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THERMAL REDUCTION OF BERYLLIUM CHLORIDE
WITH METALLIC MAGNESIUM

By
MAILAND R. STRUNK

A
THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
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Rolla, Missouri
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Approved by W. T. Schrenk

Chairman of Department of Chemical Engineer-
ing and Chemistry

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INTRODUCTION

The purpose of this research was to investigate the thermal reduction of beryllium chloride by metallic magnesium. Beryllium is a remarkable element, being characterized by its hardness, lightness and durability. Although the art of metallurgy has developed to a point at which most metals can be produced at a low cost, there are a few metals, of which beryllium is an outstanding example, which can only be obtained at high prices and in small amounts because of the difficulties of recovering the metals as such from their compounds which occur in nature. Small amounts of pure beryllium can be obtained, however, by electrolyzing molten beryllium chloride or a molten mixture of the oxide and fluoride.

At the present time, there is no complete and satisfactory method for producing metallic beryllium on a scale large enough to supply all of the demands. The supply of beryllium was insufficient during the last World War to meet the demands for master alloys to make cuproberyllium, nickel-beryllium and other alloys for military use.

Beryllium is generally not produced directly as elementary beryllium, due to the difficulties and expense involved. Present commercial practices concentrate upon the direct production of an alloy of beryllium and copper in an electric furnace by dissolving carbon in molten copper and adding beryllium oxide.

The difficulties experienced in producing elementary beryllium derive from the physical nature as well as from the chemical behavior of the metal and its compounds. Some of the properties that make the metallurgy of this element a perplexing problem are; its high melting point and high vapor pressure at the melting point, its tendency to float on slags and on fused electrolytes, the highly deliquescent properties of the halides, and its tendency to form basic and oxysalts.

The extent of the usefulness of beryllium has not yet been completely determined, due to the lack of large amounts of beryllium on the commercial market. Its most important uses to date are found in the production of alloys with copper and nickel. These alloys are extremely hard and appear to be remarkable from the standpoint of fatigue resistance and their excellent corrosion and erosion properties. These properties alone would warrant the use of large quantities of beryllium if it could be procured at a price sufficiently low to compete with other materials currently used.

From a commercial standpoint, the only beryllium ore or mineral now warranting attention is beryl, a beryllium aluminum metasilicate, which is of fairly widespread occurrence. The chief deposits are located in Brazil, Argentina, India, Canada and Portugal. In this country, most of the beryl is recovered as a by-product in feldspar and mica mines in New Hampshire, North Carolina, Georgia and Colorado.

Many methods and processes have been introduced for preparing beryllium compounds from beryl and for reducing these compounds to the metal. The chief disadvantages of the proposed processes are the use of expensive and hard to obtain chemicals and elaborate equipment that prohibit the method from being classed as a commercial process. Most of the methods that have been published, with the possible exception of electrolytic methods, are more on the order of complex large scale laboratory procedures.

Metal reductions of chlorides are generally rapid. However, the main disadvantage of a process of this type, as compared with the fusion electrolysis, is that the crystals have no time to grow and are produced in a very fine form. This, however, is not too great a disadvantage, considering the progress that has been made in powder metallurgy in recent years.

Magnesium, because of its cheapness and availability, was selected as the reducing agent. The preparation of beryllium by magnesium reduction is direct and inexpensive, and should be adaptable to large scale or commercial operations. The optimum conditions for the production of beryllium by this method must be determined. The per cent purity of the beryllium is also an important factor.

All of these facts led to the consideration of a study of the variable factors dealing with the production of beryllium by magnesium as a desirable research and thesis subject.

REVIEW OF PREVIOUS WORK

A considerable amount of work has been done in trying to obtain suitable methods and procedures for extracting beryllium and beryllium compounds from beryllium ores. The following review of the various methods are representative of the different procedures that have been tried for the production of beryllium by thermal reduction. Since this thesis is primarily concerned with the thermal production of beryllium, only previous work done along those lines will be cited. For a more comprehensive review, the reader is referred to the bibliography at the end of this thesis.

Beryllium was first produced by the Wohler Process.⁽¹⁾ Beryllium chloride and flat pressed balls of calcium were placed in layers in a platinum crucible and heat applied externally. The reduction took place instantaneously while the crucible attained white heat. After cooling, the resulting mass was washed with water and beryllium was obtained in the form of a dark gray powder.

According to the Debray Process,⁽²⁾ beryllium was also obtained in granular form through the conversion of the chloride by sodium. Debray conducted gaseous beryllium

(1) Wohler, F. *Annalen der Physik*
Vol. 13, p. 577 (1828).

(2) Debray, H. *Comptes Rendus*
Vol. 38, p. 784 (1854).

chloride over molten metallic sodium.

Another process was that of Nilson and Petterson.⁽³⁾ These investigators filled a massive cylinder of soft iron, having walls about 3 cm. thick, with molten beryllium chloride, on top of which was placed a cylindrically molded piece of sodium. The amount of beryllium chloride and sodium was such that a small excess of the latter was present. The cylinder was closed by means of an air tight screw cover and heated in an air furnace to red heat. At the end of the reduction, beryllium was found in the upper part of the iron cylinder in the form of a tissue of glittering, microscopically small metal crystals.

Kruss and Morath⁽⁴⁾ used a steel crucible with walls about 20 mm. thick which could be closed air tight by an iron cover. These investigators carried out the reduction of potassium beryllium fluoride by means of metallic sodium. They covered the bottom of the crucible with common salt and on top of this a layer of metallic sodium was placed sufficient for the reduction. Another layer of salt was added and then a layer of potassium beryllium fluoride. The entire mass was pressed together by a pestle and the remaining space filled with common salt. After heating

(3) Nilson, L. F. and Petterson, O. Chemical News. Vol. 45, p. 13 (1880).

