

Beryllium (CAS No. 7440-41-7) and Beryllium Compounds

Known to be a human carcinogen
First Listed in the *Second Annual Report* (1981)

Carcinogenicity

Beryllium and beryllium compounds are *known to be human carcinogens* based on sufficient evidence of carcinogenicity in humans. Beryllium and beryllium compounds were first listed in the *Second Annual Report on Carcinogens* as *reasonably anticipated to be human carcinogens* based on carcinogenicity in experimental animals; however, the listing was revised to *known to be human carcinogens* in the *Tenth Report on Carcinogens* in 2002.

Epidemiological studies indicate an increased risk of lung cancer in occupational groups exposed to beryllium or beryllium compounds (Steenland and Ward 1991, Ward *et al.* 1992), supporting the conclusion that beryllium and beryllium compounds are carcinogenic in humans. An association with lung cancer has consistently been observed in several occupational populations exposed to beryllium or beryllium compounds, with an excess relative risk of 1.2 to 1.6. Groups with greater exposure or longer time since first exposure show higher risks, which supports a cause-and-effect relationship. Acute beryllium pneumonitis, which is a marker for high exposure to beryllium, is associated with higher lung cancer rates (with relative risks as high as 2.3) (Steenland and Ward 1991). Although smoking could be a factor in the cancers observed in these studies, no evidence was found in any of the published epidemiology studies to indicate a difference in smoking habits between the groups of workers exposed to beryllium or beryllium compounds and the non-exposed workers used as control groups.

These conclusions are supported by data from animal studies (IARC 1993, Finch *et al.* 1996), which have shown consistent increases in lung cancer in rats, mice, and monkeys exposed to beryllium or beryllium compounds (by inhalation or intratracheal instillation). Beryllium metal and several beryllium compounds, including beryllium-aluminum alloy, beryl ore, beryllium chloride, beryllium hydroxide, beryllium sulfate tetrahydrate, and beryllium oxide, caused lung tumors in rats exposed by either a single intratracheal instillation or a one-hour inhalation exposure. Beryllium oxide and beryllium sulfate caused lung cancer (anaplastic carcinoma) in monkeys after intrabronchial implantation or inhalation. Bone cancer (osteosarcoma) has been induced in rabbits exposed to beryllium metal, beryllium carbonate, beryllium oxide, beryllium phosphate, beryllium silicate, or zinc beryllium silicate by intravenous injection and/or implantation into the bone.

Additional Information Relevant to Carcinogenicity

Beryllium compounds do not cause mutations in a variety of *Salmonella typhimurium* tester strains, but they do induce genetic transformations in a variety of cultured mammalian cells (IARC 1993). These genetic transformations may result from binding of ionic beryllium to nucleic acids, which can cause infidelity of DNA replication (Leonard and Lauwerys 1987).

Properties

Beryllium is a Group II metallic element. It is silver-gray to grayish-white, with an atomic weight of 9.01, melting point of 1,287°C, boiling point of 2,970°C, and density of 1.85 at 20°C. It has a close-packed hexagonal crystal structure and has several unique chemical properties. It is the lightest of all solid and chemically stable substances and has a very high melting point, specific heat, heat of fusion, and strength-to-weight ratio. Beryllium is lighter than aluminum, but it is over 40% more rigid and approximately one-third

more elastic than steel. It is insoluble in water and soluble in acids and alkalis. It has excellent electrical and thermal conductivity and is not magnetic. At ordinary temperatures, beryllium resists oxidation in air; however, a thin film of beryllium oxide forms on the surface, making it highly resistant to corrosion. In alloys, beryllium contributes hardness, strength, and high electrical and thermal conductivity and enhances resistance to corrosion, wear, and fatigue (WHO 1990, IARC 1993, HSDB 2003).

