

THE THRESHOLD LIMIT VALUE FOR VARIOUS FORMS OF AMORPHOUS SILICA

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Silica is the common name for silicon dioxide (SiO_2). In silica each silicon atom is covalently bound to four oxygen atoms which are arranged tetrahedrally around it. Each oxygen atom is bound to two silicon atoms. In the crystalline forms of silica the silicon and oxygen atoms are arranged in a highly ordered lattice which extends infinitely in all directions. Of course, the lattice is not truly infinite since it must end at the surface of the solid. The surfaces of crystalline silica particles or macroscopic pieces are bounded by flat surfaces joined at sharp straight edges. In some forms of crystalline silica such as tripoli or quartzite, the surfaces and edges may have been worn away to produce what appears to be amorphous particles.

All naturally occurring crystalline silica was formed by crystallization from aqueous solution or from molten magma. Depending on the temperature and pressure at which the crystallization takes place, one of three different geometrical arrangements of the silicon and oxygen atoms will be formed. The most common crystalline form of silica is quartz, which occurs as solid crystals from several inches in size down to microscopic dimensions. Other forms of crystalline silica are cristobalite and tridymite.

Under several natural and artificial conditions, silicon dioxide will form solids with no overall spatial ordering of the atoms. These products are amorphous silicas. Solid objects and particles of amorphous silica do not display flat faces and sharp edges. More importantly, amorphous silicas do not display X-Ray diffraction patterns as do the crystalline forms. The several forms of amorphous silica display different physical and chemical properties and substantially different toxicological characteristics.

The only naturally occurring form of amorphous silica is diatomaceous earth whose particles are the fossil skeletons of microscopic marine plants known as diatoms. While alive these organisms extract silica from the sea water and deposit it in complex regular forms with numerous voids. In California and other parts of the world there are very large deposits of the mineral diatomite or diatomaceous earth consisting almost entirely of fossilized diatoms, and which is a highly porous substance with a very low bulk density. The overlying and surrounding rock frequently contains quartz which contaminates the final product. Some deposits contain traces of cristobalite, apparently formed by metamorphism.

Fused quartz, or more properly, fused silica, is formed by the relatively slow solidification of molten quartz. In the melt

there is no long range order. As it cools, the molten material becomes highly viscous and then solidifies so that the atoms become immobilized in their random positions. Fused silica is produced as lumps of glassy material but during crushing and grinding, respirable particles can be produced.

Glass or silica dissolves in sodium hydroxide to form a solution of sodium silicate, also known as water-glass. On acidification, this forms the insoluble flocculent precipitate of silicic acid (H_4SiO_4 or $\text{Si}(\text{OH})_4$). As water is eliminated between nearby SiOH groups Si-O-Si bridges are formed. Depending on the dehydration process, precipitated silica or silica gel is produced. These both can be considered to be partially hydrated silicon dioxide. Silica gel can be dried to a very low moisture content to form a granular product which absorbs water and polar organic substances with great avidity.

Fumed silica is produced synthetically by a vapor phase hydrolysis of silicon tetrachloride in a flame of hydrogen and oxygen. It is a widely used filler in paints, plastics and rubber and as an antiskid and antislip agent.

Elemental silicon is produced by reacting coke and silica sand (crystalline) in an electric arc furnace. If iron is included in the charge, the product is ferrosilicon. In both cases, silicon monoxide is apparently produced as a byproduct which escapes from the furnace and is oxidized by ambient oxygen to produce what can be called silica fume. Although it is not a deliberately manufactured product, baghouse dust from silicon and ferrosilicon furnaces has been used in the same way as fumed silica. Although both fumed silica and silica fume are fumes in the usual industrial hygiene sense (they are finely divided solids produced by condensation from the gas phase) their mode of formation and worker exposure are different. As is discussed below, the toxic effects are also quite different.

Precipitated silica and silica gel could be considered to be the prototypical nuisance dusts. The ACGIH considers a material to be a nuisance dust if it causes no adverse health effects when exposures are kept under reasonable control (e.g. near or below 10 mg/m^3) and further does not alter the lung air spaces, does not form collagen to a significant extent and whose tissue reactions are potentially reversible.³ Klosterkotter showed that silica gel injected intratracheally in rats did not cause fibrosis.⁶ Schepers et al observed no fibrosis in guinea pigs and rabbits exposed by inhalation at 126 mg/m^3 for two years.⁷ There were macrophage accumulations and mild proliferation of reticulin fibers. In a group of 165 workers exposed to precipitated silica estimated

to be near or below 10 mg/m^3 for an average of 8.6 years, Wilson et al observed no serial changes in pulmonary function or chest radiographs.⁹

The TLV or 10 mg/m^3 (total dust) assigned to precipitated silica and silica gel was not chosen to avoid any known adverse health effect.³ Rather it represents a recommendation for good industrial hygiene practice. Airborne exposure above this level may reduce visibility, may cause unpleasant deposits in the eyes and nasal passages and may cause injury to the skin and mucous membranes by purely mechanical action.

