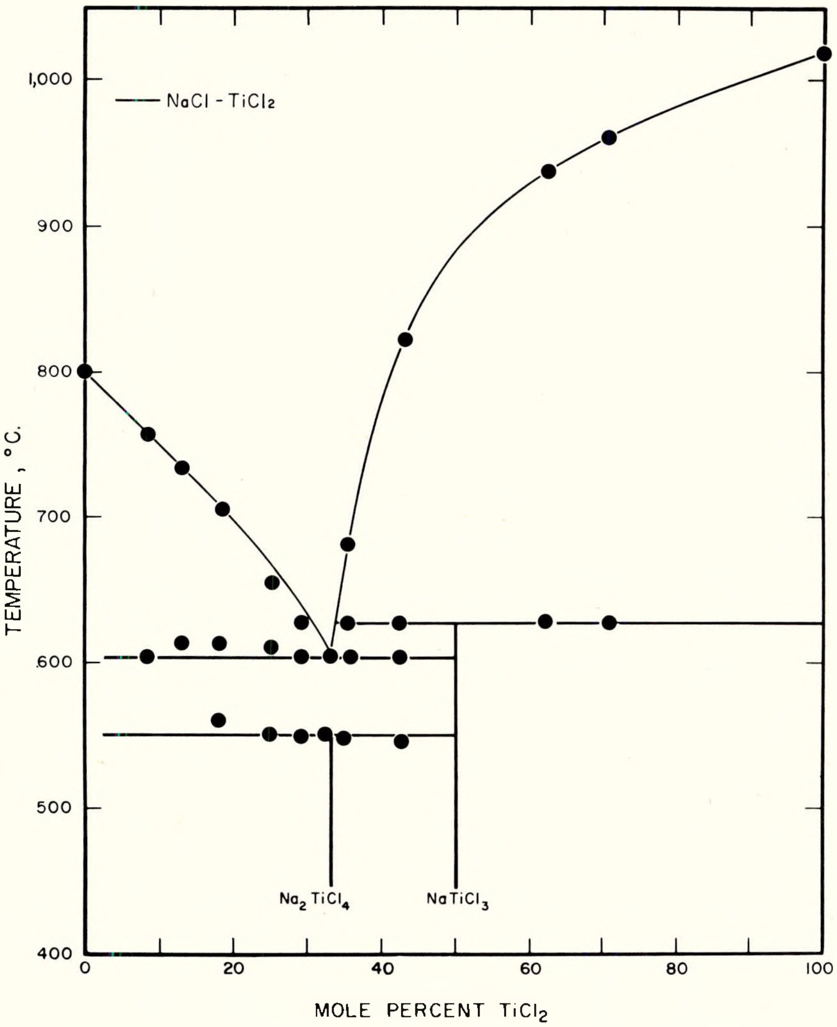


FIGURE 17. - Phase Diagram for the NaCl-$TiCl_2$ System.

diagram, the melting point of an electrolyte containing 5 percent soluble titanium is 770° to 780° C. The short-time proportional limit of low carbon steel approaches zero at 650° C. It is therefore, desirable to keep the electrolyte as close to the freezing point as possible. A temperature of 850° ± 20° C. was used in all work with the prototype cell. Below 830° C. dragout became prohibitive, while at 870° C. the anode and cathode receivers began to lose alinement.

Time of deposition is a most important variable since it largely determines major operating costs such as labor. This fact was first realized when the prototype cell was operated on a continuous basis to obtain cost data. Both cost and current efficiency consistently decreased as the number of ampere-hours per deposit was increased, using the same initial cathode current density in each case. There exists, of course, a point of maximum return in relation to cell design. In tests with the prototype cell, the optimum deposition time was found to lie between 36,000 and 40,000 ampere-hours, shown in table 7.

TABLE 7. - Effect of time of deposition on current efficiency and cost of refining

	Ampere-hours per deposit	Current efficiency, percent	Cost per pound of refined metal, dollars
1st continuous run...	28,000	67.3	0.84
2d continuous run....	36,000	63.1	.52
3d continuous run....	40,390	56.5	.53

The decrease in current efficiency with deposition time is believed to be caused by a drop in cathode current density. During electrolysis the cathode surface area increases enormously. The current density decreases proportionally until the re-solution rate finally become equal to the deposition rate as shown in equation (2).

$$Ti + TiCl_3 \rightleftarrows TiCl_2 \qquad (2)$$

Since the optimum number of ampere-hours per deposit is influenced by cell design, it must be determined experimentally.

