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A CONTINUOUS ELECTROLYTIC PROCESS
FOR THE PRODUCTION OF BERYLLIUM
METAL

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April 23, 1956

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THE PRODUCTION OF BERYLLIUM METAL

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Atomic Energy Division
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ABSTRACT

A brief description of the process is given and details of work over a three-year period are summarized.

The continuous production of beryllium metal by low-temperature fused salt electrolysis into a continuously circulating mercury cathode has been demonstrated. The product is amenable to direct hot pressing or to powder preparation by distilling off the mercury.

The production of pure beryllium chloride in good yield by direct chlorination of beryllium oxide has been demonstrated.

The production of pure beryllium chloride in good yield by direct chlorination of beryl has been studied. The status of this work is not sufficiently advanced to permit valid conclusions as to ultimate success.

The electrolytic cell and associated equipment and the chlorination equipment are described in detail. Operating procedures and representative results are given. The course for continued work is indicated.

I. INTRODUCTION

Very early in the atomic energy program, intense interest was centered on the metal beryllium because it was the only metal (barring isotopic separation of lithium) among all the potential reactor moderators. Sufficient pure metal, however, was not available, and a government-sponsored facility was finally constructed for its production by magnesium reduction of BeF_2 . The metal proved very difficult to work, being extremely brittle.

The accepted operating procedure as developed involved the production of massive metal by magnesium reduction of beryllium fluoride, followed by attrition to a fine powder. Then, using powder techniques, the desired pieces were produced. The metal so produced was very expensive, almost prohibitively so. The Atomic Energy Commission therefore continued to encourage development of cheaper processes for beryllium production, including the electrolytic deposition of beryllium in flake form on a metal cathode.

In 1952 work was started at Sylvania on an exploratory basis. Experiments indicated that beryllium could be electrolyzed from a low-melting molten salt solution into a mercury cathode. An amalgam, or more accurately a quasi-amalgam, was formed which appeared to have attractive possibilities for direct pressing, a marked simplification over the production process. An advantage over the usual electrolytic techniques was also apparent, since a washing operation to free the metal deposit of occluded salts would not be necessary. In addition, the fine grain size of the first compacts appeared most desirable from the neutron scattering standpoint. A small-scale program for pursuing this approach was therefore set up with AEC support.

After an investigation of various low-melting salt mixtures, the $\text{NaCl}-\text{BeCl}_2$ system was chosen. The BeCl_2 available at that time from outside sources was not satisfactory in quality, and consequently BeCl_2 was prepared at Sylvania by chlorination of beryllium metal pebble. The first electrolytic cell utilized a small Vycor test tube. It was in this tube that the production of "amalgam" was first demonstrated.

During the first year's operation several difficult problems were solved and the nature of others were determined. It was found that under the conditions prevailing, hydrogen was necessary for consistent production of amalgam. Foaming of the electrolyte, which hampered many of the early runs, was finally eliminated by very careful handling of the BeCl_2 feed to prevent contamination by moisture. Anode disintegration during electrolysis was a serious problem. After trial of numerous types of graphite, a graphite obtained from the Wilson Carbon Co. proved satisfactory as an anode. The problems which remained to be solved were consistent electrical shorting in the cells and clean separation of the amalgam from the electrolyte. Several compacts were made during this period, the "amalgam" being hand-picked free of salt inclusions. Water-leaching was tried but the resultant compact contained 27% oxide.

The second year's operation was concentrated on determining and eliminating the cause of cell shorting and on obtaining salt-free amalgam. During this period another problem arose in the form of hydrogen-chlorine explosions in the cell. Substitution of argon for hydrogen proved unsatisfactory and confirmed the earlier results of the need for hydrogen for consistent amalgam production. The shorting problem was traced to two possible sources: bridging of amalgam dendrites between anode and cathode and a "metal fog" formation in the salt layer. In several runs the amalgam was observed to have climbed the cell walls and grown toward the anode. Different cell materials were tried but did not prevent the climbing. Mercury circulation was tried, the mercury circulation line being centered in the cell. This was not successful because the amalgam, which concentrated at the top of the mercury cathode, was too thick to flow. A magnetic stirrer in the mercury improved the cell operation considerably by more uniformly distributing the beryllium in the cathode. An increase in cell size also helped the situation by increasing the distance between anode and cathode (including cell wall). Finally a short side-arm pour-off spout was placed on the cell for pouring off the amalgam after a run. Trouble still persisted, however, with shorting and with separation of the amalgam from salt. The magnetic stirrer was not reliable and was finally replaced by a motor-operated stirrer. There were still runs where no amalgam was formed. This was traced to use of old electrolyte. Subsequent to this, the side arm to the cell was lengthened and used to withdraw the mercury from the cell after electrolysis. This system worked fairly well. However, large quantities of black powder appeared in the take-off line with the amalgam (this was later shown to be caused by oxygen and/or moisture in the cell system). At the end of the second year shorting was still a problem, and occasionally no amalgam was produced.

The third year's operation began with construction of the prototype for the final mercury circulation system. Operation of the short side-arm cell continued for production of amalgam. The new circulation system, though satisfactory in principle, did not operate well because of difficulties in temperature balance (cold mercury returning to the cell froze the electrolyte), system leaks and inadequacy of the separator and pump. The cell was now five inches in diameter and consisted of a glass sleeve inside of a stainless steel pot - as opposed to the previous all-glass cells. Even at this time shorting was still a problem. Another serious problem was produced by salt freezing in the side arm, which necessitated complete dismantling of the cell. Hydrogen-chlorine explosions and too low a mercury level in the cell were the principle causes of this difficulty. The entire cell and circulation system were redesigned, with every attention being given to leak tightness and efficient operation. This redesigned five-inch cell and circulation system worked very well (at 6 and 12 amperes) and were run for about two months. Amalgam was consistently collected and appeared to be very good. Shorting occurred but seldom and minor hydrogen-chlorine explosions occurred from time to time.

The last three months of the project were devoted to installation and operation of a ten-inch cell and associated equipment. No shorting occurred in this cell (at 30 and 60 amperes) and it was found that hydrogen was not needed for amalgam formation, thereby eliminating the hydrogen-chlorine explosion problem. Hydrogen apparently had been necessary previously because of the purification it effected on the cell atmosphere. Thus all major process problems had been solved and a good understanding had been obtained of the electrolytic production of amalgam.

Construction of a 17-inch diameter cell capable of producing one to two pounds of beryllium metal per day (200 to 300 amperes) was stopped at the project's termination.

Because of the encouraging progress on the electrolytic program, a project was started in 1954 for preparing BeCl_2 , needed as feed, from BeO and beryl ore. The chlorination of BeO was straightforward and the yield and product very satisfactory.

The chlorination of beryl ore was more difficult - a clean separation of BeCl_2 and AlCl_3 was not made. The principal difficulties were with high temperature seals and with a BeCl_2 or $\text{BeCl}_2\text{-AlCl}_3$ "smoke" that crept along the condensers rather than settling out directly.

Some effort has been devoted to hot pressing of amalgam but optimum conditions have not been established. Compacts in the range of 1.2 to 1.8% BeO and 0.00 to 0.3% Cl^- have been obtained. More satisfactory hot pressing conditions will undoubtedly improve the compact quality. Powder has also been prepared though not under optimum conditions.

