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ABSTRACT

Studies on the production of beryllium metal powder by the electrolysis of a molten BeCl_2 -NaCl mixture using a mercury cathode were continued in order to produce ultrafine beryllium powder for metallurgical evaluation. Beryllium amalgam was successfully produced from which the metal powder was recovered by distilling off the mercury. Studies on the beryllium metal powder and an amalgam oxidation product in the form of a fine black powder were also made. Electron microscope studies show an agglomerate particle size of 1 - 2 μ , with definite evidence that individual metal particles are 0.1 - 0.2 μ in diameter.

INTRODUCTION

This report discusses additional work that has been accomplished on the amalgam process¹⁾ in an effort to produce an ultrafine beryllium powder. The process involves the electrolysis of a molten eutectic mixture of BeCl_2 -NaCl at 300°C using a graphite anode and a mercury cathode. Since the solubility of beryllium in mercury is only 0.001%,²⁾ the deposited beryllium forms a quasi-amalgam composed of extremely small metal particles suspended in the mercury. On passing this amalgam through a 100 mesh screen, it is possible to separate the metal particles from most of the mercury. The metal particles separated still entrap large amounts of mercury which can be further removed by pressing and finally by distillation.

ELECTROLYTIC TESTS

The electrolytic cell system is shown in Fig. 1. It is composed of the cell where electrolysis takes place, the vacuum filtration unit for separating beryllium quasi-amalgam from mercury, and a tank for storing the mercury collected³⁾.

The electrolytic cell system was charged with 1009 lb of mercury. Of this amount, 550 lb were charged to the cell while the remainder was pumped into the holding tank. Additional mercury was added to the system as needed via the filter screen. The mercury used was checked spectrographically and found to compare favorably with a laboratory sample of triple-distilled material.

The anode was placed in the cell at a distance of 2" from the mercury surface. The stirrer shafts were put into place, the cell was sealed, and nitrogen was admitted. Dew point readings were taken regularly to ensure

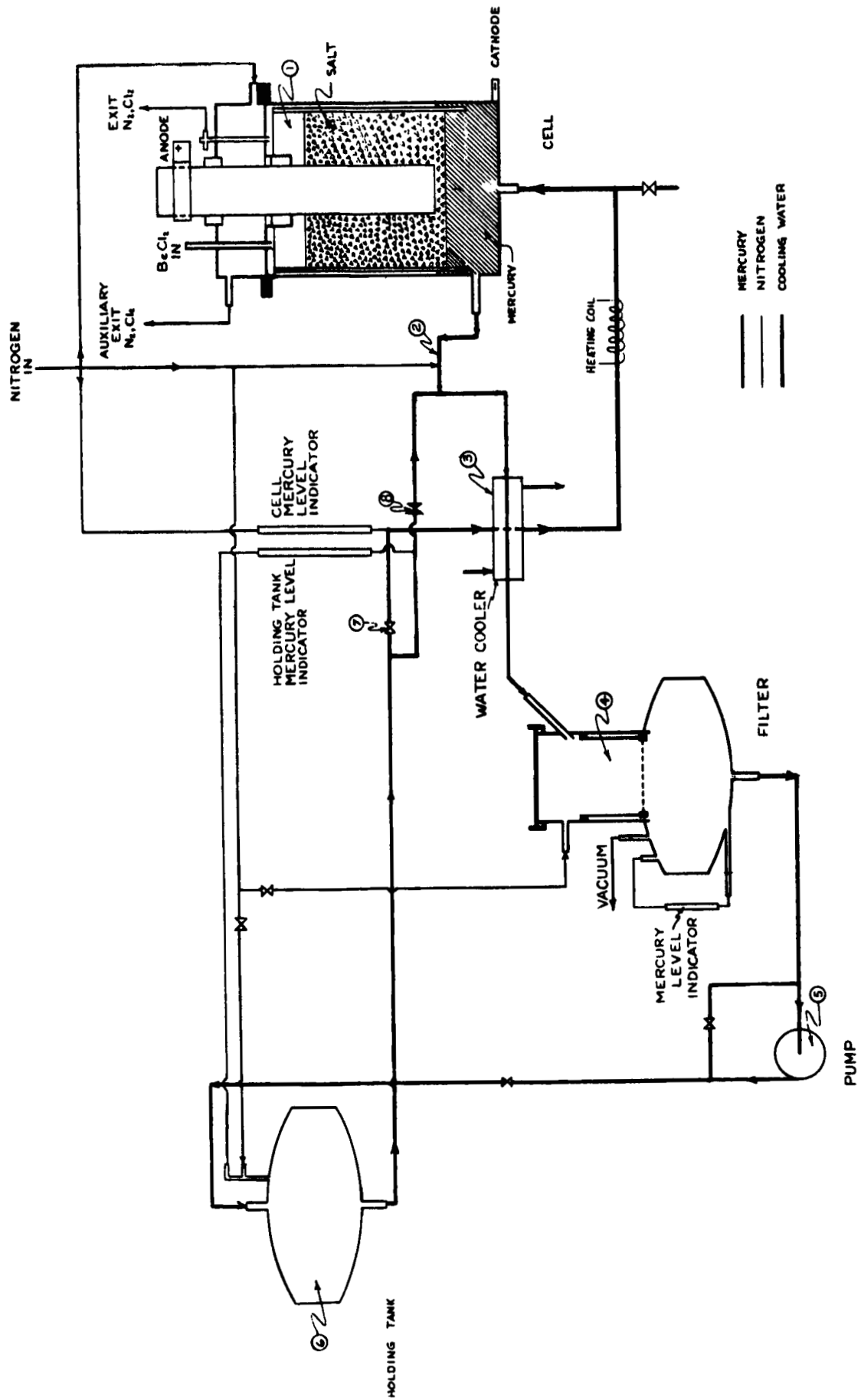


Fig. 1 - Electrolytic Cell System

proper moisture-free atmosphere throughout the system. Typical readings were around -25°F .

Electrolyte in the amount of 86 lbs was charged to the cell. Its composition was that of an approximately eutectic mixture of $\text{BeCl}_2\text{-NaCl}^{4)}$, Fig. 2, within the range of 58 to 60% BeCl_2 . Sodium chloride used was reagent grade, and beryllium chloride was re-sublimed commercial grade. Re-sublimation was carried out in our laboratory⁵⁾ and a typical analysis of the purified BeCl_2 is given in Table 1.

Table 1 - Typical Spectrographic Analysis of Re-Sublimed BeCl_2 Charged to Cell⁵⁾.

	ppm
Ag	1
Al	78
B	2
Ca	31
Cd	6
Co	50
Cr	6
Cu	37
Fe	105
Mg	125
Mn	3
Mo	3
Na	56
Ni	90
Pb	19
Si	39
Ti	9
Zn	40

Samples of the electrolyte were taken before and after electrolysis to control the BeCl_2 content. Electrolysis was conducted at 300 to 330°C . The current was held constant at 250 amps. requiring a potential of about 8 volts. The top heaters were turned off during electrolysis to aid in keeping a constant temperature, since the temperature of the bath tends to rise due to the heating effect of the current. The stirrers were operated during electrolysis to ensure proper mixing of the amalgam.