Beryllium chloride occurs as white-to-colorless deliquescent crystals. It is very soluble in water, alcohol, benzene, ether, chloroform, and carbon disulfide, and insoluble in ammonia and acetone. Beryllium fluoride occurs as a colorless amorphous mass that is readily soluble in water but only slightly soluble in alcohol. Beryllium hydroxide exists in three forms: a metastable tetragonal crystalline solid, a stable orthorhombic crystalline solid, and a slimy, gelatinous substance with a slightly basic pH. It is soluble in acids and alkalis and insoluble in water. Beryllium oxide occurs as a white powder or gel that is insoluble in hot water and soluble in acids, alkalies, and ammonium carbonate. Beryllium metaphosphate is a white porous powder or granular material that is insoluble in water. Beryllium orthophosphate is soluble in water and acetic acid. Beryllium sulfate occurs as colorless crystals that are insoluble in cold water and alcohol but decompose in hot water. Beryllium sulfate tetrahydrate occurs as colorless crystals that are soluble in water, practically insoluble in ethanol, and slightly soluble in concentrated sulfuric acid. Beryl ore occurs as colorless, blue-green, yellow, or white transparent hexagonal crystals that are insoluble in acid. Beryllium-copper alloy usually contains 4.0-4.25% beryllium by weight. It has a melting point of 870-980°C and produces toxic fumes of beryllium oxide upon heating. Beryllium-aluminum alloy may contain 20% to 60% beryllium (IARC 1993, ATSDR 2000, ChemFinder 2003).

Use

Beryllium's unique properties (it is a light metal with a very high melting point) make it very useful in industry. When used as an alloy, it increases thermal and electrical conductivity and strength; addition of just 2% beryllium to copper forms alloys that are six times stronger than copper alone (IARC 1993). The use of beryllium as an alloy, metal, and oxide in electrical components and aerospace and defense applications account for approximately 80% of its total use in the United States (USGS 2003).

Pure beryllium metal is used in aircraft disc brakes, X-ray transmission windows, space vehicle optics and instruments, aircraft and satellite structures, missile parts, nuclear reactor neutron reflectors, nuclear weapons, fuel containers, precision instruments, rocket propellants, navigational systems, heat shields, mirrors, high-speed computers, and audio components. Beryllium alloyed with copper, aluminum, or other metals is used in the electronics, automotive, defense, and aerospace industries. More specifically, beryllium alloys are used in electrical connectors and relays, springs, precision instruments, aircraft engine parts, non-sparking tools, submarine cable housings and pivots, wheels, pinions, automotive electronics, molds for injection-molded plastics, telecommunications devices, computers, home appliances, dental applications, golf clubs, bicycle frames, and many other applications (WHO 1990, IARC 1993, USDOE 1998, ATSDR 2000). Beryllium-copper alloy is used in a wide variety of applications, including electrical connectors and relays, wheels and pinions, nonsparking tools, and switches in automobiles (ATSDR 2000). Beryllium-aluminum alloy has been used in light aircraft construction (Merian 1984). It also may be used in casting alloys, where it refines the grain size, resulting in better surface polishing, reduces melt losses, and improves casting fluidity (Kirk-Othmer 1978, IARC 1980).

Beryllium oxide is the most important high-purity commercial beryllium chemical produced (Kirk-Othmer 1978). It is used in high-technology ceramics, electronic heat sinks, electrical insulators, microwave oven components, gyroscopes, military vehicle armor, rocket nozzles, crucibles, nuclear reactor fuels, thermocouple tubing, laser structural components, substrates for high-density electrical circuits, and automotive ignition systems and as an additive to glass, ceramics, and plastics (IARC 1993, ATSDR 2000). Beryllium oxide also is used in the preparation of beryllium compounds, as a catalyst for organic reactions, and in high-temperature reactor systems. Beryllium oxide was used in the past for the manufacture of phosphors for fluorescent lamps. Beryllium chloride is used primarily to manufacture beryllium metal by electrolysis in the laboratory. It also is used as an acid catalyst in organic reactions. Beryllium fluoride and beryllium hydroxide are used commercially in the production of beryllium metal and beryllium alloys. Beryllium fluoride also is used in the manufacture of glass and nuclear reactors (Sax and Lewis 1987).

Beryllium sulfate is used primarily for the production of beryllium oxide powder for ceramics, while beryllium nitrate is used as a chemical reagent and for stiffening mantles in gas and acetylene lamps (HSDB 2003). The primary use of beryllium sulfate tetrahydrate is as a chemical intermediate in the processing of beryl and bertrandite ores (Sax and Lewis 1987). Beryllium metaphosphate has limited use as a raw material in special ceramic compositions and as a catalyst carrier. A former use of beryllium zinc sulfate was as an oxygen-dominated phosphor in luminescent materials (IARC 1980, Sax and Lewis 1987).

