MICROSILICA– CHARACTERIZATION OF AN UNIQUE ADDITIVE

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ABSTRACT

Microsilica, or silica fume (CAS-no. 69012-64-2), is an amorphous type of silica dust mostly collected in baghouse filters as by-product of the silicon and ferro-silicon production. The paper summarizes important physical and chemical properties of microsilica and uses those results for an evaluation of microsilica from a Health Safety and Environment (HSE) standpoint.

Microsilica consists of spherical particles with an average particle size of 150 nm and a specific surface area of typically 20 m^2/g. The chemical and physical properties of this inorganic product are different as compared to other amorphous and crystalline silica polymorphs. More than 500.000 MT of microsilica are sold to the building industry world-wide and are used in fibre cement, concrete, oil-well drilling, refractories, and even in polymers.

Microsilica contains trace amounts of heavy metal oxides and organic deposits, which originate from natural raw materials. Since the concentration of these impurities is very low, microsilica complies with company policies and international regulations. Traces of crystalline silica in microsilica do not seem to represent a health risk, neither for silicosis nor for lung cancer, due to the low levels and the large particle size.

According to the International Agency for Research on Cancer (IARC), there is insufficient evidence for the carcinogenicity of silica fume, in contrast to crystalline silica.

In order to assess potential health risks of microsilica and compliance with international regulations from an occupational hygienist's point of view, one has to collect fragments of information from different analytical techniques. Putting these fragments together results in a cohesive picture. All evidences indicate that microsilica is not a hazardous product when applied as advised.

KEYWORDS:

microsilica, silica fume, amorphous

INTRODUCTION

In order to tailor or enhance concrete properties for specific applications, a multitude of concrete additives is available on the market. Among these are also pozzolans. According to ASTM C618, pozzolans are defined as "siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties". Typical pozzolans are for example volcanic ashes, mineral slag, fly ash, and silica fume.

Elkem Microsilica® is Elkem's tradename for silica fume, an amorphous type of silica dust collected in baghouse filters as a by-product of the silicon and ferro-silicon production(CAS-no. 69012-64-2). Due to its

unique chemical and physical properties, microsilica has become a versatile mineral admixture for a multitude of applications. The basic effects of microsilica in e.g. concrete are illustrated in

Figure 1.

An extensive documentation of the use of silica fume in concrete has been published by the American Concrete Institute (ACI, 1996).
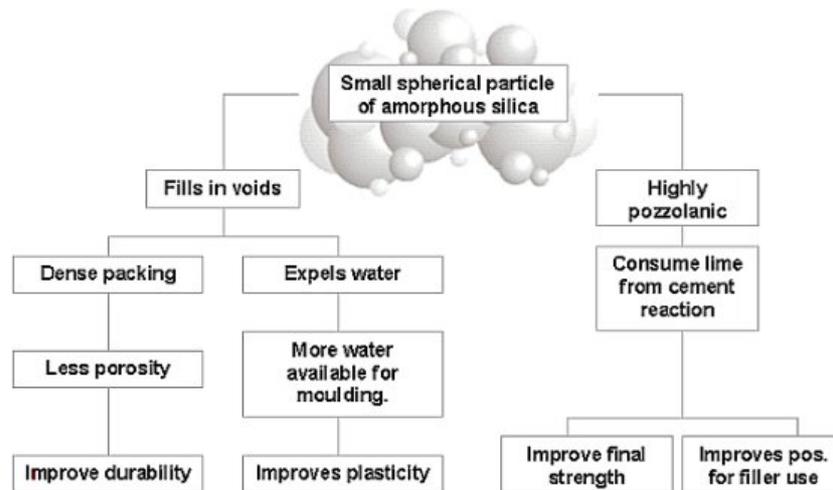
Figure 1 – Effects of silica fume in concrete

