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ELECTROREFINING BERYLLIUM

Two-Cycle Electrolysis

By M. M. Wong and D. A. O'Keefe

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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ELECTROREFINING BERYLLIUM

Two-Cycle Electrolysis

by

M. M. Wong[1] and D. A. O'Keefe[2]

ABSTRACT

To obtain beryllium metal of higher purity, flakes produced from electrorefining scrap metal were used as cell feed for a second cycle of electrorefining at 500° C in an electrolyte composed of 51.7 mole-percent LiCl, 36.9 mole-percent KCl, and 11.4 mole-percent $BeCl_2$.

Metallic impurities in the flakes totaled more than 108 ppm, the metallic impurities in the metal obtained from the two-cycle electrorefining were, with the exception of 35 ppm of calcium, below the spectrographic determination limits.

INTRODUCTION

To investigate the effect of impurities on the ductility of beryllium (3-5, 8),[3] numerous attempts have been made to prepare beryllium in as pure a form as possible. The refining methods used have included zone melting (8), distillation (6-7), and crucibleless vacuum melting (2). A higher purity starting material is desirable for use in these methods to obtain a still purer product. Bunshah pointed out that electrorefining was a promising source for high-purity beryllium metal (1).

Beryllium purer than that commercially available has been prepared by fused-salt electrorefining (9-10). The Bureau of Mines work reported in this paper is an investigation of advancing the purity of the metal by two-cycle electrorefining; that is, using an electrorefined metal as the cell feed for another cycle of electrorefining.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

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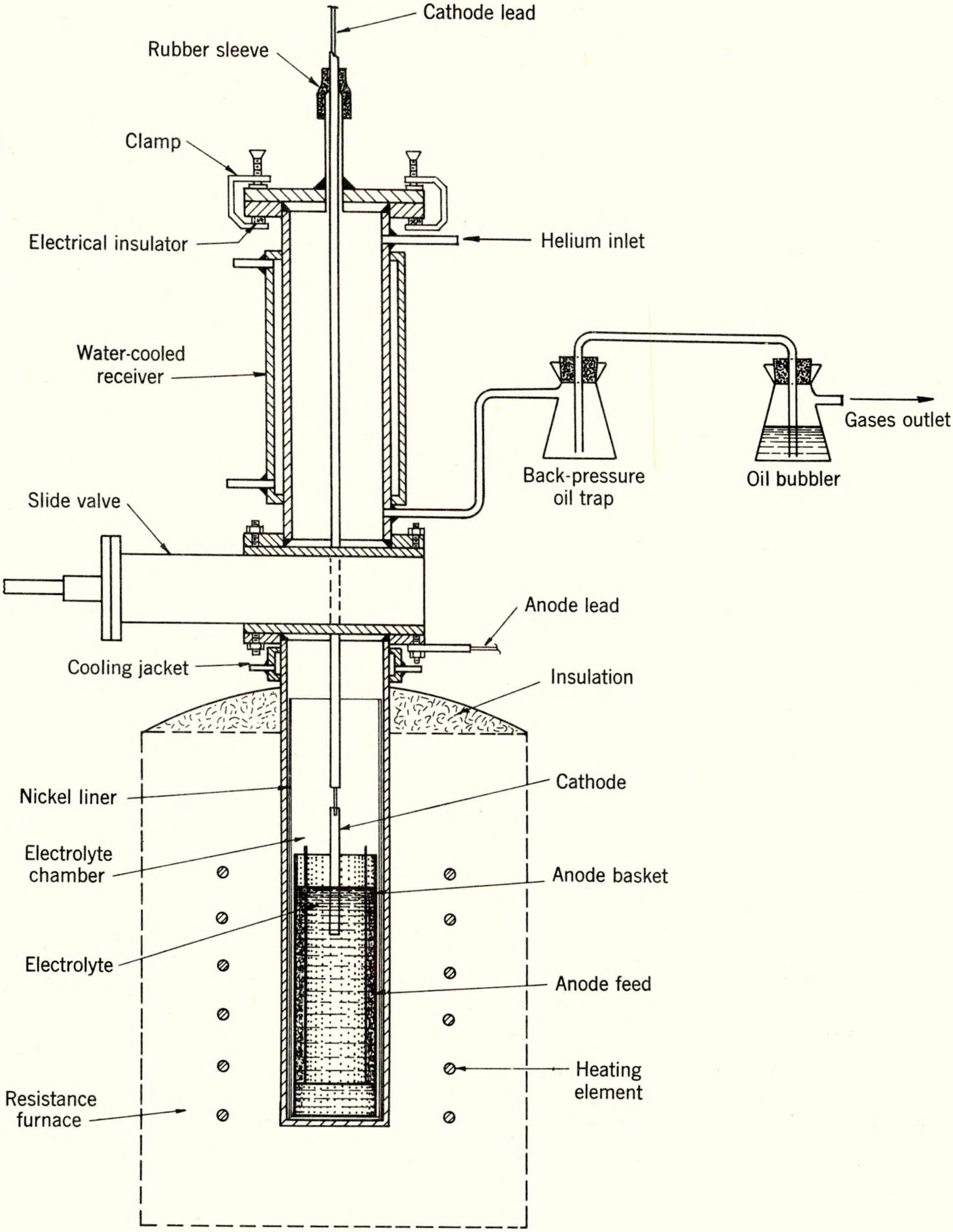

FIGURE 1. - Electrolytic Cell.