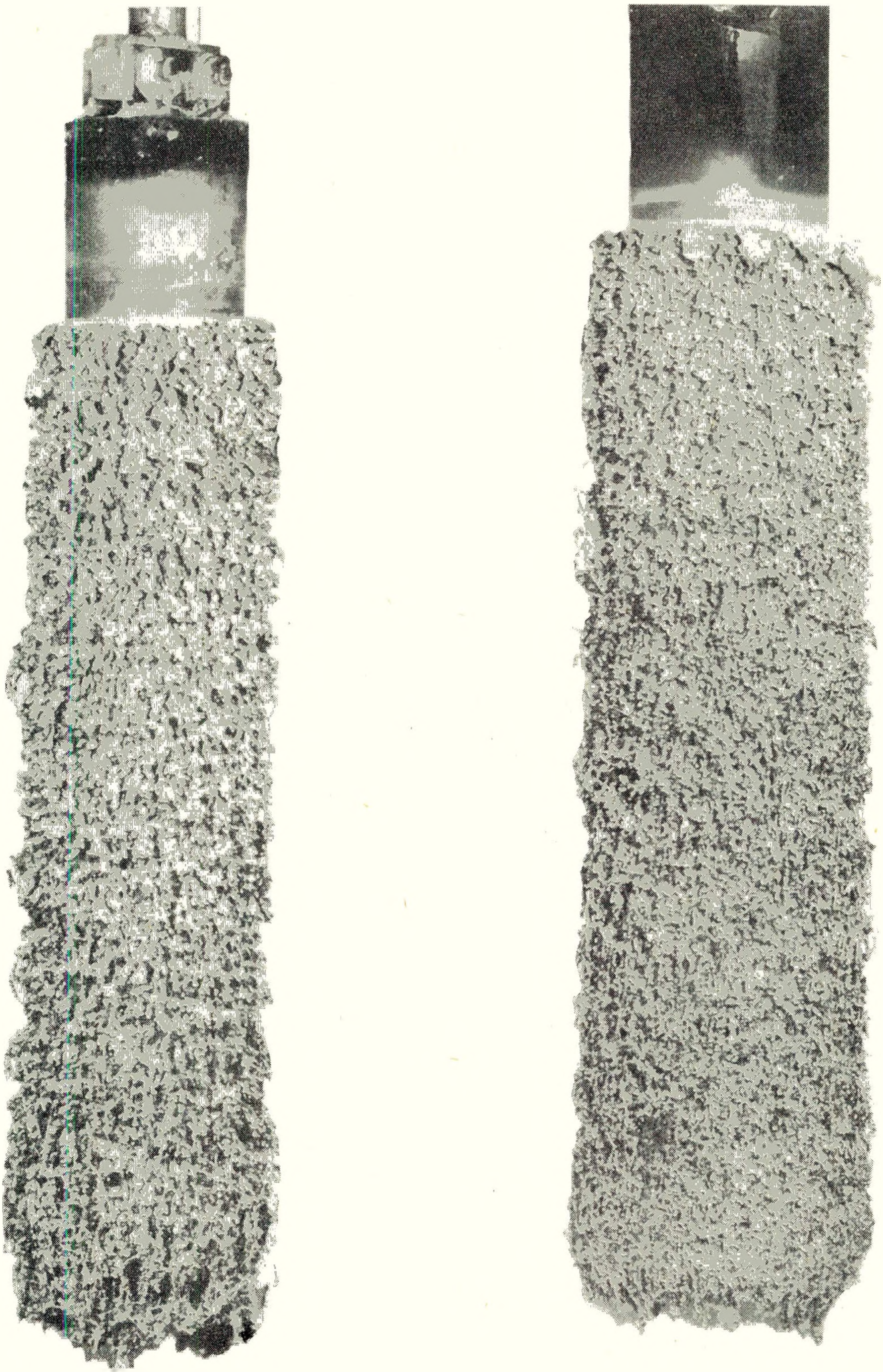
Current density is another very important variable since it affects crystal size, dragout, capital cost, and power consumption. Before any continuous runs were made, the cell was operated at 4,000, 6,000, 8,000, and 10,000 amperes, while other variables, including the total number of ampere-hours (24,000), were kept as constant as possible. Table 8 shows the average results from 24 tests which were made to establish the effect of cathode current density on the previously mentioned production characteristics.

TABLE 8. - Effect of cathode current density on cell operation

D.c. input			A.c. input,	Total power consumption,	+34-mesh fraction		Current efficiency,	Bath dragout,
A.	V.	Kw.-hr.	Kw.-hr.	kw.-hr./lb.	Pct. of deposit	B.h.n.	pct.	pct.
4,000	2.3	56	238	10.0	69.6	93	62.4	40.0
6,000	3.5	85	122	7.0	80.1	86	62.8	32.7
8,000	4.6	109	68	5.7	84.9	82	65.9	22.9
10,000	5.7	135	16	5.1	84.0	88	63.0	24.0

The test series shown in table 8 indicated that an initial cathode current density of approximately 1,000 amperes per square foot (8,000 amperes d.c. input) would give the best results. This density was used in all subsequent tests. Power consumption, for heating plus electrolysis, was very low, reaching a minimum of 9,000 amperes. With a d.c. current of such magnitude, the heat required to maintain an operating temperature of 850° C. was supplied entirely by the electrolytic current. Using 10,000 amperes, the capacity of the rectifier, the temperature of the cell increased slowly (about 4° C. per hour) with the internal heater disconnected.

