Silica, Crystalline (Respirable Size)*

Known to be a human carcinogen
First Listed in the *Sixth Annual Report on Carcinogens* (1991)

Carcinogenicity

Respirable crystalline silica, primarily quartz dusts occurring in industrial and occupational settings, is *known to be a human carcinogen*, based on sufficient evidence of carcinogenicity from studies in humans indicating a causal relationship between exposure to respirable crystalline silica and increased lung cancer rates in workers exposed to crystalline silica dust. Respirable crystalline silica was first listed in the *Sixth Annual Report on Carcinogens* in 1991 as *reasonably anticipated to be a human carcinogen* based on evidence of carcinogenicity in experimental animals; however, the listing was revised to *known to be a human carcinogen* in the *Ninth Report on Carcinogens* in 2000.

Hazardous human exposure to respirable crystalline silica, primarily quartz dusts, occurs mainly in industrial and occupational settings (discussed in "Exposure"). The link between human lung cancer and exposure to respirable crystalline silica was strongest in studies of quarry and granite workers and workers involved in ceramic, pottery, refractory brick, and diatomaceous earth industries. Human cancer risks are associated with exposure to respirable quartz and cristobalite but not to amorphous silica. The overall relative risk is approximately 1.3 to 1.5, with higher risks found in groups with greater exposure or longer latency. Silicosis, a marker for exposure to silica dust, is associated with elevated lung cancer rates, with relative risks of 2.0 to 4.0. Elevated risks have been seen in studies that accounted for smoking or asbestos exposure, and confounding is unlikely to explain these results (IARC 1997).

The findings in humans are supported by studies in experimental animals demonstrating consistent increases in lung cancers in rats chronically exposed to respirable crystalline silica by inhalation or intratracheal instillation. No lung tumors were observed in hamsters exposed to quartz by intratracheal instillation. Single intrapleural or intraperitoneal injections of various forms of respirable crystalline silica caused lymphomas in rats (IARC 1997).

Additional Information Relevant to Carcinogenicity

Respirable crystalline silica deposited in the lungs causes epithelial injury and macrophage activation, leading to inflammatory responses and cell proliferation of the epithelial and interstitial cells. In humans, respirable crystalline silica persists in the lungs, culminating in the development of chronic silicosis, emphysema, obstructive airway disease, and lymph node fibrosis. Respirable crystalline silica stimulates (1) release of cytokines and growth factors from macrophages and epithelial cells; (2) release of reactive oxygen and nitrogen intermediates; and (3) oxidative stress in lungs. All these pathways contribute to lung disease. Marked and persistent inflammation, specifically inflammatory cell-derived oxidants, may provide a mechanism by which respirable crystalline silica exposure can result in genotoxic effects in the lung parenchyma. In a human study, subjects exposed to respirable crystalline silica had increases in sister chromatid exchange and chromosomal aberrations in peripheral blood lymphocytes. Most cellular genotoxicity studies with quartz samples were negative; however, *in vitro* exposure to some quartz samples induced micronuclei or cell transformation in several cell types, including Syrian hamster embryo cells, Chinese hamster lung cells, and human embryonic lung cells (IARC 1997).

Properties

Silica, a group IV metal oxide, exists as colorless or white trigonal crystals. The molecular weight of silica (silicon dioxide) is 60.1. It occurs naturally in crystalline and amorphous forms, and the specific gravity and melting point depend on the crystalline form. The basic structural units of the silica mineral are silicon tetrahedra (SiO_4). Slight variations in the orientation of the silicon tetrahedra result in the different polymorphs of silica; crystalline silica has seven polymorphs. In crystalline silica, silicon and oxygen atoms are arranged in definite regular patterns throughout (Parmeggiani 1983).