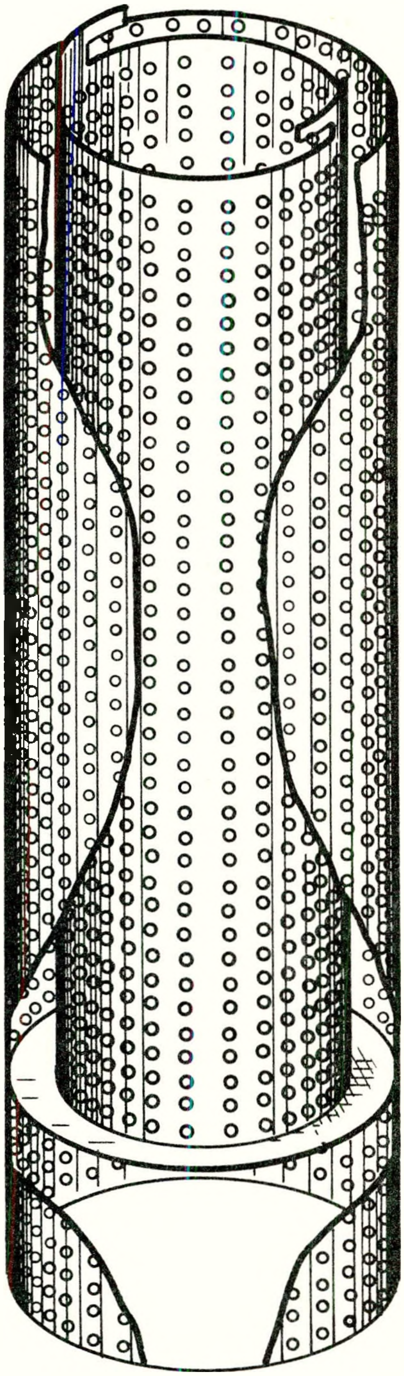

FIGURE 2. - Anode Basket.

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APPARATUS

Figure 1 is a schematic drawing of the electrolytic cell. The cell consisted of two sections separated by a slide valve. The section below the slide valve was the electrolyte chamber, which was made from a 30-inch piece of 6-inch-diameter mild steel pipe with a 3/8-inch-thick mild steel plate welded into the bottom, a flange welded to the top, and a cooling jacket welded to the wall 1 inch below the flange. The electrolyte chamber contained a 16-gage nickel liner and a perforated, annular anode basket of 16-gage nickel (shown in figure 2). The inside diameter of the anode basket was 3-3/4 inches. An electrical resistance furnace provided heat for the electrolyte chamber.

The section above the slide valve was a water-cooled, 6-inch-diameter, 16-inch-long receiver which served as an inert gas lock for the cell. The lid of the receiver, sealed to and electrically insulated from the cell body, had a port with a rubber sleeve for the passage of the cathode lead.

The cathode lead was made from a 3/4-inch-diameter nickel tube and was internally water cooled. A ½-inch-diameter nickel rod was bolted to the lead and used as the cathode; the electrolyte chamber was anodically connected to a selenium rectifier which furnished direct current for electrolysis.

PROCEDURE

The cell was assembled and evacuated to a pressure of 40 μ Hg to check for leaks. When the leak rate was less than 2 μ Hg per minute with the pump blanked off, the vacuum integrity was considered acceptable and the cell was ready for use.

An eutectic mixture of 3,062 grams of KCl (potassium chloride) and 2,438 grams of LiCl (lithium chloride) was prepared and charged in the cell. These chemically pure, anhydrous salts had been separately predried at 250° C under vacuum for 24 hours and then mixed in the eutectic proportion, melted under vacuum, and filtered at 400° C under a slight helium pressure through a sintered stainless steel element which had a mean pore opening of 10 microns. A black residue consisting of iron oxide and some carbon was filtered from the melt.

The cell was purged of air by evacuating and backfilling with helium three times. When the cell was filled with helium for the third time, it was heated to 500° C. In subsequent operations, atmospheric contamination of the cell was prevented by closing the slide valve above the electrolyte chamber whenever the receiver was opened to the outside for the introduction or removal of material. The receiver was sealed and purged of air before the slide valve was reopened.

The $BeCl_2$ (beryllium chloride) component of the electrolyte was produced in situ by reacting chlorine with beryllium metal (<u>10</u>), $Be + Cl_2 \rightarrow BeCl_2$. The nickel chlorinator consisted of a reaction tube and a delivery pipe. Electrorefined beryllium metal equal to twice the stoichiometric requirement was a added to the reaction tube which was packed with a layer of nickel pellets in the bottom to prevent the reaction residue from blocking the perforated bottom plate of the reaction tube. Chlorine was introduced to the reaction tube through the delivery pipe.