Production

Beryllium was discovered in 1798, but it did not become commercially important until the 1930s. Although more than 40 beryllium-bearing minerals are known, only two (beryl and bertrandite) currently are commercially important. Beryl ($3\text{BeO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$), which contains approximately 11% beryllium oxide (up to 4% beryllium), is the predominant beryllium-containing mineral mined in the world. Beryl is found largely in Brazil and the former Soviet Union. Impurities in beryl include alkali metals, alkaline-earth metals, iron, manganese, and phosphorus. Emeralds (beryl containing chromium), aquamarine (beryl containing iron), and other semiprecious gems are examples of beryl at its purest gem quality (IARC 1993).

U.S. companies have produced beryllium and some beryllium compounds commercially since the 1940s and beryllium oxide since 1958 (IARC 1972). Bertrandite ($4\text{BeO}\cdot 2\text{SiO}_2\cdot \text{H}_2\text{O}$) is the principal beryllium-containing mineral mined in the United States, accounting for approximately 85% of U.S. consumption. Bertrandite contains less than 1% beryllium, but it can be efficiently processed into beryllium hydroxide (IARC 1993). The Spor Mountain area of Utah is currently being mined for beryllium; it contains a large reserve of bertrandite, totaling about 18,000 tons (16,300 metric tons) of beryllium. The other area in the United States containing beryllium reserves is the Seward Peninsula area of Alaska (USGS 2003).

The U.S. is the world's largest producer of beryllium; other countries producing beryllium (in order of amount of production) are Russia, China, and Kazakhstan. U.S. beryllium production decreased from 423 metric tons (933,000 lb) in 1998 to 100 metric tons (220,000 lb) in 2002. Imports rose in the same time period from 50 metric tons (110,000 lb) to 120 metric tons (265,000 lb), and exports also increased from 60 metric tons (132,000 lb) to 100 metric tons (220,000 lb) (USGS 2003).

Two chemical suppliers were identified for beryllium in 2004 (ChemSources 2004). The U.S. imported 274,284 kg (604,682 lb) and exported 25,741 kg (56,748 lb) of beryllium ores and concentrates in 2002 and imported 250 kg (551 lb) of beryllium powders in the same year (ITA 2004). Seventeen chemical suppliers were identified for beryllium oxide, and 2 chemical suppliers were identified for beryllium

hydroxide (ChemSources 2004). One producer was identified in the United States for beryllium oxide (SRI 2004), with the U.S. importing 5 kg (11 lb) of beryllium oxide and hydroxide in 2002 (ITA 2004). There were 4 identified chemical suppliers for beryllium sulfate and 11 for beryllium sulfate tetrahydrate (Chem Sources 2004) and 1 chemical producer for beryllium sulfate (SRI 2004). Five chemical suppliers were identified for beryllium chloride, 7 for beryllium fluoride, and 1 for beryllium copper alloy (ChemSources 2004). One chemical producer was identified for beryllium nitrate (SRI 2004).

Natural sources of beryllium and beryllium compounds in the atmosphere consist of windblown dust (5 metric tons/yr [11,000 lb/yr]) and volcanic particles (0.2 metric tons/yr [441 lb/yr]). Anthropogenic sources include industry (0.6 metric tons/yr [1,323 lb/yr]), metal mining (0.2 metric tons/yr [441 lb/yr]), electric utilities (3.5 metric tons/yr [7,716 lb/yr]), and waste and solvent recovery (0.007 metric tons/yr [15 lb/yr]) (ATSDR 2000).

