Health hazards due to the inhalation of amorphous silica

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Abstract Occupational exposure to crystalline silica dust is associated with an increased risk for pulmonary diseases such as silicosis, tuberculosis, chronic bronchitis, chronic obstructive pulmonary disease (COPD) and lung cancer. This review summarizes the current knowledge about the health effects of amorphous (non-crystalline) forms of silica. The major problem in the assessment of health effects of amorphous silica is its contamination with crystalline silica. This applies particularly to well-documented pneumoconiosis among diatomaceous earth workers. Intentionally manufactured synthetic amorphous silicas are without contamination of crystalline silica. These synthetic forms may be classified as (1) wet process silica, (2) pyrogenic (“thermal” or “fumed”) silica, and (3) chemically or physically modified silica. According to the different physicochemical properties, the major classes of synthetic amorphous silica are used in a variety of products, e.g. as fillers in the rubber industry, in tyre compounds, as free-flow and anti-caking agents in powder materials, and as liquid carriers, particularly in the manufacture of animal feed and agrochemicals; other uses are found in toothpaste additives, paints, silicon rubber, insulation material, liquid systems in coatings, adhesives, printing inks, plastisol eel undercoats, and cosmetics. Animal inhalation studies with intentionally manufactured synthetic amorphous silica showed at least partially reversible inflammation, granuloma formation and emphysema, but no progressive fibrosis of the lungs. Epidemiological studies do not support the hypothesis that amorphous silicas have any relevant potential to induce fibrosis in workers with high occupational exposure to these substances, although one study disclosed four cases with silicosis among subjects exposed to apparently non-contaminated amorphous silica. Since the data have been limited, a risk of chronic bronchitis, COPD or emphysema cannot be excluded. There is no study that allows the classification of amorphous silica with regard to its carcinogenicity in humans. Further work is necessary in order to define the effects of amorphous silica on morbidity and mortality of workers with exposure to these substances.

Keywords Non-crystalline · Amorphous · Silica, Silicosis · Bronchitis · Emphysema · Airway disease · Carcinoma

Introduction

Recently, the American Thoracic Society has reviewed a great number of studies on the adverse health effects of crystalline silica (American Thoracic Society 1997). The most prominent effects of exposure to crystalline silica are silicosis, tuberculosis, chronic bronchitis/chronic obstructive pulmonary disease (COPD) and lung cancer. A review of the health effects of amorphous silica with particular reference to cancer has been published recently (McLaughlin et al. 1997). The authors concluded that epidemiological investigations for any potential cancer risk were not informative because the effects of
crystalline and amorphous silica have not been separated. In the same year, amorphous silicas were considered not classifiable with regard to their carcinogenicity in humans by the International Agency for Research on Cancer (1997). Both reviews focused on carcinogenicity. The present review concentrates on the definition, classification, uses and pulmonary effects of amorphous silica and describes in more detail the data on synthetic amorphous silica not contaminated with crystalline silica.

**Definition and use of amorphous silica**

Silica is the common name for silicon dioxide (SiO₂). Silica may have a crystalline or a non-crystalline (amorphous) structure. In crystalline silica, the silicon and oxygen atoms are arranged in a fixed geometric pattern. In contrast, in amorphous silica, no spatial ordering of the atoms is present. The most common form of crystalline silica is quartz, but cristobalite, tridymite and others also have crystalline structures. Amorphous silica may be divided into (1) naturally occurring silica, (2) silica obtained under uncontrolled conditions, and (3) intentionally manufactured synthetic silica.

1. The most important naturally occurring amorphous silica is diatomaceous earth whose particles are the fossil skeletons of microscopic marine plants known as diatoms. Dust from uncalcined diatomaceous earth was reported to contain between 0.1 and 4% crystalline silica, whereas processing (particularly calcining) leads to contamination with crystalline silica such as cristobalite up to 60% (International Agency for Research on Cancer 1997; Hughes et al. 1998). Exposure to other naturally occurring biogenic (originating in living matter) amorphous silicas has been described in farmers during harvesting, crop burning or incineration (Rabovsky 1995).

2. “Fused” silica is silica heated to a liquid phase and cooled down without allowing it to crystallize (silica glass). The processing of these silicas leads to exposure to crystalline forms of silica. Contamination with crystalline silica occurs also in fly-ashes from power stations or silica fumes due to metallurgical processes such as the production of ferrosilicon.

3. The group of amorphous silica produced under controlled conditions may be classified as:

   - Wet process silica, i.e. precipitated silica and silica gels
   - Pyrogenic (“thermal” or “fumed”) silica
   - After-treated silica, e.g. chemically modified, surface-coated or physically treated silica.

None of these intentionally manufactured synthetic amorphous silicas contain crystalline silica.

The wet manufacturing process carried out in aqueous solution or dispersion (alkali metal silicate solution) may provide two different kinds of synthetic amorphous silicas, namely precipitated silica and silica gels. Pyrogenic silicas are obtained by decomposition of a precursor from a vapour or gas phase at elevated temperature (Legrand 1998). All kinds of synthetic amorphous silicas can be after-treated either physically, chemically, or by surface modification. The methods of after-treatment are various and depend on the product application (Ferch and Toussaint 1996).

Depending on the manufacturing process, amorphous silicas have a wide range of physico-chemical properties (Table 1). The major applications depend upon the silica type (Table 2). Approximately 60% of precipitated silicas are used as fillers in the rubber industry. Increasing amounts are used in tyre compounds for reduced rolling resistance and better wet-grip “green” tyres. They are used as free-flow and anti-caking agents for powder materials and as carriers of liquids which are transformed into free-flowing powders, particularly in the manufacture of animal feed and agrochemicals. Toothpaste, paints, and silicon rubber represent further important applications. More than half of the worldwide pyrogenic silica production is used as reinforcing filler for silicon rubber, a particularly high and low temperature resistant elastomer with major applications in wires, cables and automotive components. High performance thermal insulation materials utilize the low heat conductivity of pyrogenic silica. These substances are also used as thickening and anti-setting agents in liquid systems of coatings, adhesives, printing inks, plastisol car undercoats, cosmetics and many other systems. The high purity makes pyrogenic silica a preferred carrier and free-flow agent for many pharmaceutical and food applications, for toners or fire extinguisher powders.

The estimated 1995 production of amorphous silica was about one million tons (Table 3). The table includes by-products generated in more or less uncontrolled procedures. About 2,400 subjects worldwide are exposed

<table>
<thead>
<tr>
<th>Property</th>
<th>Pyrogenic</th>
<th>Precipitated</th>
<th>Gels</th>
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<tr>
<td>Specific surface area (m²/g)</td>
<td>50–400</td>
<td>30–800</td>
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<td>pH</td>
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<td>5–9</td>
<td>3–8</td>
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<tr>
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<td>3–100</td>
<td>not applicable</td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>–</td>
<td>&gt; 30</td>
<td>2–20</td>
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