During the chlorination, the reaction tube was partially immersed in the LiCl-KCl melt. The product $BeCl_2$ passed through the perforated bottom of the reaction tube and was dissolved in the melt. After the stoichiometric amount of chlorine to yield the desired concentration of $BeCl_2$ in the electrolyte was added, the chlorinator was removed and the electrolyte was sampled and analyzed.

Approximately 1,000 grams of electrorefined beryllium flakes was loaded into the annular space of the anode basket. The basket was then lowered into the electrolyte chamber. Electrolysis was performed with the electrolyte chamber connected anodically to a direct-current power source.

At the end of a deposition cycle, the cathode was raised just above the electrolyte and the salt was allowed to drain from the deposit for 5 minutes. The deposit was then sealed in the receiver and cooled to room temperature.

After removal from the receiver, the cathode with deposit was disconnected from the electrode lead and then leached in 1-percent HNO_3 solution. Subsequently, the deposit metal was stripped from the cathode, broken into flakes (optional), stirred in a fresh 1-percent HNO_3 solution and then in distilled water, soaked in fresh distilled water overnigh, filtered, washed, rinsed with acetone, and dried.[4]

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[4] Tests were made on vacuum distillation of salt from the deposits at 850° C and 40 μ Hg for 3 to 25 hours. Salt on the crystal surface was distilled off, but salt entrapped between crystal layers could not be completely removed. A noticeable amount of beryllium metal was volatilized.

RESULTS AND CONCLUSIONS

The cell feed used as the soluble anode material was prepared from electrorefining scrap beryllium (10) in a manner that was basically identical to the procedure described in this report for the second-cycle electrorefining. This feed material was in flake form and was very low in metallic impurities (table 1). To make possible the reduction of the already very low level of impurities in the feed material by electrorefining, extra care was taken in cleaning the apparatus, purifying the electrolyte components, and handling the deposits to prevent extraneous contamination.

TABLE 1. - Analyses of anode feed and electrorefined metal, ppm[1] [2]

Material	Cl	O	N	C	Al	Ca	Cu	Fe	Mg	Mn	Si
Cell feed................	600	930	20	300	<20	38	<15	41	<5	13	16
Electrorefined metal:											
Group A................	400	540	20	300	<20	36	<15	<20	<5	[3]<10	<15
Group B................	900	630	20	400	<20	34	<15	<20	<5	[3]<10	<15
Group C................	700	650	20	400	<20	35	<15	<20	<5	[3]<10	<15

[1] The electrorefined metal contained approximately 530 ppm of K and 80 ppm of Li. Melting the metal, however, would greatly reduce the content of the alkali metal chlorides. Other metallic elements that were not detected in the electrorefined metal include Ag, B, Bi, Co, Cr, Mo, Ni, Pb, Sn, Ti, and V.

[2] Tabulated results are averages of from 2 to 7 samples.

[3] Also not detected.

The operating conditions employed in the second-cycle electrorefining were selected on the basis of previous work (9-10); namely, the electrolyte was 51.7 mole-percent LiCl, 36.9 mole-percent KCl, and 11.4 mole-percent $BeCl_2$, and the cell temperature was 500° C. The cell was operated at currents ranging from 5 to 15 amperes. The results of the operation are shown in table 2. Generally, the performance of this cell was very similar to that of those for electrorefining low-purity beryllium beads and scrap metal (9-10). However, the cathode current efficiency in this work was somewhat lower, primarily owing to working in a smaller diameter cell, where deposits were more liable to mechanical loss.

TABLE 2. - Cell operation with various amperages[1]

Test group	Amperage	Average voltage	Cathode current density, amp/sq ft[2]	Ampere-hours	Deposit metal weight, grams	Cathode current efficiency, percent
A..............	5	0.10	147	117.5	9.3	47
B..............	10	.15	294	80	7.1	53
C..............	15	.20	440	120	11.2	55

[1] Tabulated results are averages of 4 tests.

[2] Current divided by initial cathode area.

Coarse, platelike crystals were produced. Figure 3 shows the crystals, and the analysis is listed in table 1. Except for approximately 35 ppm of calcium, the metallic impurities were either not detected or below the limits of spectrographic determination. Comparing the metallic impurities in the anode feed with those in the electrorefined product indicates a reduction of iron, manganese, and silicon. Electrorefining in regard to aluminum, copper, magnesium, and other elements cannot be determined because the level of these impurities was below the spectrographic determination limits in both the feed and the product. Reduction of calcium to below 35 ppm by electrorefining does not appear promising. The source of calcium in the product is not clear. It could possibly be transported from the anode feed, or acquired from the impurities of the LiCl to form a stable calcium-beryllium compound. Some reduction of oxygen in the product has been shown, but the second-cycle electrorefining did not have any noticeable effect on the reduction of nitrogen, carbon, and alkali metal chlorides.

FIGURE 3. - Metal Produced by Two-Cycle Electrorefining (X 2.5).

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