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PURIFICATION OF BERYLLIUM COMPOUNDS: A LITERATURE SURVEY

R. E. Moore

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REACTOR CHEMISTRY DIVISION

PURIFICATION OF BERYLLIUM COMPOUNDS: A LITERATURE SURVEY

R. E. Moore

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ABSTRACT

Industrial production of technical and nuclear grade beryllia, laboratory-scale preparations of purer oxide, and separate purification processes are discussed. Several American and a French process for making nuclear-grade beryllia (300-500 ppm impurities) are described. In the U.S.S.R. oxide with only 50 - 110 ppm impurities is made from commercially distilled basic acetate, and metal with 200 ppm impurities is produced by commercial distillation. Beryllia which is purer than that commercially available has been made by laboratory-scale extraction and distillation of acetate, recrystallization of oxalate, and extraction of the perfluorobutyrate.

Precipitations and crystallizations from solution and ion exchange may be useful preliminary steps in procedures aimed at preparing ultra-pure beryllia. Liquid-liquid extraction and vacuum sublimation meet the requirements for final processes because of their theoretical capabilities and because closed systems using plastic equipment may be used to minimize contamination. Extraction methods discussed involve organic extractions of aqueous solutions of the basic acetate, acetylacetonate, and organic salts.

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INTRODUCTION

The great interest in beryllium oxide in the nuclear energy field stems from its low neutron absorption cross section, high moderating capacity, very high melting point, and very low vapor pressure at high temperatures. These qualities make it ideally suited for use as a moderator in nuclear reactors designed to operate at high temperatures.

Beryllium oxide for nuclear applications must be virtually free from contamination by elements of high neutron absorption cross section such as boron, cadmium and lithium. For refractory use, it should also contain very little of elements such as the alkali metals and fluorine which lower the melting point substantially.

This report is the result of a literature survey of methods for purifying beryllium oxide and compounds which may be converted to the oxide. The following topics are discussed in separate sections: (I) Industrial production of technical oxide; (II) Industrial manufacture of beryllia suitable for nuclear use; (III) Laboratory-scale preparations of higher purity beryllia; (IV) Details of separate purification processes. The state of the art is summarized and the various purification processes are evaluated in the final section.

Spectrographic analysis appears to be the most convenient analytical tool for studies of the purification of beryllium. It should be noted, however, that this method is only semi-quantitative for most elements and very poor for some such as

phosphorus. Also, there may be sizeable discrepancies between results from different laboratories because of the use of different standards. Spectrographic results for the products prepared by the various methods are presented in terms of parts per million in beryllium oxide so that comparisons can be readily made.

I. INDUSTRIAL PRODUCTION OF TECHNICAL OXIDE

The source of nearly all beryllium oxide and other beryllium compounds is beryl ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$), a mineral so widely scattered that it can be mined economically only in conjunction with several other minerals. Stoichiometrically, beryl contains 14% beryllia, but beryl ore generally ranges from 8-12%. There are two commercial processes in use in the United States for converting beryl into technical grade beryllium compounds such as BeO and $Be(OH)_2$.

In the fluoride process,[1,2] used by the Beryllium Corporation, Reading, Pa., a mixture of finely pulverized beryl, sodium ferric fluoride, sodium fluosilicate, and soda is heated to 750°C. The soluble sodium beryllium fluoride which is produced is leached out of the mass by water, leaving an insoluble residue of silica and oxides of iron and aluminum. Beryllium hydroxide is precipitated from the solution by caustic soda, and calcined to the oxide at 1000°C.

The sulfate process,[3,4] used by Brush Beryllium Company, is based on the fact that if molten beryl, fused about 1700°C, is quenched in cold water, the resulting frit is reactive to sulfuric acid. Leaching of the ground frit with acid yields a solution

containing mainly aluminum and beryllium sulfates. Aluminum is removed as ammonium alum by the addition of ammonium sulfate. Sequestrants are added to the mother liquor to keep impurities such as iron in solution, and beryllium hydroxide is precipitated and calcined to the oxide at approximately 800°C.

Beryllia produced by the two processes briefly described above is sufficiently pure to be used for the production of beryllium copper, but further purification is required to produce a material satisfactory for refractory or nuclear use.

II. INDUSTRIAL MANUFACTURE OF BERYLLIA SUITABLE FOR NUCLEAR USE

Several industrial processes have been used to convert technical beryllium products into beryllium oxide and metal which meet the purity requirements for general nuclear application. These processes and the degrees of purity of the products are described below.

The Pechiney Process

The Pechiney Company[5] of France produced beryllia containing more than 99.95% BeO for the French Atomic Energy Commission. The procedure consisted of a series of precipitations of impurities and crystallizations of beryllium compounds from solution.

Technical beryllium hydroxide was converted to sulfate with sulfuric acid, and silica was rendered insoluble by heating to 105°C. Insoluble sulfides were precipitated with hydrogen sulfide; the sulfide precipitate coated the silica making filtration

possible. After removal of hydrogen sulfide by air bubbling, iron was oxidized with chlorine, and ammonia was bubbled in to pH 4.5 to precipitate ferric hydroxide. A medium purity beryllium hydroxide was precipitated with ammonia, leaving Ca, Mg, Cu, Na, and others in solution, and then it was dissolved in an excess of sulfuric acid. Beryllium sulfate was allowed to crystallize from the cooled solution and then dissolved in water. Pure beryllium hydroxide was precipitated with ammonia. Beryllia made from the hydroxide by calcination contained more than 99.95% BeO and less than 100 ppm each of iron and silicon, approximately 100 ppm aluminum, and less than 0.3 ppm boron.

Basic Acetate Distillation in the U.S.S.R.