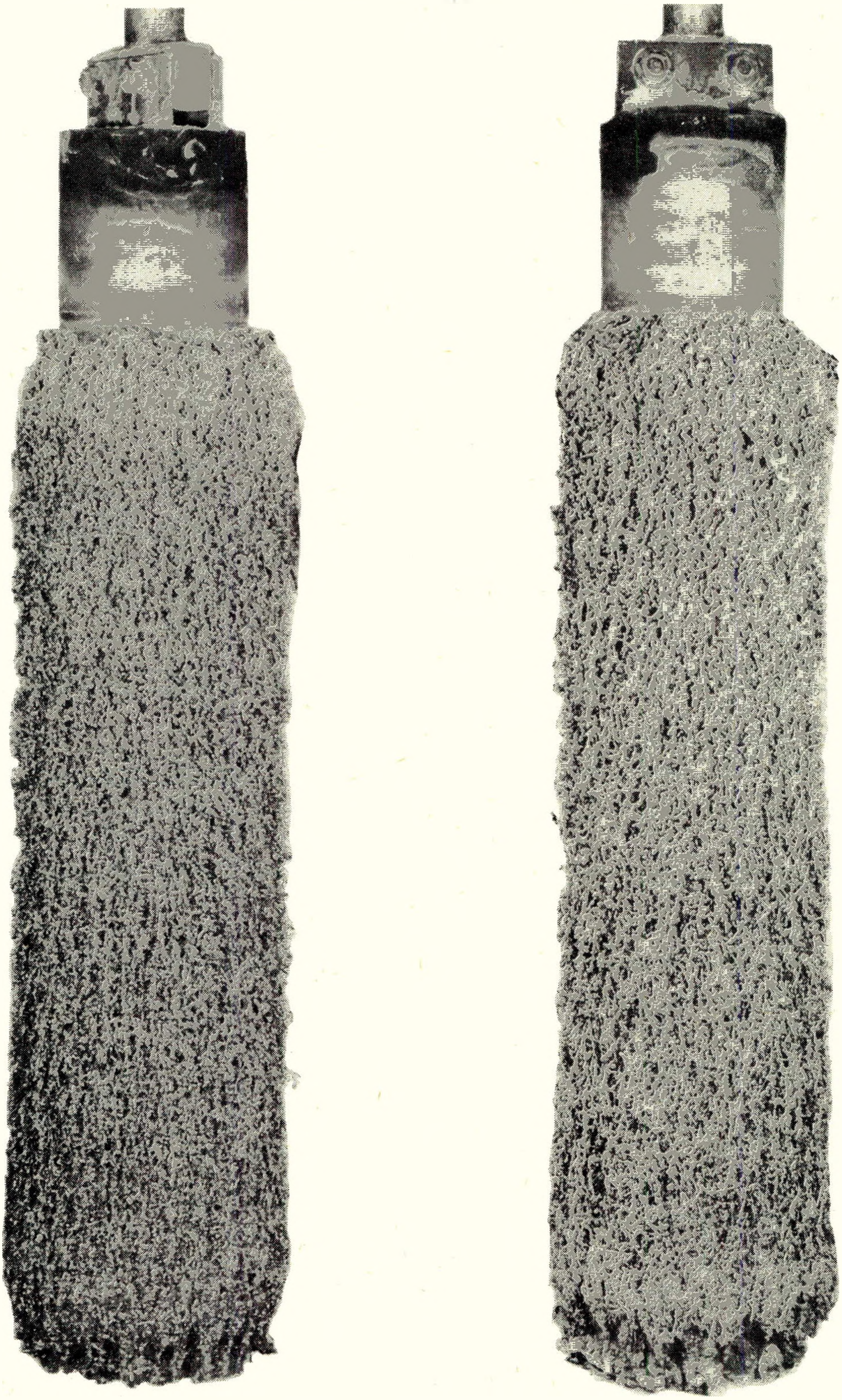
Figures 18 and 19 show the type of deposit obtained at each of the four current densities. Deposits formed at the lower densities (500 and 750 amperes per square foot) contained larger crystals but also had a greater proportion of fines. At 1,000 amperes per square foot, the crystal size was very uniform. In all of the tests, the high rate of crystal growth relative to the rate of nucleation caused titanium to deposit in a dendritic form that was relatively easy to strip. Titanium occurs in two crystalline forms. At about 882° C. the hexagonal close-packed alpha structure changes to a body-centered cubic (beta) crystal. The deposits consisted largely of six-sided crystals of alpha titanium, indicating that the alpha-beta transition temperature had not been reached at the cathode during electrolysis. The uniformity of the deposits from top to bottom (see figures 18 and 19) demonstrates the excellent throwing power of the bath.



A

B

FIGURE 18. - Deposits Obtained at Cathode Current Densities of (A) 500 Amperes per Square Foot and (B) 750 Amperes per Square Foot.



A

B

FIGURE 19. - Deposits Obtained at Cathode Current Densities of (A) 1,000 Amperes per Square Foot and (B) 1,250 Amperes per Square Foot.

Conditions to be used in leaching cathode deposits were also investigated, since this is an important part of the electrorefining process. The best solid-to-liquid ratio, that is, the maximum amount of deposit per unit of solution that could be kept in suspension by the agitator used with the prototype cell, was about 2.5 pounds per gallon. Large-scale leach tests using agitation times of 30 minutes, 1 hour, and 2 hours showed the 1-hour period to be adequate. In the 30-minute test, the cathode deposits were not completely broken down into individual crystals, and in the 2-hour test, the results were no better than in the 1-hour test.

To determine the effect of acid concentration, cathode deposits were leached for 30 minutes with 5, 10, 15, 20, and 25 percent by volume of concentrated HCl in water, using the solid-to-liquid ratio that was just given. The leach time was deliberately kept short to bring out any differences in the rate of disintegration. Table 9 shows the results that were obtained.

