Industrial Hygiene

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Beryllium: Associated Hazards, Safety Evolution & Safety Limits

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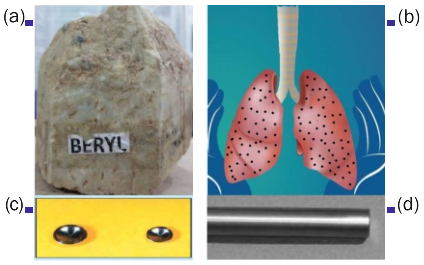

(a) Beryl ore extracted in India (b) Lungs affected by chronic beryllium disease (c) & (d) Some Beryllium metal components manufactured by BARC

ABSTRACT

In addition to conventional industrial safety and associated hazards, Industrial Hygiene and Safety Section of Health, Safety & Environment Group have been providing safety surveillance as well as monitoring for BARC Beryllium facilities since inception. This includes regular air monitoring, surface swipe sampling as well as monitoring of waste effluent so as to comply the limits as stipulated by BARC Safety Council. As on-line detectors are not available for Beryllium, its surveillance is a challenge and engineering, medical & administrative controls are quite helpful in this regard. In addition, cautious and conservative approach along with use of personnel protective equipments, continued education, training and awareness plays an important role in ensuring beryllium safety of individuals as well as the environment.

KEYWORDS: *Beryllium safety surveillance, Limits, Chronic and acute beryllium diseases, and estimation of beryllium*

Introduction

Beryllium (Be) is one of the most remarkable element in the nature & is used in nuclear, space, defense as well as in many other household items of day-today use. It has very low density, high specific heat, high strength to weight ratio, good thermal conductivity and good dimensional stability over wider temperature range. It is lighter than Aluminium but more rigid than steel. Due to low atomic number, the K shell energy is ~218 eV (0.218 KeV), so poses little attenuation (via photoelectric effect) to X-ray photons and thin Be metal windows are used in X-ray machines as well as in synchrotron beam lines. Properties like low atomic weight, low absorption and high scattering cross section for neutrons, low photon neutron reaction threshold value and low mass absorption, favour Be as a nuclear material [1].

In combination with α emitters like Ra, Am etc., Be releases neutrons (neutron source) as α particles having energy of few MeV available naturally are capable to cause (α, n) reaction with Be nucleus i.e. easily overcome coulombic repulsion barrier. Further, Be or BeO is used as a neutron reflector in research reactors as well as in many reactor physics experiments. However, Be is one of the most toxic element in periodic table and was the first element to have environmental exposure limit.

Beryllium and its Prevalence in Environment

Beryllium occurs in rocks, minerals etc. and its average concentration in earth crust have been reported to be 1-10 ppm. Many minerals are known to contain Be, but Beryl ($3BeO.Al_2O_36SiO_2$) and bertrandite ($4BeO.2SiO_2$) ores have been commercially exploited. The commercial grade Indian beryl ore (Fig.1) contains ~12 % BeO and fairly large deposits are found in Andhra Pradesh, Bihar, Rajasthan, Tamil Nadu and Chhattisgarh. Beryllium has many isotopes out of which ^{9}Be is a stable isotope, whereas ^{7}Be and ^{10}Be are radioactive and are produced by cosmic rays in the upper atmosphere in trace amount. The typical concentration of ^{7}Be in atmospheric air is reported to be ~5 mBq/m^3 and is being considered as a radioactive tracer for studying global atmospheric changes.

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In addition to this, Be is present in air, soil, water and food. The typical concentration of Be in air is reported to be <0.05-0.30 ng/m^3. However, coal combustion in thermal power plants and use of hydrocarbons further increases the ambient background levels to values >0.30 ng/m^3.

The fly ash is reported to contain Be up to few hundreds ppm. Similarly, Be is prevalent in the soil and its concentration is reported to be few ppm although it varies from place to place and is the main contributor to the background levels in food, air and water. It needs to be mentioned that typical Be concentration in water is reported to be < 1 ppb whereas in fruits and vegetables, it is generally ≤ 1-10 ppb; although many factors like uptake of Be from soil, water etc. influence these values [1].

Health Hazards Associated with Beryllium

Typical health hazards associated with Be exposures are mainly to lung and are classified as chronic or acute beryllium diseases. It is generally believed that Acute Beryllium Disease (ABD) occurs when human are exposed to Be air concentration normally exceeding 100 µg/m^3 and is characterized by irritation in respiratory system, chest pain, fever, dry cough with blood etc., whereas chronic beryllium disease (CBD) (Fig.2) is known to occur even after 20-30 years after cession of exposure and exposure response relationship is not much understood. Further, ABD is reversible (but it was found that many a times ABD causes CBD later),whereas CBD in neither curable nor reversible [2-4].