High-purity beryllia for nuclear use is produced industrially in the U.S.S.R. by a process involving distillation of the volatile basic acetate, $BeO \cdot Be_3(CH_3COO)_6$, in continuous-flow apparatus at 360-400°C.[6] After two distillations, the basic acetate is decomposed at 600-700°C to form beryllium oxide as a highly dispersed powder. Impurities reported to be present in the purified oxide in parts per million are Fe, 4-11; Al, 11-25; Si, 36-72; Mn, <1; Cu, <2; Ni, <7; B, 0.04.

High-Vacuum Distillation of Beryllium Metal in the U.S.S.R.

Sinelnikov, et al.[7] reported in 1958 that commercial scale production of very high purity beryllium metal is being carried out in the U.S.S.R. by vacuum distillation and condensation on heated surfaces. Commercial beryllium containing 1.2% of Fe, Si,

Al, Mn and other metals is distilled from beryllia crucibles under a vacuum of 10^{-5}-10^{-6} mm. and condensed on a heated surface in the upper part of the furnace. Beryllium metal as pure as 99.98% was obtained with Mn, Al and Si reduced to 10-20 ppm. If the purified beryllium metal from the Russian process were converted to oxide without introducing contaminants, a beryllia containing only about 73 ppm total impurities with between 4 and 7 ppm each of manganese, aluminum, and silicon would result.

High-Purity Hydroxide Made by the Beryllium Corporation

Grade I beryllium oxide is the purest oxide commercially available from the Beryllium Corporation. According to B. J. Sturm[8] of ORNL, the hydroxide used to make Grade I BeO is employed as a starting material at ORNL for attempts at further purification. Spectrographic analysis at ORNL* gave the following impurities in ppm based on oxide:

Al <50T	Cu < 5	P present
B T	Fe 35	Pb <2
Ba <5	Mg 35	Si 150
Ca <35	Mn <5	Sn <5
Co <5	Na 500	V <5
Cr 20	Ni <20	Zn <25

(T = trace)

* All spectrographic analyses at ORNL given in this report were performed by J. A. Norris and co-workers.

Beryllium Oxalate Made by the Beryllium Corporation

The Beryllium Corporation has produced pure $BeC_2O_4 \cdot 3H_2O$ in sizeable quantities by leaching and recrystallizing impure oxalate made by reacting a beryllium compound with molten oxalic acid dihydrate. This is a method originally developed by workers at General Electric Corporation.[9] A spectrographic analysis at ORNL gave the following amounts of impurities in ppm based on beryllium oxide:

Al 15	K <10	Si 25
B <1	Li <10	Sn <5
Ca 240	Mg 25	V <10
Co <5	Mn <20T	Zn <25
Cr <20	Na 50	P not detected
Cu 5	Ni <20T	
Fe 60	Pb 75	

(T = trace)

Beryllia Made by Brush Beryllium Company

The Brush Beryllium Company produces several grades of beryllia for various purposes. Their purest commercially available product is known as UOX Grade which is made by further purification of technical grade oxide.[10] A spectrographic analysis at ORNL gave the following impurites in ppm:

Al 100	Fe 20	Na 20
B 2	K <100	Ni <20T
Ca 50	Li 10	Pb 5
Co <5	Mg 70	Si 110
Cr 20	Mn <20	Sn <5
Cu 5	Mo <50	(T = trace)

III. LABORATORY-SCALE PREPARATIONS OF HIGHER PURITY BERYLLIA

Beryllia of a higher purity than that commercially available may be desirable for spectrographic standards, basic research, sintering studies, and special nuclear applications. Several laboratory-scale purifications aimed at producing beryllia for such uses have been reported and are described in this section. The reduction of each impurity to a very low level is a very difficult problem because extreme precautions must be taken to avoid contamination of the product by the reagents, apparatus, and atmospheric dust.

Extraction and Distillation of the Basic Acetate

Tomkins, Cressman and Tolmach[11] of the University of Chicago Metallurgical Laboratory reported a procedure consisting of repeated extractions of a chloroform solution of beryllium basic acetate with water followed by several distillations of the basic acetate at 335-340°C. The acetate was converted to sulfate and ignited at 1000°C to oxide. Spectrographic results given in ppm for their product are as follows:

Ag < 10	Cr <20	Na <10
Al 1	Cu <10	Ni <50
B <0.05	Fe <5	P <20
Bi <0.1	Li <5	Pb <10
Ca 1	Mg 2	Sb <5
Cd <0.2	Mn <5	Si <5
Co <50	Mo <50	Sn <2
		Zn <50

The Pechiney Company[5] has prepared spectrographic standards by chloroform extraction and distillation of the basic acetate. The beryllium oxide obtained from the purified acetate contained less than 50 ppm impurities.

Beryllium Oxide Made from Crystallized Oxalate

A special lot of beryllium oxide from the Beryllium Corporation was prepared by calcining beryllium oxalate which had been subjected to repeated washing and recrystallizing.[8] Spectrographic analysis at ORNL gave the following impurites in ppm:

Al <10T	Li <50	V <5
B 0.5	Mg 10	Zn <25
Ba <5	Mn <20	
Ca 20	Mo <10	T = trace
Co <5	Na 50	FT = faint trace
Cr <20	Ni <20T	
Cu <5FT	Pb <5	
Fe <10	Si 20	
K <100	Sn <5	

Laboratory-scale purifications have been carried out at ORNL by B. J. Sturm[8] by crystallization of beryllium oxalate. Spectrographic analyses of two preparations which are typical of the better batches are given below in ppm based on beryllium oxide:

(1)	Al <50	Li <10	Ti not detected
	B 1	Mg <20T	V not detected
	Ca <35T	Mn <10	Zn <25
	Co <5	Na 100	F present
	Cr <20T	Ni <20T	
	Cu <5FT	Pb <5	T = trace
	Fe <25T	Si <25T	FT = faint trace
	K <25	Sn <5	
(2)	Al 10	Li <10	Sr <10
	B 5	Mg 10	Zn <25
	Ba <10	Mn <10T	
	Ca 30	Na 35	T = trace
	Co <5	Ni <20T	
	Cr <20T	P present	
	Cu <5T	Pb <5T	
	Fe 25	Si 50	
	K <100	Sn <5	

A Special Purity Beryllia from the Brush Beryllium Company

Brush Beryllium Company has made small lots of a specially purified beryllia for experimental purposes.[10] Details of the purification process do not seem to be available. A spectrographic analysis carried out at ORNL gave the following results in ppm:

Al <50	Fe <25FT	Na <100
B 2	K <100	Ni <20T
Ca <35	Li <50	P not detected
Co <5	Mg <35T	Pb <5T
Cr <20	Mn <10	Si <80T
Cu <5T	Mo <20	Sn <5

T = trace

FT = faint trace

Ether Extraction of Beryllium Perfluorobutyrate

Sturm and Whetsel[12] of ORNL (1960) prepared about one gram of beryllia from beryllium perfluorobutyrate which had been extracted by ether from an aqueous solution of beryllium nitrate containing an equivalent quantity of freshly distilled perfluorobutyric acid and a small amount of sodium ethylenediaminetetraacetate to complex impurities. Extractions from solutions adjusted to pH 2.5 and pH 3 with freshly distilled aqueous ammonia were evaluated.

The original starting material was commercial hydroxide from the Beryllium Corporation (see page 5). Beryllium oxide made by igniting the nitrate obtained upon treatment of the ether phase with nitric acid was found by spectrographic analysis to contain the following quantities of impurities:

Al < 10 T	Cu 5-100	Na 10
B 10	Fe <25 T - 25	Ni <20-20
Ba 5	K < 20	Pb 5
Ca 15	Li < 10	Si 200
Co < 5	Mg 10	Sn <5
Cr 30	Mn < 10	Zn <25

(T = trace)

Except for phosphorus, which was not detected in this product, there was no significant improvement over oxide made from hydroxide by crystallization of oxalate. Spectrographic analysis is not good for determining phosphorus.

IV. DETAILS OF SEPARATE PURIFICATION PROCESSES

There are many purification processes which have been used in practice or which might be profitably incorporated into purification schemes. Actual procedures often consist of the successive application of two or more of these processes, discussed in detail in this section, because any one process may effectively remove certain impurities but leave unaffected or even concentrate others.

Distillation of Beryllium Compounds

Successful purification by distillation requires the use of a beryllium compound that is reasonably stable at its distillation temperature and has a vapor pressure appreciably different from those of analogous compounds of impurities. Beryllium basic acetate has received by far the greatest attention; other compounds which have been considered are the acetylacetonate, fluoride and chloride.

Beryllium Basic Acetate.--The basic acetate, $BeO \cdot Be_3 (CH_3COO)_6$, was first prepared by Urbain and Lacombe[13] in 1901 by treating the hydroxide or carbonate with acetic acid. It melts to a mobile,

colorless liquid at 283°C and boils without decomposition at 330°C. The compound is insoluble in cold water and alcohol, but it is soluble in most ordinary organic solvents including chloroform in which it dissolves to the extent of 33 g per 100 g of chloroform.

Kling and Gelin[14] in 1914 found that beryllium could be separated from aluminum and iron by sublimation of the acetate obtained by treating a mixture of the hydroxides with acetic acid. The sublimation was carried out at 160-170°C for four hours at 19 mm pressure followed by 250°C for one hour.

Tomkins, Cressman and Tolmach[11] (1946) carried out successive distillations in quartz apparatus at 335-340°C to purify further the basic acetate after a series of chloroform extractions (see page 7).

Ishibashi and Motojima[15] (1951) purified the compound by vacuum sublimation through a glass filter, and produced a material which was reported to be spectrographically free from iron and aluminum. A U. S. patent issued to H. C. Kawecki[16] (1953) describes a process for making high purity beryllia by distillation of the basic acetate at 330-350°C followed by vapor-phase combustion in air.

In 1955, Hutter and Pingard[5] reported that the Pechiney Company prepared beryllium oxide standards by acetate distillation and chloroform extraction (see page 8). Their experiments showed that zinc acetate sublimes with the beryllium compound.

Meyerson[6] reported in the same year that an industrial distillation process is in operation in the U.S.S.R. (See page 4).

Other Basic Beryllium Compounds.--Compounds of the type $BeO \cdot Be_3(RCOO)_6$, typified by the basic acetate, are very general. In addition to the acetate, Lacombe[17] (1902) prepared the formate, propionate,

n-butyrate, isobutyrate and isovalerate. Properties reported for these compounds are tabulated below:

Compound	Melting Point (°C)	Boiling Point at 760 mm (°C)	Boiling Point at 19 mm (°C)
Formate	Sublimes	--	--
Acetate	283-284	330-331	Sublimes
Propionate	119-120	339-341	221
Isobutyrate	76	336-337	216
n-Butyrate	Liquid	336-337	239
Isovalerate	Liquid	336-337	254

Tanatar and Kurovsky[18] (1908) prepared the basic crotonate, levulinate and succinate, and stated that the crotonate volatilizes with decomposition. These investigators also prepared the mixed compounds $BeO \cdot Be_3 (C_3H_7COO)_4 (CH_3COO)_2$, which boils at 351°C, and $BeO \cdot Be_3 (C_2H_5COO)_3 (CH_3COO)_3$, which melts at 127°C and boils at 330°C without decomposition.