II. ELECTROLYSIS

A. Brief Process Description

The process as presently conceived is as follows: The cell feed is beryllium chloride (present in the cell as an essentially eutectic $\text{BeCl}_2\text{-NaCl}$ mixture) prepared by direct chlorination of a beryllium oxide - carbon mix at about 1000°C . The beryllium chloride produced is condensed at about 300°C in a dilute chlorine atmosphere which provides effective separation from iron impurity. Since BeCl_2 and beryllium metal are extremely reactive, every precaution must be taken to exclude air and moisture from the process systems. The BeCl_2 is added to the cell periodically to maintain the BeCl_2 concentration. The operating temperature is maintained between 300° and 330°C . The cell is essentially a metal container with an internal refractory sleeve (pyrex was used in the experimental cells) with provisions for stirring and continuously circulating the mercury cathode. A special carbon

anode is used, and a purified argon atmosphere is maintained over the electrolyte. The beryllium metal formed at the cathode distributes throughout the mercury in the form of a quasi-amalgam. This amalgam is continuously circulated to a separation unit consisting of a 200 mesh screen held in a metal container. The screen effectively holds the quasi-amalgam while excess mercury runs through. The beryllium concentration in the "amalgam" is about 2 w/o after vacuum filtration. When sufficient amalgam has been collected, the mercury flow is switched to a second separator, and the full separator is taken to a dry box for removal of amalgam. This separator is then returned to the circulation system. (This procedure was used only long enough to demonstrate feasibility. Since, in the experimental cells, a single separator could handle sufficient amalgam for a day's needs, generally only a single separator was used in the circulation system, thereby amplifying operation.) Amalgam is produced at a current efficiency of about 70%.

The amalgam is handled in either of two ways. It is hot pressed directly or the mercury is distilled away from it at low temperature and the resulting "sinter cake" ground to a fine powder. (Although optimum conditions have not been established in either case, hot pressed compacts have been produced having oxygen contents of less than 0.8% and chlorine contents from 0.00 to 0.3%. There is no mercury, within the detection limits, in these compacts).

The attractive features of this electrolytic process are primarily:-

1. Low operating temperature: 300° to 330°C.
2. Continuous operation made possible by cathode mercury circulation.
3. Fine particle size of beryllium metal produced, permitting direct pressing or direct preparation of powder.

B. Electrolytic Cell and Associated Equipment

1. Cell Feed

After preliminary investigations of various fused bromide systems and organic solvents for BeCl_2 , the $\text{NaCl} - \text{BeCl}_2$ system was selected for cell feed. This system has a eutectic at about 50 mol percent BeCl_2 and 215°C, and a melting point below 300°C in the range of 40 to 65 mol percent BeCl_2 (Fig. 1). Since the cathode is mercury, the temperature of electrolysis is limited by the boiling point, 356°C. A low temperature of electrolysis is desirable to minimize the volatilization of both mercury and

Fig. 1- SYSTEM BeCl_2 - NaCl

BeCl₂. Pure BeCl₂ has a vapor pressure of about 2 mm of mercury at 330°C, but its vapor pressure is less than this in the cell feed solution. On the other hand, a high operating temperature is desirable because of decreased cell resistance and lower decomposition potential resulting in lower energy requirement per unit of product. The best situation from the viscosity standpoint would be to run the cell at eutectic composition by continuous feed addition. However, as a practical matter the feed solution was kept between about 45 and 60 mol percent BeCl₂ by batch BeCl₂ addition. Operating temperatures were kept between 300° and 330°C. (The vapor pressure of mercury is about 247 mm mercury at 300°C and 460 mm mercury at 330°C.)

In the usual fused salt electrolysis where solid metal is deposited a metal cathode is used. After build-up of electrolyzed metal, the cathode is removed from the bath taking with it a high percentage of feed salt. The aim in that case is to use a low-cost solvent salt and to deplete the feed of product metal.

In the process under study, essentially no salt is removed from the cell because the metal is removed as a quasi-amalgam by continuous circulation of the mercury cathode. More expensive solvent salts are thus feasible. An improved cell feed might contain two or more of the following salts: NaCl, KCl, CaCl₂ and possibly MgCl₂, although its decomposition potential is not so favorable.

The NaCl used for cell feed was of commercial purity grade, oven dried at 120°C. Since no BeCl₂ of reasonable quality was commercially available during the first two years of this project, the BeCl₂ used was made by chlorination of beryllium metal pebble. The apparatus consisted of a Vycor tube with a two-liter bulb on one end - essentially a Vycor flask - and a short exit tube on the bulb (Fig. 2). An inner sleeve was loaded with beryllium pebble and the tube heated by a nichrome resistance-winding. Argon was used as an inert atmosphere. At about 600°C chlorine (or HCl) was introduced, and the BeCl₂ produced deposited in the air-cooled bulb. At the end of the chlorination (200 to 300 gms BeCl₂) the entire unit was transferred into a dry box and the BeCl₂ collected. The NaCl and BeCl₂ were then mixed in proper proportion and fused under argon. This cold-fused mix was fed into the cell. Additional BeCl₂ was then added to the cell as required.

BeCl₂ of good quality was obtained from the Beryllium Corporation of America in June, 1955. This material was light green in color and not as pure as the material obtained from chlorination of pebble. This purchased BeCl₂ had the following analysis:

Fig. 2 Be CHLORINATOR

<u>Material</u>	<u>Percent</u>
Ni	0.060
Fe	0.013
Al	0.02
Si	0.07
O ₂	0.68

This material was mixed directly with NaCl and used for cell feed. Since nickel and iron are electrolyzed preferentially to beryllium, the first "amalgam" obtained was high in iron and nickel (contained about 20% nickel and 4% iron based on beryllium). As operation continued, the beryllium quality improved until new BeCl₂ was added to the cell when the nickel and iron contents rose sharply as expected. Since pre-electrolysis in a continuously operating cell is not feasible, very pure feed is required and ideally should be added continuously so as to give a uniform product. BeCl₂ may be separated from nickel and iron chlorides by distillation. However, results of chlorination of BeO, to be described later, indicated that a very pure BeCl₂ product could be obtained directly, thereby eliminating a further purification step.