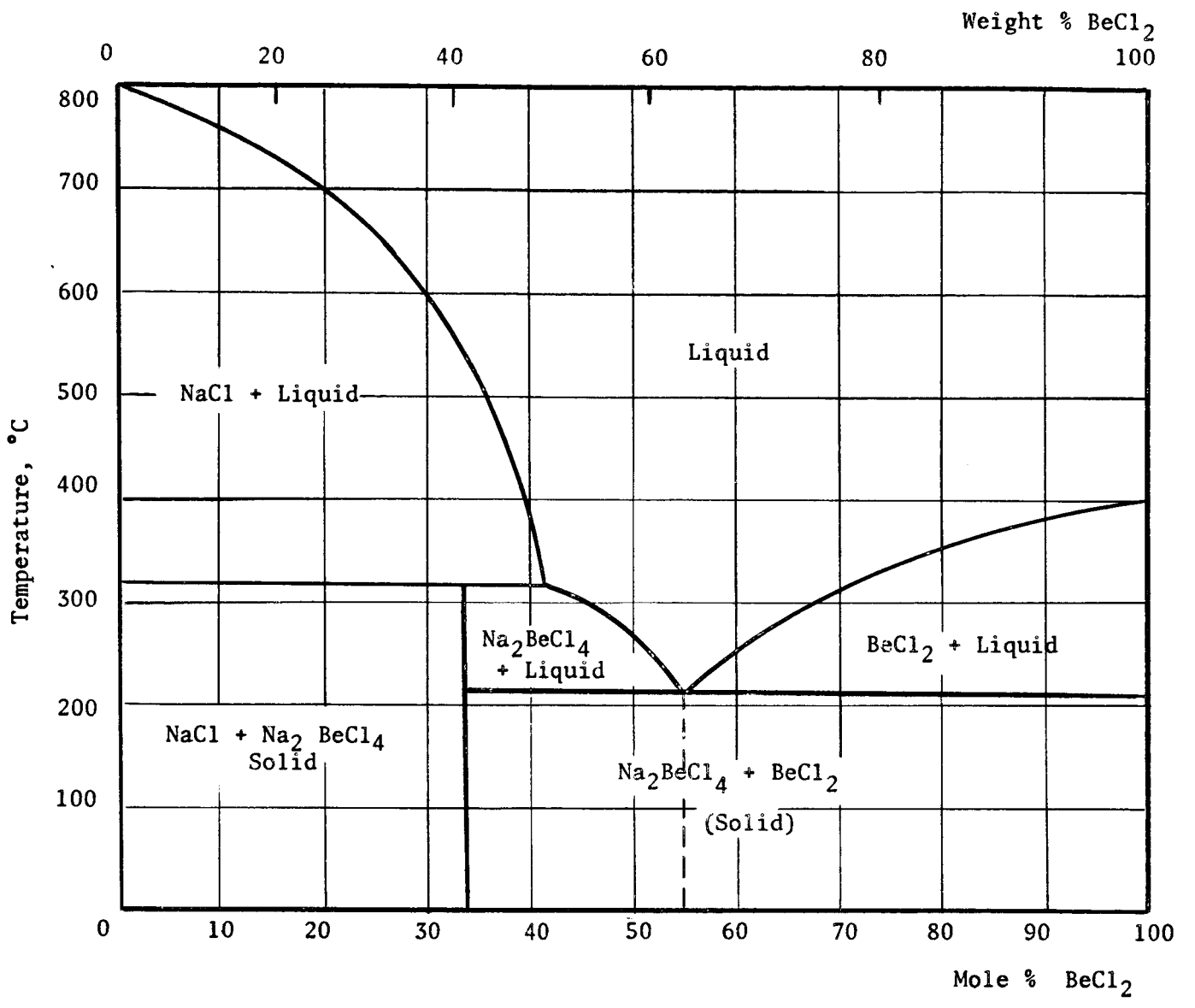


Fig. 2 - Beryllium Chloride - Sodium Chloride Phase Diagram⁴⁾

Each test was conducted for about 5 hours. After this period, the cell was tapped by introducing mercury from the holding tank into the cell to force the amalgam from the cell.

The amalgam was filtered, collected in the vacuum filtration unit, and transferred into air-tight containers. The mercury which passed through the filter was pumped to the holding tank. The cell was idled at 250°C by turning on the top heaters, and a nitrogen atmosphere was maintained in the cell until the next run.

Data for a typical test is shown in Fig. 3. It can be seen that within one half hour after switching power on to the cell, a current of 250 amps. can be readily passed. Also, the heating effect due to the resistance of the bath causes a gradual increase in temperature resulting in a voltage drop.

Current efficiency was calculated by comparing the amount of BeCl_2 depleted during electrolysis with the theoretical amount predicted by Faraday's Laws. The results (Table 2) are approximate because the analytical method for determining BeCl_2 in the bath was only empirical. The method used was based on the fact that BeCl_2 is soluble in many organic solvents while NaCl is not. Therefore when a sample of the bath is extracted with an alcohol mixture and filtered, the undissolved residue may be weighed and considered as NaCl . The drawback of this method, however, is that any BeO present in the bath which is insoluble in the alcohol will remain in the residue thus introducing an error in calculating the amount of BeCl_2 depleted.

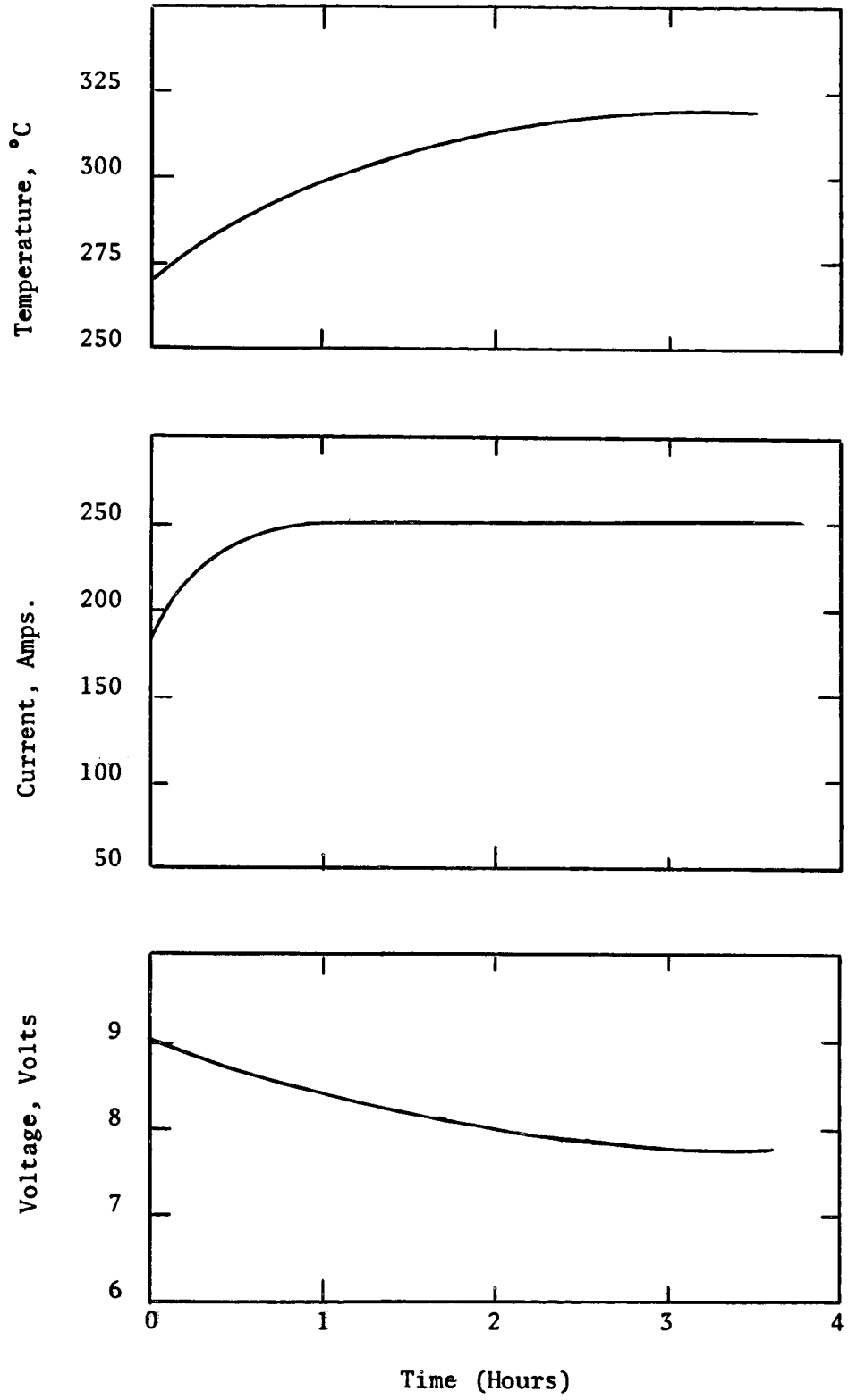


Fig. 3 - Typical Operational Data⁶⁾

TABLE 2
Experimental Results 6)