(4) Kruss, G. and Morath, H. Annalen der Chemie. Vol. 260, p. 161 (1890).

for about thirty minutes to a bright red heat, a grayish black mass was obtained in which small hexagonal prisms of metallic beryllium were clearly visible. Through washing with water, both crystalline and powdered beryllium were obtained. The latter, however, contained impurities of iron and iron oxide.

Beryllium was also produced by the Engle and Hopkins⁽⁵⁾ Process. By reducing sodium beryllium fluoride with sodium granulated under xylene, the beryllium was obtained in a pulverized form, provided the oxidation was prevented by suitable apparatus. A suitable procedure for this process was worked out by Engle and Hopkins. A mixture of 20 grams of sodium beryllium fluoride and 30 grams of finely granulated sodium was heated for 45 minutes at 850 degrees centigrade and under a pressure of 7 mm. Along with the metallic beryllium, undecomposed fluoride and beryllium oxide was produced.

A more recent process of the Dow Chemical Co.⁽⁶⁾ reduced $\text{BeF}_2 \cdot 2\text{NaF}$ with molten magnesium instead of $\text{NaF} \cdot \text{BeF}_2$ as was used in the Engle and Hopkins process. The magnesium was covered with common salt during the reduction.

Winkler⁽⁷⁾ stated that magnesium could be employed in

- (5) Engle, E. A. and Hopkins, B. S. Transactions American Electro. Chem. Soc. Vol. 45, p. 483 (1924).
- (6) Dow Chemical Co. Reduction of Halogen Compounds of Beryllium, U.S. Pat. 1,515,082 (1920).
- (7) Winkler, C. Berichte der Deutschen Chemischen Gesellschaft, Vol. 23, p. 120 (1890).

the reduction of beryllium oxide. This statement has been contradicted by many investigators who found that no reduction of beryllium oxide occurred by aluminum, calcium, magnesium, potassium or sodium whether alone or in combination in different molecular proportions. These statements have been supported by Matignon and Marchal.⁽⁸⁾

According to Warren,⁽⁹⁾ the reduction to the metal took place by passing a strong stream of hydrogen gas over the beryllium oxide enclosed in a lime tube heated by an oxy-hydrogen flame. If, however, the hydrogen stream was passed too slowly over the mixture, a decomposition of the lime tube was noticed due to the result of the water formed.

Since the heats of formation of the reduction metals commonly used are lower than the heats of formation of beryllium oxide, it is not surprising that the processes for reducing beryllium oxide have yielded contradictory results. For economic reasons, all of the above methods were unsuitable for the production of beryllium. The beryllium thus obtained was recovered in a very impure state.

Hunter and Jones⁽¹⁰⁾ investigated the reduction of

(8) Matignon, C. and Marchal, G. *Comptes Rendus*.
Vol. 185, p. 812 (1927).

(9) Warren, H. N. *Chemical News*.
Vol. 72, p. 310 (1895).

(10) Hunter, M. A. and Jones, A. *The reduction of Some Rarer Metal Chlorides by Sodium*. *Trans. Electrochem. Soc.* Vol. 45, pp. 474-482 (1924).

beryllium chloride with metallic sodium. The beryllium obtained was always found to be in an impure form in which considerable oxide was present.

Schmidt⁽¹¹⁾ reduced beryllium chloride with metallic sodium and obtained a metal with 81 per cent beryllium, and also with lithium and produced a metal with 71 per cent beryllium. The remainder was beryllium oxide. The reasons for the above percentages were that the chloride was contaminated to some extent from exposure to air and from water vapor, and that the work was carried out on too small a scale.

Kangro and Lindner⁽¹²⁾ developed a process for producing beryllium oxide from beryl by first recovering the beryllium as the chloride and then forming the oxide.

Hanawalt and Peake⁽¹³⁾ as well as Dolan⁽¹⁴⁾ developed processes for the reduction of beryllium oxide by means of carbon and atomic hydrogen respectively. In the former process, the oxide and the carbon were mixed and formed into briquettes using a tar or pitch binder. Even after this

(11) Schmidt, J.M. Study of Beryllium and Its Chloride. Ann. Chem., Vol. 11, p. 352 (1929).

(12) Kangro, W. and Lindner, A. Separation of Beryllium Compounds from Beryllium Minerals. U.S. Pat. 1,893,331 Jan. 3, 1933.

(13) Hanawalt, J.D. and Peake, J.D. Production of Light Metals. U.S. Pat. 2,256,161 Sept. 16, 1941.

(14) Dolan, P.M. Method and Apparatus for Reducing Chemicals. U.S. Pat. 2,226,525 Dec. 24, 1940.

elaborate preparation, the charge was rarely an intimate mixture. In the latter process hydrogen was converted to atomic hydrogen and then allowed to react with the beryllium oxide. Both of these processes took elaborate equipment and control.

Another typical reduction process was that of Wilhelm Rohn⁽¹⁵⁾ for producing alloys of beryllium. Beryllium carbide and beryllium oxide were reduced in molten copper to form an alloy of copper and beryllium.

In general, modern processes⁽¹⁶⁾ for beryllium production have been based on bringing beryllium into solution as an alkaline fluoberyllate or as beryllium sulfate or chloride, dissolving the beryllium after a preliminary decomposition of the beryl by an alkaline hydroxide or carbonate or an alkaline earth oxide or carbonate. High temperature chlorination has also been resorted to for the direct production of chloride using chlorine, hydrochloric acid, carbon tetrachloride or various combinations of them. These compounds were then used in electrolytic methods or converted to other compounds more suitable for thermal reduction as described briefly in the methods mentioned above.