Quartz, cristobalite, and tridymite are the three most common crystalline forms of free silica. Quartz is by far the most common; it is found abundantly in most rock types, including granites and quartzites, and in sands and soils. Cristobalite and tridymite are found in volcanic rocks. All three forms are interrelated and may change their form under different temperature and pressure conditions. The quartz structure is more compact than that of tridymite or cristobalite (IARC 1987, 1997). Quartz melts to a glass, and its coefficient of expansion by heat is the lowest of any known substance. Silica is practically insoluble in water at 20°C and in most acids; but its solubility increases with temperature and pH, and is affected by the presence of trace metals. The rate of solubility also is affected by particle size, and the external amorphous layer in quartz is more soluble than the crystalline underlying core. Silica dissolves readily in hydrofluoric acid producing silicon tetrafluoride gas (Merck 1989, IARC 1997).

Use

Crystalline silica has many uses because of its unique physical and chemical properties. Commercially produced silica products include quartzite, tripoli, gannister, chert, and novaculite. Crystalline silica also occurs in nature as agate, amethyst, chalcedony, cristobalite, flint, quartz, tridymite, and in its most common form, sand (IARC 1997). Naturally occurring silica materials are classified by end use or industry. Sand and gravel are produced almost exclusively for road building and concrete construction, depending on particle size and shape, surface texture, and porosity (IARC 1987).

Silica sand deposits, commonly quartz or derived from quartz, are high in silica content, typically 95%, although impurities may be present up to 25%. Silica sand has been used for many different purposes over many years. In some instances, grinding of sand or gravel is required, increasing the levels of dust containing respirable crystalline silica. Sand with low iron content and more than 98% silica is used in the manufacture of glass and ceramics. Silica sand also is used in foundry castings, abrasives (such as sandpaper and grinding and polishing agents), in sandblasting materials, in hydraulic fracturing to increase rock permeability to increase oil and gas recovery, as a raw material for the production of silicon and ferrosilicon metals, and as a filter for large volumes of water, such as in municipal water and sewage treatment plants (IARC 1997).

Extremely fine grades of silica sand products are known as flours. Silica flour, not always labeled as containing crystalline silica and often mislabeled as amorphous silica, is used industrially as abrasive cleaners and inert fillers. Silica flour may be used in toothpaste, scouring powders, metal polishes, paints, rubber, paper, plastics, wood fillers, cements, road surfacing materials, and foundry applications (NIOSH 1981). Cristobalite is a major component of refractory silica bricks; the high temperatures at which the bricks are fired convert the quartz mainly to cristobalite (IARC 1997).

Production

Silica used in commercial products is obtained mainly from natural sources (IARC 1997). U.S. production of silica sand was estimated at 27.9 million metric tons (61.4 billion pounds) in 2001 and 28.5 million metric tons (62.7 billion pounds) in 1997. It was estimated that the U.S. exported 1.5 million metric tons (3.3 billion pounds) and imported 172,000 metric tons (378 million pounds) of silica sand in 2001 (USGS 2003).

In the past, natural quartz crystals were mined in the United States; however, mining no longer occurs today. U.S. production of high-purity quartz was 315,000 lb (143 metric tons) in 1979, decreased to 174,000 lb (79 metric tons) in 1981, and rose to 800,000 lb (364 metric tons) in 1983 (IARC 1987). Today, synthetic quartz crystals (hypothermally cultured quartz crystals) are used as the raw material for quartz production. Lascas, the precursor material for synthetic quartz crystals, was mined in the United States for many years, but mining and processing ended in 1997. Lascas mining production was estimated at 1 million pounds (455 metric tons) in 1985 and 600,000 lb (273 metric tons) in 1988. Currently, 3 U.S. firms continue to produce cultured quartz crystals using imported and stockpiled lascas. In 2002, exports of cultured quartz crystals were estimated at 38 metric tons (84 million pounds) and imports at 14 metric tons (31 million pounds) (USGS 2003).