Electrolysis No.	Electrolyte			BeCl ₂ Depleted During Electrolysis, lb	Amount Collected, lb	Filtered Amalgam			Current Efficiency %
	BeCl ₂ Before Electrolysis, %	BeCl ₂ After Electrolysis, %	BeCl ₂ Depleted During Electrolysis, lb			Beryllium Content %	Sodium Content %		
3	-	-	-	10.1	1.14	0.08	-	-	
4	-	-	-	9.2	1.60	0.23	-	-	
5	-	-	-	20.0	-	-	-	-	
6	60.0	56.3	7.6	21.7	1.87	0.10	100	100	
7	58.6	57.6	2.1	20.1	2.28	0.09	51	51	
8	59.6	57.4	4.6				100	100	
9	58.6	56.9	3.3	8.1	-	-	79	79	
10	58.6	56.9	3.4	13.8	-	-	82	82	
11	59.6	58.7	1.9	7.0	-	-	46	46	

BERYLLIUM AMALGAM

The beryllium content of the amalgam as it left the cell was found typically to be 0.04%. Vacuum filtration of the amalgam on the 100 mesh screen resulted in a pasty cake having a shiny and silvery appearance. The beryllium content of such cakes was 1.1 to 2.3 % (Table 2). Additional mercury could be squeezed from the cake by pressing; the higher the pressure applied the more mercury can be expressed out, until a limiting value is approached beyond which no mercury can be removed. By measuring the density of amalgams pressed at various pressures, it was found that under these conditions the limiting pressure required to squeeze the maximum amount of mercury was about 18 tons/sq. in., and the density of pressed amalgam reached a limiting value of about 5.2 g/cc, as shown in Fig. 4. This density corresponds to an amalgam containing 24% Be, or 87.5 atom % Be and 12.5 atom % Hg, coinciding with a formula Be_7Hg .

Analysis of mercury obtained after passing through the filter showed that it contained 0.0014 % Be, in close agreement with the known value of the solubility of beryllium in mercury²⁾.

Amalgam which was tapped after remaining in the cell for an extended period of time was coarse-grained and contained a higher beryllium content. This was attributed to the phenomenon of aging (or agglomeration) which is accelerated by increase in temperature, and the subsequent separation of the agglomerates on the surface of mercury due to the difference in specific gravity.

Since aged amalgam will flow only with difficulty, the stirrers installed in the cell proved unable to handle the load and the amalgam could not be tapped properly as a result. In an attempt to alleviate this

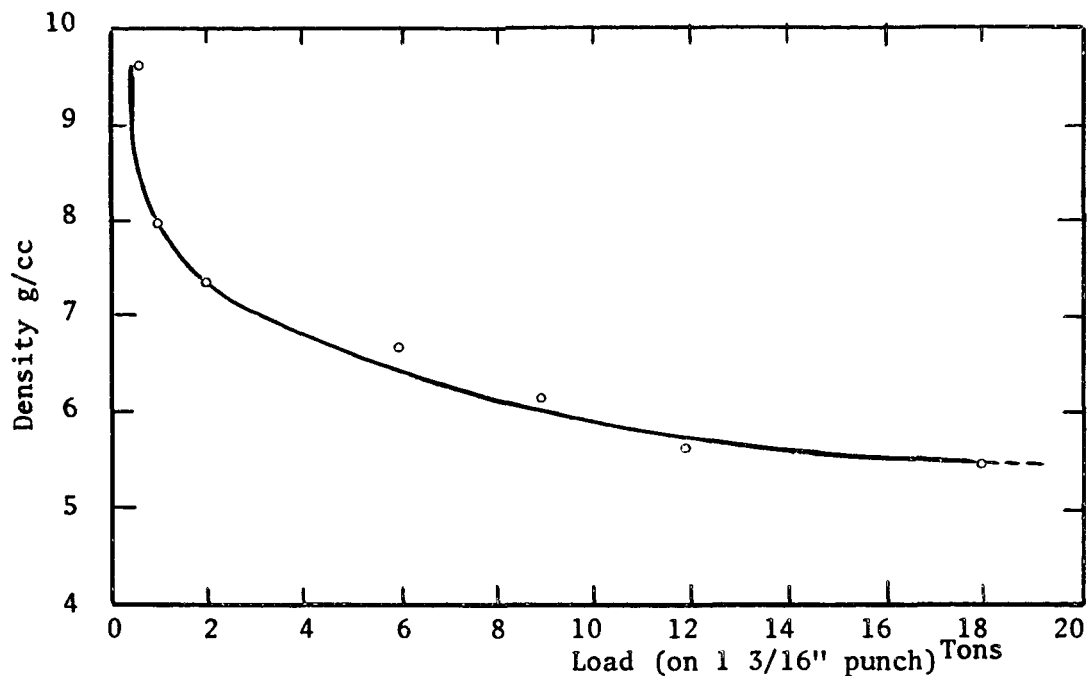


Fig. 4. Cold-Pressing of Amalgam⁷⁾

difficulty the two 1/10 horse power stirrer motors were replaced by one 3/4 horse power stirrer motor driving the two stirrers.

The amalgam readily decomposes when exposed to air, forming a black powder that separates from the amalgam phase and floats on the surface of the mercury. Studies of the black powder are reported in a later section of this report. In an attempt to find out whether or not beryllium forms a compound with mercury an x-ray investigation was undertaken. The amalgam could not be placed into the sample tubes used for Debye-Scherrer photographs unless it was diluted with mercury. Films obtained with such diluted amalgam showed no lines which could be recorded. Attempts to obtain a diffractometer trace of the amalgam were also unsuccessful because any window transparent enough to x-rays was not thick enough to prevent the amalgam from oxidizing. As a result either no useful patterns were obtained, or patterns characteristic of black powder were obtained.

BERYLLIUM METAL POWDER

A sample of the amalgam produced was heated in an all-glass vacuum distillation unit housed in a nitrogen inert atmosphere dry box (dew point -30° F) to distill off the mercury. A black fine powder remained behind in the distillation flask. A sample of this powder was examined by the Debye-Scherrer method. Beryllium, beryllium nitride (Be_3N_2) and carbon were identified, with 3 lines being unaccounted for. Figure 5 shows the x-ray pattern of this distillation residue as compared with that for commercially available beryllium metal powder (General Astrometals, GB-2).