(15) Rohn, W. Process for Producing Beryllium Alloys. U.S. Pat. 2,025,614 Dec. 24, 1935.

(16) Liddell, D.M. Handbook of Nonferrous Metallurgy. 2nd ed., N.Y., McGraw-Hill, 1945, pp. 67-70.

CHEMICALS USED

The anhydrous beryllium chloride used in these experiments was of technical grade and purchased from the Brush Beryllium Company of Cleveland, Ohio. This material was found, by analysis, to contain 1.8 per cent beryllium oxide.

The beryllium oxide was also technical grade and was donated by the Brush Beryllium Company for this research.

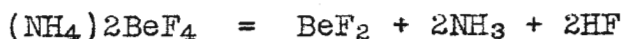
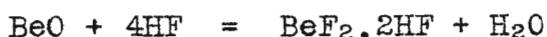
Magnesium, employed in these experiments, was purchased from the Dow Chemical Company and was obtained in standard commercial ingot form.

Helium gas was procured from the U. S. Bureau of Mine's helium plant at Amarillo, Texas and was 99.9 per cent pure.

All other chemicals used in this research, with the exception of beryllium fluoride, were either CP or reagent grade chemicals.

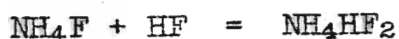
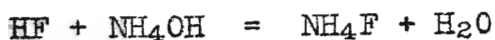
PREPARATION OF ANHYDROUS BERYLLIUM FLUORIDE

Anhydrous beryllium fluoride was prepared by two methods. Six grams of beryllium oxide were transferred to a platinum crucible containing 34 ml of 48 per cent hydrofluoric acid and digested until solution was complete. The excess hydrofluoric acid was then neutralized with ammonium hydroxide and a slight excess of hydrofluoric acid added. The solution was carefully evaporated to dryness and heated in order to volatilize the remaining water and the ammonium fluoride. The following equations represent the reaction:



Approximately eleven grams of beryllium fluoride were made in this manner.

In the second process, 25 ml of hydrofluoric acid were neutralized with ammonium hydroxide and 25 ml more of hydrofluoric acid added to the solution. After eight grams of beryllium oxide were dissolved in the solution, it was carefully evaporated to dryness and heated. The following equations represent the reaction:



Approximately fifteen grams of beryllium fluoride were prepared by this method.