Exposure

Crystalline silica is an abundant and commonly found natural material. Human exposure to respirable crystalline silica, primarily quartz dusts, occurs mainly in industrial and occupational settings. Respirable quartz levels exceeding 0.1 mg/m^3 are most frequently found in metal, nonmetal, and coal mines and mills; in granite quarrying and processing; in crushed stone and related industries; in foundries; in the ceramics industry; in construction; and in sandblasting operations (IARC 1997). The National Occupational Exposure Survey (NOES), conducted by NIOSH from 1981 to 1983, estimated that 944,731 total workers, including 112,888 females, were occupationally exposed to quartz and 31,369 total workers, including 2,228 female workers, were exposed to cristobalite. NIOSH's National Occupational Hazard Survey (NOHS), conducted from 1972 to 1974, estimated that 81,221 workers were exposed to quartz (NIOSH 2003). NIOSH (2002) estimated that 522,748 workers in nonmining industries and 722,708 workers in mining industries were potentially exposed to respirable crystalline silica in 1986.

Potential exposure to respirable crystalline silica has been studied in metal and nonmetal mining and milling operations. Workers in sandstone, clay, and shale, and in miscellaneous nonmetallic mineral mills had the highest exposures to silica dust. Within the mills, the workers with the highest exposures were the baggers, general laborers, and personnel involved in the crushing, grinding, and sizing operations. Granite and stone industry and construction personnel also are potentially exposed to respirable crystalline silica. Sculptors and carvers, stencil cutters, polishers, and sandblasters had the highest potential exposures; the silica content of respirable dust ranged from 4.8% to 12.2%. Respirable crystalline silica exposures in clay pipe factories ranged from 0.01 to 0.20 mg/m^3; 10% of 348 samples collected from glass manufacturing industries had silica concentrations at least two times the permissible exposure standards; 23% to 26% of samples from clay products and pottery industries had concentrations more than twice the exposure limits; one-third of dust samples from fibrous glass plants had concentrations of respirable crystalline silica in excess of 0.10 mg/m^3; levels of respirable crystalline silica in a ceramic electronic equipment parts plant ranged from 0 to 0.18 mg/m^3; and 23% of samples collected in iron and steel foundries had concentrations in excess of 0.20 mg/m^3 respirable crystalline silica (IARC 1987). Occupational exposure to cristobalite may occur in industries where silica products are heated, including refractory brick and diatomaceous earth plants and ceramic and pottery manufacturing plants (IARC 1997).

Nonoccupational exposure to respirable crystalline silica results from natural processes and anthropogenic sources; silica is a common air contaminant. Residents near quarries and sand and gravel operations are potentially exposed to respirable crystalline silica. A major source of cristobalite and tridymite in the United States is volcanic rock in California and Colorado (NIOSH 1986). Local conditions, especially in deserts and areas around recent volcanic eruptions and mine dumps, can give rise to silica-containing dust (IARC 1987).

Consumers may be exposed to respirable crystalline silica from abrasives, sand paper, detergent, cement, and grouts. Crystalline silica also may be an unintentional contaminant, for example, diatomaceous earth, used as a filler in reconstituted tobacco sheets, may be converted to cristobalite as it passes through the burning tip of tobacco products (IARC 1987).

Regulations

OSHA

Permissible Exposure Limit (PEL) = Crystalline Quartz (respirable): 250 mppcf (millions of particles per cubic feet of air)/(%SiO_2 +5); 10 mg/m^3/(%SiO_2 + 2); Quartz (total dust): 30 mg/m^3/(%SiO_2 + 2); Cristobalite and Tridymite: Use ½ the value calculated from the count or mass formula for quartz

Guidelines

ACGIH

Threshold Limit Value - Time-Weighted Average Limit (TLV-TWA) = 0.05 mg/m^3 (cristobalite, quartz, tridymite - respirable fraction); 0.1 mg/m^3 (tripoli - respirable fraction)

NIOSH

Recommended Exposure Limit (REL) = 0.05 mg/m^3

Immediately Dangerous to Life and Health (IDLH) = 25 mg/m^3 (cristobalite, tridymite); 50 mg/m^3 (quartz, tripoli)

Listed as a potential occupational carcinogen

*No separate CAS registry number is assigned to silica, crystalline (respirable size).

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