2. Electrolytic Cell

The ten-inch electrolytic cell (see Fig. 3), which was the last one operated, consisted of a type 304 stainless steel pot (1) ten inches in diameter and fourteen inches high having two stainless steel tubes (6, 10) welded into the sides at the base. The 3/8-inch diameter tube (6) is the mercury return line from the mercury circulation system (to be described later) and the 1-inch diameter tube (10) is the amalgam exit. A water condenser (11) on this side-arm cools the hot amalgam from the cell to room temperature. A 9-inch diameter pyrex battery jar (2) with the base cut off was used for the feed container. A rectangular piece was cut out of the base of the sleeve to uncover the exit tube (10) opening and permit amalgam to flow out of the cell. The cell top prevented vertical movement of the sleeve. The mercury cathode was stirred by a stainless steel stirrer (4) with two-inch long blades. The rod passing through the molten salt was protected by a glass sleeve (3) held down against the blades by a stainless steel pin (7) through the rod. The anode (9) was a 7/8-inch diameter rod of "calcined carbon black" obtained from the Wilson Carbon Company, New York. A stainless steel rod (8) was threaded into the carbon anode, and being offset permitted considerable lateral movement of the anode. Electrical shorting in earlier smaller cells had indicated that this movement might be helpful. However, there was no shorting in this larger cell. Heat was supplied to the cell by a

nichrome ribbon-winding (5) and by a hot plate beneath the cell. The cell sat in a low-melting metal bath on the hot plate. The winding was heavily insulated with asbestos. The upper part of the cell was not insulated and thus ran much cooler than the heated part. It therefore acted as an efficient mercury condenser and also permitted the use of rubber stoppers for making the top seals. The cell top was bolted to the base, the seal being effected by a metal O-ring (1,2). The stirring rod acted through a mercury seal (13). Silicone grease was used on the bearing surface and stood up well. A ball bearing welded to the stirring rod below the blades was positioned in a small cup in the cell base and prevented the stirrer from wobbling. Feed was added to the cell through an opening (14) at the top. The anode opening (15) was large enough to permit insertion of the 7/8-inch anode. Use of a larger anode required the removal of the cell top. Temperature control and mercury and salt depth measurements were effected through a separate opening (16). A thermocouple tube (19) extended to the bottom of the cell. One thermocouple was positioned at the center of the salt layer (20) and the other down in the mercury (22). The salt temperature controlled the current to the nichrome heater (5). The two temperatures were continuously recorded. A nichrome wire (21) sealed, except at the tip, in a glass capillary rod served to determine the mercury and salt depth by resistance measurements between the wire and ground (cathode). Argon and hydrogen were admitted to the cell through a tube on the top (17) and these gases as well as chlorine and some BeCl_2 exited through another tube on the top (18).

The 17-inch cell (see Fig. 4) as designed incorporated a number of improvements over the 10-inch cell. The interior metal ring (23) serves as a base for the pyrex sleeve and eliminates cutting and positioning of the sleeve. The side-arm contains a heat exchanger for obtaining operational data for production design. The top of the cell has a double wall, increasing operational safety. It can handle a three-inch anode and the upper seals (rubber stoppers, etc.) are protected from chlorine and BeCl_2 by argon maintained in the interior and entering at a tube in the cell top (24). An extra opening at the top serves for removal of molten salt from the cell as required for cell cleanup, new feed insertion, etc. The 17-inch cell was to be constructed from type 316 stainless steel which proved considerably better than type 304 in corrosion tests with NaCl - BeCl_2 feed at 330°C . For production use, Hastelloys B and C should be considered.

Fig. 3 10" ELECTROLYTIC CELL

Fig. 4 17" ELECTROLYTIC CELL

Results of corrosion tests of 264 hours duration at 330°C in BeCl₂-NaCl feed were as follows:

	Change in Weight (mg/in ²)
Hastelloy B	+0.36
Hastelloy C	-0.51
Stainless 317	-3.0
Stainless 316	-12.2
Stainless 304	-55.8

Mercury and chlorine attack upon materials of construction is of course a vital consideration. In this respect, type 304 stainless appeared to be quite satisfactory and the other materials should be even better.

3. Mercury Circulation System

The mercury circulation system (see Fig. 5) was designed to remove amalgam from the cell continuously, to separate the beryllium from the majority of the mercury and to return the filtered mercury back to the cell. A vacuum pump (oil diffusion pump plus mechanical forepump) attached to the glass "viewer" (25) maintained the mercury level in the viewer and also served for prior evacuation of the separators (26) when they were placed in the system. The mercury pump (a Milton Roy Simplex pump) took the mercury which passed through a 200 mesh screen (27) in the separator and returned it to the cell. The safety bypass line (30) was designed to prevent system damage if a plug developed in the return heating coils of the preheater (31). The water cooler (11) and the preheater (31) were used with the 10-inch cell rather than a heat exchanger because of time considerations. In a production cell a heat exchanger would naturally be used. The 17-inch cell was to have provided a start in that direction. Mercury was added to or removed from the system through the storage reservoir (28).

Connections between the various elements of the circulating system were made with tygon tubing except the mercury return line (6) to the cell from the pump, which was stainless steel. The tygon (29) worked quite well on the laboratory scale and could be effectively closed with pinch clamps. These tygon joints would be replaced with valves in a production unit.

The viewer (25) is a holdover from earlier 5-inch cells. It provided a means for checking the mercury level visually and also gave an indication of amalgam quantity and quality. Occasionally there was difficulty in getting the

collected amalgam down into the separator. Washing the amalgam down could thus be followed visually through the glass. Continuous pumping, using the oil diffusion pump, started with the 10-inch cell and essentially eliminated the need for the viewer. The viewer was about 4 inches in diameter and 5 inches high. The separators (26), 3-1/2 inches in diameter and 4-1/2 inches high, were made of mild steel. A 200 mesh stainless steel screen backed by a 20 mesh screen (27) served to retain the beryllium in the separator while allowing the mercury to pass through. A rubber gasket made the seal on the facing plates of the top section of the separator and the screw-on type base. Larger separators 5 inches in diameter by 4-1/2 inches high made of 316 stainless steel were received just prior to the project's termination. The upper and lower parts were sealed using flanges and an O-ring. The screen was to be supported by a metal cross in the bottom section. The mercury storage reservoir (28) was simply a glass separatory funnel. It was opened to the system only when additional mercury was needed. The mercury pump used was a Milton Roy Simplex pump capable of delivering 4.9 gallons per hour. It was actually run at 25 to 60 percent of capacity. It was housed in a metal box so that it would operate in an argon atmosphere, thereby eliminating possible air contamination in the system. The mercury preheater was a Woods' metal bath. It was resistance-wound with nichrome ribbon. A 2500 watt quartz immersion heater was used in the bath. The temperature of the bath served as the control for the heaters.

4. Gas Supply and Discharge System

The gas supply and discharge system (see Fig. 6) served two purposes; first, to maintain an inert atmosphere in the cell and second, to measure the current efficiency of cell electrolysis by measuring the chlorine generation over a fixed period of time. The gases originally supplied to the cell were hydrogen and argon passed through a Deoxo unit (32), a Lectrodryer (33), and hot calcium chips (34). Hydrogen caused some problems because of mild explosions on reaction with the chlorine generated in the cell. It had originally been thought that hydrogen was necessary for the formation of amalgam. However, when the entire cell system had been scrupulously made gas tight, the hydrogen proved to be unnecessary and thereafter only argon was used. The dew point of the treated argon was better than -60°C. The gases passed into the cell through a tube in the cell top (17). A sulfuric acid bubbler (35) acted as a safety release valve in case of system plugging. The gases left the cell through another tube in the cell top (18) and passed through a BeCl₂ condenser bulb (36) and then through a sulfuric acid bubbler (37) which served to maintain a slight positive pressure in the cell with

Fig. 5 MERCURY CIRCULATION SYSTEM

Fig. 6 GAS SUPPLY AND DISCHARGE SYSTEM

respect to atmospheric pressure. The gases then passed up the stack. When current efficiencies were measured the chlorine-containing gases were routed through a comparable head of sodium hydroxide solution (38) for a fixed period of time, usually 15 minutes, and the chlorine determined by titration with sodium arsenite solution. The amount of BeCl_2 caught in the trap (36) was not large and provisions could easily be made to return it to the cell.