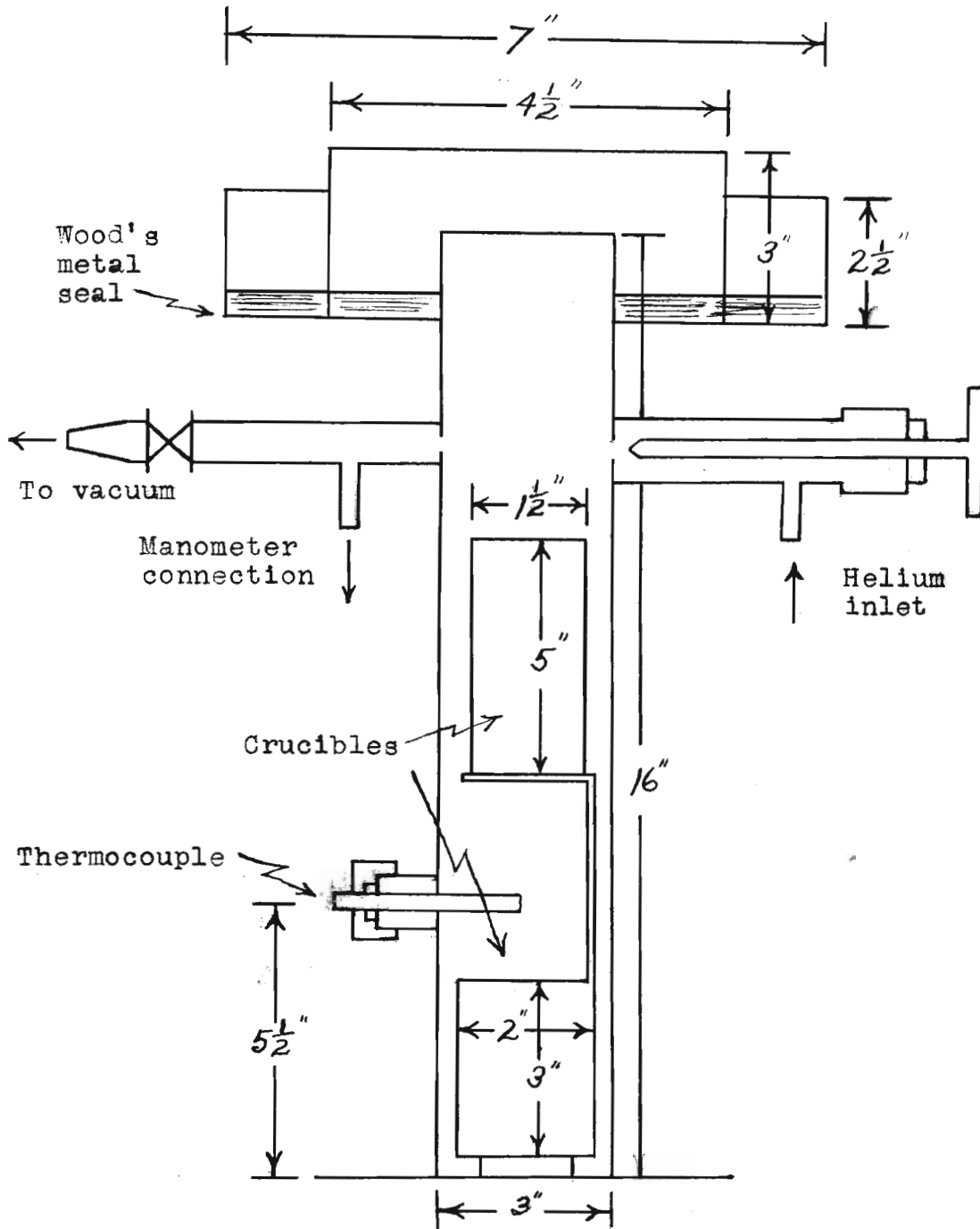


Fig. 1. Schematic diagram of apparatus used in experiments ten and eleven.

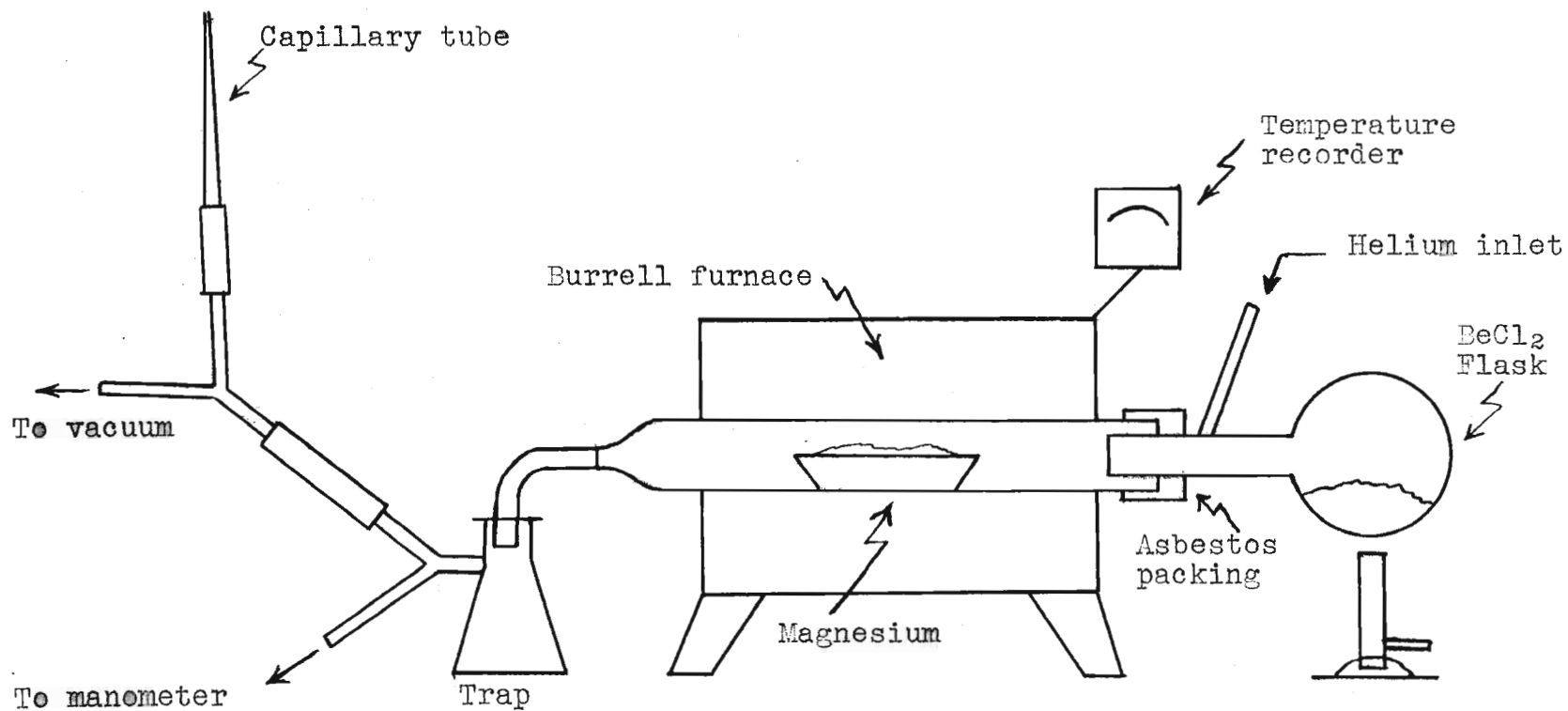


Fig. 2. Schematic diagram of apparatus used in experiments four, five and six.

