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BERYLLIUM, ACTUAL AND POTENTIAL RESOURCES, TOXICITY,
AND PROPERTIES IN RELATION TO ITS USE IN
PROPELLANTS AND EXPLOSIVES (U)

14 NOVEMBER 1960



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BERYLLIUM, ACTUAL AND POTENTIAL RESOURCES, TOXICITY,
AND PROPERTIES IN RELATION TO ITS USE IN
PROPELLANTS AND EXPLOSIVES (U)

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ABSTRACT: Those who wish to consider beryllium as an ingredient of propellants or explosives should be familiar with the current and potential supply of this element. Likewise they should comprehend the toxicity of beryllium and its compounds. The objectives of this report are provision of information about the actual and potential supply of beryllium and about the toxicology of beryllium and its compounds.

Metallic beryllium will not be available in quantity if nothing better than the primitive methods of mining now in use, utilization of only the richest ores, and complex and inefficient methods of extracting beryllium oxide do not make way for better methods. If mining and extraction of beryllium are not improved, plans should not be made to use more than small quantities of beryllium in explosives or in propellants.

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CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

14 November 1960

The collection of information on the toxicity and supply of beryllium was part of the Bureau of Naval Weapons task, Study of Explosives Properties, RUUO-3-E-012/2121 WF008-10-004, to develop new and improved solid high explosives. The information recorded herein is to assist those who may want to decide whether evaluation of beryllium in high explosives or propellants is likely to be feasible and profitable.

W. D. COLEMAN
Captain, USN
Commander

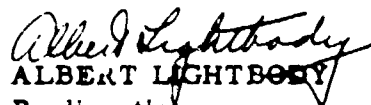

ALBERT LIGHTBODY
By direction

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BERYLLIUM, ACTUAL AND POTENTIAL RESOURCES, TOXICITY,
AND PROPERTIES IN RELATION TO ITS USE IN
PROPELLANTS AND EXPLOSIVES (U)

INTRODUCTION

Beryllium has been suggested as an ingredient of propellants and explosives at various establishments at various times by various people. Those who suggest that beryllium be used as aluminum or magnesium is used, present certain facts in support of their conclusion that it should be superior to the latter metals. The most cogent of these facts is that the heat of formation of beryllium oxide is higher than that of aluminum or magnesium. Therefore, the heat of explosion of explosives or heat of combustion of propellants containing beryllium, will be higher than similar compositions containing other metals. It cannot be concluded, a priori, that the advantage of higher heat of oxidation of beryllium will cause explosives and propellants containing beryllium to perform substantially better than those based on other fuels. Superiority of beryllium as an ingredient in explosives and propellants will have to be established by experimental evaluation.

The factors which should be considered while deciding whether to undertake experimental evaluation of beryllium include the actual and potential supply of the metal and the toxicity of the metal and its compounds. The actual and potential supply of beryllium will define the magnitude of plans for its use and the effort which can justifiably be expended on its evaluation. Toxicity will increase the cost of evaluation, production of metal of suitable form, and production of products. Facts about the actual and potential foreign and domestic resources of beryllium are presented herein. These facts and discussion thereof are presented to assist those who wish to decide for themselves whether beryllium can be expected to be superior to other metallic fuels, for what propellant and explosive uses it should be evaluated, and the quantity that will be available for expendable uses.

To recapitulate, the author's primary objective is to describe the beryllium supply situation and to present the facts and opinions about toxicity.

SUMMARY AND CONCLUSIONS

1. Commercial beryllium ore (beryl) is mined and prepared for market by quite primitive methods. The methods of recovering beryllium oxide or beryllium are complex and inefficient and under no probable economic conditions can they ever be expected to separate more than about 600 short tons of beryllium from presently known ore deposits. This, 600 short tons of beryllium, must therefore be considered to be the total available domestic supply until mining and metallurgical methods have been improved. The ratio of domestic to foreign potentially available beryllium has been assumed to be 1:14. Therefore, the total foreign resources are, under existing circumstances about 10,000 short tons of beryllium. In emergency foreign powers will bid for the limited supplies and nations having beryllium ores may choose to retain them or they will sell to the highest bidder.

2. The Atomic Energy Commission will probably want to use large amounts of beryllium relative to the supply and in time of emergency will probably demand and get priority in the use of the metal. Also beryllium will be in great demand for use in airplanes and missile machines for special parts. Under the circumstances mentioned here and in the preceding paragraph, there may be little, if any, beryllium remaining for use in explosives and propellants. It would then be unwise to plan to use more than small quantities of beryllium in explosives and propellants.

3. However, there are relatively vast quantities of beryllium in the U. S. in low grade ores, containing at least 0.1% beryl, reference (4), estimated to contain 270,000 tons of beryl. If economical means of recovering beryllium from these sources are developed much more pretentious plans for use of beryllium in explosives and propellants can be justified. Discovery of an acid leachable ore of considerable magnitude would lead to the same result. The following news item quoted from the September 12, 1960 issue of Chemical and Engineering News indicates that there is reason to believe that such ores may be found.

"Vitro Minerals Corp. has received the first loan for beryllium exploration (previously only beryl ores were eligible) from the Office of Minerals Exploration of the U. S. Department of Interior. The loan will be used to explore Vitro's property in the Topaz Mountain area of Juab County, Utah, which seems to contain an acid-leachable type of

beryllium ore." There is at least one other development in the Topaz Mountains, supported by strong engineering and financial interests, whose objective is a source of leachable beryllium ore.

4. Workers can be protected from the toxic effects of beryllium during manufacturing processes by good ventilation of working places, rigorous screening of exhaust gases, and conformation to the highest standards of personal hygiene.

5. The toxic hazards of underwater evaluation of beryllium explosives are believed to be negligible. Air blast evaluation of beryllium explosives should be performed in isolated areas. Operating employees must not re-enter the evaluation area until the beryllium concentration in the air is less than one microgram per cubic meter.

COMPARISON OF BERYLLIUM WITH OTHER ELEMENTAL FUELS

In 1951, reference (1), David Hart and W. R. Tomlinson, Jr. of Picatinny Arsenal published a paper in which various metals, silicon, phosphorus (red), and boron were compared as ingredients of explosives. The table of physical and thermochemical properties presented by these authors is given in this report as Supplement A. The author of this report has compiled a more comprehensive table of physical properties and thermodynamic data for beryllium, aluminum, boron, and magnesium. This table is presented herein as Supplement B. The coefficients to be substituted in the specific heat equations for various physical states of the four elements and their oxides are recorded in Supplement C. Reference (5) contains discussions of the physical and chemical properties of beryllium as well as a tabulation of many of its physical properties. These are reproduced herein as Supplement D.