Besson and Hardt[19] (1954) made beryllium basic monochloroacetate from the basic carbonate and monochloroacetic acid in a slurry of silica gel in benzene. It was purified by sublimation in a nitrogen stream above 130°C.

Kurdyumov and Semenko[20] (1957) prepared beryllium basic benzoate, which melts at 315-318°C and sublimes at 305-310°C. The basic 1-naphthoate and 2-naphthoate, which melt at 246.5° and 335.5-336.5°C, respectively, were prepared by Krasnec, Kratsmar-Smogrovic and Pivoda[21] (1957).

It is conceivable that basic beryllium compounds such as those mentioned above could be profitably used in distillation processes.

Beryllium Acetylacetonate.-- Combes[22] (1894) first prepared beryllium acetylacetonate, $Be(C_5H_7O_2)_2$, an inner complex formed by the chelating agent acetylacetone with beryllium ion. The compound melts at 108°C and boils at 270°C. Although acetylacetone forms complexes with nearly 60 metals, the beryllium complex is sufficiently more volatile than most that distillation under reduced pressure has been proposed (Bubes[23] (1944)) for purification. Parsons[24] (1904) used sublimation followed by recrystallization from alcohol to prepare a pure material.

Beryllium Chloride.-- Beryllium chloride melts at 405°C and boils at 488°C (Rahlfs and Fischer).[25,26] A method of purification based on differences in the volatilities of chlorides should be possible, but there are no references to the actual use of the process except as a preliminary step in processing of raw materials for metal production.[27,28]

Beryllium Fluoride.-- Brush Beryllium Company has attempted the purification of beryllium fluoride by sublimation under vacuum or reduced pressure. Sublimation at 900°C in a vacuum of 70-100μ yielded a product containing about 0.03% iron.[29] In later work,[30] the crude fluoride with 2% beryllium metal added was first pretreated with hydrogen at 500-550°C for two hours, and then was sublimed under hydrogen at 1038°C with a sublimation pressure of less than 1 mm. Spectrographic analysis of the product by National Spectrographic Laboratories, Inc., Cleveland, Ohio, gave the following impurities in parts per million:

Al 15	Cu 65	Si 14
B <1	Fe 150	Sn <10
Ca 50	Mg 65	
Cr <5	Mn <7	

Each value should be multiplied by 1.88 to convert to parts per million based on beryllium oxide. Larger scale attempts at vacuum sublimation did not give as pure a product.[31,32]

Distillation of Beryllium Metal

Until the last few years attempts to purify beryllium metal by distillation have not been very successful. A. J. Martin[33] (1955) reviewed the history of these attempts. In general, there were reductions in some impurities but enrichments in others, and there were vast discrepancies among the results of the various investigators. As a result of a theoretical analysis, Martin came to the following conclusions: Starting with an initial charge of 100 g of metal,

a. All calcium, sodium, and magnesium should be removed in the first 2 g of distillate. Manganese should be 90% evaporated in the first 24 g.

b. Aluminum and silicon should be difficult to remove because their rates of evaporation are comparable to that of beryllium.

c. Iron should be almost all retained in the furnace after 90% of the original charge has distilled.

d. Sublimation at 1200°C would have little advantage over distillation at 1400°C.

Research programs at the Massachusetts Institute of Technology have included purification of metal by distillation. A. R. Kaufmann[34,35] (1946-1947) reported the preparation of metal containing only 1 ppm boron by distillation of 920 g at 1500°C. A metal containing only 0.1 ppm boron, determined by chemical analysis, was obtained by distillation at 1300-1400°C under pressures varying from 90-500 μ. Pearsall[36] (1952) prepared distilled metal containing about 800 ppm impurities by the use of an electron bombardment furnace and a vacuum

of 5×10^{-9} to 4×10^{-10} mm.

In 1955 Meyerson[6] (U.S.S.R.) reported a distillation process for preparing a very pure metal with the following amounts of impurities in parts per million: Fe, 50; Al, 30; Cu, 40; Ni, 30; Cr, 50; Mn, 20. Converted to oxide, the impurities would be: Fe, 18; Al, 11; Cu, 14; Ni, 11; Cr, 18; Mn, 7. The metal was distilled at 1300-1400°C under a residual pressure of 1×10^{-5} mm Hg, and condensed in a zone at 1120-1150°C. A molybdenum reflux condenser was used.

Sinelnikov and associates[7] reported in 1958 that metal distillation is on a commercial scale in the U.S.S.R. The purified metal was reported to contain as little as 0.02% total impurities. If converted to oxide, the total impurities would be only about 73 ppm with Mn, Al, and Si between 4 and 7 ppm each (see page 4).

The mechanism of beryllium evaporation under high vacuum has been studied by Amonenko and associates[37] (1959), who stated that one of the sources of oxygen in distilled beryllium is the compound Be_2O, which is more volatile than BeO and which is produced in the reaction $Be + BeO \rightarrow Be_2O$ at 1400°C and upward.

Volatilization of Beryllia by Water Vapor

A U. S. patent issued to Hutchison and Malm[38] (1950) suggests that the transport of beryllium oxide by water vapor at high temperatures may form the basis for a purification process.

Several observers, including Norton[39] (1947), have noted that beryllium oxide is quite volatile when heated in air at temperatures below 1800°C. Berkman and Simon [40] (1948) found that beryllia loses weight when maintained above 1000°C in the presence of water vapor.

Measurements of the vapor pressure of beryllium oxide by Erway and Seifert[41] (1951) showed that the high volatility in air cannot

be explained by the vapor pressure. For example, to attain a vapor pressure equivalent to that of mercury at 26°C, beryllia must be heated to 2096°C in vacuum. Beryllia may be used up to 2000°C in vacuum or inert atmosphere without appreciable loss by vaporization.