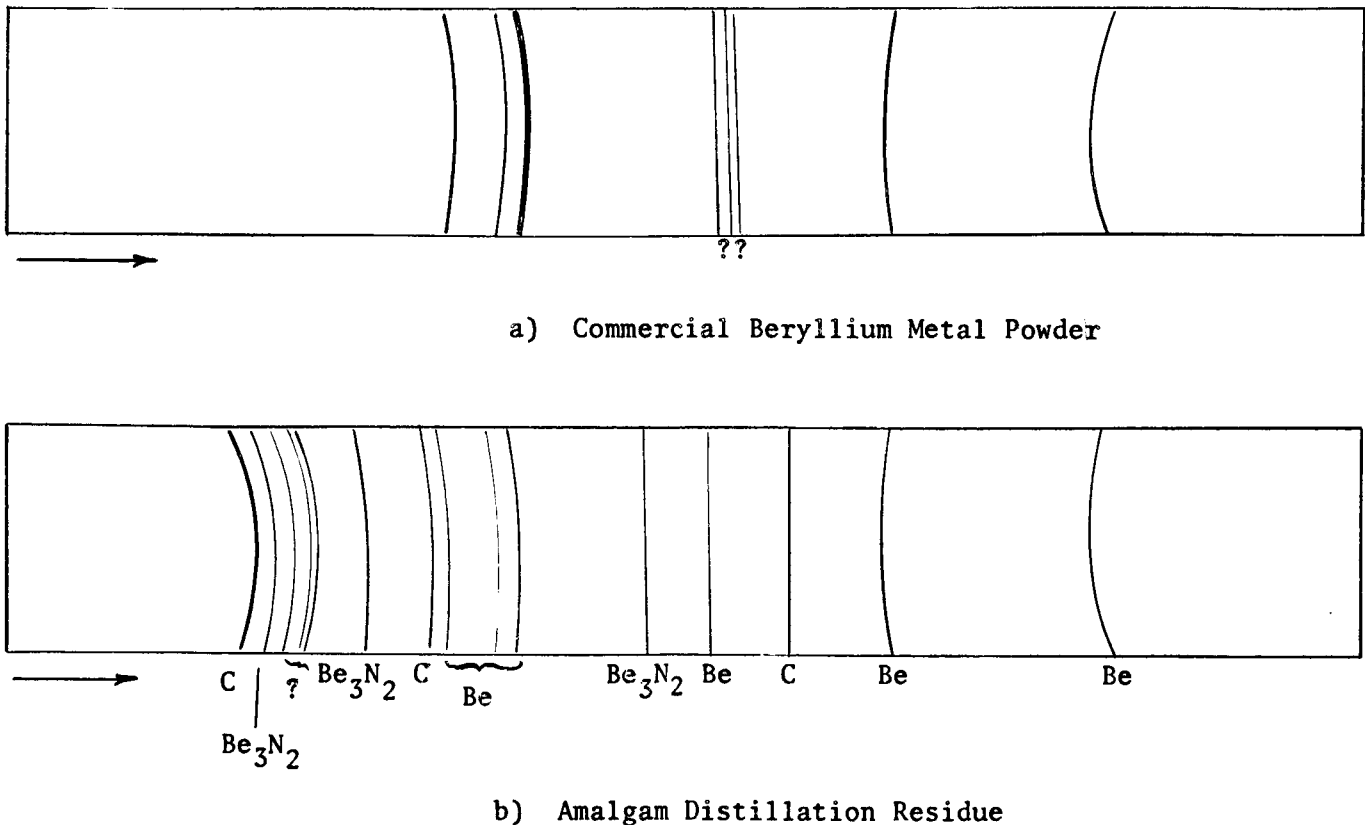


Fig. 5 - X-Ray Diffraction Patterns⁸⁾

THE BLACK POWDER

A sample of the black powder, formed by exposing the amalgam to air, was collected from the surface of the mercury and submitted to the following studies:

Microscopic Analysis

Microscopic examination revealed that this material is of extremely small particle size at least in the micron range. Droplets of mercury, about 20 μ diameter, always contaminated the product as shown in Fig. 6. Attempts to separate these mercury droplets by a simple sink-and-float method using dibromoethylene removed only a part of the mercury. Shaking overnight in this medium did not help to achieve the separation of mercury (Fig. 7).

Chemical Analysis

Total beryllium content and BeO content were determined⁹⁾ from which the metal content was calculated as shown in Table 3. The balance 32.9% is most probably the residual mercury.

Table 3 - Chemical Analysis of Black Powder

	%
Metallic Be	15.6
BeO	40.0
C	10.0
Fe	1.5

X-Ray Diffraction Analysis

A 114.6 mm Debye-Scherrer camera was used to examine black powder samples for identification of the phases present by reference to the A.S.T.M. Diffraction Card File and to the patterns obtained on relatively pure Be and BeO samples. A sample of black powder from the amalgam of No. 3 electrolysis was shown to contain Be, carbon, and mercurous chloride (Hg_2Cl_2) together with some unidentified lines, but not BeO which is in contradiction to chemical analysis. The grain structure of BeO may be too small to be resolved by x-rays. Figure 8 shows an x-ray pattern of the black powder as compared with that of commercial beryllium powder.

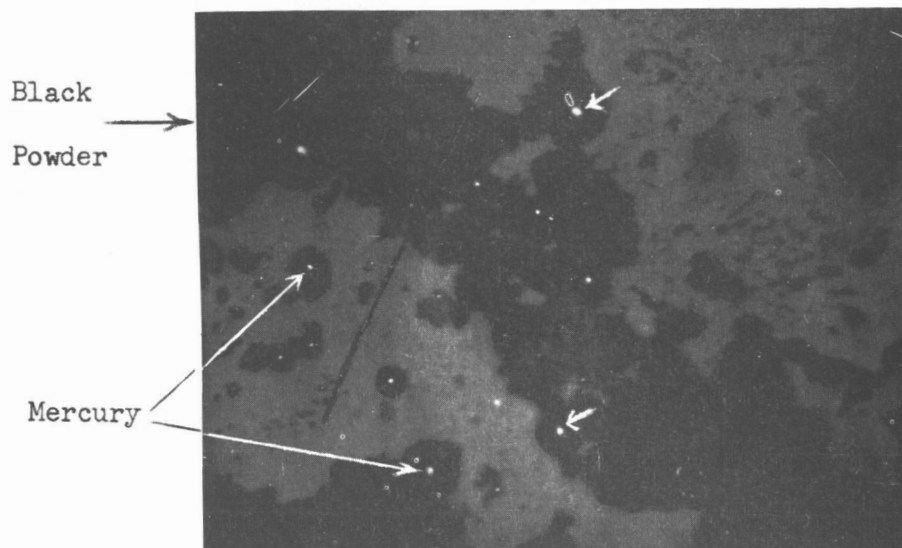


Fig. 6 - Photomicrograph of Black Powder Showing Mercury Droplets About 20μ Diameter, (100X)⁷.

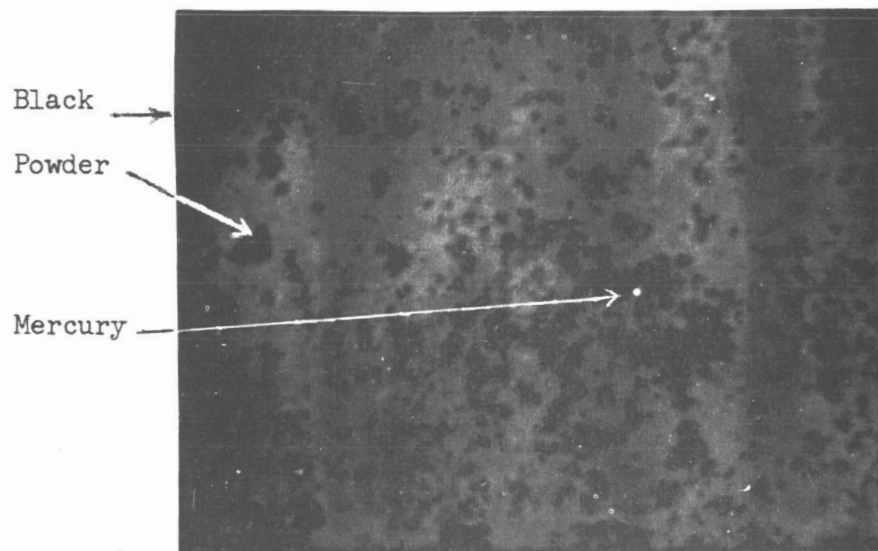


Fig. 7 - Photomicrograph of Black Powder After Sink-and-Float in Dibromoethylene Showing Unremoved Mercury Droplets, (100X)⁷.