5. Cell Feed System

The cell feed system (see Fig. 7), which was detached from the cell when not in use, consisted simply of a flask (39) and a metal T (40) with a tygon connector. A short tygon tube pinched off at the center was connected to the opening (14) in the cell (Fig. 3). The flask was filled with cell feed in a dry box and the tygon connector pinched off. An open end of the "T" was then forced into the tygon on the cell top (14), shown in Fig. 3. The "T" was evacuated through the remaining opening and then filled with argon. The two clamps on the tygon connectors were then opened and the feed dropped into the cell.

6. Power Supply

The d.c. power supply used was a simple unit consisting of appropriate sized selenium rectifiers operating off a transformer with a rated output of 25 volts at 90 amperes. Control of voltage and/or current was manual. In general, operation of the 10-inch cell was quite stable. Changes in cell operating characteristics were noted by recording variations in voltage while maintaining constant current.

C. Operation of the Cell

1. Setting up for Operation

Since BeCl_2 and beryllium "amalgam" are both extremely sensitive to air and moisture, every precaution must be taken to prevent access of the latter to the system. Every unit going into the system should be checked for leak tightness. For this purpose a mass spectrometer-helium leak detector was used regularly. This tightness is also very desirable from the standpoint of health and safety considerations since beryllium compounds are very toxic. The mercury pump used was very satisfactory. However, at higher speeds there appeared to be some air leakage. Consequently, the pump was housed in an argon-filled box. Distilled mercury was added to the leak-tight system in sufficient quantity to fill the circulation system and to fill the cell to a point about 1/2 inch

Fig. 7 CELL FEED SYSTEM

above the rectangular cut in the glass sleeve (2), shown in Fig. 3. (If the mercury level falls below the sleeve opening during cell operation salt gets into the side-arm and freezes, disrupting operation of the cell.) The cell was again leak tested using the mercury-seal tube (13) for the vacuum connection and of course closing the entrance and exit gas (17, 18) and mercury lines (6, 10) by pinching off the nearest tygon connectors. When the system was leak tight, argon was introduced and the mercury seal stirrer attachment made. The cell was then heated and the mercury circulated while purging the cell with argon. Preparations were then made for adding the NaCl-BeCl₂ feed to the cell. This operation was described previously (II. B. 5.) The original feed to the 10-inch cell consisted of approximately 13.5 pounds BeCl₂ and 6.5 pounds of NaCl (a 60:40 mol ratio), giving a fused salt depth of about 6-1/2 inches as measured by the resistance element (21). Since essentially no NaCl was lost during operation, the salt depth was a fair measure of the BeCl₂ concentration in the molten feed.

The mercury level in the cell changed when the salt was added. The mercury height was adjusted to a point 1/4 to 3/8 inch above the sleeve outlet using the storage reservoir (28). If the level is set too high above this point, there may be trouble in getting the amalgam, which is less dense than mercury, out of the cell and into the side-arm. If the level is set too low, salt may get into the side-arm because of the fluctuating surface level caused by stirring and/or by changes in barometric pressure which cause gas pressure fluctuations in the cell. If the "viewer" (25) had been completely filled with mercury and sealed or had had a small surface area, there would of course have been no appreciable mercury level change with changes in pressure. However, continuous evacuation above the separator appeared to give better quality amalgam in our experimental set up since it eliminated contact with vacuum grease and also provided for continuous removal of small amounts of gas which appeared from time to time and will be discussed in the following section. In any event the cell mercury level was easily controlled and no trouble was experienced on the 10-inch cell from this source. The anode height above the mercury surface was finally readjusted and was generally run 3/4 of an inch above the cathode surface. The cell was now ready for operation.

2. Operating Procedure

The cell was brought up to operating temperature (300°-330°C), the circulating pump set to a predetermined delivery speed (in the range of 1.2 to 3 gal/hr) and the stirrer set to the desired speed (in the range of 50 to 125 rpm). The argon flow to the cell was arbitrarily set

at about 1-1/2 liters per minute. Electrolysis was then started and the current set to the desired figure (30 or 60 amperes for the 10-inch cell). The cell voltage and temperature (salt temperature by potentiometer measurement) were read at 15-minute intervals. After about two hours operation a current efficiency measurement was made as discussed previously (II. B. 4.) One of the variables (i.e. stirring speed) was then changed and after two hours another current efficiency taken. A day's operation is shown in Table I. While these data were being obtained, amalgam was being continuously pumped into the viewer. Since amalgam is lighter than mercury it tended to float and remain in the viewer rather than travel down to the separator. When enough amalgam accumulated, it would essentially plug the viewer and the circulating system would stop functioning. The amalgam was then tapped and washed into the separator with the aid of alternate use of argon pressure and vacuum above the amalgam (see 25). In the separator most of the mercury was pumped out of the amalgam, and since the viewer was also empty, the mercury level in the cell rose considerably. This appeared to have no undesirable effect. The four tygon connectors (29) for the separator were then pinched off with screw clamps and the separator removed to a dry box where the amalgam was unloaded. Meanwhile, a second separator previously leak tested was immediately put into the system and evacuated. The pinch clamps were then removed and the separator and viewer filled with mercury. Additional mercury was added to the system through the reservoir to make up for the mercury removed in the amalgam, the amount being determined by the mercury level in the cell. With large separators, such as those last received, some mercury would have to be added to the system before filling the separator and viewer for otherwise the mercury level in the cell might drop too far and let salt into the side-arm. With the viewer and separator filled, the electrolysis proceeded as before. Beryllium chloride was added to the cell as needed. Since the operating range was 45 to 60 mol percent BeCl_2 or 7.3 pounds to 13.5 pounds of BeCl_2 in the 10-inch cell (6.5 pounds of NaCl used), a 2400 ampere-hour run at 80% current efficiency was possible before recharging was necessary. Actually, to minimize effects of concentration changes in the cell, additions were made at about 600 ampere-hour intervals.

Before continuous evacuation was maintained on the viewer, the procedure had been to pull the mercury into the viewer and then shut off the stopcock. This left a stagnant argon atmosphere at low pressure above the mercury. Any gas leaking into this section finally caused the mercury level to recede to the point where circulation was

TABLE I

OPERATIONAL DATA FOR THE 10-INCH CELL

Mercury Level 1-7/16"
 Salt Depth 4-9/32"
 Argon Flow 1.66 l/min.
 Anode Height Above Mercury 3/4"

<u>Time</u>	<u>Current (amps)</u>	<u>Voltage (volts)</u>	<u>Stirring Rate rpm</u>	<u>Current Efficiencies %</u>	<u>Salt Temp. °C</u>
10:40 A.M.	30	7.8	100		308
11:05	30	6.6	↓		326
11:20	30	6.7	↓		322
11:35	30	8.3	↓		306
11:50	30	6.7	↓		310
12:05 P.M.	30	6.6	↓		318
12:20	30	6.8	53	87.1	318
1:10	30	6.6	↓		315
1:25	30	6.7	↓		315
1:40	30	6.6	↓		315
1:55	30	6.8	↓		314
2:10	30	6.8	75	43.6	314
2:25	30	6.8	↓		314
2:40	30	6.6	↓		314
2:55	30	6.5	↓		314
3:10	30	6.5	↓		314
3:25	30	6.5	↓		314
3:40	30	6.5	↓		314
3:55	30	6.5	↓		314
4:10	30	6.5	↓	66.2	314
4:25	30	6.5	↓		314

prevented. These gases, aside from small direct leaks as in the pump section, appeared to come from two sources: the first was from incompletely degassed separators and the second and larger source was leakage from inside the cell - down the cell wall and up the side-arm. Intermittent evacuation was therefore required to enable the circulation system to operate.