Beryllium Resources of the Earth

After only slight study of the resources of beryllium the student can justifiably conclude that the available and potentially available beryllium obviously is not adequate for extensive use in explosives and propellants. At this early stage in his studies he also concludes that consideration of any proposed use of beryllium must include estimation of the amount of beryllium required and comparison of the requirement with United States and world resources of beryllium. As previously stated one of the two primary objectives of writing this report is to present in one document the information of world beryllium resources which will enable those

considering beryllium for use in explosives and propellants to decide whether beryllium for their expected need can be provided.

References (4) and (7) contain much of the information presented herein. This information is presented rather fully in this report for the benefit of readers who may not have the references.

Beryllium Resources of the United States

The resources of beryllium in the United States are fairly well known as a result of an intensive study carried out by the Geological Survey, Supplement E, in recent years, largely on behalf of the Atomic Energy Commission. The principal known resources are in pegmatites. The greatest domestic production of beryl has come from feldspar, lithium, and mica mines in the southern Black Hills, South Dakota. The principal sources of cobbable (separable by hand sorting) beryl, most of which can be produced only as a by-product of other minerals under present conditions, are in South Dakota, New Hampshire, Maine, Connecticut, Colorado, and New Mexico. The largest known source of milling rock is in the Kings Mountain area of North Carolina, where pegmatites of 0.04 to 0.05 percent BeO content are estimated to contain about 823,000 tons of beryl or beryl equivalent to a depth of 300 feet. Spectroscopic methods of analysis do not distinguish between beryllium in beryl and beryllium in other minerals, such as chrysoberyl. Nearly all non-pegmatitic deposits of beryllium in the United States are very low grade and contain very small reserves.

In 1957, it was reported that the United States had the following reserves: 8,800 tons of beryl (440 tons of beryllium) in pegmatite deposits containing at least 1 percent beryl and at least 100 tons of beryl, and 3,300 tons of beryl or beryl equivalent (165 tons of beryllium) in non-pegmatite deposits having the same tenor. The distribution of this 605 tons of beryllium is as follows: in pegmatites 175 tons in South Dakota, 180 tons in New England, 50 tons in Colorado, and 35 tons in Idaho, Nevada, and New Mexico; and in non-pegmatite deposits, 165 tons in various States, reference (8).

Another estimate indicates that the United States has 271,800 tons of beryl (13,590 tons of beryllium) in pegmatite deposits containing at least 0.1 percent beryl and 7,200 tons of beryl or beryl equivalent (360 tons of beryllium) in non-pegmatite deposits of the same tenor. The beryl in individual deposits containing less than ten tons are excluded from these figures. The distribution of this 13,950 tons of beryllium is as follows:

In pegmatites, 12,190 tons in North Carolina, 800 tons in South Dakota, 350 tons in New England, 175 tons in Colorado, 65 tons in Idaho, Nevada, and New Mexico, and 10 tons in other States; and in non-pegmatite deposits, 360 tons in various States, reference (8).

The tin-spodumene belt, which is about 25 miles long and less than 2 miles wide and is in North Carolina, contains 823,000 tons of disseminated beryl (41,150 tons beryllium) to a depth of 300 feet, reference (9). Most of this beryl is excluded from the figures of the previous paragraph because the concentration is less than 0.1% beryl equivalent.

Beryllium Resources of Foreign Countries

Beryl has been found in many foreign countries, but little quantitative data on grade or reserves are available. The principal known resources are in Brazil, India, Australia, Argentina, and various parts of Africa. Large beryl resources may yet be discovered in these and other parts of the world, especially in lithium pegmatites. A large part of any such newly discovered beryl may be too fine grained to be of commercial interest at the present time.

The literature indicates that the deposits of foreign countries are very similar to the deposits of the United States. Aside from a small quantity of scrap from emerald mines, all of the world's beryl obtainable under present conditions is from pegmatites or from eluvial deposits derived from pegmatites. A large proportion of the total beryl mined has been by-product or co-product, but an increasingly larger quantity is being mined without the concomitant production of other minerals.

This general information about the resources of foreign countries precedes specific descriptions of the principal deposits of beryllium bearing minerals throughout the world. For more details of these the reader should see reference (4). Because of special interest in Russian resources the summary paragraph about the deposits in that country is quoted here from reference (4).

"The reports of Sinogub, reference (11), and Ames, reference (12), strongly imply that Russian beryl resources are meager. An inordinate interest seems to have been taken in the extremely inaccessible Tigiretz pegmatite, which is only 19 meters long and 6 meters thick. Furthermore, the emphasis on the Ural deposits seems scarcely justified, in view of the fact that figures for size, grade, or productive capacity seem

to be lacking. The Zabaikal deposits are in tungsten veins, a type of deposit that cannot be economically mined for beryl under present conditions in other parts of the world. Only the deposits on the north slope of the Turkestan Range seem to be sufficiently similar to deposits worked elsewhere in the world to indicate that the beryl could be mined under existing economic and technological conditions and sold at a profit in an uncontrolled market."

SUMMARY OF WORLD RESOURCES

The beryllium reserves of the world are not known with certainty. In order to estimate world resources in 1953, the ratio of the beryllium mineral resources in the United States to those of the world was assumed to be the same as the ratio of beryl production, 1935-51. For each ton of beryl that the United States produced during that period, the world produced 14; thus, a ratio of 1 to 14 was established for calculating world resources of beryllium minerals. Using this ratio, the world resources of beryllium in deposits containing more than 1 percent beryl or equivalent beryl were calculated to be about 200,000 tons (19,000 tons of beryllium). The total resource of world deposits containing 0.1% beryl or beryl equivalent was calculated to be about 4 million tons (200,000 tons of beryllium), reference (10). These estimates have not since been confirmed. It appears from these figures that the U.S. beryllium reserves amount to 55,000 tons (41,000 tons in the tin-spedumene belt and 14,500 tons elsewhere) of beryllium and that the world reserves amount to 200,000 tons in deposits containing over 0.1% beryl or beryl equivalent.