Hutchison and Malm[42] (1949) found that the rate of volatilization of beryllium oxide in the presence of water vapor increases with increasing temperature. They concluded that water reacts with the oxide to produce a compound which is volatile at 1250°C or above and which condenses with decomposition to beryllium oxide.

According to Grossweiner and Seifert[43] (1952), the weight loss in the presence of water vapor is approximately a linear function of the partial pressure of water. The authors concluded that volatilization results from the reaction

$$BeO(s) + H_2O(g) \rightarrow BeO \cdot H_2O(g),$$

and stated that although beryllium hydroxide is unstable above 300°C at atmospheric pressure, it is not necessarily unstable in the gas phase.

Elliott[44] (1952) showed that oxygen is not a product of the major volatility reaction and inferred that the equation

$$XBeO(s) + H_2O(g) \rightarrow XBeO \cdot H_2O(g)$$

is the proper one, but said that both his data and those of Grossweiner and Seifert suggest a minor volatile species with an oxygen dependence.

Livey and Murray[45] (1956) have studied the stability of beryllia and magnesia in different atmospheres at high temperatures. The conclusions were that beryllia is stable in vacuum or reducing atmospheres but not in water vapor, and that magnesia is stable in water vapor but dissociates rapidly in vacuum or reducing atmospheres.

The volatilization of beryllia by water vapor may be an important factor in the operation of beryllia-moderated – air-cooled reactors. Corrosion testing of beryllia in moist air has been studied by Elston and Caillat[46] (1958) and also by McKisson[47] (1959), who concluded that the $BeO-H_2O$ interaction would not limit the feasibility of operating an open-cycle BeO-moderated power reactor at passage surface temperatures up to 1560°F.

The patent of Hutchison and Malm claims that silver, aluminum, iron and silicon are effectively removed from beryllia by transporting the oxide at 1483-1528°C with water vapor at one atmosphere. Needles approximately 0.2 mm in length are produced. In one example given, an original sample containing less than 0.01% silver, more than 1% aluminum, and about 1% each of iron and silicon was purified to such an extent that silver and iron could not be detected, and aluminum and silicon were reduced to about 0.01% each. Grossweiner and Seifert mentioned that there are other oxides such as SiO_2, B_2O_3, WO_3, W_4O_{11}, WO_2 and MoO_3 whose vapor pressures are increased in the presence of water vapor. Consequently, successive transportations may be required to reduce all impurities to low levels.

Precipitation and Crystallization Processes in Aqueous Solution

In this category is a variety of processes involving precipitation of impurities from solutions containing beryllium, and precipitation or crystallization of beryllium compounds which leaves impurities in solution. In general, an actual purification procedure would consist of a series of these processes, successively removing groups of impurities until a pure beryllium compound is isolated. The procedure used by the Pechiney Company for making reactor-grade beryllia is an example of such an operation (see page 3).

There are many precipitation processes used in quantitative analysis for the separation of beryllium from other elements. Some of the more general methods, listed below, have been used in purification procedures as well as in analytical schemes.

Precipitation of Impurities.--

1. Silica can be precipitated from hot acidic solutions containing beryllium. In the Pechiney process[5] the insoluble silica is made more easily filterable by coating it with a sulfide precipitate (page 3).

2. Hydrogen sulfide will precipitate elements forming insoluble sulfides leaving the alkali metals, alkaline-earth metals, aluminum, chromium, and others in solution.[48]

3. Sodium hydroxide in excess will precipitate Sc, Y, La, Ac, Ti, Zr, Hf, Th, Pa, U, Cr, Fe, Co and In from other members of the ammonium hydroxide group including Be, Al, Zn, Ga, and P.[49] Cottin[50] (1939) has reported that a quantitative separation of Be and Al is attained above pH 9.75 where aluminum is transformed into aluminate.

4. Sodium hydroxide with sodium carbonate is useful for separating the other alkaline earths from beryllium. This reagent will precipitate Mg, Ca, Sr, Ba, Ra, Sc, Y, La, Ac, Ti, Zr, Hf, Th, Pa, Cr, Mn, Fe, Co, Ni, Cu, Ag, Cd, In, and Tl, leaving beryllium and several other elements in solution.[51]

5. 8-Hydroxyquinoline in acetic acid-acetate solution will precipitate Fe, Al, Co, Ni, Cu, Zn, Ga, Pd, Ag, Cd, In, Hg, Bi, Ti, Zr, Hf, Th, Cb, Ta, Pa, Mo, W, and U from solutions containing beryllium. The alkali and alkaline earth metals and a few others are also left in solution.[52]

Precipitation or Crystallization of Beryllium Compounds.--

1. Precipitation of Beryllium Hydroxide.-- Beryllium hydroxide is precipitated from aqueous solution by ammonia and also by sodium hydroxide if not in excess.[53] The alkali metals remain, but the other alkaline earths may be caught in the precipitate. Aluminum, iron, chromium and a number of other elements will be precipitated with the beryllium.

2. Crystallization of Beryllium Sulfate.--Crystallization of the sulfate from acid solution has been used in purification procedures.[4,5] The system $BeO-SO_3-H_2O$ has been studied by Parsons[54] (1904) and by Campbell, Sukawa and Koop[55] (1951). The latter determined isotherms at 25, 50, 75, 85 and 95°C.

3. Crystallization of Beryllium Nitrate.-- Sieverts and Petzold[56] (1933) studied the system $Be(NO_3)_2-H_2O$, and Nowasselowa and Nogorskaya[57] (1935) determined the solubility of beryllium nitrate in water and nitric acid at 0°C and 20°C. There is nothing in the literature concerning actual processes based on crystallization of the nitrate, but the possibility has been mentioned by several investigators.