Apart from its use in construction concrete for tunnels, bridges, parking structures and skyscrapers, the use of microsilica in non-asbestos fibre cement enhances bending strength and density, while it reduces porosity and water absorption. This has a positive effect on the freeze-thaw properties. (SCHREINER & HOLMEN 2002). Furthermore, microsilica is a key ingredient in refractories (MONSEN et al. 1984, MYHRE et al. 2000), and special grades are even used as impact modifier and process aid in polymers (GILBERT et al. 2005).
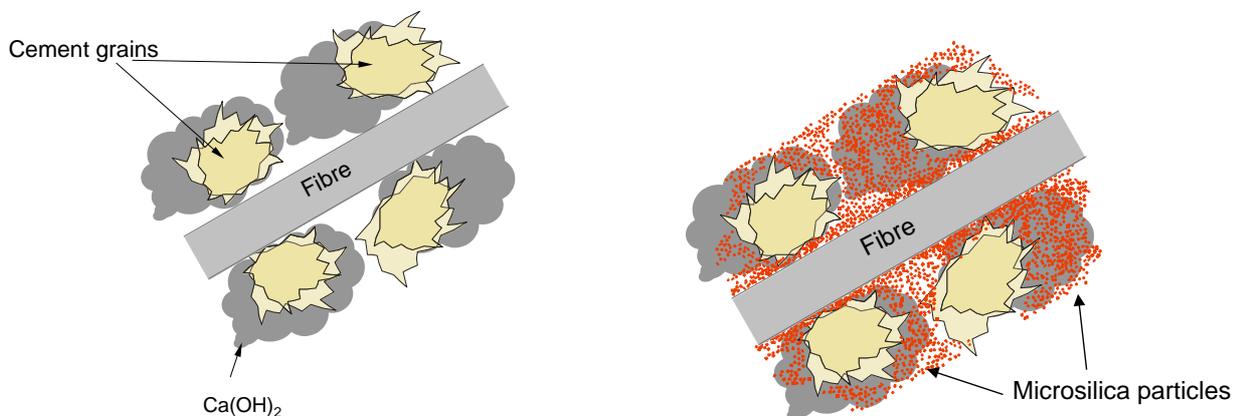
Figure 2 – Effects of microsilica in fibre cement: cement reacts with water, creating binder and dissolved calcium hydroxide (left); the dissolved calcium hydroxide reacts with microsilica that fills the voids, creating more binder and more binding points on the fibers (right).

As the beneficial effects of microsilica are based on its physico-chemical properties, thorough analytical studies are the key for understanding this product and developing new applications. Taking into account the large amounts of silica fume that are consumed every year (approximately 500.000 metric tons), health, safety and environmental issues (HSE) become very important.

This article summarizes important physical and chemical properties of microsilica and uses those results for an assessment of microsilica from an HSE standpoint.

CHEMICAL AND STRUCTURAL CHARACTERIZATION OF MICROSILICA

Characteristics of microsilica

The chemical composition of microsilica depends strongly on the choice of raw materials and the production process parameters. According to international standards (e.g. ASTM 1240-01, prEN 13263-1), the silica content of silica fume for the use in concrete must be at least 85 %. Typical impurities are carbon, silicon, phosphorus, sulfur, silicon carbide, chloride, and a variety of metal oxides. The specific surface area is between 15 and 30 m^2/g, which is relatively high, compared to crystalline silica flour (e.g. 4 m^2/g). The color of microsilica varies from dark black to almost white, depending on the carbon content. Undensified microsilica is a fluffy powder with low bulk density around 100-300 g/l.