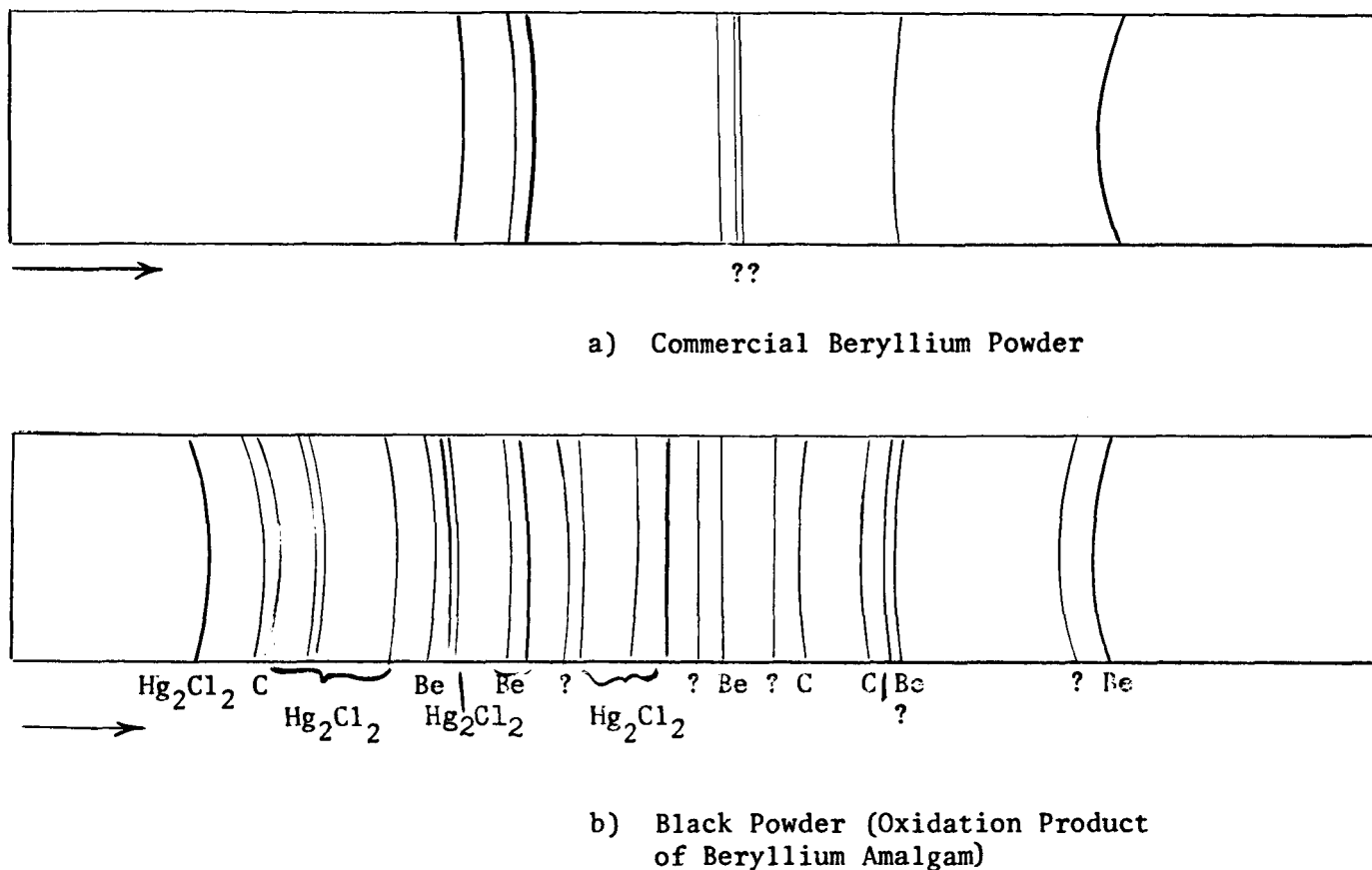


Fig. 8 - X-Ray Diffraction Patterns⁸⁾

Table 4 - Spectrographic Analysis of Calcined Black Powder
Values Expressed in Ppm Based on BeO

	Product from Electrolysis No. 10 (Ref. 6)	Product from Electrolysis No. 11 (Ref. 6)	Early Amalgam (Ref. 3)
Ag	140	140	250
Al	375	800	1,300
B	45	75	13
Ca	100	200	240
Cd	40	35	6
Co	85	92	120
Cr	~ 10,000	~ 10,000	1,500
Cu	600	750	450
Fe	~ 10,000	~ 9,000	15,000
Mg	55	150	60
Mn	1,500	1,200	660
Mo	300	400	700
Na	3,000	4,000	300
Ni	620	660	3,000
Pb	1,000	120	--
Si	350	450	150
Ti	120	125	--
Zn	170	500	170

Owing to the low atomic number of Be, x-rays are not strongly scattered so that a lengthy exposure of 32 hours is necessary with FeK_α radiation. Consequently, since small quantities of higher atomic number impurities may scatter much more strongly, there may well be diffraction lines after 32 hours from quite small quantities of impurity. The quality of such photographs is not especially high and so given the presence of several phases it is not easy to positively identify all lines. It is for this reason that in a typical film there are three to seven unidentified lines.

X-Ray Fluorescence Analysis

An x-ray fluorescence analysis was carried out using an air path, LiF crystal and tungsten radiation. Owing to overlap of Hg emission wavelengths with the very strong tungsten spectra from the tube it was not possible to identify the presence of mercury. Identified qualitatively were Fe, Cr, Ni, Mn, Zn, Pb, As. Elements below Ti are not detectable, hence the absence of Be.

Calcination of Black Powder

In order to identify the trace impurities in the black powder by spectrographic analysis, it was necessary to calcine this powder at 1000°C so that it could be compared with a BeO spectrographic standard. Spectrographic analysis of the calcined material is given in Table 4. The high values of iron and chromium are attributed to the corrosion of the stainless steel from which the cell is made. Sodium present is a result of some electrolysis of NaCl in the bath; the amalgam always contained 0.1-0.2% Na as shown in Table 2. It is not possible at this time, however, to account for the high values of lead and manganese since these were practically absent in the raw materials fed to the cell (See Table 1).

Figure 9 shows an x-ray diffraction pattern of this calcined black powder compared with commercial beryllium oxide. It can be seen that calcined black powder is mainly BeO with small amounts of Be still evident. There are some lines in the pattern unaccounted for.