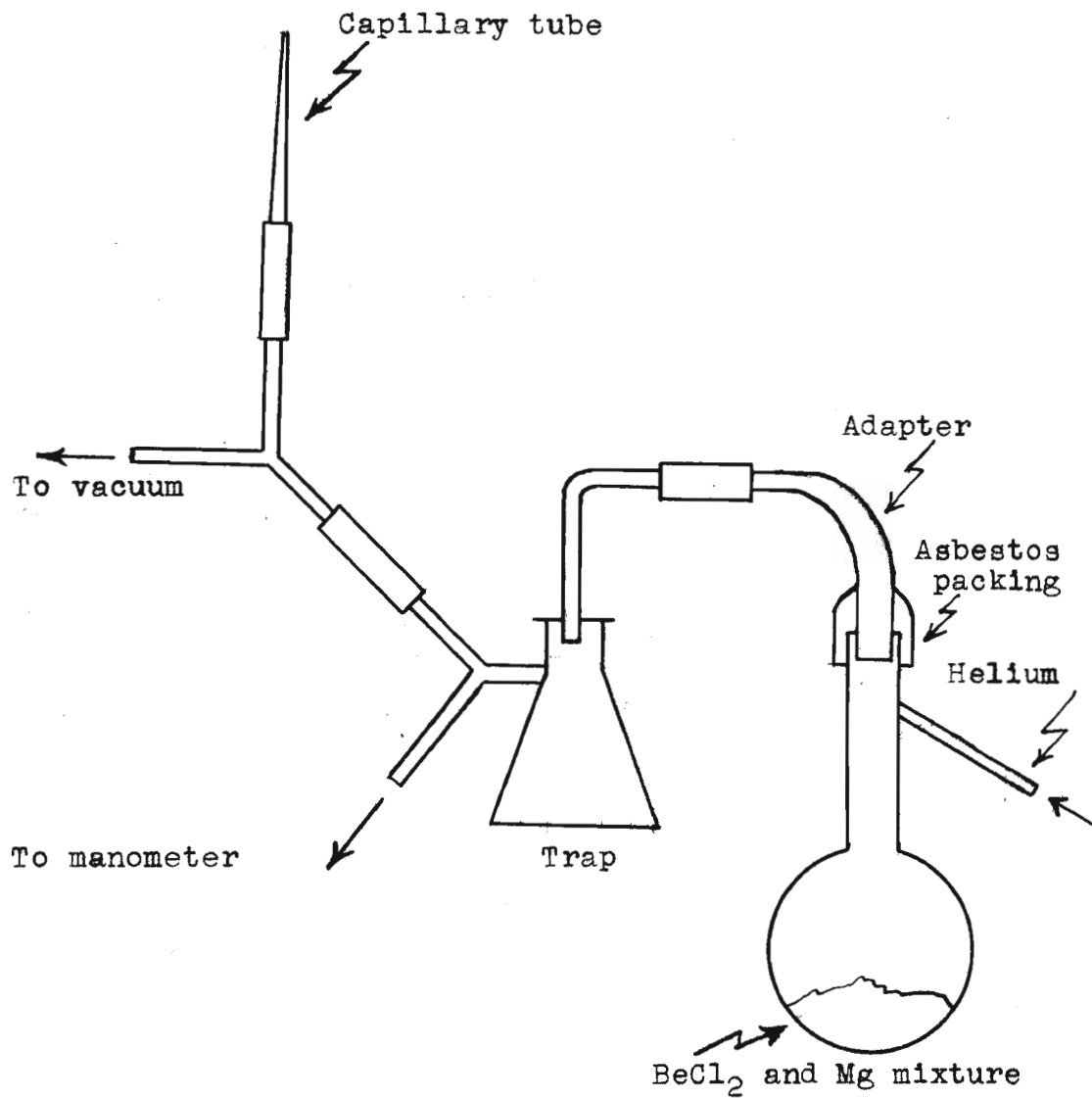


Fig. 3. Schematic diagram of apparatus used in experiments one, two and three

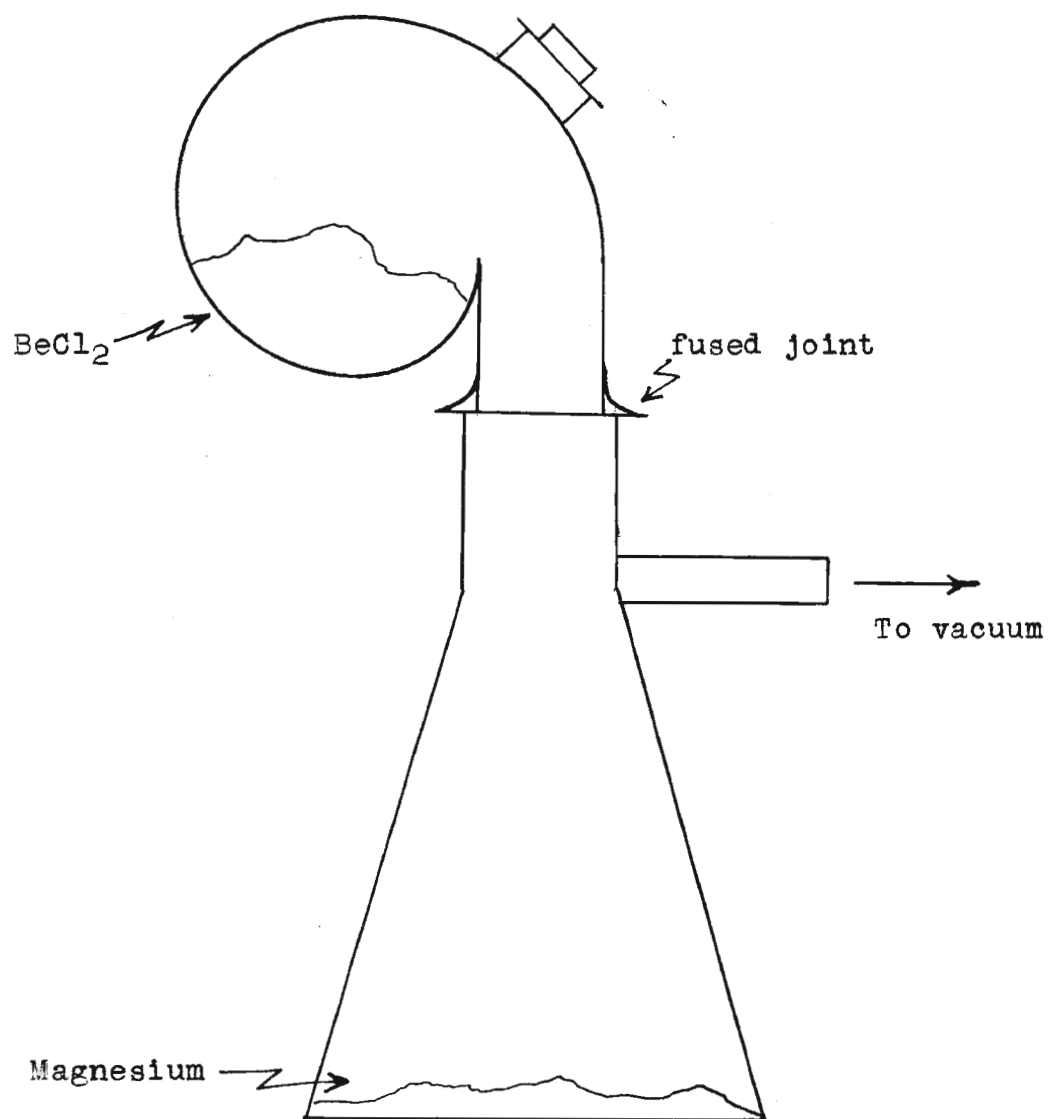


Fig. 4. Diagram of apparatus used in experiments eight and nine.

EQUIPMENT

Several of the reduction reactions were performed in a two tube Burrell high temperature furnace. This furnace was equipped with a thermocouple attached to a temperature indicator, which was calibrated to 2800°F.

Other experiments were conducted in a specially built furnace similar to one used by other investigators⁽¹⁷⁾ for the reduction of zirconium. This furnace, as shown in figure one, page 12, was constructed of stainless steel and welded together. The cap or cover was made gas tight by means of a molten metal seal of Wood's metal. The reactions were carried out in the crucibles inside the vertical tube of the furnace. Helium could be introduced into the furnace by means of an iron needle valve, which could be closed or opened manually. The furnace could be evacuated through another connection located on the opposite side from the point where the helium was introduced. A stop cock enabled one to control the vacuum. A removeable thermocouple well was installed near the base of the furnace and was designed so it could be screwed tightly into place. The temperature of the furnace was measured by a potentiometer, using an iron-constantin thermocouple. The vertical tube was covered with alundum cement and wound with 25.5 feet of nichrome wire.

(17) Kroll, W.J., Schlechten, A.W., and Yerkes, L.A.
Ductil Zirconium from Zircon Sand. Electrochem. Soc.
Preprint. No. 89-29 (1946).

The furnace was designed to use 110 volts and alternating current. The entire surface was insulated with standard magnesia pipe insulation. The maximum temperature attained in the furnace was 900°C.

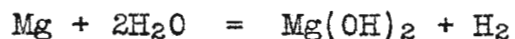
Some experiments were carried out in an apparatus shown in figure two, page 13. The neck of a 250 ml distilling flask, containing the beryllium chloride, was inserted into the tube of the Burrell furnace, held securely and made gas tight by means of asbestos packing. A porcelain boat was used to contain the magnesium. In addition to the trap, manometer and vacuum connections, a capillary tube was installed in order to control a steady flow of helium through the apparatus.

An apparatus, shown in figure three, page 14, was also used in some of the experiments. A 1000 ml distilling flask was connected to an adapter and made gas tight with asbestos packing. The rest of the apparatus was identical to that shown in figure two.