This information about the economic geology of beryllium was extracted from Chapter III of reference (4). This chapter was written in 1950 but was modified in 1953 to fit conditions as they existed then. Reference (4) was chosen as the source of information rather than reference (7), a later publication because there is much more detail in the former. Comparison of references (4) and (7) shows clearly that there have been only minor changes in the beryllium supply situation since 1953, the date of reference (7). Cf. reference (17).

Submarine sources of beryllium should be mentioned because there may be some curiosity about these sources. Beryllium isotopes having mass numbers 7 and 10 are produced in the upper atmosphere by cosmic ray bombardment. These isotopes are carried into the ocean by rain. The accumulation of ⁷Be is negligible because of its short half life.

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The half life of ^{10}Be is 2.5 million years and accumulation can be expected to be much larger. However, analysis of sediment cores from the Pacific Ocean indicate that concentration of ^{10}Be is of the order of only a few parts per million. Obviously recovery of beryllium from this source is not feasible. No other information about submarine sources was found.

ANALYSIS OF WORLD BERYLLIUM RESOURCES

The estimates of the U.S. and world beryllium resources are misleading without analysis and much complementary information. Specific qualifications of these estimates are given herein in explanation of that statement.

The sources of U.S. beryllium ore which are estimated to contain 605 tons of beryllium, are either pegmatites or non-pegmatites. The 165 tons and larger quantities from poorer deposits of beryllium estimated to exist in non-pegmatite deposits cannot be recovered by hand methods and recovery must await development of ore milling techniques, page III-3, reference (4). All commercial beryl is hand-cobbed and seldom are crystals and fragments recovered that are less than 1 inch in size. Furthermore, the author of reference (7) on page 4 goes on to state that "probably not more than one-third of the beryl in the average commercial deposit is recovered by the crude hand methods now employed". Therefore, in order to interpret the estimates of reserves as precisely as possible much more extensive analysis is necessary. This we propose to present here.

In order to understand the beryllium supply situation it will be necessary to develop a general comprehension of the geology of beryllium, mining methods, ore improvement, and production of beryllia and beryllium.

BERYLLIUM GEOLOGY

Beryllium has been found in many different types of rock, but it occurs principally in granitic and syenitic intrusive, igneous rocks chiefly pegmatites, granites, and nepheline-syenites and in a few sediments derived from these rocks. These intrusives result from the solidification of molten rock forced upward into crevasses, cracks, and other voids in over-lying solid rock by the pressure of this solid rock on deep seated molten magma. This intruded molten rock solidified under conditions that caused formation of large crystals. Beryl, the only mineral found in sufficient quantity rich enough to qualify as an ore mineral of beryllium, occurs in intrusive pegmatites in crystals or aggregates which range in size from crystals too small to be cobbed (hand sorted) to an occasional 60 tons. The world's

principal sources of beryl are heterogeneous granite pegmatites, where the mineral occurs in enriched zones, filled fractures, and replacement bodies. The principal beryl deposits are found in zones that usually contain only a few thousand tons of pegmatitic rocks. A few deposits contain a million tons or more.

Beryllium reserves and resources may be grouped into four economic categories: (1) Beryllium in beryl produced as the principal mineral of a pegmatite mine; (2) beryllium in by-product beryl; (3) beryllium in beryl and other pegmatite minerals recoverable only by milling; and (4) beryllium in non-pegmatitic deposits. All of the beryllium produced at the present time is in the first two categories.

Beryl, Principal Product of a Mine

In the United States only the few deposits that contain at least 2% beryl recoverable by hand-sorting can be mined profitably for beryl alone under existing economic conditions. Possibly somewhat lower grade material can be mined profitably in some foreign countries. Nevertheless, deposits that can be mined for beryl alone are rare. Most, and possibly all, such deposits are small but rich shoots or pods in larger, lower grade units of zoned pegmatites. Few of these deposits contain more than 100 tons of beryl, but 1 deposit in Argentina, presumably of this kind, contained at least 3,000 metric tons of beryl. Large masses of beryl-rich rock capable of sustaining a mining operation on their own merits either are found in the course of mining for other minerals or are exposed at the surface. Additional deposits may yet be found at the surface in foreign countries, but the search for beryllium throughout the world has been extensive enough to suggest that appreciable quantities of beryl in such deposits will be found only in extremely inaccessible regions.

By-Product Beryl

A large proportion of the beryl used commercially is a by-product or co-product from mines that produce other pegmatite minerals. The beryl crystals must be sufficiently large and free of inclusions to be concentrated by hand-sorting. Pegmatite deposits from which beryl is obtained as a by-product may contain 0.1% beryl or less. Beryl is produced as a by-product of mica, feldspar, and lithium mining in the United States.

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Reserves in known or easily found deposits that can be mined for beryl alone under present conditions should not be expected to exceed a few tens of thousands of tons of beryl in the entire world.

Beryllium Minerals Recoverable from Pegmatites by Milling

Most of the resources of beryl in the United States, and presumably elsewhere in the world, can be recovered only by milling because the beryl crystals either are too small or contain too many inclusions to be sorted by hand and obtain a clean product. A successful beneficiation method for the recovery of beryl has not yet been developed. Nevertheless, if world production is to be greatly increased, the recovery of beryl by milling will be necessary. If other beryllium minerals occur in sufficient concentration in any pegmatite, they may also be milled at some future time. Milling is not an end process. It is preliminary to extraction of values by flotation or leaching. Even if milling methods were to come into general use, beryl mining probably would continue to be largely a by-product industry. Consequently, the beryl, to be recoverable at a profit, would have to pay only for the concentration unit set up for beryl in a mill.

Beryllium in Non-Pegmatitic Deposits

The beryllium minerals of non-pegmatitic deposits are too fine grained to be concentrated by hand methods and cannot be recovered under present conditions. Furthermore, the present day beryllium industry is adapted only to the use of beryl and possibly chrysoberyl as sources of beryllium; other minerals are not being used. Non-pegmatitic deposits, like deposits of pegmatites, should contain, at the very least, the equivalent of 0.1% to be considered possible future sources of beryllium.

MINING AND ORE PREPARATION

Beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ or $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) the mineral from which nearly all of the world's supply of beryllium is obtained contains 5% of beryllium. It occurs in pegmatites in the form of crystals and is separated, for commercial use, by cobbing (hand-sorting). It is either a by-product or co-product of mining other minerals. Consequently, beryl production is not and cannot be varied independently and it is governed by demand for another product. Another consequence of such

relationship is that the mining methods may be less efficient in separating the beryl because the recovery or condition of the co-product or main product ore must be considered or given first consideration. For example in mining beryl as a co-product with mica, blasting must be done so that maximum size mica sheets can be obtained. This may mean that the beryl is not entirely separated from gangue and some of it may not be separable by hand-sorting. On the other hand, if more brisant blasting is done some of the beryl will be lost as "fines".