Analysis of the cell-operating data showed that the current efficiency was very sensitive to changes in stirring speed (Table II) and that efficiencies of 80% were obtainable at 100 rpm. As is to be expected, an increase in amperage resulted in a decrease in efficiency. The voltage change with temperature at 30 amperes appeared to be not greater than -0.042 volts/ $^{\circ}\text{C}$ in the range 300° to 330°C . Other factors, however, appeared to obscure this effect as results were not consistent.

TABLE II

STIRRING RATE VS. CURRENT EFFICIENCY

<u>Date</u>	<u>Anode Height</u>	<u>Amperage (amps)</u>	<u>Stirring Rate ppm</u>	<u>Current Efficiency</u>	<u>Temperature $^{\circ}\text{C}$</u>
9/8	3/4"	30	85	63.5%	308
		30	75	43.6	307
		30	100	84.6	302
9/13	3/4	30	75	$\sim 100?$	310
9/21	3/4	30	100	87.1	315
		30	53	43.6	314
		30	75	66.2	314
9/26	3/4	60	100	68.2	325
10/4	3/4	60	80	45.4	324
		60	100	$\sim 100?$	317
		60	125	63.3	311

D. "Amalgam"

1. Nature and Properties

The amalgam produced by this electrolytic process is a very interesting material. It can be diluted with mercury in all proportions and on stirring becomes essentially homogeneously dispersed. However, if allowed to stand, a relatively thick amalgam forms as an upper layer leaving essentially pure mercury below. If the material is left standing for a considerable time, a black powder appears on the surface - the less pure the atmosphere the faster

the black powder appears. If left long enough, essentially all of the beryllium appears as a black powder. The quantity of black powder in the electrolytic cell system thus indicates the extent of air contamination.

Although argon gas was used for cell purging and amalgam storage, preliminary tests indicated that pure tank nitrogen might be just as effective.

Vacuum filtration of the amalgam produced a semi-solid cake having a shiny and silvery metallic appearance. This cake contained 1.7 to 2.0 percent beryllium by weight. This composition corresponds to $\text{Be}(\text{Hg})_2$ with a slight excess of mercury. $\text{Be}(\text{Hg})_2$ is suggested in analogy to the known compound $\text{Mg}(\text{Hg})_2$ although the presence of $\text{Be}(\text{Hg})_2$ was not proved. Since the viscosity of the amalgam increases with increasing beryllium content, the mercury circulation in the cell system must be sufficient to prevent plugging by amalgam. An arbitrary limit of 0.25% beryllium was set. Amalgam of this concentration or less flowed readily through a capillary of 1 mm radius, while more concentrated amalgam would not. In actual practice flows 10 to 100 times the minimum were used, giving a large safety factor.

Stainless steel screens of 100, 120, 170 and 200 mesh were used in the separators. They all appeared effective in holding the amalgam back. Analysis of mercury below the screens was inconclusive because of sampling and analytical difficulties. However, except in one case, the 200 mesh screens showed no "plugging" and consequently they were used as standard practice. In the one case of "plugging", the difficulty appeared to be that the amalgam wet the screen. Since this occurred after the changeover to the Beryllium Corporation BeCl_2 , the iron and/or nickel may have been responsible.

The chlorine content of the amalgam varied somewhat with the batch in the range from less than 0.3% to about 2% based on the beryllium present. Since electrolysis variables were constantly being changed, this variation is not surprising. From the results obtained on the compacts made from good amalgam, the oxygen content of the amalgam appears to be less than 0.7% based on the beryllium present.

2. Pressing and Sintering

In the early phases of the project, before a continuous circulation system was developed, the small amounts of amalgam produced were generally contaminated with small pieces of electrolyte. At this stage the amalgam was cold pressed and then vacuum sintered. In this way several compacts were obtained with oxygen as low as 1.2

to 1.3%. When larger quantities of purer amalgam became available, direct hot pressing of the thick amalgam (excess mercury was removed by vacuum filtration) was used.

The hot pressing apparatus is shown in Fig. 8. The outer unit was made of stainless steel and the top sealed to it using a stainless steel O-ring (41). Difficulties in obtaining a vacuum tight seal were completely overcome by use of aluminum foil above and below the ring. The die body (42) and two inserts (43) as well as the lower (44) and upper (45) punches and ram (46) were made of Inconel X. The lubricant used on the die walls was aquadag. This was sprayed on hot. The amalgam was loaded into the unit in a dry box, 1000 to 1500 grams being used. The upper punch was then inserted and the top, with the ram, bolted on. The unit was then leak tested in the dry box by replacing the argon atmosphere with helium and using the mass spectrometer leak detector attached through the dry box wall to the side-arm (47). The rubber tubing on the side-arm (48) was then pinched off and the entire unit taken to the pressing stand. The unit was set into a vertical 3 coil furnace tube, each coil being separately controlled. The pressing temperature was measured by a thermocouple in the well (49) at the bottom of the pressing unit. Water cooling coils (50) on the top prevented damage to the Wilson seal (51). A mercury trap (52) was attached to the rubber tube (48) on the side-arm and a diffusion pump attached to the other arm of the trap. The trap was cooled with trichlorethylene and dry ice. After the unit was evacuated, the temperature was raised to the pressing point as rapidly as possible. As the temperature rose during the heating, a large amount of outgassing took place. This was undoubtedly a source of contamination. Plans were made to preheat the empty die unit under vacuum and then fill with argon. After cooling, the unit was to be taken to the dry box for loading. A difficulty arose, however, in that the aquadag tended to peel off and blister thus putting carbon into the product. On one run the lubricated die was prebaked at 350°C in air and cooled in argon. Analyses of the product showed that the center material (about 80% of the total) contained about 0.10% carbon and 0.75% oxygen while the outer material contained about 0.50% carbon and 5% oxygen.

The hot pressing conditions used for the runs were generally 3 to 4 minutes at 1000°C and 1000 psi and then 15 minutes at 900°C at 4000 psi. However, only a small number of runs were made in all. The runs made indicated that continuous pressure applied during heating produced compacts with low oxygen content, 0.7 to 0.8%, but relatively high chlorine content, 0.1 to 0.3%; while pressing only when the pressing temperature was reached produced compacts with low chlorine, 0.00 to 0.07%, but relatively high

Fig. 8 HOT PRESSING APPARATUS

oxygen content, 1 to 7%. The longer the time at pressing temperature, the higher the oxygen content and the lower the chlorine content. From the above it is evident that, as in the electrolysis, atmosphere control is all important. The compacts obtained had grain sizes of less than 50 microns. However, complete sintering was not obtained with the conditions used (see Fig. 9). No residual mercury was detected.