The remainder of the experiments were performed in an apparatus shown in figure four, page 15. The arm of a 500 ml retort was cut off and the retort fused to the top of a 1000 ml suction flask. The entire apparatus could be evacuated through the side arm on the suction flask and a vacuum maintained.

TREATMENT AND ANALYSIS OF RESIDUES

The residue, obtained in the various experiments, was leached in a ten per cent ammonium chloride solution containing twice the theoretical amount of ammonium chloride needed to dissolve all the magnesium. All residues remained in the leach solution ten to twelve hours. This removed all the magnesium and magnesium oxide, as well as other salts that were soluble in ammonium chloride. The reactions involving the magnesium and magnesium oxide are shown by the following equations:



The extracted residue was then filtered, washed with water, alcohol and dried. The residue, obtained in this manner, was analyzed by the following procedures.

Approximately .1 gram of the sample to be analyzed was dissolved in concentrated sulfuric acid. After the sample was in solution, dilute ammonium hydroxide was added to neutralize the sulfuric acid. The solution was then heated to 50-60°C and an excess of 10 to 50 per cent acetic acid solution of 8-hydroxyquinoline was added. The 8-hydroxyquinoline solution was prepared by dissolving enough finely powdered 8-hydroxyquinoline in 2N acetic acid to form a five per cent solution. A 2N solution of ammonium acetate was slowly added until a permanent precipitate was

produced and several ml in excess added to insure complete precipitation. The precipitate was removed by filtering and washed with cold distilled water. The precipitate, $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$ or an analogous precipitate of iron, was then ignited and weighed as the oxide.

The filtrate from the 8-hydroxyquinoline precipitation was analyzed for the beryllium. At least five grams of ammonium chloride per 200 ml of solution was added to prevent the magnesium from precipitating as the hydroxide. A few drops of methyl red (0.2% alcohol solution) were added and the solution heated to boiling. Dilute ammonium hydroxide was then added and the solution boiled for one or two minutes. The precipitate of beryllium hydroxide was filtered, washed with hot ammonium chloride-ammonium hydroxide solution and ignited to the oxide and weighed.