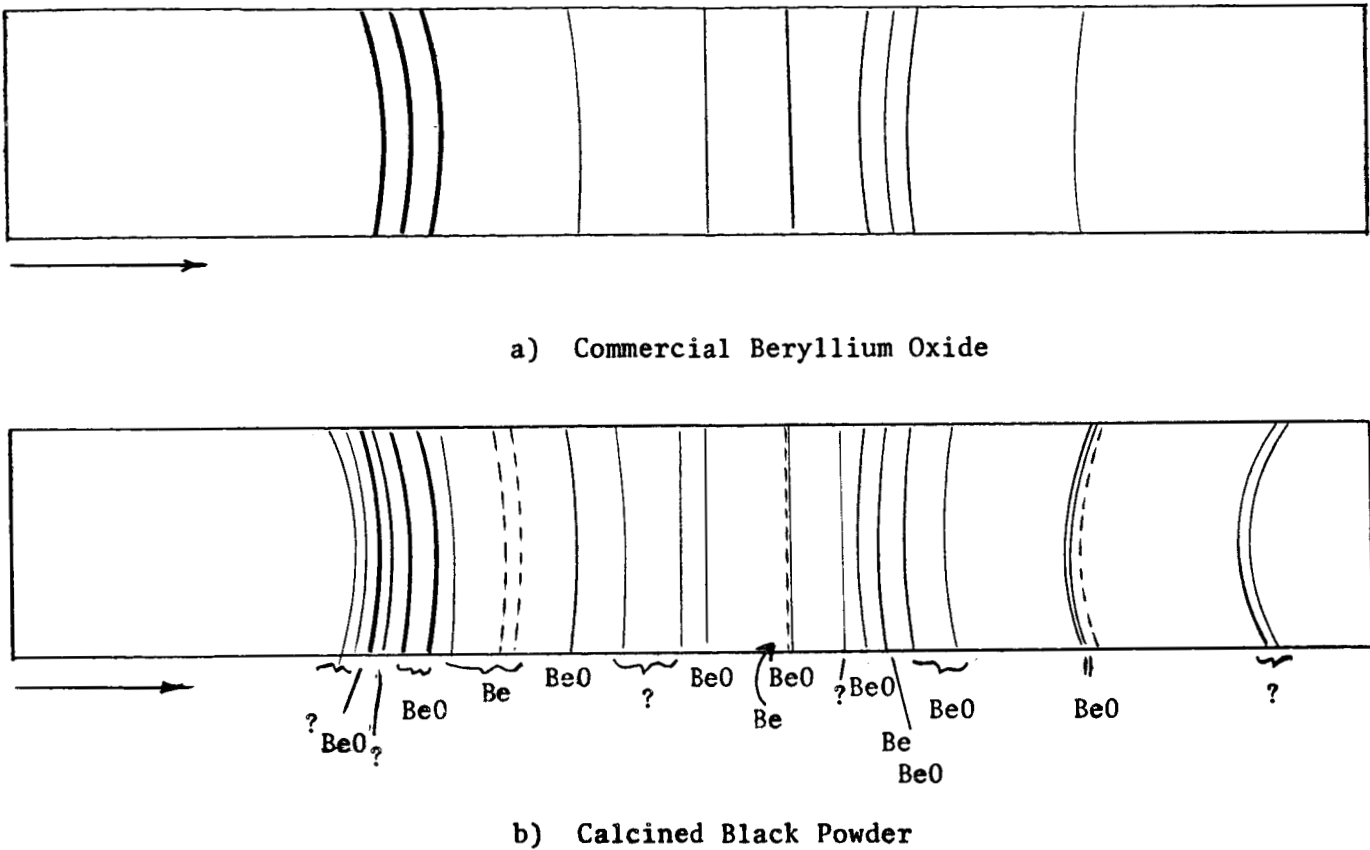


Fig. 9 - X-Ray Diffraction Patterns⁸⁾

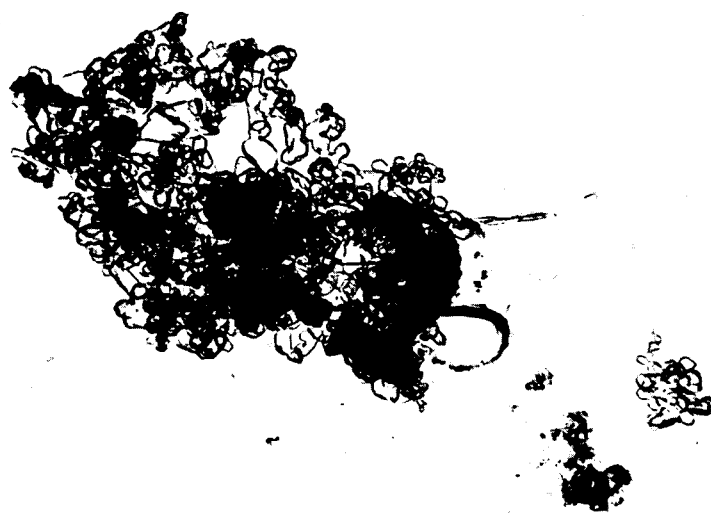
Particle Size Evaluation

Since no work has yet been done on evaluating the particle size of the ultra-fine beryllium powder because of the difficulty in handling such a reactive material, most of the effort was directed in evaluating the particle size of the black powder. Samples of black powder were suspended in different media and examined microscopically. Only agglomerates were observed and it was not possible to see individual particles.

Electron microscopic studies using a Philips EM-75C electron microscope are under way. A small amount of the black powder was dispersed in iso-propyl alcohol, siphoned into a fine-tipped eyedropper, and subsequently allowed to drop onto a Formvar coated copper specimen grid and allowed to dry. Once the material had dried, a carbon evaporated surface was applied, and the larger particles were shaken loose by gently tapping the grid. The Formvar was removed by dissolving it



a) Direct Observation, (15,360X)



b) Replica Technique, (29,000X)

Fig. 10 - Electron Microscope Photographs of
Black Powder⁸⁾.

in 0.5% ethylene dichloride. Direct observation of the specimen is now possible (Fig. 10a).

The replica technique utilized the same procedure with the exception that the black powder was removed from the carbon coating by dissolving it in 1:1HCl. Direct observation of the black powder revealed the powder to be composed of agglomerated material (Fig. 10a). Generally speaking the particles appear to have angular surfaces and range in size from 0.1 to 1.5 micron. These figures are arrived at by measuring only a relatively small number of particles. The replica revealed similar results (Fig. 10b).

The blackened portions of the replica may be due to insufficient removal of the powder, the presence of carbon, or a combination of the two. The latter alternative seems to be the most logical as sufficient time was allowed to dissolve most of the powder from the carbon film.

SHUTDOWN AND INSPECTION OF CELL

After 60 hours of actual cell operating time (from January to May 1966), erratic results became evident. It was observed that two hours were required to achieve the maximum current passed of 235 amps (Fig. 11) while for earlier runs a current of 250 amps was readily achieved in half an hour (Fig. 3). Further, the impurity level in the black powder was found to be much higher than in the amalgam previously produced³⁾ as shown in Table 3. Subsequently, the cell was shut down, drained, and then opened for inspection. Pictures in Plates 1 and 2 were taken when the cell was opened. The following was observed:

1. The graphite anode lost 5" of length, so that it was in fact barely touching the electrolyte (Fig. 12). The increased cell resistance accounts for the difficulty in achieving the required current during electrolysis.
2. The electrolyte contained fine black material which, on separation by dissolving away the electrolyte, was revealed to contain about 20% carbon⁹⁾. This can be accounted for by the disintegration of the anode.

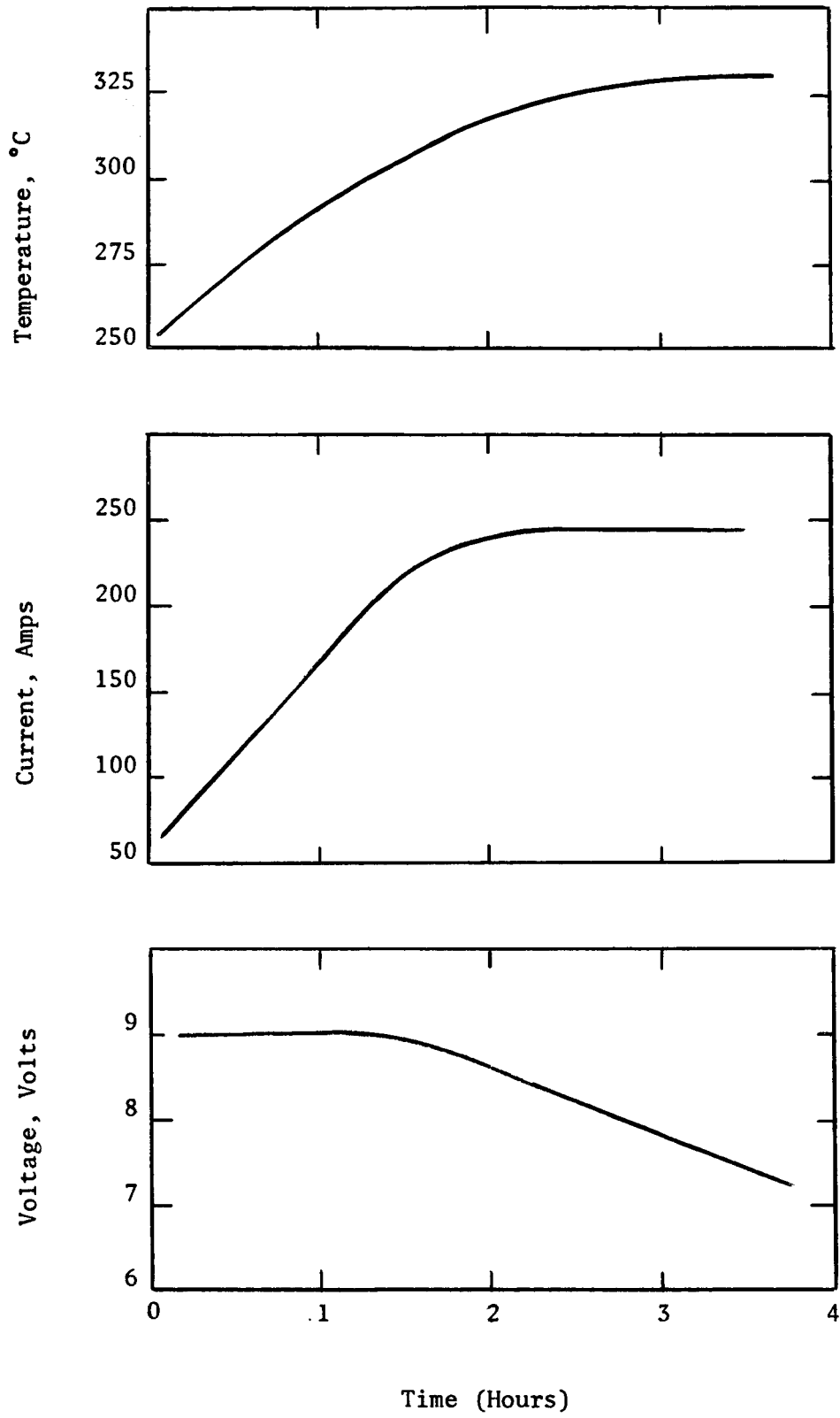
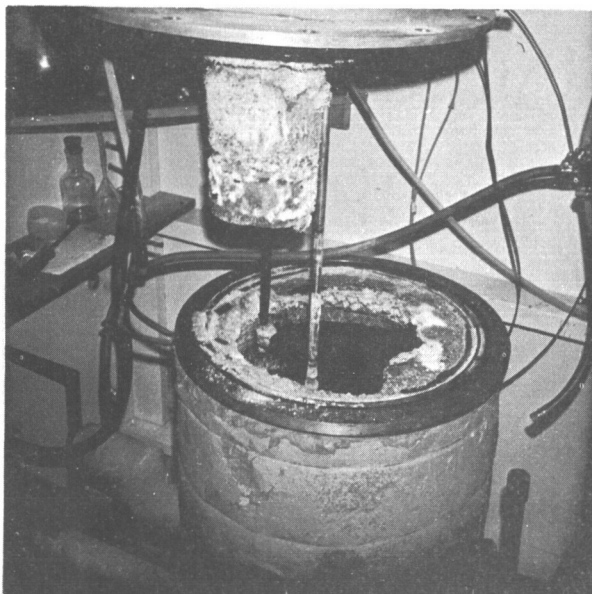
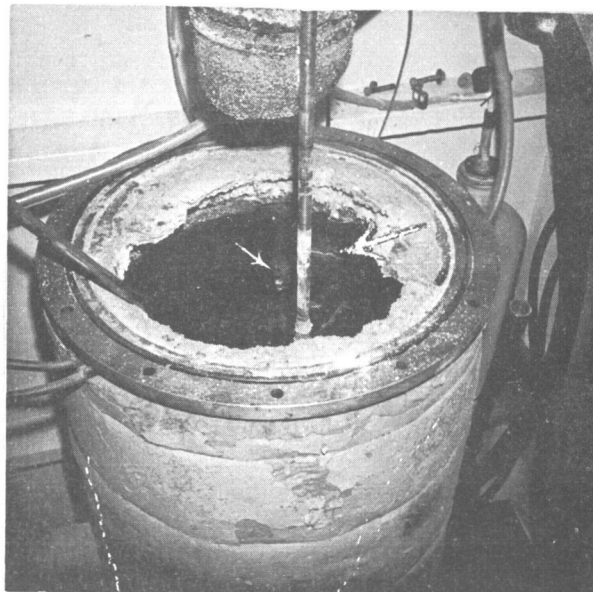