Heretofore, pegmatites have been mined by underground methods on a limited scale only, chiefly because of higher costs, compared with opencut mining, adequate access to deposits amenable to the opencut mining method, and the lack of initiative and capital to undertake underground exploration of potential beryl-bearing deposits. To exploit beryl pegmatites more effectively, many deposits will have to be mined underground by using mechanized mining and transportation where possible to increase efficiency and offset high labor costs.

Nearly all beryl mined in the United States is recovered as a by-product from the mining of pegmatites exploited primarily for feldspar, mica, quartz crystals, lithium-bearing minerals, and gemstones. However, some foreign deposits are worked for beryl alone. The beryl content is usually very small; generally about 100 tons of rock must be broken to recover 1 ton of hand-cobbed beryl. Hand-cobbing is a laborious and time-consuming operation; therefore, the matter of adequate price becomes an increasingly important factor in efforts to augment the supplies of beryl. An unfortunate aspect as regards beryl recovery lies in the fact that most of the richest beryl-contained zones of a pegmatite dike contain the poorer grades of feldspar; therefore, they often are avoided in the normal course of recovering feldspar, and the opportunity for any potential economic recovery of beryl is thus limited.

Ore Preparation

The specific gravity of beryl (2.65 to 2.84) is slightly higher than that of feldspar or quartz, but the difference is not enough to favor gravity methods of separation, such as the "sink and float" process. Liberation of the free mineral has not been commercially successful heretofore; processes suitable for treating coarse sands are desirable because the optimum size for crushing the associated minerals--quartz and feldspar--for use in the glass industry is about 14 mesh.

Considerable work on the beneficiation of beryllium ores was done by the Bureau of Mines in conjunction with its exploratory work for other ore deposits, chiefly the beryl-bearing pegmatites from various localities in the Black Hills. Flotation has proved to be the most applicable method although various concentration methods were more adaptable economically for removing small quantities of certain accessory minerals. Some of the ores were amenable to flotation only after scrubbing with an alkali to remove the alteration products, and still others did not respond even after this treatment.

Under memorandum agreement with the Defense Materials Procurement Agency and in cooperation with the Foote Mineral Company, the Bureau of Mines is* conducting an investigation of the recovery of beryl as a by-product from the Kings Mountain, N. C., spodumene mining operation. Preliminary results indicate that beryl can be recovered economically by flotation.

Intensive studies are being conducted by industry and other Bureau of Mines laboratories to develop a commercial process, and it is believed to be only a question of time before the problem will be solved, reference (13).

METALLURGY

Beryl is a compound of beryllium with alumina and silica. In general separation of elements from silica combinations such as this have been difficult and usually other ores are chosen as sources of the desired element. The difficulty of the metallurgical processes for recovery of beryllium may be illuminated by examination of the beryl-beryllium price structure. The prices for beryl and beryllium used in this analysis are in the following paragraphs quoted from reference (7).

"In July 1959, E&MJ Metal and Mineral Markets quoted domestic beryl, 10 to 12% BeO, at \$46 to \$48 per short ton unit of BeO, f. o. b. mine. On term contracts, quotations for imported beryl, 10 to 12% BeO, c. i. f. United States ports, was \$31 to \$33 per short-ton unit of BeO, however, the spot price was \$30 to \$31 per unit of BeO."

"Unit prices paid by the Government under its program for purchasing domestically produced hand-cobbed beryl are as follows: 8 to 8.9% BeO, \$40; 9 to 9.9% BeO, \$45; and 10% or more BeO, \$50."

*As of 1953, date of reference (4).

"In July 1959, the American Metal Market quoted the following prices: Beryllium metal, 97% pure, lump or beads, f.o.b., Cleveland, Ohio, and Reading, Pa., \$71.50 per pound. Beryllium-copper master alloy was quoted f.o.b. Reading, Pa., Detroit, Mich., and Elmore, Ohio, at \$43 per pound of contained beryllium, with the balance paid as copper at the market price on date of shipment. Beryllium-aluminum was quoted f.o.b., Reading, Pa., Detroit, Mich., and Elmore, Ohio, at \$74.75 per pound of contained beryllium, plus the value of the aluminum at the market price."

Eighteen months later in its September 15, 1960 issue the E&MJ Metal and Mineral Markets published the following quotations: Domestic beryl 10-12% BeO \$46 to \$48 per short ton unit, imported beryl same tenor, \$34.00 to \$34.50, and spot \$31.75 to \$32.50. Price for metal 97% was quoted as \$71.50 per pound. Comparison of these prices with those quoted in July 1959 by the same publication shows that the slight changes have been inconsequential.

One short ton unit is 20 pounds. Therefore, in September 1960, the quotation for beryllium in domestic beryl was \$6.39-\$6.67 per pound. Beryllium in imported ore in September 1960 was \$4.31 - \$4.58 per pound. The quotation for metallic beryllium was \$71.50 per pound. Therefore, beryllium metal cost \$65 more per pound than beryllium in domestic beryl which amounts to an increase of 900% through separation of the metal from the ore. The percentage increase is less if allowance is made for the 65% recovery which is the accepted normal. If a substantial reduction in the apparently large cost of extraction could be made and shared with the beryllium consumer and the beryl miner, the latter would be stimulated to increase production of beryl and insure a reliable supply. This might encourage the miners to install more efficient mining machinery and thereby reduce costs.

The difficulties which must be overcome in the separation of beryllium as metal or oxide from ore are well stated in the following quotations from page II-7 of reference (4):

"The production of beryllium metal and its alloys has been acknowledged as one of the most difficult tasks in metallurgy. It has been termed 'the world's No. 1 metallurgical headache', since the metallurgy of the element has always presented a perplexing problem. The metal has a high fusion point and a high vapor pressure at a temperature not much above the fusion point, thereby creating a critical

metallurgical situation. The pure metal is exceedingly light, tending to float on slags and fused electrolytes*, the halides, highly deliquescent, cannot be reconverted to the desired form as an anhydrous salt by simple heating after they absorb water from the air, as all halides hydrolyze readily; when beryllium hydroxide is precipitated it tends to occlude and adsorb other salts in addition to forming basic salts and oxysalts."