The filtrate from the precipitation of beryllium was then tested for magnesium in order to determine whether all or only part of the magnesium was removed by the leach solution. The filtrate was boiled down to a small volume until salts began to crystallize. Water was added to bring everything into solution again and heated to boiling. 25 ml of disodium ammonium phosphate was slowly added. Dilute ammonium hydroxide was added until the solution smelled of ammonia and an excess of 10 per cent by volume stirred in. The solution was allowed to stand several hours in a cool place. The precipitate was then ignited to the pyro

phosphate and weighed.

No aluminum nor magnesium were found in any of the residues. This showed that the magnesium was quantitatively removed by the leach solution and that aluminum and iron were not an impurity in any of the materials used. This made it unnecessary to examine each residue for their magnesium and aluminum content.

When the stainless steel crucible was used, iron was found in the residues and was determined by two methods. It was precipitated by 8-hydroxyquinoline as previously described, and the precipitate ignited to ferric oxide and the iron calculated.

The iron was also determined by dissolving the residue in sulfuric acid and reducing any ferric iron present with an excess of hydrogen sulfide gas. The excess hydrogen sulfide was removed by boiling and the ferrous iron titrated with potassium permanganate.

EXPERIMENTAL RESULTS

Typical Data Showing Per Cent of Metallic Beryllium⁺
Produced By Thermal Reduction of Beryllium Chloride With
Magnesium Under Given Conditions

Exp. No.	Percent Be	Conditions During Experiment
1	69.50	solid Mg powder mixed with BeCl ₂ in 1000cc glass flask under He.
2	91.50	same conditions as Exp. 1
3	66.40	same conditions as Exp. 1
4	13.75	Mg heated above M.P. in porcelain boat with BeCl ₂ vapor passed over it in high temp. Burrell furnace
5	10.01	same conditions as Exp. 4
6	10.73	same conditions as Exp. 4
7	42.80	Mg powder mixed with BeCl ₂ in porcelain boat and heated in Burrell furnace under He gas
8	29.60	BeCl ₂ vapor passed over heated solid Mg powder in glass flask under vacuum
9	26.40	same conditions as Exp. 8
10	50.30	Mg mixed with BeCl ₂ in iron crucible under He gas in special furnace
11	20.20	same conditions as Exp. 10 except clay crucible was used

+ Per cent beryllium expressed on a basis of total weight of sample analyzed

EXPERIMENTAL PROCEDURES

In experiments one, two and three, powdered magnesium in excess was mixed with beryllium chloride and placed in a 1000 ml distilling flask as soon as possible in order to prevent too long an exposure of the beryllium chloride to the atmosphere. The side arm of the flask was connected to the helium source as shown in figure three, page 14. The connection leading to the vacuum pump, trap and manometer was fastened to the top of the flask by means of an asbestos stopper or plug. Asbestos was used since cork or rubber stoppers could not stand the temperature attained. The flask was evacuated and helium introduced. Helium flowed through the flask and out through a small capillary, thus maintaining a steady flow of helium through the apparatus and keeping the pressure constant at one atmosphere. Heat was applied at the bottom of the flask by means of a bunsen burner. The reduction reaction was complete in approximately thirty five minutes. A reddish orange flame indicated that a chemical reaction was taking place. The temperature during the reaction was approximately 600°C. After the reaction was completed, the mass was allowed to cool and the residue leached and analyzed.

The apparatus, shown in figure two, page 13, was used in experiments four, five and six. A porcelain boat, containing an excess of magnesium, was placed in the high temperature Burrell furnace. The beryllium chloride was placed in a 250 ml distilling flask and the top of the flask

placed two inches inside the combustion tube and sealed with asbestos packing. The other end of the tube was connected with a vacuum pump and helium to the distilling arm of the flask. The apparatus was evacuated and flushed with helium and a helium atmosphere maintained continually throughout the remainder of the run. The Burrell furnace was now raised to a temperature of 900°C. After this temperature was obtained in the furnace, the distilling flask was heated by means of a bunsen burner and the beryllium chloride volatilized. The vapor of beryllium chloride passed over the heated magnesium in the tube. When all of the beryllium chloride was volatilized, the apparatus was permitted to cool and the residue examined and analyzed by the standard procedure.

This same apparatus was used for experiment seven. All conditions were maintained the same as in experiments four, five and six, except that an excess of magnesium was mixed with the beryllium chloride in a porcelain boat. This mixture was placed in the tube of the furnace as soon as possible. The apparatus was evacuated and placed in a helium atmosphere. The tube was then heated to 1000°C and maintained at this temperature for a period of three hours. The apparatus was permitted to cool and the residue recovered, examined and analyzed by the usual procedure.

The apparatus, shown in figure four, page 15, was used in experiments eight and nine. Beryllium chloride was placed in the retort and an excess of magnesium powder placed in

the suction flask. The apparatus was then evacuated. The flask, containing the magnesium powder, was heated by a bunsen burner to a temperature of approximately 600°C. The retort, containing the beryllium chloride, was heated until the beryllium chloride volatilized. The vapors passed from the retort into the flask. When all the beryllium chloride was volatilized, after a period of one hour, the apparatus was allowed to cool and the residue recovered, examined and analyzed by the usual procedure.

The apparatus, shown in figure one, page 12, was used for runs ten and eleven. The beryllium chloride and an excess of magnesium were mixed and placed in the stainless steel crucible and the charge covered with magnesium. The furnace was heated to the melting point of the Wood's metal and the crucible placed as quickly as possible in the furnace. The cover was replaced and the Wood's metal allowed to solidify. The furnace was then evacuated and a helium atmosphere introduced and maintained as nearly as possible at one atmosphere in order to prevent excessive loss of helium through the metal seal. The furnace was heated to approximately 900°C and powdered carbon placed over the Wood's metal to prevent excessive oxidation. These conditions were maintained for a period of three hours. The furnace was then permitted to cool to about 90°C. The crucible and contents were removed from the furnace and the residue was later examined and analyzed by the usual procedures.