TABLE 9. - Effect of acid concentration on results obtained in leaching

HCl concentration, pct. by vol.	Size distribution of leached metal, pct.					Hardness of leached metal, B.h.n.		
	+8	-8 +34	-34 +48	-48 +120	-120	+8	-8 +34	-34 +48
SOP[1]	49.5	38.3	9.0	1.2	2.0	68	76	91
5	52.4	38.3	6.3	.9	2.1	73	82	144
10	59.2	31.5	6.1	1.0	2.2	71	92	161
15	55.2	35.0	6.8	1.2	1.8	71	91	139
20	56.9	33.2	7.6	.9	1.4	73	92	167
25	46.5	42.3	6.7	.6	3.9	76	92	176

[1] Procedure used in small-scale work.

Acid concentration had little effect on either the rate of disintegration (relative size distribution of crystals in final product) or the purity of the metal produced. Titanium from the special leach tests was harder than that treated in the usual way, because the leach period used in the special tests was too short to effectively separate fines from coarser crystal sizes.

To determine how acid concentration affected metal recovery (that is, how much titanium was dissolved by acid during leaching), several cathode deposits were blended and washed with tap water until free of salt. This was accomplished by running a continuous stream of water into the bottom of a container holding the cathode deposits. The water percolated up through the titanium and overflowed to waste. Most of the $TiO_2.XH_2O$ formed by hydrolysis was removed in the overflow. Care was taken in handling the deposits to avoid breaking up aggregates of crystals. After treatment, the metal appeared clean and bright, but when dried, it turned various shades of blue and yellow. The discoloration was probably caused by a thin film of $TiO_2.XH_2O$ on the surface of the metal. Five hundred gram portions of the washed and dried metal were leached with 5- , 10- , 15- , 20- , and 25-percent (by volume) concentrations of HCl in water, using the same conditions as those in the preceding test. One control portion was treated only with water. The results of these tests are shown in table 10.

TABLE 10. - Effect of acid concentration on metal recovery during leaching

HCl concentration, pct. by vol.	Metal weight after leaching, g.	Size distribution of leached metal, pct.					B.h.n.	
		+8	-8 +34	-34 +48	-48 +120	-120	+8	-8 +34
SOP[1]...........	-	17.1	66.8	13.1	1.1	1.9	68	72
0[2]............	495.0	20.3	62.7	13.9	.5	2.6	83	94
5.............	497.5	20.5	62.4	13.6	.6	2.9	79	89
10............	496.9	23.0	59.1	14.6	.5	2.8	80	87
15............	498.0	22.8	61.7	12.7	.4	2.4	76	83
20............	495.7	14.7	65.4	16.6	.5	2.8	73	81
25............	495.6	21.4	60.7	13.9	1.0	3.0	74	81

[1] Procedure used in small-scale work.

[2] Metal leached with water only.

Metal for this test was deposited at a higher current density and therefore contained more minus 8- plus 34-mesh material than that obtained in the preceding tests. No hydrogen evolution from, or coloration of, the leach solution occurred, and samples that were leached in the 15- , 20- , and 25-percent acid solutions were not discolored after being dried. The resistance of titanium to attack by the more strongly acidic solutions was surprising, since the metal is said to react with concentrations of HCl above 3 percent. There was a small decrease in the weight of all lots treated, but this was probably the result of handling losses during leaching, washing, drying, and screening. As in the first series of tests, acid concentration had little effect on the rate of "chopping" or hardness of the metal. The test results indicate that only enough acid should be used during leaching to prevent hydrolysis of subvalent titanium compounds. However, since considerable acid is consumed by the $TiCl_2$ in the salt removed and bath with the deposits, 5 percent by volume of HCl in water is considered to be the minimum amount suitable for general use.

To determine if deionized water, which adds to the expense of the process, was required for washing leached metal, a series of cathode deposits was treated in the usual way, and then portions were thoroughly washed with both raw and demineralized water. Table 11 gives the results of the experiment.

TABLE 11. - Comparison of raw and deionized water for washing final product

Deposit screen size	Metal washed with raw water				Metal washed with deionized water			
	B.h.n.	Na[1]	Cl[1]	O[1]	B.h.n.	Na[1]	Cl[1]	O[1]
+8........	65	0.018	0.04	0.015	66	0.017	0.04	0.014
-8 +34.......	73	.025	.05	.015	73	.022	.05	.015
-34 +48.......	87	.021	.05	.035	81	.020	.07	.028

[1] Analysis in percent.

There appeared to be little advantage in the use of deionized water. Washing with raw water, however, left a film on the titanium after it dried which gave the metal a dull, grayish appearance. This film was evidently too thin to affect the chemical analysis, but it detracted from the appearance of the metal.

COST DATA

The cost of electrorefining offgrade Kroll sponge was determined by continuous operation of the prototype cell for 10-day periods. Enough metal was produced in this time to permit a realistic evaluation of cell performance. One 20-day run was also made to confirm cost data and determine the effect of prolonged operation.