Termination of the program has left incomplete the evaluation of the beryllium metal produced from amalgam. Additional work will be required to fully assess the quality of the material.

3. Preparation of Powder

An alternative to direct pressing of the amalgam and one which may be more attractive on a commercial basis is the preparation of beryllium powder from the amalgam by low temperature vacuum distillation of the mercury. Several preliminary runs were made, the final and maximum temperature being 340°C. The distillation was not done in the optimum way, but rather the temperature was raised slowly to determine the effect of temperature on the rate and quantity of mercury distilled. Some black powder came over with the mercury and a small amount of BeCl_2 condensed above the flask. A mechanical pump was used. The long duration of the experiments coupled with the moderate vacuum resulted in considerable oxygen pick-up. The residual beryllium was loosely sintered and could easily be ground to a fine powder. Analysis showed 6.5 to 8.5% oxygen and 1.4 to 2.1% chlorine. The contamination problem here is obviously of the same order of magnitude as in the hot pressing. Storage of the powder presents an additional problem. At present it appears that satisfactory powder can be obtained by close control of atmosphere and minimum processing time. Further high temperature operations (hot pressing, vacuum sintering) will serve to remove the chlorine.

III. PREPARATION OF BeCl_2

With the success of the electrolytic program assured, effort was devoted to methods of preparation of BeCl_2 from BeO and beryl ore. The chlorination of BeO was successful but work was curtailed when BeCl_2 of satisfactory quality became commercially available. Work continued on the chlorination of beryl but the problems had not been resolved at the time of the project's termination.

Fig. 9 - Hot Pressed Beryllium. Mag. 250X

Plate No. 15684

A. BeO as Feed

1. BeO Analysis

Two lots of BeO were used with analyses of important impurities as follows:

	<u>Lot No. 1</u>	<u>Lot No. 2</u>
% SiO ₂	0.19-0.34	0.00
% Fe	0.12-0.19	0.12-0.28
% Al	0.25-0.39	0.28-0.31

As far as was determined, there was no difference in behavior between the two lots during chlorination.

2. Feed Preparation

The chlorination feed was prepared by mixing BeO with about 15% excess acetylene black in a ball mill and then adding water and rolling overnight. The spheres produced in this manner were quite uniform in each batch and varied from batch to batch in the range of 1/16 to 3/8 inch in diameter. Occasionally it was necessary to scrape down the sides of the jar and re-roll. A typical batch consisted of 250 grams of BeO, 140 grams of carbon, and 250 ml of water. The wet balls were stored in closed containers until use. The balls maintained their shape on firing to 1000°C but could be crumbled by finger pressure when cold.

3. Chlorination Apparatus

The original Vycor BeO chlorination unit (Fig. 10a) was similar to the beryllium-pebble chlorinator (Fig. 2) but was longer and larger in diameter (1-1/2 inches) and had provisions for a water condenser (9) at the top. A resistance-wound alundum tube served as the heating unit. The incoming argon or chlorine flowed through the check valve (1), H₂SO₄ bubbler (2), ballast volume (3) and then through the H₂SO₄ flowmeter (4) to the reactor. The H₂SO₄ container (5) served as a flow regulator aid prior to admission of the gases to the reactor, and then, by turning the 3 way stopcock (6), as a safety release in case of a reactor plug. The base of the reactor was sealed with a rubber stopper (7) through which passed the gas inlet and the Vycor thermocouple well (8). The exit gases from the reactor traveled through the SiCl₄ condenser (11) (by-pass pinch clamp (10a) closed) which was cooled by a eutectic Mg(NO₃)₂-water mixture (-29°C) in a Dewar flask (12). The gases then passed through a tube of Anhydrite (CaSO₄) (13) and finally through a solution of NaOH (15). An argon entrance (14) between the drier and NaOH served to prevent backup of NaOH and to maintain a positive pressure beyond

Fig.10b MODIFIED VYCOR BeO CHLORINATOR

Fig.10a BeO CHLORINATOR APPARATUS

the water condenser if the system plugged or when the entrance gas was shut off. A pressure release H_2SO_4 bottle (16) was used in conjunction with the argon inlet. A second chlorine inlet (17) to the reactor was added later (Fig. 10b). The chlorine from this inlet emerged above the charge (18). The temperature of the bulb was at this time controlled using heating tape and a section of a Glass-col mantle.

4. Operation

(a) Charging the Reactor

The reactor (Fig. 10b) was charged from the top after seating the rubber stopper containing the chlorine and thermocouple tubes in the base of the reactor. Quartz wool approximately 2 inches deep was packed at the bottom. Silica chips (pre-chlorinated) were next added to a depth of about 6 inches and then another 2 inches of quartz wool. A feed charge containing close to 125 grams of BeO was next added and generally extended to a height of 8 to 9 inches. Finally, another 2 inches of quartz wool was packed in. This layer came within an inch or so of the base of the bulb. The silica chips and wet charge pebbles were introduced through a tube to prevent contamination of the bulb. In general the percent of BeO in the wet feed was roughly determined by weighing a sample, drying, igniting and reweighing. The charge equivalent to 125 grams of BeO was then determined and weighed out.

(b) Setting up for Operation

The charged reactor was lowered into the tube furnace and extended about 4 inches below the bottom. A small blower was used to assure that the base of the reactor remained cool. The gas inlet lines were connected and the thermocouple inserted. The water condenser was not attached. Argon was passed into the reactor and the temperature raised to 1000°C and maintained for an hour or so to dry out the charge. Meanwhile the rest of the system was set up and with the line pinch clamps (10) (Fig. 10a) closed, the $\text{Mg}(\text{NO}_3)_2$ solution in the Dewar (12) was cooled by dry ice until a large amount of solid eutectic had formed. The water condenser was then attached using a high-temperature silicone grease and the system well flushed with argon, closing the bypass pinch clamp (10a) and opening the line clamps (10). The three-way stopcock (6) in the gas inlet line was then set for two-way operation into the H_2SO_4 pressure release bottle (5), the head of which was adjusted to equal the head of the NaOH solution (15). The chlorine flow

was then set and the inlet lines filled with chlorine. With the reactor bulb temperature properly set, the H_2SO_4 head (5) was raised and the stopcock (6) set for three-way operation. When the second chlorine inlet tube was used, a separate flowmeter was placed in the line and the flow regulated by pinch clamp. All connections were made with tygon tubing.

(c) Operation and Results

The chlorine flow rate was set such that chlorine equivalent to the charge would pass through the reactor in about six hours. When this equivalence point was reached or a deep chlorine color appeared in the exit lines, the chlorine flow was stopped and an argon purge started. Flow rates and temperatures were recorded regularly during the run, and adjustments made as necessary. The bulb temperature required special attention because of the heat released as the BeCl_2 condensed. After the system had been purged with argon, the line pinch clamps (10) were closed and the bypass clamp (10a) opened. The SiCl_4 condenser (11) was removed and the volume of liquid noted. The condenser (11) was then cleaned, all power to the system turned off, and the system left to cool with argon flowing through it. When the system was cool, the argon flow was increased. The water condenser was quickly removed and the top of the reactor plugged with a rubber stopper. The tygon leads to the reactor were then pinched off. The reactor was removed from the furnace and taken into a dry box where the weight of BeCl_2 obtained was determined. The unreacted charge was assayed and also the material in the water condenser. Finally the chlorine in the NaOH bottle was determined. The above data were used for calculation of the percent conversion of BeO to BeCl_2 and the chlorine efficiency. The product BeCl_2 was analyzed for iron.