Fumed silica and silica fume display entirely different toxicities. This contrast illustrates the confusion created by misidentification of the toxic substance in epidemiological studies and the risk of predicting toxicity on the basis of chemical similarity. As noted above, both products are true fumes, ultrafine solid particulates formed in gas phase reactions. However, fumed silica appears to be only slightly more toxic than precipitated silica and silica gel. ASTM standard E1156-87 reviewed three studies involving a total of 353 workers exposed for up to 32 years to fumed silica concentrations from 1.6 to 53 mg/m^3 .¹ No pulmonary dysfunction was observed except in smokers. Schepers exposed rats, rabbits and guinea pigs to fumed silica at 53 mg/m^3 for a year causing emphysema which reversed after exposure ceased and fibrosis which partially reversed.⁷ Groth observed significant interstitial hyperplasia and collagen deposition in monkeys exposed to 15 mg/m^3 of fumed silica for 13 months.⁴ However, the monkeys' lungs showed the presence of mineral dust which had apparently been inhaled in the wild or in captivity prior to purchase of the animals. No changes were observed in rats and guinea pigs similarly exposed.

On the other hand, several studies in the elemental silicon and ferrosilicon industries show that silica fume produces a unique complex of acute and chronic effects which are reversible after exposure ceases. The observations of Bowie at an African ferrosilicon plant are typical.² Brief high exposures to silica fume produce the symptoms of metal fume fever, which can persist for up to three months. Chronic exposure produces X-Ray and pulmonary function evidence of silicosis which regresses or disappears after cessation of exposure.

The TLV for fumed silica has been set at 10 mg/m^3 ; the value assigned to nuisance dusts.³ No value has been established for silica fume but a TLV of 0.2 mg/m^3 (twice the TLV for quartz) seems reasonable.

It is tempting to speculate on the causes of the radical difference between the two silica fume materials. In the case of silica fume, the effects may be produced by repeated high exposures but no airborne measurements are available to sup-

port this hypothesis. It is also possible that silicon and ferrosilicon workers are exposed to a much more freshly formed fume since they work at the tapping ports of the furnaces while the synthetic fumed silica may have aged for a few minutes before reaching the workers' breathing zones. Again there is no evidence to support this.

In contrast to the other forms of amorphous silica, the TLV for fused silica is based on very little actual data, animal or human. The Documentation references only two studies both published in the early 1950s; one an acute intraperitoneal injection in rabbits, the other an intratracheal instillation in rats.^{3,8,5} No inhalation experiments in animals or epidemiological studies in exposed workers have been published since then. Both references indicated that fused silica was less active in inducing a tissue reaction than crystalline quartz but no comparisons with nonfibrogenic forms of amorphous silica were performed. On the basis of the fact that there was a tissue reaction at all, a TLV of 0.1 mg/m^3 was established; the same as for quartz.³

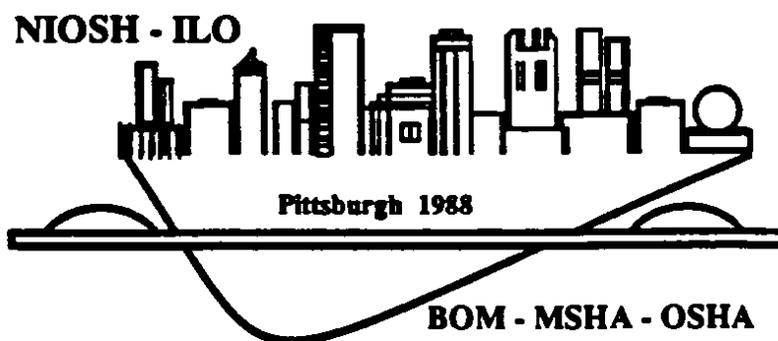
Fused quartz is now used in several advanced technological products such as ablative surfaces for rocket reentry vehicles and in fiber optics. It is anticipated that more workers will be exposed to this hitherto exotic material and it is unfortunate that more solid toxicological data is not available.

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