The first 10-day period was started on September 22, 1959, and completed on October 1, 1959. Two 6-inch-diameter cathodes were used with their immersion adjusted to 30 inches. Electrolyte composition, temperature, and the amount of anode material in the cell were held as constant as possible. Forty-two deposits were made, 11 at 9,000 amperes for 3 hours, and 31 at 7,000 amperes for 4 hours. Overheating of the rectifier prevented making all deposits at 9,000 amperes. Two men were employed per shift, one operator and one assistant.

The molten sodium chloride electrolyte (total weight = 10,900 pounds) contained 4.06 percent soluble titanium with an average effective valence of 2.19 at the start of the production period. The high valence indicates that the electrolyte was not fully conditioned. In normal operation, the A. E. V. varies between 2.05 and 2.10. Electrolyte depth was 36 inches, and the nominal temperature was 850° C. No salt was added to the cell at any time during the 10-day run. When the 10-day period ended, the electrolyte contained 4.32 percent soluble titanium with an A.E.V. of 2.13. The depth had decreased to 34 inches, which was brought back to 38 inches by the addition of 800 pounds of vacuum-refined salt.

The maximum number of ampere-hours per deposit was limited to approximately 30,000 by the physical dimensions of the cell (that is, by the 12-inch slide-valve openings). Larger deposits stuck in the cathode nozzles. During the 10-day production run, anode material (roughly equal in weight to that withdrawn in deposits) was dropped into the cell on alternate shifts. Its composition is given in table 5. Total weight of all deposits produced was 1,865 pounds. The weight of refined metal remaining after leaching was 1,190 pounds. The difference, 675 pounds, represents salt removed from the electrolyte with the deposits. A screen-size analysis of a 364-pound sample of refined metal is given in table 12.

TABLE 12. - Screen size and hardness of refined metal from first 10-day period

Screen size (Tyler)	Weight of fraction, lb.	Size distribution, pct.	Hardness, B.h.n.
+8......	21	5.8	89
-8 +34....	292	80.2	95
-34 +84....	45	12.4	189
-84........	6	1.6	264

An accurate record was kept of all costs (labor, power, dragout, maintenance, helium, and utilities). A time study was also made to determine the labor required for each manipulation involved in cell operation. To determine labor costs, only actual working time was considered. The total time needed to refine 1,190 pounds of metal was 194.9 man-hours, distributed as shown in table 13.

TABLE 13. - Labor distribution, first 10-day period

Job	Man-hours
Adjusting controls......................	12.0
Changing receivers......................	69.0
Purging receivers.......................	20.4
Stripping cathodes......................	71.8
Adding anode metal......................	9.3
Miscellaneous tasks.....................	12.4

Some operations, such as changing receivers and stripping cathodes, required both an operator ($3.05 per hour) and an assistant operator ($2.68 per hour). Other operations required either an operator alone (adjusting controls) or an assistant operator alone (purging receivers and adding anode material to the cell). Miscellaneous tasks included changing helium cylinders, minor repair jobs, checking cooling water rates, and correcting leaks (the cell had to be given a static-pressure test occasionally, since not even the smallest leak could be tolerated if high-purity metal was to be produced). Table 14 gives the cost of labor per pound of refined metal on the basis of the wage rates just given.

TABLE 14. - Cost of labor per unit operation, first 10-day period

Job	Per pound
Adjusting controls..............	$0.031
Changing receivers..............	.166
Purging receivers...............	.046
Stripping cathodes..............	.173
Adding anode metal..............	.021
Miscellaneous tasks.............	.028

The total labor cost was $0.46 per pound. Labor is the major expense in electrorefining titanium.

Power was required both for electrorefining (d.c.) and to maintain the cell at operating temperature (a.c.). During the first 10-day series, the internal heater operated continuously at an average current input of 2,640 amperes at 11.0 volts. Total power consumption was 6,970 kilowatt-hours or 5.86 kilowatt-hours per pound of metal refined. Electricity was available from Hoover Dam at a cost of 1 cent for 2 kilowatt-hours; therefore, the cost of heating the cell was $0.029 per pound. Average electrolyte temperature (at the location of the thermocouples) was 847° C. during the 10-day period. The germanium rectifier supplied 897,700 ampere-hours. Based on the 1,190 pounds of metal recovered, current efficiency ($Ti^{++} \rightarrow Ti$) averaged 67.3 percent. Total power consumed in electrolysis was 5,019 kilowatt-hours (11 deposits--9,000 amperes--5.5 volts; 31 deposits--7,000 amperes--3.9 volts). Average power consumption for electrolysis was, therefore, 4.22 kilowatt-hours per pound of metal refined. This is equivalent to a cost of $0.021 per pound. The overall power cost was $0.05 per pound of metal.

A total of 675 pounds of salt was removed from the electrolyte with the deposits. This salt was not recovered from the leach solution. Average soluble titanium content of the electrolyte during the 10-day period was 4.19 percent. The quantity of titanium, in the form of dichloride, lost in dragout was, therefore, 28.3 pounds. The cost of reducing $TiCl_4$ to $TiCl_2$ with sodium to make the "master mix" used as electrolyte is not known, but it will be assumed that titanium in the form of $TiCl_2$ has a value of $1.00 per pound. On this basis, loss of titanium in salt removed with deposits amounted to $0.024 per pound of metal refined. The vacuum-refined sodium chloride cost $2.26 per 100 pounds (all prices shown in this report are less-than-carload lot, f.o.b. Boulder City Laboratory). Makeup came to $15.25, or $0.013 per pound of metal produced. The overall cost of dragout was $0.04 per pound of refined titanium.