4. Crystallization of Beryllium Oxalate.--Crystallization of the oxalate, $BeC_2O_4 \cdot 3H_2O$, from aqueous solution is a method used by the Beryllium Corporation and B. J. Sturm of ORNL (see pages 6,8,9).Most of the oxalates of impurities are less soluble in water than beryllium oxalate, but Sturm states that the impurity oxalates become more soluble in a solution containing an excess of oxalate ion because of complex formation. According to Sturm, filtration of beryllium oxalate solution before crystallization is an effective method for removing silica.

Parsons and Robinson[58] (1906) have studied equilibria in the system $BeO-H_2O$-oxalic anhydride. The authors prepared $BeC_2O_4 \cdot 3H_2O$ by treating basic beryllium carbonate with a slight excess of oxalic acid. On evaporation, oxalic acid crystallized out first, but repeated recrystallization did not completely remove all the oxalic acid. After nine recrystallizations, the exact amount of beryllium carbonate was added to neutralize the excess acid. Parsons and Robinson also prepared the monohydrate by heating the trihydrate to 100-105°C. They concluded from their work that acid oxalates of beryllium do not exist, that anhydrous beryllium oxalate is difficult, if not impossible, to prepare and that the so-called basic oxalates do not exist as separate and definite compounds even though beryllium oxide can be dissolved in beryllium oxalate solutions.

Sidgwick and Lewis[59] (1926) studied the system BeC_2O_4-$H_2C_2O_4$-H_2O at 25°C. It was determined that solid $H_2C_2O_4 \cdot 2H_2O$ dissolves in $BeC_2O_4 \cdot 3H_2O$ to some extent. The authors explained the difficulties encountered by Parsons and Robinson in removing the last of the acid impurity from $BeC_2O_4 \cdot 3H_2O$ on this basis.

Liquid-Liquid Extraction Methods

For the successful purification of beryllium by liquid-liquid extraction, it is necessary to use a beryllium compound which is much more soluble in one solvent of an immiscible pair than are analogous compounds of impurities. Extraction of impurities by water from a chloroform solution of beryllium basic acetate and extractions of beryllium acetylacetone have received the most study.

Beryllium Basic Acetate (Chloroform-Water).-- The high solubility of beryllium basic acetate in chloroform (see page 12) has been used as a basis for an extraction process for purifying beryllium. Haber and Van Oordt[60] (1904) purified the acetate by extraction with chloroform and noted that it is soluble in acetone, benzaldehyde, molten monochloroacetic acid, PCl_3, malonic and acetic acid ester as well as chloroform.

Bubes[23] (1944) used the method to prepare spectrographic standards. He stated that Mg, Mn, B, and Fe and - to a lesser extent - Si and Na remain in the water layer. A spectrographic analysis of the beryllium oxide made from the purified acetate gave the following amounts of impurities in parts per million:

Cd <0.1	Mg 2
B <0.1	Mn 1
Si 100	Li <0.3
Fe 6	Na 150

Tomkins, Cressman, and Tolmach[11] (1946) found that repeated extractions did not result in a purer product than that obtained by Bubes. Distillation of the acetate after extraction gave a very pure product (see page 7). Hutter and Pingard[5] (1955) also combined extraction with distillation to obtain very pure spectrographic standards (see page 8).

Cairo and Crespi[61] (1955) determined the following separation factors in the basic acetate-chloroform-water system: Zn, 650; Tl, 134; Cr, 124; Ce, 116.

Beryllium Acetylacetonate.-- Extraction of beryllium acetylacetonate, an inner complex formed by the chelating agent, acetylacetone, with beryllium ion, has been studied by a number of investigators

for use as an analytical separation method. Since inner complexes are generally more soluble in polar solvents than in water, and since acetylacetone forms compounds with nearly 60 metals, the proper conditions for the selective separation of beryllium from other metals must be determined.

Steinbach[62] (1953) studied the distribution of metals in the solvent pair acetylacetone-water and obtained percent extracted - pH curves at constant reagent concentrations for many metals. He predicted that beryllium and aluminum could be quantitatively separated by proper pH adjustment, and that beryllium could be quantitatively separated from Mg, Co(II), Hg, Ni and Na because these five are not extracted by acetylacetone.

Bolomey and Broido[63] (1948) used the extraction of beryllium acetylacetonate with benzene to separate Be^7 from lithium. Toribara and Chen[64] (1953) and Toribara and Sherman[65] (1953) used a benzene solution of acetylacetone to extract beryllium selectively from aqueous solution for the determination of micro quantities. The authors noted that aluminum accompanies beryllium in this procedure. Conditions for the back extraction of beryllium into hydrochloric acid were determined.

The extraction of beryllium acetylacetonate from solutions containing ethylenediaminetetraacetic acid to complex interfering elements has been studied by Adam, Booth and Strickland[66] (1952) and Alimarin and Gibalo[67] (1956). The latter authors found that only beryllium was extracted from aqueous solutions containing Al, Cr, Fe(III), Ni, Mn, Zn, Cd, Pb, Cu, Ca, and Mg by the solvents CCl_4, $CHCl_3$, butyl alcohol and isoamyl alcohol. The best solvent proved to be carbon tetrachloride. Tabushi[68] (1959) used chloroform extraction with

ethylenediaminetetraacetic acid added to separate beryllium from mixed fission products. The decontamination factor was approximately 10^4 with a beryllium recovery of 97%.