The original experiments were made with the single chlorine inlet and a cold bulb. At the start of chlorination, a deep red material deposited on the walls of the bulb. BeCl_2 , which is white, deposited on this red layer with increasing purity as the run proceeded. Tests indicated that this red material was an iron compound (believed to be FeCl_3) and that it would not deposit in a bulb heated to 300°C . Since a considerable amount of this iron was found to be coming from the silica chips, these were thereafter pre-chlorinated before use. Heating the bulb to 300°C effectively eliminated the red compound from the bulb as expected. However, the BeCl_2 deposit

was greenish in color. Two runs were made without changes and yielded BeO to BeCl₂ conversions of 93.2 and 94.3% with chlorine efficiencies of 99% and >99%.

Iron determinations were made on the products of these runs and were 0.016 and 0.020%. At this point, in the belief that the greenish color was caused by ferrous chloride, FeCl₂, the additional chlorine inlet above the charge was added to reoxidize the FeCl₂ to FeCl₃ and thus prevent iron deposition in the bulb. This procedure proved effective. The iron content of the product dropped to 0.002% with a BeO conversion greater than 90% and a chlorine efficiency of about 93%. The drop in chlorine efficiency from previous runs is accounted for by the chlorine added above the charge. The BeCl₂ produced was very slightly off-white in color. Since optimum conditions were not established, further improvement can be expected. This product compares very favorably with the Beryllium Corporation BeCl₂ purchased for the electrolytic program, described earlier, which appears to have been made in a nickel reactor. However, the quartz used in the experimental reactor was attacked by the BeCl₂ in the hot zone and a heavy white BeO scale developed. Some form of internal heating appears desirable although impervious carbon sleeves might solve the problem in a properly designed reactor. Unfortunately no experience was obtained on the use of the nickel condensers which were received at the project's termination. It is believed though that at condenser temperatures (<350°C) nickel will not contaminate the product. The BeCl₂ can of course be purified by distillation but this added step is not desirable from an overall cost standpoint.

B. Beryl Ore as Feed

1. Beryl Analysis

Ground beryl ore as received was screened through -200 and -325 mesh screens. The fraction passing through the -325 mesh screen was analyzed with the following results:

<u>Material</u>	<u>Percentage</u>
BeO	11.7
Al ₂ O ₃	17.6
SiO ₂	61.3
Fe	0.57
H ₂ O	{ 2.36 at 1000°C 0.045 between 1000° and 1200°C

One of the important considerations connected with work on beryllium and beryllium compounds is the difficulty of analysis which can sometimes result in deviations of 5 to 15% on duplicate aliquots. The above figures are averages of several determinations.

2. Feed Preparation

The chlorination feed was prepared by mixing -325 mesh beryl ore with 10 to 25% excess acetylene black in a ball mill, adding water and rolling overnight. The spheres were similar to those from BeO. Several experiments were made using up to 10% sugar binder (based on BeO) but the fired pellets showed no marked improvement in resistance to powdering.

3. Chlorination Apparatus

Whereas a relatively simple chlorinator proved suitable for BeO as feed, the chlorination of beryl presents certain problems that require more elaborate equipment, especially more efficient condensers with their attendant high temperature seals. These difficulties arise from the need for separation of the BeCl_2 from the relatively large quantities of AlCl_3 and SiCl_4 formed.

Preliminary chlorination experiments were undertaken in a one-inch diameter Vycor tube (lying horizontally in a tube furnace and serving as its own condenser on the outside) and in the reactor used for chlorination of BeO (Fig. 10a). Neither of these was satisfactory, because of their inefficiency in separating BeCl_2 and AlCl_3 . Resistance-wound reactors of mullite (more resistant to attack than quartz) and of quartz were tried (Fig. 11) with hot seals being made by use of ground joints. The reactors were approximately 24 inches long and 3 inches in diameter. The condenser joint was a particular problem since it had to be taken apart at the end of the run with reasonable ease. The joints which were to be hot were generally made by placing a thin wet asbestos sheet around the male joint and then forcing the joint together and holding it with fairly stiff springs. These joints were moderately satisfactory but the desirability of a metal system even on a small scale was soon apparent. The resistance wound glass tube condenser (Fig. 11) was 30 inches long and was followed by a water condenser which was connected in turn to the SiCl_4 condenser, as in Fig. 10a. The metal "chlorinator" (Fig. 12) had undergone its shakedown tests and a preliminary chlorination run using glass condensers at the time of the project's termination. Glass condensers were used because the nickel condensers ordered had not been received. Unfortunately, a small water leak developed in one of the bayonet water coolers during the run and negated the experiment. The body of

Fig. 11 REFRACTORY CHLORINATOR UNIT

the reactor (1) was a 6-inch diameter steel tube 23-1/2 inches long with a flange (2) at the upper end and three grooves for rubber O-rings at the bottom (3). A second "flange" (4) was welded above the grooves and a gas outlet (5) was located near the top. The top (6) was made of nickel and was bolted onto the body flange, the seal being made with a nickel O-ring (7). A circular groove 1/16 inch deep and 2-7/8 inches I.D. x 3-5/8 inches O.D. (8) was cut in the top nickel face and served to seat the top of the reaction tube (9). Asbestos rings were used in these grooves as seals and cushions. The exit flange (10) on the top was designed to bolt directly onto the first metal condenser. However, since the metal condensers were not available, the metal adapter (11) was used to permit attachment to a glass condenser (12). The base of the reactor (13) was fitted with a metal ring (14) which press-fit over the rubber O-rings making a gas tight seal. The base was water cooled by copper coils (15). A groove (16) identical to that on the top (8) was cut in the base and served to position and seat the reaction tube (9) with asbestos rings as above. Thin metal tubes (17, 18, 19) were soldered to the base and were used for rubber stopper connections for the gas entrance tube (20), the nickel water coolers (21), and the thermocouple well (22). The base also contained an argon entrance tube (23) outside of the reaction tube. The base was spring-loaded (24) to the body of the reactor, thus providing for differences in expansion of the body wall and the reaction tube during operation. Reaction tubes (9) of quartz, mullite and impervious carbon ("Graph-i-tite" - produced by Graphite Specialties Corp.) were available. Their dimensions were 3 inches I.D. x 3-1/2 inches O.D. x 24 inches long. The heater (25) was a split graphite "bayonet" with separation maintained at the bottom by means of a lava insert (26). The water coolers, screwed into the base of the heater, served as electrical leads. The reaction tube was insulated from the metal body with asbestos fibers (28). The gas entrance and exit systems were identical to those shown in Fig. 10a. The nickel condensers (Fig. 13) consisted of two identical units (1 and 3) and a smaller cyclone separator (2). The larger units were 14 inches long and 8 inches in diameter at the top and the smaller unit 11 inches long and 3 inches in diameter at the top. A flat plate (4) extending to within 6-1/2 inches from the discharge port (5) of the larger condensers served as a baffle for incoming gases. Condensers (1) and (2) were to serve as BeCl_2 collectors and condenser (3) as an AlCl_3 collector. Heating mantles were designed to provide uniform temperatures. The condensers with heating units were received at the time of the project's termination.