Modern processes are based largely on bringing beryllium into solution either as a beryllium sulfate or as an alkaline fluoberyllate, reference (14). The latter processes originated from the fact that alkaline fluoberyllates are soluble in water, whereas beryllium fluoride is not. Much recent metallurgical research in this field has been done in the United States, Germany, and France.

The refining of beryllium ores on a commercial scale is a problematical undertaking requiring skilled operating technicians. In the processes developed thus far, a beryllium recovery of about 65% has been accepted as normal, although efforts have been made to increase this figure. It is usually economically advisable to convert the ore to beryllium oxide, or to beryllium hydroxide, at which stage beryllium can be more readily processed into all forms. The major difficulties encountered are (1) that beryl is entirely inert to any reagent at low temperature except hydrofluoric acid and (2) that the compounds of beryllium and aluminum present as chemical constituents of beryl are very similar chemically; hence, most of the expense and difficulty in producing beryllium oxide is centered around the separation of these two elements. Only three different ore processes have been used commercially in recent years, although several hundred methods have been invented and patented.

Joy-Windecker Process-Clifton Products, Inc.

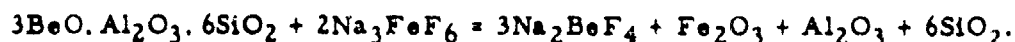
In this process the ore is fused with soda ash and the product treated with strong sulfuric acid to obtain silica in insoluble and filterable form and aluminum and beryllium in the form of water-soluble sulfates.

*The density of metallic sodium is about one-half that of the fused electrolyte from which it is produced. Therefore it floats on the electrolyte, which is not a disadvantage in the production of sodium.

The major portion of the aluminum sulfate is first separated from the beryllium sulfate by adding ammonium sulfate to the mixed sulfates. The ammonium alum crystals formed by this addition are separated, leaving a filtrate of beryllium sulfate contaminated mainly with aluminum and iron. The iron is oxidized to the ferric state, and the filtrate is diluted and treated with sodium carbonate to a pH of about 5.5. The precipitate, containing about 95% of the aluminum and iron and about 10% of the beryllium present, is filtered off and separated. This crude hydroxide is then re-dissolved in sulfuric acid, the beryllium sulfate solution produced is diluted, and the pH of the solution is adjusted with ammonia to 5.5-5.7 to precipitate the remaining aluminum and iron as hydroxides. After separation of these impurities the filtrate is completely precipitated with ammonia. The pure beryllium hydroxide formed is separated by filtration, washed, dried, and ignited to beryllium oxide of high purity, reference (15).

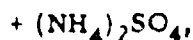
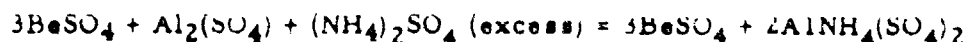
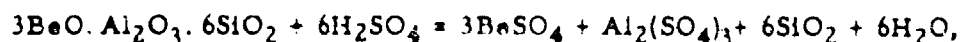
Fluoride Process-(Copaux-Kawecki)- The Beryllium Corporation

The ore is first ground in a ball mill, either wet or dry, until about 70% is minus 200 mesh (0.07 mm in diameter). It is then mixed with sodium ferric fluoride and made into wet briquets, which are heated for about an hour at 750°C. The sodium ferric fluoride reacts selectively at 750°C with the beryllium oxide in the beryl ore, forming sodium beryllium fluoride and ferric oxide according to the equation:



Sulfate Process-(Sawyer-Kjellgren Process)-Brush Beryllium Company

The beryl ore is first completely melted at approximately 1,625°C and then quenched in cold water. The melted beryl is poured into water to obtain a frit, which is ground in a ball mill. This renders the ore susceptible to attack by sulfuric acid at 275°C. The main reactions involved are:



Another sulfate process in use separates beryllium from the aluminum in the sulfate solution by careful pH control. Aluminum and iron hydroxides precipitate before the beryllium. Separation is effected by adding some basic material such as ammonia or soda ash.

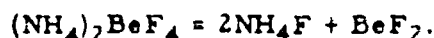
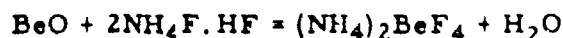
Many more details of these processes are given in Chapter II of reference (4).

Beryllium Metal

The processes described result in production of BeO instead of metallic Be. For most uses including explosives and propellants the latter is wanted.

Beryllium is produced as solid-lump metal by reducing an excess amount of beryllium fluoride in solid form with magnesium metal charged in a graphite-lined furnace at a crucible temperature of about 900°C. A slag of magnesium fluoride and beryllium fluoride is produced. Solid beryllium metal is recovered after the reaction is completed by raising the temperature to 1,300°C., somewhat above the melting point of beryllium. The molten beryllium, which floats on top of the molten slag, is collected into a pool and then quickly solidified into a floating cake of solid beryllium.

This process is based on the following reactions:



Cf. references (15) and (16).

TOXICITY OF BERYLLIUM AND ITS COMPOUNDS

The fabrication of products from finely divided beryllium and its soluble compounds has been accompanied by serious illnesses and deaths of operators. The mining of ores, recovery of beryllium as the oxide, and the reduction of the oxide have not been accompanied by toxic manifestations. It is only where finely divided metal, oxide, or compounds have been processed that serious toxic effects have been experienced among workers and others working or residing near plants from which beryllium containing dust or fumes have been ejected. The following

statement on toxicity from reference (7) is quoted because it is a good summary of the beryllium toxicity situation today.

"Some materials containing beryllium are toxic to humans, references (18) through (20) of this report. No ill effects from beryllium have been found in mining, sorting, or transporting beryl to markets. However, a disease known as berylliosis is caused by exposure to various compounds, dusts, fumes, or mists from some beryllium materials and can be injurious to health if safety precautions are not taken. It is safest to regard beryllium metal and its compounds in powder form as potentially toxic. Simple and practical industrial procedures for control of the toxicity are available.

"There are two types of beryllium-induced chronic diseases, skin and respiratory. In each type a kind of tumor is formed that affects the skin or lungs. The skin type of beryllium induced disease can sometimes be contracted by implantations with some beryllium compounds. Acute inflammatory conditions of skin and mucous surfaces can be caused by contact with dusts, fumes, or mists of certain compounds of beryllium. The respiratory types, acute and chronic, can be received from breath' g certain dusts, mists, or fumes containing the element. Most of the victims of acute beryllium-induced respiratory disease recover rapidly and without permanent injury, but a few have been afflicted by the chronic form for several years with serious consequences. Modern control practices have practically eliminated new cases of disease from beryllium.