Comprehensive information on its chemical toxicity and other adverse effects on humans became available after the appearance of lung related diseases and deaths amongst

Fig.1: Beryl ore from Jharkhand, India. *(Courtesy: AMD's exhibition at AOCRP-6, Mumbai)*

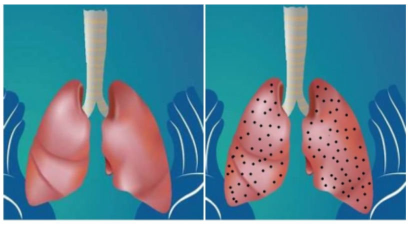

Fig.2: Lungs affected by CBD (formation of granules leading to problem of inflation/ respiration).

fluorescent lamp (handling BeO_4SiZn (Beryllium Zinc Silicate)) manufacturing workers and the use of Be based compounds in lamp industry was later discontinued. Further, during end of second world war, production and use of Beryllium increased in USA and cases of chemical pneumonia in workers extracting BeO from Be based ores, continued to be reported. All this led to the requirement of some safety standards for protection of occupational workers and public environment.

Basis of Safety Standards for Beryllium

In view of chemical toxicity of Beryllium resulting in chronic and acute diseases arising from inhalation of dust, fumes or particles, the standard of 2.0 μg/m^3 for Be in air ($Be_{Air\text{-}Conc}$) as particulate matter with time weighted average over 8 hours was defined by Department of Energy (DOE), USA in 1948 and were adopted in the end of 1949. This was the first standard which put regulations on allowable $Be_{Air\text{-}Conc}$ and was initially termed as **O**ccupational **E**xposure **L**imit (OEL) at the time of its inception [5].

The notion behind adoption of 2.0 μg/m^3 was based on the fact that during 1950s, ~100 μg/m^3 as air concentration was an established value for occupational safety at workplaces as far as chemical toxicity of heavy metals (Pb, Hg etc.) was concerned. Considering the fact that toxic heavy metals are of having atomic weight of ~200 whereas $_4Be^9$ is a light metal with a atomic weight of ~10 (ratio of mass number of heavy metal to lighter metal = 200/10 = 20) and assuming atom for atom toxicity, the typical value for Be exposure limit comes to be 100 μg/m^3 /20 = 5.0 μg/m^3 as derived from heavy metals toxicity. In addition, an adjustment factor of 2.50 was further applied as the lung disease (CBD) associated with Be exposure is not only incurable but also irreversible and there was also not much epidemiological data or details about understanding of CBD during 1950s. This finally lead to Be standard of 5.0 μg/m^3 /2.5 = 2.0 μg/m^3 or 0.002 mg/m^3 as a time weighted average over 8 hours/per shift (daily limits on **$Be_{Air\text{-}Conc}$**) for occupational Be workers/workplaces [5].

However, the questions on adequacy of 2.0 μg/m^3 to eliminate CBD always remained and cases of CBD continued to be reported till recently and it was suggested by OSHA in 2017 that "maintaining Be exposures < 0.20 μg/m^3, 95% of the time may prevent CBD in workplace" i.e. daily 8-hour time weighted average should not exceed 0.20 μg/m^3 [6]. In view of above, the overall philosophy behind Beryllium related guidelines/ standards follow from the fact that acute beryllium disease which occurs at higher Be air concentrations is ruled out by selecting much lower levels i.e. limits much below the threshold value of ABD and CBD occurrence is further minimized to lowest acceptable level.

Indian Scenario on Beryllium Activities and Related Safety Standards

In India, Be related ore mining activities date back to pre-independence era and a survey of literature shows that ~281

Table 1: Be air concentration, surface level contamination & effluent discharge criterions as stipulated by BARC Safety Council (BSC).

Category	Type	Criteria/Levels/Limits	
Air concentration -μg/m^3	Occupational workplace*	**Be air concentration μg/m^3**	
		Previous (up to 2021)	Present
		2.0$	0.20
	Public/ambient area** at any ground level location around production facility	0.01	0.01
	STEL/Peak value***	25	2.0
Surface contamination -ng/cm^2	Occupational workplace	**Surface contamination ng/cm^2**	
		10.0	
	Any equipment to be taken to public area from Be area or release of Be contaminated equipment to non-Be area	1.00	
Effluent discharge-ppm	Maximum concentration of liquid effluents dischargeable to public sewers	0.10 ppm (100 ppb)	

* Average over an 8 hour time period, $Action level of 0.10 μg/$m^3$&PLE value of 0.20 μg/$m^3$ with STEL of 2.0 μg/$m^3$is followed in DAE from February, 2021, As per Directorate General Factory Advice and Labour Institutes (DGFASLI), India, the value of 2.0 μg/m^3 is stipulated.** Averaged over 30 day period, *** Maximum peak exposure limit not defined in AEFR, 1996 but reported by various Indian researchers.