Fig. 12 METAL CHLORINATOR

Fig. 13 NICKEL CONDENSER UNIT

4. Operation

(a) Background

Based on the large separation in sublimation or boiling points of BeCl_2 , AlCl_3 and SiCl_4 - 494° , 178° and 58°C , respectively, it would appear that there should be no difficulty in obtaining pure compounds by fractional condensation procedures. SiCl_4 appears to offer no difficulties. The literature, however, is contradictory as relates to the products BeCl_2 and AlCl_3 obtained from chlorination of beryl. Winters and Yntema (Trans. Amer. Electrochem. Soc. 55: 205 (1929) claimed to have separated BeCl_2 and AlCl_3 at 375°C . Clifton Products, Inc. (see CPI 2,3,6) reported separation of BeCl_2 and AlCl_3 using hydrogen gas.

On the other hand F.K. McTaggart (J. Council Sci. Ind. Res. 20, 564-84 (1947) found that BeCl_2 and AlCl_3 were not separated on condensation but that a redistillation at 470°C produced a pure BeCl_2 product and a mixed BeCl_2 - AlCl_3 product. He concluded that lack of separation was caused by an oxy-aluminum chloride compound which was substantially involatile up to 400°C . The oxygen he believed came from hydroxyl groups in the beryl itself which were not completely eliminated even by heating to 1200°C . He suggested that his results differed from those of others possibly because of the use of beryl from a different source. Analysis of beryl used at Sylvania (p. 24) showed residual water between 1000° and 1200°C - no attempt was made to go higher in temperature. Based on operational results showing carry-through of BeCl_2 , several experiments were made using AlCl_3 and BeCl_2 directly in an effort to determine whether there was compound formation between AlCl_3 and BeCl_2 . In two of these experiments AlCl_3 vapor was passed over BeCl_2 (solid), and the amount of BeCl_2 depositing in the condenser portion of the tube compared to that depositing when no AlCl_3 was used. In both cases there was some indication of compound formation, though the evidence was not conclusive. In a third experiment on a larger scale volatilizing both BeCl_2 and AlCl_3 and using an efficient packed condenser, a pure BeCl_2 product was found at the base of the condenser, but again there was evidence, inconclusive as before, that more BeCl_2 passed through the condenser with the AlCl_3 than would be expected without the presence of AlCl_3 . There was not sufficient time to run a blank test on pure BeCl_2 , however, to check this.

Early experiments using small beryl charges in a horizontal Vycor tube, heated in a tube furnace indicated that the use of HCl was beneficial in removing residual water from the charge. Temperatures up to 900°C were possible with little volatilization of products from the charge. However, chlorine at 900°C reacted readily with the charge and produced a heavy white "fog" in the condenser part of the tube. This "fog" drifted through the system. This tendency to "fog" formation was fairly characteristic of the beryl runs and increased the separation difficulties.

(b) Charging the Reactors

The reactors (Figs. 11 and 12) were charged from the top after the bottom connections had been made. An insulating bed of mullite or silica chips was used and the charge added to fill the hot zone. A quartz wool filter was then placed in the cap and the cap sealed to the system.

(c) Setting up for Operation

Once the cap was sealed to the system the entire unit was leak tested by pressurizing the system with argon using a head of 4 or 5 inches of H_2SO_4 . If the system was satisfactory, the water condenser was removed and the power to the reactor and condensers was turned on and the temperature set. In the metal chlorinator (Fig. 12) an argon pressure was maintained outside the reaction tube slightly greater than the gas pressure inside. The procedure with the entrance and exit gas lines was the same as for the BeO operation (II. A. 4. b.)

(d) Operation and Results

The operation during a run was essentially the same as for BeO chlorination (III. A. 4. c) with special attention being given to the $BeCl_2$ condenser. When the run was over and the system cool and argon-purged, the condensers were removed and the contents analyzed. Access of air at this time was not detrimental, since the information desired was the degree of separation of $AlCl_3$ and $BeCl_2$. No clean separations were made, and an excessive carry-through of $BeCl_2$ into the $AlCl_3$ condenser was observed. This appeared to be caused by the "fog" formation discussed earlier. A chlorination temperature of 1000°C was used with $BeCl_2$ condenser temperatures of 250° to 300°C. No attempt was made to obtain complete chlorination, although chlorination data indicated about 60% conversion of the beryl to chlorides at essentially 100% chlorine

efficiency. One run made with the horizontal tube BeCl_2 condenser, having a temperature gradient established along it varying from 200°C at the cold end to 500°C at the hot end, showed regions of fairly pure BeCl_2 (95 to 99%) surrounding a region high in AlCl_3 . Even in this experiment, well over 30% of the BeCl_2 produced was found in the air condenser. An efficient vertical condenser thus appears to be a necessity to avoid BeCl_2 carry-through. As in the BeO chlorinations some attack on the reaction tube was noted in the form of a scale on the walls. This scale was found to contain considerable beryllium. Use of impervious graphite might solve the problem here also, and tubes had been purchased as was previously mentioned. In any event, the results obtained indicate the desirability for basic research on the BeCl_2 - AlCl_3 system and the effect of oxygen on the system.

IV. CONCLUSIONS

1. The electrolytic process developed by Sylvania has been established as a satisfactory method for direct continuous production of finely divided beryllium metal as a quasi-amalgam. High-quality amalgam was consistently obtained in both the 5-inch and 10-inch cells at current efficiencies above 70%.
2. The beryllium metal produced (as amalgam) is amenable to direct hot pressing. Compacts were produced with oxygen contents less than 0.8% and chlorine contents of 0.00 to 0.3%. Termination of the program left incomplete the study of hot pressing conditions and evaluation of the metal so produced. Additional work is therefore required. However, it is believed that chlorine can be essentially eliminated from the compacts and the oxygen content substantially reduced. Standard commercial powder (-200 mesh) is reported to have an oxygen content of about 0.6% and high temperature electrolytic material (which also must be attritioned to produce -200 mesh powder) has somewhat more than this. With regard to metallic impurities, the quality of metal will be a direct function of the purity of the beryllium chloride feed. Electrolytic powder as now produced is definitely superior to standard powder from the standpoint of metallic impurities.
3. Fine beryllium powder may be produced by distillation of the mercury from the "amalgam" followed by a simple grinding of the resultant "sinter" cake. An excellent vacuum system is required to prevent oxygen pickup. A small inert gas bleed may be desirable.

4. The present stage of development of this process does not enable a valid cost comparison with other production processes. However, the continuous nature of the process, unique in beryllium technology, and the simplification in operations it offers over other processes in the powder metallurgy of beryllium are distinct advantages.
5. BeO has been established as a satisfactory starting material for production of electrolytic cell feed, BeCl₂, by direct chlorination. Iron contents of 0.002% were achieved. Yields and chlorine efficiencies above 90% were obtained. Distillation of BeCl₂ provides excellent separation from all the normal impurities with the possible exception of AlCl₃.
6. The suitability of beryl ore as a starting material for production of BeCl₂ by direct chlorination has not been established. Further work is required.
7. Basic research on the Be-Hg system and on the BeCl₂-AlCl₃ system is desirable.

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