Exposure

The primary route of human exposure to beryllium is through inhalation of dusts and fumes. Beryllium also may be ingested in drinking water or food. Measurements at 100 U.S. locations revealed average daily beryllium concentrations in the air of $< 0.0005 \mu\text{g}/\text{m}^3$. Beryllium occurs naturally in soils at concentrations ranging from < 1 to 15 mg/kg. Beryllium was detected at 2,760 out of 50,000 surface water sites in the United States at an average concentration of 1.9 $\mu\text{g}/\text{L}$, and 30 out of 334 ground water sites at an average concentration of 1.7 $\mu\text{g}/\text{L}$. Beryllium content in fruit and fruit juices has been measured at levels ranging from $< 0.1 \mu\text{g}/\text{L}$ in a pineapple to 74.9 $\mu\text{g}/\text{L}$ in a papaya. Cigarettes contain beryllium at levels up to 0.0005 $\mu\text{g}/\text{cigarette}$. The average inhalation exposure to beryllium for a U.S. adult was estimated at $< 0.0006 \mu\text{g}/\text{day}$, while daily exposure from food was estimated at 0.12 μg (ATSDR 2000).

The highest levels of human exposure to beryllium are through occupational exposure, which may occur via inhalation of beryllium dust or dermal contact with products containing beryllium. Workers with the highest potential for exposure include beryllium miners, beryllium alloy makers and fabricators, phosphorus manufacturers, ceramics workers, missile technicians, nuclear reactor workers, electric and electronic equipment workers, and jewelers. Occupational exposure also may lead to at-home exposure to beryllium on work garments. Studies in the workplace found that air concentrations from personal monitors mounted on clothing increased when the amount of beryllium dust on the fabric increased (HSDB 2003). The National Occupational Exposure Survey (NOES), conducted between 1981 and 1983, estimated that a total of 13,938,000 workers, including 739 women, potentially were exposed to beryllium; 4,305 workers, including 849 women, were exposed to beryllium oxide; 1,822 workers, including 230 women, were exposed to beryllium sulfate tetrahydrate; and 1,740 workers, including 37 women, were exposed to beryllium-copper alloy. The National Occupational Hazard Survey (NOHS), conducted from 1972 to 1974, estimated that 10,510 workers were potentially exposed to beryllium (RTECS 2003).

EPA's Toxics Release Inventory (TRI) estimated that in the United States in 2001, 22 facilities released 306,481 lb (139 metric tons) of beryllium, while 55 facilities released 633,775 lb (287.5 metric tons) of beryllium compounds to the environment (TRI01 2003).

Regulations

DOT

Numerous beryllium compounds and beryllium compounds not otherwise specified are considered hazardous materials and requirements have been prescribed for shipping papers, package marking, labeling, and transport vehicle placarding for the shipment and transportation of these hazardous materials

EPAClean Air Act

NESHAP: Beryllium Compounds listed as Hazardous Air Pollutants (HAPs)
 Urban Air Toxics Strategy: Beryllium Compounds identified as one of 33 HAPs that present the greatest threat to public health in urban areas

Clean Water Act

Effluent Guidelines: Listed as a Toxic Pollutant (beryllium and compounds)

Comprehensive Environmental Response, Compensation, and Liability Act

Reportable Quantity (RQ) = 10 lb (beryllium); 1 lb (beryllium chloride, beryllium fluoride, beryllium nitrate)

Emergency Planning and Community Right-To-Know Act

Toxics Release Inventory: Beryllium and beryllium compounds are listed substances subject to reporting requirements

Resource Conservation and Recovery Act

Listed Hazardous Waste: Waste codes in which listing is based wholly or partly on substance - P015 (beryllium powder)

Beryllium Powder and Beryllium compounds each listed as a Hazardous Constituent of Waste

Safe Drinking Water Act

Maximum Contaminant Level (MCL) = 0.004 mg/L (beryllium only)

FDA

Maximum permissible level of beryllium in bottled water = 0.004 mg/L

OSHA

Acceptable Peak Exposure = 0.025 mg/m³ (maximum duration = 30 minutes)

Ceiling Concentration = 5 µg/m³

Permissible Exposure Limit (PEL) = 2 µg/m³

Guidelines**ACGIH**

Threshold Limit Value - Short Term Exposure Limit (TLV-STEL) = 0.01 mg/m³

Threshold Limit Value - Time-Weighted Average Limit (TLV-TWA) = 0.002 mg/m³

NIOSH

Immediately Dangerous to Life and Health (IDLH) = 4 mg/m³

Listed as a potential occupational carcinogen

Recommended Exposure Limit (time-weighted-average workday) = 0.0005 mg/m³

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