REDUCTION OF BERYLLIUM OXIDE WITH MAGNESIUM

In the course of this research, it was desired to determine to what extent magnesium would reduce beryllium oxide. A mixture of magnesium and beryllium oxide was placed in an alundum boat and placed in the tube of the high temperature Burrell furnace. The temperature was maintained at 1200°C for three hours. The reduction was carried out in an atmosphere of helium. After cooling, extracting with ammonium chloride solution and analyzing the resulting residue, the total beryllium content was found to be only 1.25 per cent, indicating that beryllium oxide was hardly reducible with magnesium, under the conditions in which the reduction was made.

DENSITY SEPARATION

The purpose of these experiments was to determine if the per cent beryllium could be increased by centrifuging with ethylene dibromide. Since the specific gravity of beryllium was 1.816, that of beryllium oxide 3.020 and ethylene dibromide 2.180, it was hoped that the finely divided crystals of beryllium could be separated from the beryllium oxide or any other material that might have been present. Ethylene dibromide was selected because of its ready availability and for its specific gravity.

Samples of the material produced in experiment one, containing 69.50 per cent beryllium, were subjected to this centrifuge treatment with ethylene dibromide. The results indicated that only an increase of from approximately two to three per cent could be obtained in this manner. An average increase was from 69.50 per cent beryllium to 72.34 per cent.

Hence, from these results, a separation of the beryllium from the beryllium oxide was not deemed feasible by this method.

REDUCTION OF BERYLLIUM FLUORIDE WITH MAGNESIUM

The reduction of beryllium fluoride was carried out in the furnace shown in figure one, page 12, and the same conditions, which were present when beryllium chloride was reduced in experiments ten and eleven, were maintained. The material, at the end of the reduction run, was removed from the furnace, leached and analyzed by the methods previously described.

Analysis showed a beryllium content of only 11.6 per cent. The rest of the material undoubtedly contained some magnesium fluoride, which was not dissolved by the ammonium chloride solution, and beryllium oxide. Only one run was made and hence results cannot be taken as conclusive or representative.

CONCLUSIONS

From the experimental results of this research, it was strongly indicated that the container or type of crucible, in which the reduction was carried out, effected, to a considerable extent, the per cent of beryllium obtained in the final product. This was indicated in experiments one, two and three, in which relatively high per cents of beryllium were obtained, whereas experiments four, five and six gave much lower per cents of beryllium. This was attributed to the fact that the beryllium, produced in the reduction reaction, tended to react with the silicates or other materials in the porcelain or clay crucibles and caused the final product to be contaminated with silica and oxides which in turn caused the per cent of beryllium to be low. This was verified by the fact that at the end of each run, the porcelain, clay and alundum crucibles were definitely noted to have been attacked during the reaction and in some runs, the crucibles were found to be almost disintegrated.

Reactions carried out in pyrex glass flasks were not observed to attack the glass walls of the flask and hence, no contamination from the glass was present in the sample. This tended to give the higher results shown in experiments one, two and three.

Experiments ten and eleven also illustrate the difference in the per cent beryllium obtained from using iron and clay crucibles. The clay crucible in run eleven was attacked considerably causing impurities to be found in the extract

from the leach solution and causing the per cent beryllium to be low. Some iron, however, was found to contaminate the beryllium sample made in experiment ten.

Another conclusion reached was that a greater yield and a higher per cent of beryllium was obtained when the magnesium and beryllium chloride was intimately mixed and allowed to react, than when the beryllium chloride was in the vapor state and allowed to pass over the magnesium. This was indicated when experiments eight and nine were compared with one, two and three. Glass was used as the container in each case, thus eliminating the possibility of the product becoming contaminated by the crucible itself.

This conclusion was also borne out by comparing experiments four, five and six with experiment seven. All reactions were carried out in porcelain boats. Although all samples in this case were contaminated from the crucibles, a considerably higher per cent of beryllium was obtained by comparison when the beryllium chloride and magnesium were intimately mixed and then allowed to react.

Under the conditions in which these experiments were performed, it was difficult to obtain a value for the per cent beryllium in excess of 70 per cent. However, in experiment number two, an extract containing 91.50 per cent beryllium was obtained.

It was believed that, in addition to the reasons stated previously, the lack of higher percentages of beryllium from

the reduction reactions were due to three variable factors; (a) the presence of traces or small amounts of water vapor in the apparatus; (b) exposure of the anhydrous beryllium chloride to the atmosphere during preliminary preparations before making the reduction run; and (c) the presence of some beryllium oxide initially in the technical grade beryllium chloride used.

Any one of these factors or any combinations of them would have the effect of causing a lower yield of beryllium.

SUMMARY

A study of the reduction of anhydrous beryllium chloride by magnesium was made in several different types of apparatus. Beryllium, having a purity of 91.50 per cent, was produced in one experiment. Variation of conditions gave a purity of only 10 per cent beryllium.

Alundum, clay and silicate containers or crucibles, caused the per cent beryllium in the residue to be low. The yield of beryllium was low when vapors of beryllium chloride were passed over heated, as well as melted, magnesium. Beryllium, of higher purity, was obtained when an excess of magnesium and beryllium chloride were intimately mixed and heated in an atmosphere of helium.

Further work should be performed on this method in order to study and fix other variables.

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