To maintain an inert atmosphere within the cell, 14 cylinders of helium costing $16.15 each (including $12.15 freight) was required. Total cost of helium was $226.10, equivalent to $0.19 per pound of metal refined. This expense was much higher than had been expected. Since helium is used chiefly for purging receivers between runs, the amount required might be reduced somewhat by use of a shorter purge period. The cost of helium would, of course, be drastically reduced if enough cells were in operation to justify its purchase in large quantities such as tank-car lots.

To process (crush, leach, wash, dry, and screen) deposits stripped from the cathodes, 19.5 man-hours was required. The total labor cost (one operator plus one assistant operator) was $56.00, or $0.047 per pound of metal. Six carboys of concentrated hydrochloric acid (at $5.06 per carboy) was used for leaching the combined deposits. This charge amounted to $0.026 per pound of metal produced. Approximately 1,500 gallons of de-ionized water ($0.25 per thousand gallons) for washing leached metal and 150 cubic feet of natural gas ($0.98 per 1,000 cubic feet) for drying the final product were also needed. Altogether, miscellaneous processing costs came to less than $0.01 per pound of metal. The total cost of processing was approximately $0.08 per pound.

In addition to the above there were costs for utilities used during the 10-day period. An average of 18.8 gallons per minute of treated water was required for cooling various parts of the cell. This water was circulated through a tower and reused. Utilities, including water, light, gas, and compressed air, came to $19.50, or $0.016 per pound of metal refined. The overall cost of operation (excluding amortization and overhead) was $0.84 per pound of metal refined, distributed as shown in table 15.

TABLE 15. - Direct operating costs, first 10-day period

Item	Per pound
Labor....................	$0.46
Power, d.c. and a.c......	.05
Dragout..................	.04
Helium...................	.19
Processing...............	.08
Utilities................	.02

To minimize costs, it is obvious that the greatest possible amount of metal must be deposited at the cathode before stripping. Limiting factors are anode-to-cathode spacing, current efficiency, and cell dimensions. In the first 10-day production cycle, the amount of deposit that could be built up on the cathodes before stripping became necessary was determined by the size of the openings in the cell through which the deposits were withdrawn. In the second 10-day period, smaller diameter cathodes (4-inch instead of 6-inch) were used. The maximum allowable power input then had to be reduced from 9,000 amperes d.c. to 6,000 amperes d.c. to maintain an initial cathode current density of 1,000 amperes per square foot. Use of smaller cathodes permitted the number of ampere-hours per deposit to be increased from 28,000 to 36,000. This, in turn, reduced both of the major costs of cell operation (labor and helium). The number of ampere-hours per deposit, using 4-inch cathodes, was limited not by cell dimensions but by current efficiency, which fell off rapidly after approximately 3 inches of metal had been deposited at the cathodes. The reason for the above phenomenon is not known, but it is probably the result of the rate of re-solution approaching the rate of deposition.

The second 10-day period started on December 1, 1959, and was completed on December 10, 1959. One 6-hour deposit at 6,000 amperes was scheduled for each shift. Two 4-inch-diameter cathodes were used with immersion adjusted to 30 inches. Electrolyte composition, temperature, and the amount of anode material in the cell were held as constant as possible. At the start of the second 10-day interval, the cell contained 916 pounds of anode material. Ninety pounds of offgrade Kroll sponge (Brinell hardness 189) was added to the cell on alternate shifts to compensate for metal withdrawn in deposits. The average chemical composition of this sponge is shown in table 16.

TABLE 16. - Analysis of anode material, second 10-day period

Element	Percent	Element	Percent
Fe..................	0.10	H....................	0.003
Mg..................	.30	C....................	.049
Na..................	.014	Cl...................	.15
N...................	.034	V....................	.08
O...................	.136	S....................	.008

Altogether, 1,350 pounds of material were added to the cell during the second 10-day campaign.

Total weight of all deposits was 1,951 pounds. Weight of refined metal remaining after the leaching, washing, filtering, and drying operations was 1,342 pounds. Loss of electrolyte in dragout, 609 pounds, was somewhat less than in the first 10-day period. The average rate of production was 5.6 pounds of refined metal per hour. Of the 1,342 pounds of metal produced, 161 pounds was ruined by fires which occurred in the rotary dryer. The remaining 1,181 pounds separated as shown in table 17.

TABLE 17. - Screen size and hardness of refined metal from second 10-day period

Screen size, Tyler	Weight of fraction, lb.	Size distribution, pct.	Hardness, B.h.n.
+8......	67	5.7	80
-8 +34.....	758	64.2	88
-34 +84.....	292	24.7	134
-84.........	64	5.4	265

While the hardness of the plus 34-mesh fraction was less than in the first 10-day period, only 70 percent (by weight) of the metal was in this size range. The decrease in crystal size with time was probably caused by poor anode contact. After the test series was completed, anode material at the bottom of the cell was stirred up with a poke rod to correct this condition.