"Little is known about berylliosis, but much has been done by the beryllium industry to prevent the disease. Working places are kept clean; workers are required to wash their hands frequently; clothing is laundered regularly; dusts, fumes, and mists are caught at the source and deposited in dust collectors; and numerous other precautions including medical programs have been adopted to make working conditions safe."

The toxicity situation of beryllium was summarized very well in reference (4). This is quoted as Supplement F. Other publications in which the toxicity of beryllium and its compounds are discussed are references (25), (27) and (28). A comprehensive bibliography, reference (29), in which 670 references are listed, on the toxicology of beryllium has been prepared at the University of Rochester for the Atomic Energy Commission. References (30) and (31) are other bibliographies on the same subject.

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The safe handling of metallic beryllium and its compounds are described in detail in reference (26). The abstract of this paper published in U.S. Government Research Reports, Vol. 33, No. 3, March 18, 1960 is quoted below in part.

"No recommendations for safe handling of beryllium in setting up a new operation are intended or can be given in this report. However, it is hoped that these references and brief descriptions may assist safety engineers, operators, and plant design groups in the task of setting up a reasonable program of safe handling practices to be adhered to in any shop that expects to handle beryllium for the first time."

SUPPLEMENT A

PHYSICAL AND THERMOCHEMICAL PROPERTIES OF POWDERED ELEMENTS USED IN
MODERN MILITARY AMMUNITIONS*

	Density	Melting Point C°	$\frac{-\Delta H^{***}}{n}$	Heat of Oxidation Cal./G	Adiabatic Temp. of Oxidation C°
Magnesium	1.74	651	73.05	6,000	12,200
Beryllium	1.85	1280	69.50	15,500	11,600
Aluminum	2.7	660	66.50	7,400	13,300
Zinc	6.4	1860	64.5	2,830	14,300
Boron	**	2300	56.63	15,600	11,300
Silicon	2.4	1420	50.8	7,200	11,300
Titanium	4.5	1727	56.25	4,700	12,500
Manganese	7.2	1260	46	1,680	7,700
Phosphorous (Red)	2.2		36	5,800	8,600
Iron	7.86	1535	33.3	1,770	6,600
Nickel	8.9	1452	29.2	990	4,800
Antimony	6.7	631	27.7	680	5,500
Lead	11.3	327	26	260	4,300

*From reference (1)

**Figures given in reference (2) are 3.33 for crystalline and 2.34 for amorphous boron.

***In kilocalories

[illegible]

SUPPLEMENT C

SPECIFIC HEAT COEFFICIENTS*

$C_p = a + bT - cT^{-2}$ cal. deg. $^{-1}$ mole $^{-1}$					Range of Temperature °K
Element	State	a	$b \times 10^3$	$c \times 10^{-6}$	
Aluminum	Crystals	4.80	3.22	-----	273 - 931
Aluminum	Liquid	7.00	-----	-----	931 - 1273
Aluminum Oxide	Crystals	22.08	8.971	0.5225	273 - 1973
Beryllium	Crystals	4.698	1.555	0.1210	273 - 1173
Beryllium Oxide	Crystals	8.69	3.65	0.3130	273 - 1175
Boron	Crystals	1.54	4.40	-----	273 - 1174
Boron Oxide	Glass	5.14	32.0	-----	273 - 513
Boron Oxide	Glass	30.4	-----	-----	513 - 623
Magnesium	Crystals	6.20	1.33	0.0678	273 - 923
Magnesium	Liquid	7.4	-----	-----	923 - 1048
Magnesium Oxide	Crystals	10.86	1.197	0.2087	273 - 2073

*These data were copied from reference (5). Cf. reference (6).

SUPPLEMENT D*

1. Physical Properties

Beryllium, symbol Be (or Gl), is a steel-gray, lightweight, hard, metallic element. Its ability to harden and strengthen other metals has been its chief useful characteristic. The specific gravity of beryllium is 1.846; its melting point, 1.285°C, and its hardness 6 to 7 on the Mohs scale. The atomic number of beryllium is 4, its atomic weight is 9.02, and it is unique among elements of even atomic number in that it has a single stable isotope. The oxide film that forms quite readily on the surface of the metal is hard enough to scratch glass. Pure beryllium may be somewhat ductile under certain conditions, but specimens reported to be 99.94 percent pure were brittle when cold and could only be rolled when heated. At high temperature beryllium becomes readily malleable but more difficult to handle because of its affinity for oxygen. The addition of about 0.5 percent of titanium or zirconium is said by one company to render beryllium malleable enough to be worked satisfactorily at a high temperature, apparently because the added metal reduces intergranular beryllium oxide film. Beryllium has an electrical and a thermal conductivity approximately 40 percent of that of copper. Thermal expansion of beryllium is about the same as that for iron and ordinary steel and considerably less than that for aluminum; its latent heat of fusion is higher than that for any of the other metals. Sound travels 2-1/2 times faster in beryllium than in steel. The principal physical properties of beryllium are listed in the accompanying table, which includes early data by Sawyer and Kjellgren, Claussen and Skehan, Hoyt, Hum Hume-Rothery and recently revised data from industry.

2. Chemical Properties

The theoretical chemical composition of beryl, the chief source mineral of the beryllium industry, is $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$, representing a composition of 14 percent BeO , 19 percent Al_2O_3 , and 67 percent SiO_2 . Small amounts of the alkali oxides frequently replace the beryllium oxide content. The common commercially required beryllium oxide content ranges from 10 to 12 percent BeO .

Pure beryllium is rather stable and tarnishes slightly at room temperature in dry air and pure oxygen. When it is finely ground and

*Taken from reference (4).

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blown into a flame, it burns with brilliant scintillations, reference (32). Compounds of beryllium have a sweet taste, which accounts for the name "glucinum" or "glucinium", sometimes applied to the element and currently used by the French. When beryllium is heated in air, it develops a thin, almost invisible layer of oxide -- analogous to the action of aluminum under the same conditions. This oxide coating protects the metal from attack by either hot or cold water. Beryllium is vulnerable, however, at temperatures above 800°C, to attack by a number of gases, such as nitrogen, chlorine, bromine, iodine, and oxygen, but not by hydrogen. The affinity of beryllium for oxygen makes it a strong reducing agent.