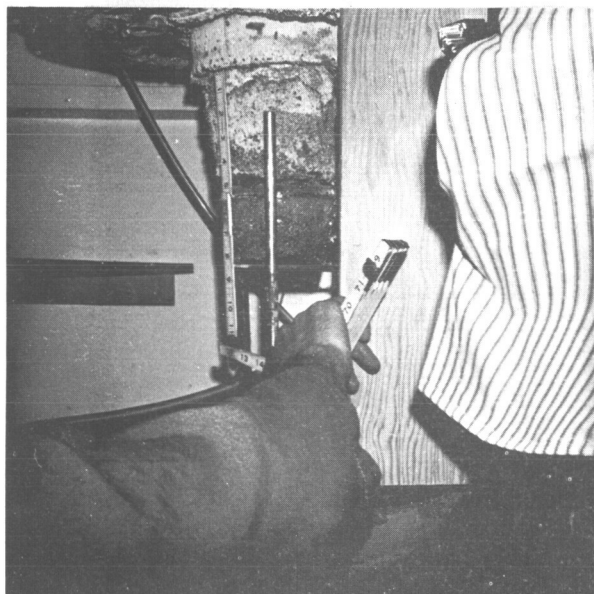
Fig. 11 - Operational Data 6)
Just Before Shutdown



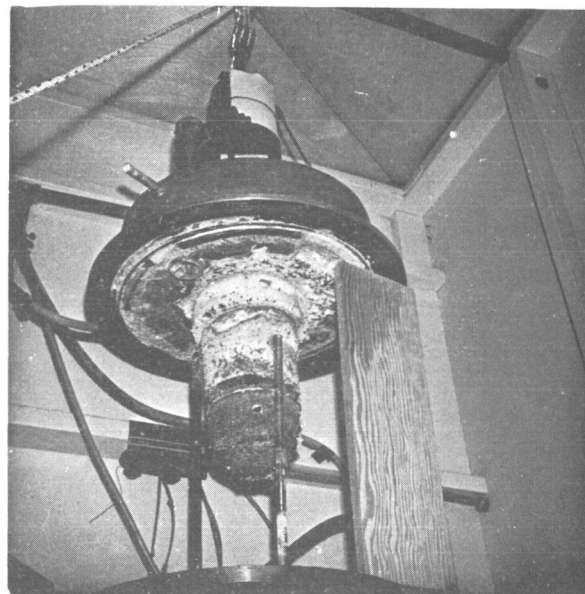
View of Cell After Lifting Lid



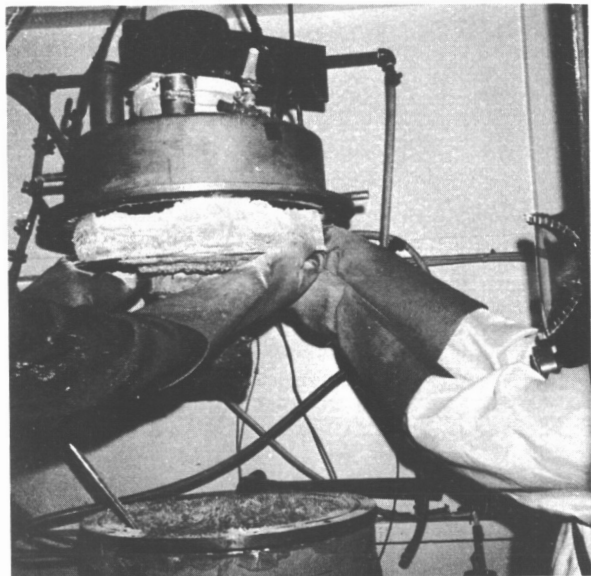
Cracked Glass Liner



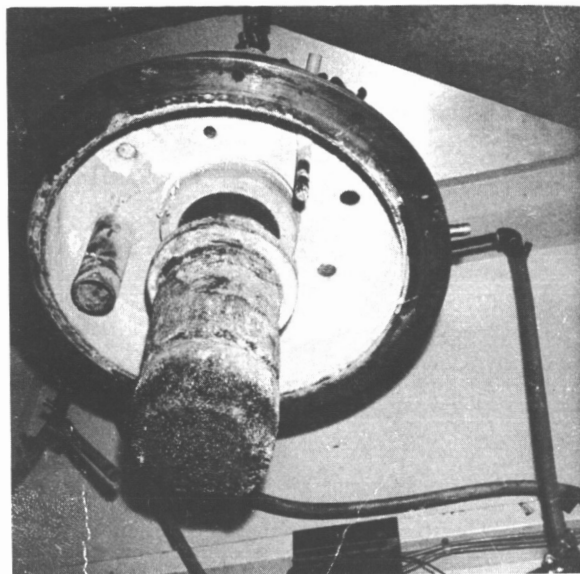
Loss of About 5" from Anode



View of Lid and Anode



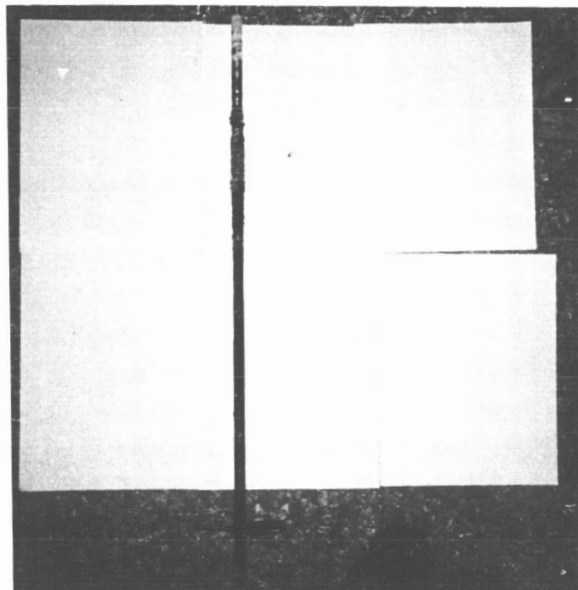
Removing False Lid. Note Build-Up of White Caked Mass of Hg_2Cl_2



Interior of Cell Lid After Removal of False Lid.