Ton beryl ore was mined in 1932 which raised to ~1500 Tons per year during second world war although whole of beryl ore was exported to Germany and USA. Post independence, because of strategic nature and associated applications of Be, export of beryl ore was banned [5]. From literature, it can be seen that the attempts for extraction of Beryllium from beryl ore were made during 1960s along with a proposal for establishing pilot plant for production of sintered Beryllium

Air sampling using dry vacuum pumps at prescribed flow rate is carried out and dust particles are deposited on 0.8 micron mixed cellulose ester filter by the air passing through it. The filter is chemically processed and Be is measured which gives information about concentration of Be in the breathing zone (μg/m^3) of the personnel working in the given area.

High volume air samplers having typical flow rate of 500 LPM are also used for Be measurements on short term basis and suitable for measuring instantaneous concentration of Be (STEL value) at a given location and such pumps can be operated for few minutes (3-15min).

Personnel air samplers are quite useful for measurement of Be concentration of individual workers and are suitable for knowing and assigning exposure in situations where high concentration gradients occur and workers may encounter higher air concentration during works. The only limitation associated with personnel air samplers is that the air flow rate is low i.e. up to 5 LPM or so and it may be difficult to get reasonable measurement signal especially for low concentration values.

Swipes are collected from floors, walls, equipment/items to check the surface contamination levels. In case of higher values, cleaning/decontamination, wet mopping of floors, equipment etc. is continued to bring the surface levels within the stipulated values.

Fluorometry is done in which Be or its compounds are leached in to the solution and this solution is capable of exhibiting fluorescence in visible in the presence of specific reagent (dye) when excited by ultra-violet (UV) rays. During measurements blank solution is prepared to adjust background/zero setting & blank is identical to various Be calibration standards or samples and after calibration, Be concentration from sub-ppm to few or higher ppm is estimated. Using this, Air concentration and surface contamination levels as low as 0.002 $\mu g/m^3$ & 0.10 ng/cm^2 are measured.

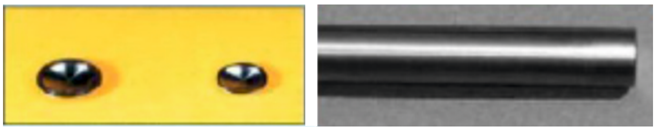

Fig.3: Beryllium metal window for X-ray tube and metal rod manufactured by BARC.

oxide from beryl ore by Department of Atomic Energy (DAE) [7]. Regarding Be protection related standards in India, survey of literature also shows that in DAE, the safety related guidelines were framed way back in 1960 by Soman and Kamath [8]. Although R&D activities about Be in DAE were started during 1960s but large-scale work in beryllium extraction/production and its applications started in 1982 with the establishment of Be plant at Vashi, Navi Mumbai by BARC prior to which the integrated flow sheet for extraction of beryllium from beryl and its consolidation by powder metallurgy was developed at a special laboratory set up for the purpose at Modular Laboratory, BARC in 1968. [9-11]. Some of the Beryllium metal components like windows for X-rays tubes and metal rod are shown in Fig. 3 [10-11]. As per the Atomic Energy Act, 1962, Be is categorized as a prescribed substance. Details about the Be safety procedures, operations and protocols can be had from Atomic Energy Factory Rules (AEFR), 1996 [12]. Historical details about various regulatory limits/levels pertaining to Be ($Be_{Air\text{-}Conc}$) for occupational workers and ambient air standards for public as adopted in India are given in Table 1 [2, 4-5].

Role of Industrial Hygiene Practices

IHSS, HS&EG plays an important role in ensuring Beryllium safety. All the processes being carried out at Powder Metallurgy Division, BARC, Vashi are under strict supervision of IHSS experts. Frequent sampling at every stage is carried out to ensure the safety limits for plant personnel and public are not exceeded.

Safety Provisions

Special provisions were made in the plant to handle toxic metal viz. negative pressure/ventilation at working areas, use of PPEs like boiler suits, hand gloves, comfo-respirator-half or full-facemask, goggles, airline breathing supply or SBCA as per requirement. These play an important role in prospective planning and minimizing Be exposures to occupational workers. Further, good and regular housekeeping practices keep spread of Be contamination in check. Personnel working in Be plants are provided with change room, shower facility and lockers. In addition to all above, medical surveillance plays an important role and periodic medical tests are performed by the management. A minimum medical surveillance program should include skin examination, respiratory history, spirometry and periodic chest x-ray. Any abnormal observation may be helpful in taking necessary steps/cautions by the management.

Conclusions

In view of high toxicity of Be, utmost precautions need to be taken while handling Be related compounds during processing, manufacture and machining, including Be items bearing loose contamination. Continued education and training of workers and awareness along with engineering, medical, housekeeping and administrative controls can be helpful in maintaining Be exposures as low as reasonably achievable. Use of appropriate PPEs further helps in reducing the exposure as well as handling emergency situations. In the absence of any online/active detectors for Be, it is preferable to adopt a cautious and conservative approach while dealing with Be safety related affairs. IHSS is playing an important role in ensuring Be safety along with the plant management from 1970s or so.

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