The fused sodium chloride electrolyte (total weight, 11,194 pounds) contained 3.64 percent soluble titanium with an A.E.V. of 2.07 at the start of the second 10-day period. Depth of the electrolyte was 38 inches, and the nominal operating temperature was 850° C. No salt was added to the cell at any time during the producing cycle. At the completion of the test, the electrolyte contained 2.07 percent soluble titanium with an average effective valence of 2.17. These analyses indicate that some electrowinning had occurred, probably because of poor anode contact. Since the soluble titanium content of the electrolyte was below the desired operating range (4 to 5 percent), 800 pounds of "master mix" was added to the cell through the anode receivers.

After the salt addition, the electrolyte separated into two distinct layers. Deposits from subsequent runs showed a striking difference in the type of crystal formed in each layer. Samples from the top and bottom of the fused salt contained 4.69 and 6.21 percent soluble titanium, respectively. Since the "master mix" addition had raised the average A.E.V. of the electrolyte to 2.46, eight deposits were made using a small amount of current to purify the electrolyte. During conditioning the line of demarcation between the two zones approached the bottom of the cathodes and finally disappeared. Samples of the hexagonal crystals from the top of the deposits and the feather-like form from the bottom showed no difference in hardness.

Operating conditions during the second 10-day production run, with the exceptions already noted, were the same as those in the first test. Total labor required to refine 1,342 pounds of sponge was 130.1 man-hours, distributed as shown in table 18.

TABLE 18. - Labor distribution, second 10-day period

Job	Man-hours
Adjusting controls	1.8
Changing receivers	57.8
Purging receivers	12.9
Stripping cathodes	44.6
Adding anode metal	7.5
Miscellaneous tasks	5.5

The pay scale at the Boulder City Metallurgy Research Laboratory, was such that the labor cost per pound of metal refined was 27 cents. Cost per unit operation is shown in table 19.

TABLE 19. - Cost of labor per unit operation, second 10-day period

Job	Per pound
Adjusting controls	$0.004
Changing receivers	.123
Purging receivers	.026
Stripping cathodes	.095
Adding anode metal	.015
Miscellaneous tasks	.011

The internal heater operated continuously at an average power input of 2,600 amperes and 10.4 volts. Average temperature of the electrolyte during the 10-day period was 864° C. Total power consumption for heating was 6,490 kilowatt-hours or 4.83 kilowatt-hours per pound of metal produced. The cost of holding the cell at operating temperature was, therefore, $0.024 per pound. During the 10-day period, the germanium rectifier supplied 1,080,000 ampere-hours. Based on the 1,342 pounds of metal recovered, current efficiency ($Ti^{++} \rightarrow Ti$) averaged 63.1 percent. This was not quite as good as the efficiency obtained in the first 10-day test. However, previous work had shown that it was about the best that could be expected with the number of ampere-hours used. Total power consumed in electrolysis was 4,640 kilowatt-hours (30 runs--6,000 amperes--4.3 volts). Average power consumption for electrolysis was 3.46 kilowatt-hours per pound of metal refined at a cost of $0.017 per pound. Overall power cost was $0.04 per pound, 25 percent less than in the first 10-day period.

A total of 609 pounds of salt was removed from the electrolyte with the deposits. Since the average titanium content of the electrolyte was 2.85 percent, only 17.4 pounds of metal was lost in this way. If a value of $1 per pound for divalent titanium in "master mix" is assumed, the loss is $0.013 per pound of metal refined. It would also cost $13.76, or $0.01 per pound, to replace the sodium chloride dissolved during the leaching operation. The overall cost of dragout was, therefore, $0.02 per pound, or half of that encountered in the first 10-day period.

Since helium had proved to be one of the most expensive items in cell operation, a very careful check was made on the volume used in the second 10-day period of operation. No attempt was made to reduce the amount used by operators for purging receivers, however. A total of 2,257 cubic feet was required, equivalent to 8.1 cylinders (280 cubic feet per bottle). At $16.15 per cylinder, the total cost was $130.82, or $0.10 per pound of metal refined. Costs for processing deposits and for utilities were exactly the same as in the first 10-day period. Since somewhat more metal was produced in the same length of time, however, the unit cost for both of these items came down slightly.

The cost of electrorefining offgrade sponge was reduced to $0.52 per pound in the second 10-day cycle by the use of smaller diameter cathodes (4-inch instead of 6-inch). These permitted a greater quantity of metal to be deposited before stripping became necessary. Unit costs for the two periods are compared in table 20.

TABLE 20. - Comparison of operation costs, first and second 10-day period

Item	First 10-day period, cost per pound	Second 10-day period, cost per pound
Labor.................	$0.46	$0.27
Power, d.c. and a.c...	.05	.04
Dragout...............	.04	.02
Helium................	.19	.10
Processing............	.08	.07
Utilities.............	.02	.02
Total............	0.84	0.52

Both labor and helium costs were drastically reduced by the use of a greater number of ampere-hours per deposit. Since the current efficiency decreases, however, as the number of ampere-hours is raised, any further reduction in cost appeared unlikely.