Beryllium metal is attacked by sulfuric, hydrochloric, and hot nitric acid but not by cold nitric acid. Organic acids, such as tartaric acid and citric acid, react with beryllium only until an oxyhydrate is formed, after which reaction the metal is no longer corroded. Beryllium is dissolved by alkaline hydroxides; it is more resistant to alkalis than aluminum but less resistant than magnesium. It forms a carbide when heated with carbon and reacts when treated with cyanides and phosphorus.

Beryllium does not react with ammonical solutions but can be converted to a nitride by gaseous ammonia at temperatures above 750°C, it is extremely reactive when molten. The extraction of metallic beryllium from beryl ore is difficult and expensive, owing primarily to its occurrence in an aluminum silicate mineral, reference (33).

PHYSICAL PROPERTIES OF BERYLLIUM

Density (specific gravity)-----	1.846 to 1.816 gm/cc*
Hardness-----	97-172 Brinell
<u>Tensile properties: **</u>	
Ultimate strength-----	35,000-95,000 lb./sq. in.
Yield strength, annealed (offset, 0.2 percent) -	30,000-45,000 lb./sq. in.
Elongation (in 2 in.)-----	2-20 percent
Reduction of area-----	2-20 percent
Young's modulus of elasticity-----	36,000,000-44,000,000 lb./sq. in.

PHYSICAL PROPERTIES OF BERYLLIUM (cont'd)

Compressive properties:

Yield strength (offset, 0.2 percent) -----	26,000-86,300 lb./sq. in.
Young's modulus of elasticity -----	42,000,000-45,000,000 lb./sq. in.
Shearing strength -----	31,000-66,000 lb./sq. in.

Electrical properties:

Electrical conductivity -----	40-44 percent of Cu
Electrical resistivity -----	3.9-4.3 microhms/cc
Electrode potential -----	minus 1.69 volts

Thermal properties:

Melting point -----	1,285°C (2,345°F)
Boiling point -----	2,970°C (5,378°F)
Linear coefficient of expansion:	
(20° - 200°C) -----	13.3 x 10 ⁻⁶ per °C
(20° - 700°C) -----	17.8 x 10 ⁻⁶ per °C
Thermal conductivity (at 20°C) ----	0.385 cal./sq. cm./cm./sec. / °C or 42 percent of Cu
Specific heat (at 20° - 100°C) -----	0.43-0.52 cal./gm./°C
Latent heat of fusion -----	250-277 cal./gm.
Vapor pressure: (at 1,400°C) -----	0.001 mm Hg
(at 3,000°C) -----	760.0 mm Hg
Heat of oxidation -----	140.15 cal. ***
Magnetic susceptibility -----	0.79 gauss/oersted c.g.s.
Reflectivity (white light) -----	50-55 percent
Velocity of sound -----	12,600 meters/sec.

PHYSICAL PROPERTIES OF BERYLLIUM (cont'd)

Atomic properties:

Atomic number -----	4
Atomic weight -----	9.02
Atomic volume -----	4.96
Crystal structure -----	Dihexagonal-bipyramidal, close-packed
Lattice constants: <u>a</u> -----	2.268 A. 2.285
<u>c</u> -----	3.594 A. 3.533
Axial ratio -----	1.585 A. 1.5682
Closest approach of atoms -----	2.223 A. 2.2211
Atomic diameter -----	2.25

*Theoretical density reported by two different sources.

**Tensile properties may vary over a wide range, according to the method of fabrication employed.

***This is quoted correctly from reference (4) in which the temperature is not given. Value is probably meant to be in kilocalories. See Supplement B for heat of formation of BeO at 298.16°K.

SUPPLEMENT E

BERYLLIUM RESOURCES OF THE UNITED STATES IN PEGMATITES
CONTAINING MORE THAN 10 TONS OF BERYL AND NON-
PEGMATITIC DEPOSITS CONTAINING MORE THAN
1 TON OF BeO *

Pegmatites

Location	Resources in deposits con- taining 1.0 percent beryl or more /1	Resources in deposits con- taining 0.1 percent beryl or more /1
Colorado, Larimer County, Crystal Mountain district	700	2,400
Colorado, Gunnison County, Quartz Creek district	200	300
Colorado, other districts	500	800
Connecticut, Middlesex and Hartford Counties, Middletown district		2,100
Idaho, Latah County	100	400
Maine, Oxford County	2,700	3,800
Nevada		300
New Hampshire, Cheshire and Sullivan Counties	200	300
New Hampshire, Grafton County, Grafton district	300	400
New Hampshire, Rockingham County, Raymond district	100	300
New Hampshire, other districts		100
New Mexico	600	600
North Carolina, Tri-County district		<50
North and South Carolina, tin- spodumene belt		243,800/2
South Dakota, Pennington County, Keystone district	5,400	10,300
South Dakota, Pennington County, Hill City district		200

Pegmatites (cont'd)

Location	Resources in deposits con- taining 1.0 percent beryl or more	Resources in deposits con- taining 0.1 percent beryl or more
South Dakota, Custer County, Custer district	300	5,500
Wyoming	100	200
Total, excluding tin-spodumene belt (round)	11,000	28,000
Grand total (round)	11,000	270,000

/1 To the nearest 100 tons.

/2 Based on incomplete work. Beryllium recognized spectrographically
is assumed to be in beryl.

*Taken from reference (4).

Non-Pegmatitic Rocks

Location	Resources in deposits con- taining 0.1 percent BeO or more <u>/3</u>	Resources in deposits con- taining 0.01 percent BeO or more <u>/3</u>
Arizona	30	110
Arkansas		60 (?)
Colorado		10
Montana		100 (?)
Nevada		10
New Hampshire	<5	<5
New Jersey		200 (?)

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Non-Pegmatitic Rocks (cont'd)

	Resources in deposits con- taining 0.1 percent BeO or more	Resources in deposits con- taining 0.01 percent BeO or more
New Mexico, Sierra and Socorro Counties, Iron Mountain district	400	400
New Mexico, other districts		50
Utah		?
Virginia	<5	<5
Total (round)	400	900
Total, equivalent beryl ^{/4} (round)	3,000	7,000

^{/3} To the nearest 10 tons.

^{/4} Based on the assumption that beryl contains 12.5 percent BeO.