Interior of Cell Showing Damage of Glass Liner, Protective Glass Tubing Around Stirrer Shafts Lost. (White Lump in Cell is Dry Ice).



Attack and Reduction in Diameter of Stirrer Shaft at the Gas-Salt Interface.

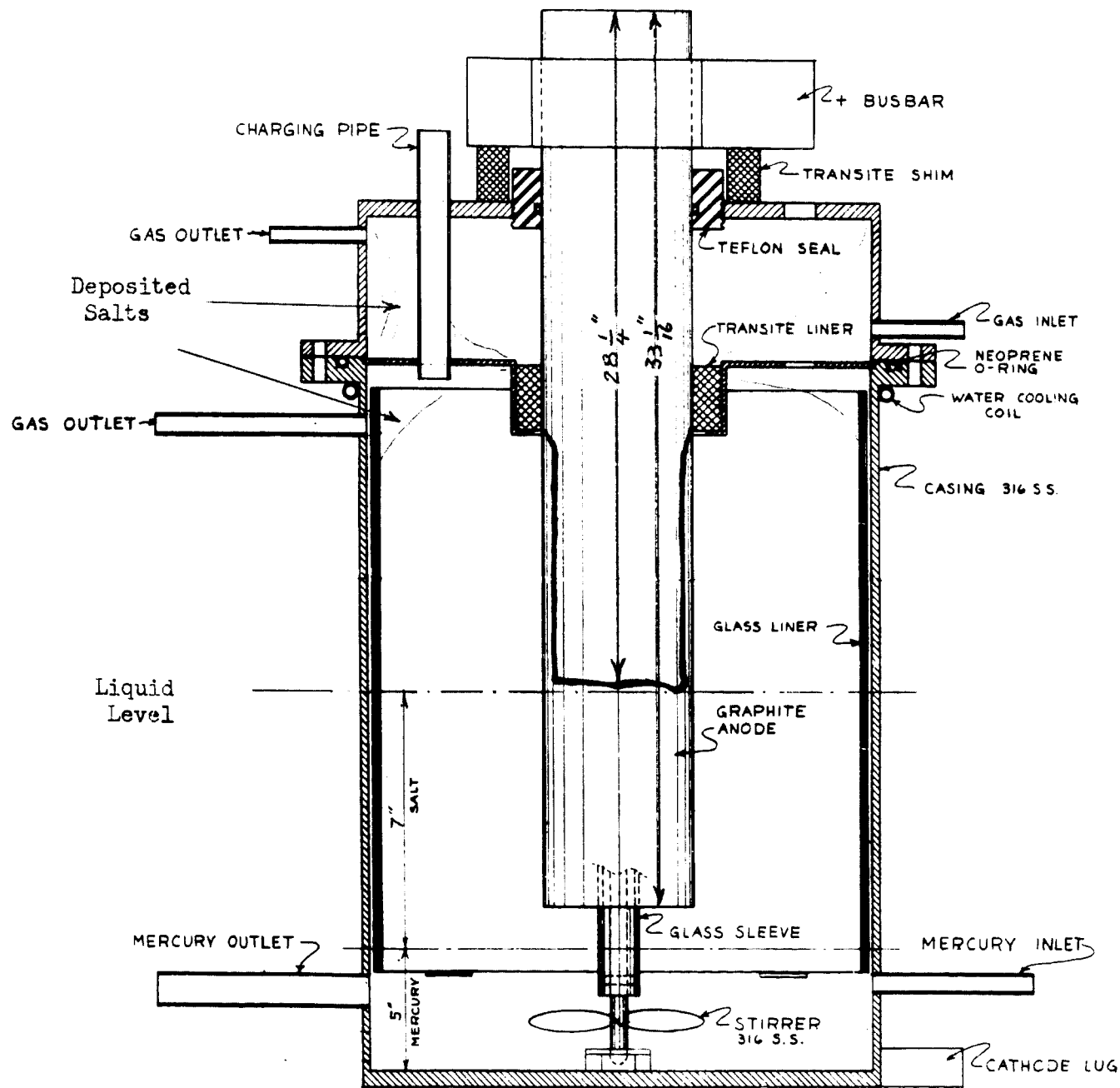


Fig. 12 - Electrolytic Cell Showing Disintegration of Graphite Anode.

3. Mercury droplets, in considerable amount, were found entrained with a large white mass that condensed at the false lid.
4. A large amount of white powder, identified as mercurous chloride, (Hg_2Cl_2), was deposited on the upper part of the false lid. It seems evident that mercury vapor volatilized from the cathode pool, passed between the Pyrex liner and the stainless shell, and reacted with the chlorine in the space above the false lid forming Hg_2Cl_2 .
5. The glass liner and the glass tube surrounding the stirrer shaft were found to be broken, and therefore the electrolyte was in direct contact with the stainless steel. This accounts, at least in part, for the increased impurities in the black powder. Since the anodic cross sectional area was 16.8 sq. in., at 250 amps the current density used during these tests was 15 amp./sq. in. This is considered high and may be the cause of the disintegration of the anode.

The presence of the high carbon in the black powder can be explained as follows: Graphite particles from the anode suspended in the electrolyte were wetted by the amalgam and when the amalgam was exposed to the air, the graphite was expelled from the amalgam phase along with the beryllium powder. Some of the impurities reported in the black powder may be traced at least partially, to the impurities present in the graphite anode which on disintegration were dissolved in the electrolyte and subsequently entered the amalgam. The electrodes were found to contain 0.03% ash, analysis of which is given in Table 5.

Table 5 - Spectrographic Analysis of Graphite Electrode Ash

	%
Al	0.4
Ca	80.0
Co	0.2
Cr	0.2
Fe	4.0
Ni	2.4
Si	4.0
Ti	trace
V	0.5

CONCLUSIONS

1. It has been demonstrated that the beryllium metal in the amalgam has a particle size of 0.1-0.2 microns as determined from electron microscopic examination of the oxidation product.
2. Impurities in the powder resulted from disintegration of the anode and from corrosion of the stirrer shafts.
3. Removal of the mercury from the amalgam by distillation in a nitrogen atmosphere at a dew point of -20° F apparently results in formation of some beryllium nitride.
4. A more complete evaluation of the metal powder must await refinement in the process to eliminate carbon and metal impurities.

FUTURE WORK

1. Cell Operation

- a) In order to better study operation of the cell and the other auxiliary equipment, it is planned to operate the cell on an intermittent basis with brief shut downs for inspection and evaluation of the cell and the product. This will enable varying the conditions of operation and other parameters, and to evaluate their effect on performance of the cell and purity of the powder.
- b) In order to prevent or minimize disintegration of the anode, electrolysis will be conducted at current density lower than previously attempted.

2. Product Evaluation

- a) Two types of beryllium will be produced for evaluation:
 - i) By controlled oxidation of the amalgam and skimming off the black powder from the surface, and
 - ii) By distilling of the amalgam to remove the mercury thus leaving an unoxidized powder.

- b) Both powders will be evaluated for purity, particle size and shape, and for other powder characteristics.
- c) Hot pressing of the two types of powder will be studied in order to consolidate the material.
- d) The hot pressings will be evaluated to determine mechanical and physical properties.
- e) Samples of both types of powder will be submitted for strand burning tests in rocket fuel formulations.

ACKNOWLEDGEMENTS

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