A 20-day production experiment was started February 24, 1960, to confirm cost data and determine the effect of prolonged operation. All deposits to date had been made at constant amperage. Tests using constant voltage indicated some possibility of producing acceptable metal at slightly higher average current densities. This would in turn permit the use of a greater number of ampere-hours per run and might lower costs somewhat. During the 20-day test, the cell was, therefore, operated at constant voltage rather than at constant amperage. In the first four tests, the d.c. input was held at 4.5 volts for 8 hours, using 30-inch immersion on two 4-inch-diameter cathodes. Difficulty was experienced in closing the slide valves at the bottom of the cathode receivers because of the side of the deposits. Immersion on the following runs was reduced to 28 inches, and the voltage was cut back to 4.0 to maintain approximately the same current density.

The appearance of the refined metal remained excellent until March 3, when the amperage suddenly dropped. The next nine deposits consisted of very fine, dark crystals heavily loaded with salt. The 20-day experiment was interrupted for 8 hours on March 6 so that the anode material at the bottom of the cell could be stirred up with a poke rod. This led to an immediate improvement in the appearance of the deposits. No further trouble was encountered during the rest of the 20 days.

The total weight of all deposits produced was 3,421 pounds. After crushing, leaching, washing, drying, and screening, 2,472 pounds of metal remained. The difference, 949 pounds, consisted of salt removed from the cell with the deposits. Dragout was 27.7 percent, slightly less than in the second 10-day test. Deposits were divided into "good" and "bad" lots before processing. "Bad" lots consisted of the nine deposits noted, plus one that was badly oxidized when a slide valve failed to close properly as the receiver was removed from the cell. Table 21 shows some of the results obtained in the 20-day program.

TABLE 21. - Results obtained in 20-day period

Item	"Bad" metal	"Good" metal
Total weight of deposits..........pounds	945	2,476
Weight of contained salt.............do.	473	476
Weight of refined metal..............do.	472	2,000
Dragout ratio....................percent	50.0	19.2
Amount of +34-mesh metal.............do.	68.3	85.4
Hardness of +34-mesh fraction.....B.h.n.	140	90

During the time that the cell was operating properly, 1,708 pounds of excellent metal (100 percent plus 34-mesh, Brinell hardness 90) was produced. Results, however, did not approach those obtained in small-scale work. In preliminary tests, where greater care could be used, hardnesses as low as 66 Brinell were commonplace. However, in continuous operation, simulating possible commercial practices, an average hardness of 80 to 90 Brinell (plus 34-mesh fraction) was the best that could be expected. Table 22 indicates the degree of purification obtained when the cell was operated continuously over a 20-day period using offgrade Kroll sponge with a Brinell hardness of 195 as the anode material. The "product" was representative of all the plus 34-mesh refined metal.

The overall cost (excluding amortization and overhead) of refining titanium amounted to $0.53 per pound during the 20-day period. This figure is very close to that obtained in the second 10-day period, and it is believed to represent a minimum using the present cell design. Unit costs for the two last tests are compared in table 23.

TABLE 22. - Analyses of titanium before and after electrorefining, 20-day period

Element	Analysis, percent	
	Feed, 195 B.h.n.	Product, 90 B.h.n.
Fe..........	0.08	0.01
Mg..........	.14	.008
Na..........	.002	.022
N...........	.032	.002
O...........	.119	.034
H...........	.002	.003
C...........	.10	.02
Cl..........	.17	.04
V...........	.02	.005
S...........	.008	.001

TABLE 23. - Direct operating costs, 20-day period

Item	2d 10-day period, cost per pound	Final 20-day period, cost per pound
Labor...............	$0.27	$0.26
Power, d.c. and a.c.	.04	.04
Dragout............	.02	.02
Helium.............	.10	.12
Processing.........	.07	.07
Utilities..........	.02	.02
Total.........	$0.52	$0.53

When the cell was operated at an initial cathode current density of 1,000 amperes per square foot, approximately 85 percent of the metal produced was coarser than 34-mesh. The minus 34-mesh material was usually recycled to the cell. Considering only the plus 34-mesh fraction in calculating costs, the refining charge would be increased to about $0.60 per pound. This figure is still very conservative, since all major expenditures (labor, helium, and processing) would be reduced to a considerable degree in large-scale operation.

CONCLUSIONS

These investigations indicate that it is possible to produce high-purity titanium from offgrade scrap or sponge for less than $0.60 per pound, exclusive of capital and crude titanium costs. When operated at 850° C. using a cathode current density of 1,000 amperes per square foot and a molten sodium chloride electrolyte containing 5 percent by weight of soluble titanium, the prototype cell produced coarse (85 percent plus 34-mesh), compact deposits of premium-grade (<100 Brinell) metal.

Labor charges appeared to be largely dependent upon the number of ampere-hours per deposit. By proper cell design, it was possible to carry out electrolysis at an amperage high enough to maintain the temperature of the bath, thus reducing power consumption to less than 5 kilowatt-hours per pound of metal refined. Dragout was found to be influenced by temperature, bath composition, and current density. The best deposits from the prototype cell contained about 20 percent by weight of salt.

While the prototype cell produced acceptable metal at 10,000 amperes with low labor and power consumption, it is not necessarily the best cell that can be developed for the electrorefining of titanium. For example, means of stripping deposits from the cathodes without removing them from the cell would lower the cost of both labor and helium. As knowledge of fused-salt electrolysis increases, it will be possible to improve the methods for producing high-purity titanium.