Beryllium Salts of Carboxylic and Perfluorocarboxylic Acids.--The extraction of beryllium butyrate from aqueous solution by $CHCl_3$ ethyl acetate, ethyl ether, benzene, amyl alcohol and CCl_4 was studied by Sundaram and Banerjee[69] (1953). The maximum extraction (90-94%) was obtained with chloroform with the pH of the solution at 9.3 - 9.5. Banerjee, Sundaram and Sharma[70] (1954) separated beryllium from aluminum and iron by extraction with chloroform with sodium ethylenediaminetetraacetate present in the solution. Phosphate was said to interfere.

Mills and Whetsel[71,72] (1955) have used ether extraction of salts of perfluorobutyric acid to separate Be, Fe(III), Al, Cr(III) and UO_2(II) from univalent and other divalent cations. The extractions were found to proceed best at a pH value just less than that at which the cation would form an insoluble hydroxide. Basic salts such as $Be(OH)(C_3F_7COO)\cdot 5H_2O$ are generally extracted.

Sturm and Whetsel[12] (1960) employed this process with the use of sodium ethylenediaminetetraacetate to complex interfering impurities for the preparation of purified beryllium oxide (see page 10).

Other Compounds.--Bolomey and Wish[73] (1950) purified radioberyllium by benzene extraction of beryllium thenolytrifluoroacetonate. West[74] (1956), in a review of liquid-liquid extraction processes, said that with the exception of the 1,3-diketones, such as acetylacetone and thenoyltrifluoroacetone, none of the common chelating agents seem to be capable of extracting beryllium from aqueous solution. Przheval'skii and Moiseeva[75] (1959) prepared a number

of beryllium complexes with 1,3-diketones and determined their properties. These compounds and compounds of the general type, $BeO \cdot Be_3(RCOO)_6$, besides the acetate (see page 12), may be useful in extraction processes.

Ion-Exchange Methods

Ion-exchange techniques have been used for quantitative analytical separations of beryllium from other elements.

Kraus, Nelson, Clough and Carlston[76] (1955) have studied the absorbability of metal ions from lithium chloride solution by the anion exchange resin, Dowex-1. The absorbability of Be(II) in concentrated lithium chloride solution was found to be sufficient to permit separation from alkali metals, magnesium, and others.

Honda[77] (1950) separated lithium, beryllium and aluminum salts by successively eluting a cation exchange column containing the absorbed salts with 0.1 N HCl, 0.05 N $CaCl_2$ and 4 N HCl. The first effluent contained lithium, the second beryllium, and the third aluminum salts.

Beryllium spectrographically free from aluminum was obtained by Kakihana[78] (1951) by passing a solution containing both ions through a phenolsulfonic acid type exchanger saturated with calcium ions. Aluminum was completely absorbed while most of the beryllium was in the effluent.

Ryabchikov and Bukhtiarov[79] (1954) developed an analytical method for separating beryllium, aluminum, and iron in solution by passing an oxalate solution through a cationite (SBS) where only beryllium is retained.

Nadkarni, Varde and Athavale[80] (1957) separated beryllium from iron, aluminum, and titanium by passing a solution at pH 3.5

containing ethylenediaminetetraacetic acid and H_2O_2 through a column of the cation exchange resin Amberlite IR-120. Beryllium was retained while the other metal ions appeared in the effluent.

A quantitative separation of all the alkaline earths including radium was achieved by Milton and Grummit[81] (1957) in 5 hr by elution of Dowex-50 resin with ammonium lactate.

Schubert, Lindenbaum and Westfall[82] (1958) quantitatively separated trace amounts of beryllium from macro-concentrations of salts including Cu, U, and Ca. Beryllium was eluted selectively from a cation exchange resin with 0.02 to 0.10 *m* sulfosalicylic acid at pH 3.5 - 4.5. These investigators noted that a separation of aluminum from beryllium should be possible by adding ethylenediaminetetraacetic acid at approximately pH 4 before passage through a cation exchanger.

Kennedy and Wheeler[83] (1959) separated beryllium quantitatively from alkaline earths (Ca and Sr), Fe(III), divalent cations of the first transitional period, Al, lanthanides, Cd, Hg(II) and Po(IV) by using the complexing polymer sodium diallyl phosphate in conjunction with sodium ethylenediaminetetraacetate.

Other Processes

Precipitation from Molten-Salt Solutions.-- J. H. Shaffer[84] (1960) of ORNL has recently prepared crystalline beryllium oxide by the action of water vapor on a molten mixture of lithium and beryllium fluorides. It is not known as yet whether this procedure is capable of producing highly purified beryllium oxide.

The phase diagram compilation by Levin, McMurdie and Hall[85] with Part II by Levin and McMurdie[86] lists diagrams of binary and ternary systems of beryllium oxide with many metal oxides. The compilation also includes a number of binary and ternary fluoride systems containing

beryllium fluoride. Crystallization of beryllium compounds from fused mixtures of oxides or fluorides may possibly be used as a purification method. Oxide systems have the disadvantage of requiring very high temperatures; the low melting point of beryllium fluoride (545°C) makes the fluoride systems appear more attractive. The success of the process would depend on whether the impurities are left in solution as the beryllium-containing phase crystallizes out. Even a very small range of solid solution of an impurity fluoride in beryllium fluoride would mean that the impurity would not be eliminated. Trapping of impurities during crystallization may be troublesome, but successive recrystallization should overcome the difficulty.

Directional Crystallization of Metal.--Pearsall[87] of MIT (1952) showed that beryllium metal could be refined by directional crystallization.

Reducing Gases.--A French patent[88] (1938) claims that if a reducing gas, such as carbon monoxide or hydrogen, is passed over a heated, impure beryllium compound containing oxygen, impurities are eliminated and a purified beryllia results. It does not seem likely that this method would be capable of producing beryllia containing very low levels of impurities.