SUPPLEMENT F*

HEALTH AND SAFETY FACTORS

Compounds of beryllium are considered by medical authorities as possibly dangerous to health, and precautions must therefore be taken in their production. Health problems may be encountered when mists, dust, or fumes of these compounds are inhaled, and such encounters must be prevented. The sensitivity of individuals varies greatly. It is also recognized that a few individuals are super-sensitive and therefore cannot be employed in the beryllium industry. This applies especially to the production of primary beryllium products in the extraction plants.

The exact role played by the beryllium atom itself is not clearly understood, especially because the intensity of the attack on the skin or lungs varies greatly with the element or elements combined with the beryllium atom and also with the individual.

Various investigators have studied the physiological action of beryllium in regard to lung irritation and general toxic effects. The results of this work, much of which is of a conflicting nature, were summarized in 1943 by the U. S. Public Health Service, whose own investigations at that time indicated that beryllium was not toxic. It is now recognized, however, that exposure to in-process materials in any one of the important beryllium-production processes may be toxic to certain supersensitive individuals. Furthermore, certain beryllium salts, for example, the oxyfluoride and sulfate, readily hydrolyze to free acids and, if permitted on the hands of workers, may cause skin irritation and ulcers on those dermatologically susceptible. A domestic producer has reported several cases, one of which was that of a worker who milled beryl and had no contact with fluorides. The SAPPI organization in Italy lost four employees, all of whom contracted the characteristic shortness of breath. Heraeus Vacuumachmelze A. G. in Germany experienced no deaths from beryllium assimilation, but an associated company that worked up beryllium-copper furnace dross reported a fatality of unascertained cause. Due to the toxicity of beryllium compounds, DEGUSSA in Germany is reported to have lost 8 men, 6 in working up crude beryllium fluoride, 1 at the drying and ball-milling of melted ore and lime, and 1 at the filter-press operation for preparing crude sulfate solution. All eight deaths were characterized by acute chemical inflammation of the lungs, shortness of breath, and edema. The company's new plant at Rheinfelden provided

*Taken from reference (4).

for pneumatic feeding and conveying of beryllium materials under reduced pressure to minimize the health hazard. In the United States the beryllium health hazard was recognized by Texas in 1947, when beryllium was included in the list of minerals that may cause occupational diseases and are compensable, (22).

The beryllium health hazard may be effectively reduced, according to authorities, by proper ventilation, frequent washing of the hands, arms, face, and neck, and showers at the end of each shift. Personal cleanliness should be emphasized; and in very hot and humid weather, the operator may be provided with a clean set of working clothes at the beginning of each shift to combat dermatitis. It is also advisable to have the plant physician check the chest of every employee at frequent intervals and to X-ray all employees at least once a year. An employee showing signs of lung irritation should immediately be given a period free from work long enough for recovery to take place, thus reducing the danger of acute pneumonitis that might end fatally. By taking these and other precautions, the number of cases of dermatitis and acute pneumonitis are greatly reduced and kept under control.

A more serious health hazard resulting in a number of fatalities has appeared since approximately 1930 in some industries, particularly in the fluorescent lamp industry, in which beryllium-zinc silicate was used. The chronic lung disease, related to beryllium, was first noted in this industry. It develops relatively slowly and may extend over a period of years; hence it has been called delayed pneumonitis or berylliosis. This health hazard is less understood than the health hazards encountered in the production of beryllium and its compounds from beryl ore. United States health authorities and other medical groups are now investigating the causes of delayed pneumonitis to establish what part beryllium plays in the development of this disease.

In 1951, investigations of the Argonne National Laboratory, Chicago, (23), demonstrated that aurin tricarboxylic acid (ATA) reacts with beryllium salts by fixing the beryllium into an inactive, non-poisonous compound. This observation has no immediate application in humans.*

During the last few years the AEC, along with others, has amassed considerable evidence that beryllium is a toxic material under certain circumstances. Although the mechanism by which beryllium produces disease is not yet clearly understood, it has been found that inhalation of relatively minute quantities of beryllium dispersed in the air can be
*Nov (1960) has been proposed and used for human prophylaxis, references (21) and (23).

extremely dangerous, with one exception, beryl ore, all of the beryllium compounds of industrial importance have been considered as possible causative agents in the production of either pulmonary disease or one or more types of dermatitis. Evidence points to the dust of pure beryllium metal, the oxides, and other compounds as creating health hazards; beryllium alloys have never been pinpointed as trouble makers.

The occupational diseases produced by exposure to beryllium or its compounds are of two types: Dermatologic and respiratory.

The dermal manifestations are caused by direct contact with certain beryllium material. There are several recognized dermal responses:

1. A typical industrial dermatitis which usually appears on the face and hands. It produces severe irritation and itching. Areas subject to excessive perspiration and abrasion by clothing, gloves, goggles, or face masks are susceptible to attack.
2. Skin ulcers may develop after the introduction of some beryllium materials in a cut or wound on the skin.
3. Skin lesions have developed spontaneously in patients who have contracted the chronic form of pulmonary disease.
4. Tumors have developed beneath the surface of the skin after it has been cut with a fluorescent tube containing beryllium phosphors.

There are two principal respiratory responses, acute pneumonitis and chronic pulmonary granulomatosis (berylliosis). These may be disabling or fatal.

Acute pneumonitis is produced by exposure to relatively high concentrations of airborne beryllium. (The use of the word beryllium here implies either metallic beryllium or one of its compounds.) It has been known to develop after a single short exposure to soluble beryllium salts. No personnel should be exposed to concentration greater than 25 micrograms per cubic meter for any period of time, however short, (24).

"Chronic berylliosis is an insidious disease that may develop after exposure to concentrations considerably lower than those responsible for acute pneumonitis. Its onset may be delayed from a few months to several years after exposure.

"An inplant daily average concentration of 1 to 2 micrograms per cubic meter of air has been widely adopted as a safe operating criterion by plants handling beryllium (24). The essentials of a hygienic program for beryllium plants are: Careful plant design, effective local exhaust ventilation, routine dust monitoring, rigorous housekeeping, enforced personal hygiene, and strict medical supervision.

"A hazard may develop in the vicinity of a plant which processes large quantities of beryllium materials if the process gases and ventilating air are not properly controlled. A maximum allowable average concentration of 0.01 microgram per cubic meter has been recommended for the neighborhood around a beryllium plant (24). Dust-collecting equipment must be employed where such a problem may exist."

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