Purification of Beryllia with Phosgene.--Chauvenet and Duchemin[89] (1927) purified commercial beryllia containing 1.5% iron, aluminum, and calcium by passing phosgene over it at 455°C. Iron and aluminum chlorides sublime under these conditions, and chlorides of beryllium and calcium must be washed out.

Single Crystals of Beryllium Metal.--Garber, Gindin, and Shubin[90] (1959) reported that single crystals of pure (99.98%) beryllium metal were obtained by slow cooling of the melt in vacuum.

V. SUMMARY AND DISCUSSION

There are several beryllium preparations commercially available in the United States which are quite pure by the usual chemical standards and satisfactory for ordinary nuclear or refractory applications. These products, containing 300-500 ppm total impurities, may be conveniently used as starting materials for further purification. Nuclear-grade oxide of a comparable purity has also been made by the Pechiney Company of France. Distillation of beryllium basic acetate has been used on a laboratory scale by a number of investigators to give products of about as high a purity as has been achieved by any method, but has not been conducted on an industrial scale except in the U.S.S.R., where the process has been in use for at least five years. Total impurities reported for the oxide made from the purified acetate of the Russian process were between 50 and 110 ppm.

It is also noteworthy that although distillation of beryllium metal has not been very successful elsewhere, an industrial process is reported to have been in use in the U.S.S.R. for at least two years. If the metal produced by the Russian process were converted to oxide without introducing contaminants, the total impurities would be only about 73 ppm.

Laboratory-scale or small-batch preparations of beryllium compounds of generally higher purity than those commercially available in the United States have been reported by several investigators. The combination of chloroform extraction and distillation of basic acetate has been used by the University of Chicago Metallurgical Laboratory and the Pechiney Company to prepare spectrographic standards of beryllium oxide. Oxide made by the latter was reported

to contain less than 50 ppm total impurities. Repeated washing and recrystallization of beryllium oxalate has been employed by the Beryllium Corporation and ORNL to prepare small batches of material containing somewhere between 150 and 350 ppm total impurities based on beryllium oxide. In addition, Brush Beryllium Company has made small lots of special purity beryllium oxide with considerably less impurities than are contained in Brush commercial UOX Grade.

Achievement of impurity levels substantially below those in the best commercial preparations is a difficult problem. Most investigators who have attempted such purifications have emphasized the need to take special precautions to avoid contamination of the product by the reagents and apparatus. When the aim is to reduce impurity contents to a few parts per million, even laboratory dust can cause serious contamination. Consequently, processes should be chosen which (1) can be conveniently carried out in closed systems, (2) are amenable to the use of equipment which will not introduce contaminants, and (3) use reagents which can be easily purified to very high levels. Using large amounts of material is desirable because the effect on the product by most of the sources of contamination will be minimized.

Distillation of metal and volatilization of beryllia by steam have the disadvantages of requiring very high temperatures. In the latter method the oxide is purified directly, thus avoiding an additional conversion step, but there may be serious interference by other oxides also transportable by steam. Although a remarkably pure metal is reported to be produced by distillation, further processing is required if the goal is to make a pure oxide. Also, it is not known whether redistillation would improve the purity much beyond the reported level.

Processes consisting of precipitation of impurities, crystallization of beryllium compounds, and ion exchange may be useful as preliminary stages to remove certain elements which may interfere in the final purification process. Precipitation by hydrogen sulfide or 8-hydroxyquinoline, for example, will virtually eliminate many elements, while others will not be affected. The limiting factor is the solubility product of the impurity sulfide or 8-hydroxyquinolate. Recrystallization of beryllium salts such as the sulfate and oxalate has been successfully used in several procedures, but the loss of a large fraction of the beryllium to the mother liquor with each step is a serious drawback. Furthermore, a leveling-off of the impurity content may be expected as the process is continued. Ion-exchange methods have usually been limited to separations of beryllium from ions with which it is often associated in analytical procedures involving small quantities of material. Not enough quantitative data is available to evaluate their efficiencies for purifying beryllium to very low impurity levels.

Liquid-liquid extraction and vacuum sublimation of compounds such as the basic acetate or acetylacetonate are processes which meet the requirements for a final purification step. Extraction processes can be carried out with plastic equipment at room temperature in closed systems, and with favorable separation factors there is no theoretical limit to the degree of purity which can be achieved upon repeated extraction. An attractive feature is the adaptability to a large scale using counter-current extraction equipment. Sublimation processes require higher temperatures, of course, but apparatus could be made from teflon or other plastics capable of withstanding the required temperatures.

The basic problem in extraction processes is finding a system in which (1) separation factors for beryllium and the impurities are favorable, (2) the reagents are easily purified, and (3) the final product can be readily converted to a useful beryllium compound without introducing contaminants. Organic extractions of aqueous solutions of the acetylacetonate, carboxylates, and perfluorocarboxylates, with ethylenediaminetetraacetate added to complex interfering impurities, have been reported favorably in the literature. One of the advantages of these beryllium compounds is that they can be readily decomposed by strong acids. Besides acetylacetone, other 1,3-diketones such as thenoyltrifluoroacetone possibly may be useful in extraction schemes. Water extraction of impurities from chloroform solutions of beryllium basic acetate has been employed in practice with success. A serious disadvantage is apparent, however, if it is desired to use the process to achieve levels of impurities significantly below those already attained: The acetate is not easily converted to the oxide without introducing contaminants.

The sublimation of the basic acetate would have the same disadvantage as extraction with respect to conversion to oxide. Purification by subliming beryllium acetylacetonate has been proposed, but it is not certain whether interference by acetylacetonates of impurities would limit the efficiency of the process.

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