As depicted in Figure 3, microsilica is amorphous to X-rays and thus, lacks long range order. This means that the primary building units of amorphous silica, SiO_4 tetrahedra, are randomly connected to each other and do not exhibit a regular pattern, in contrast to the crystalline silica polymorphs quartz, cristobalite or tridymite.
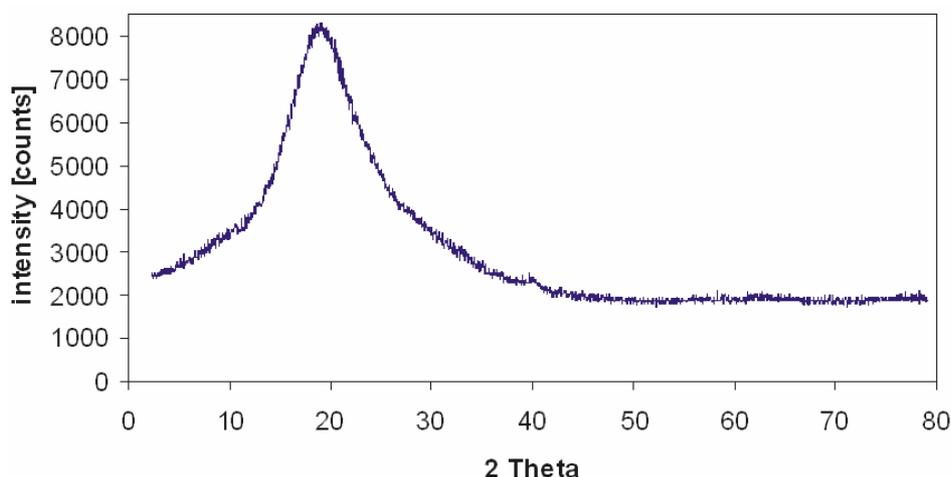
Figure 3 – X-ray diffraction pattern of amorphous microsilica. STOE Stadi P XRD instrument, Cu-K$_\alpha$

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[33-1161] Si O2 / Silicon Oxide / Quartz, syn (Range 1)
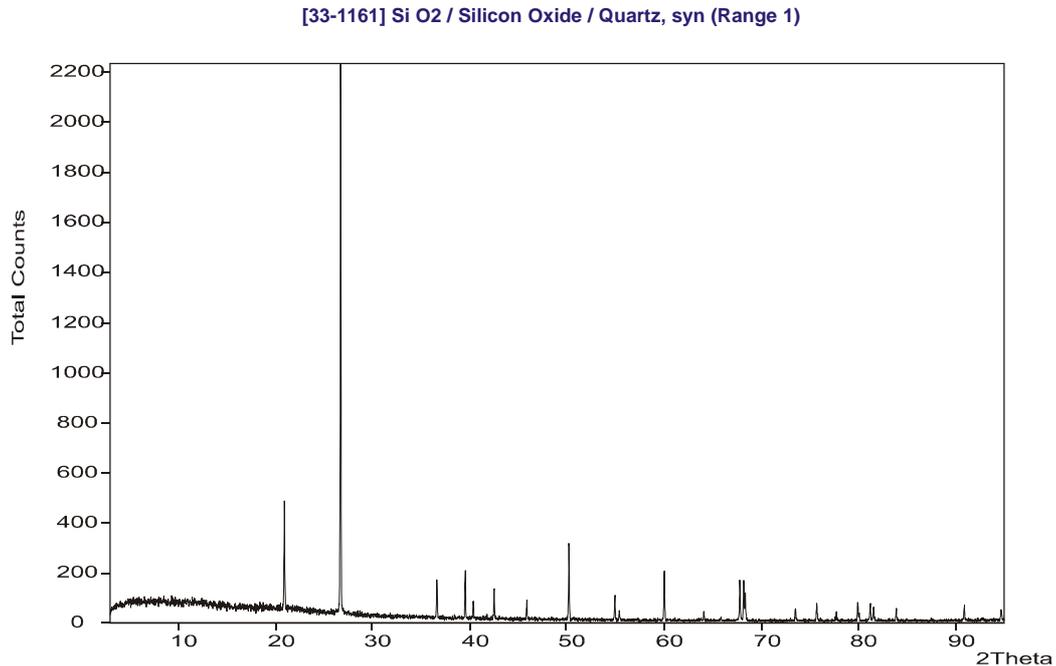
Figure 4 – X-ray diffraction pattern of quartz. STOE Stadi P XRD instrument, Cu-K$_\alpha$

The particle size distribution of microsilica in an aqueous dispersion is displayed in Figure 5 and shows that the majority of particles is smaller than 1 µm. In order to disperse the microsilica agglomerates, ultrasonic energy must be applied. In applications, mixing energy and shear forces between cement particles are responsible for the dispersion of microsilica agglomerates.
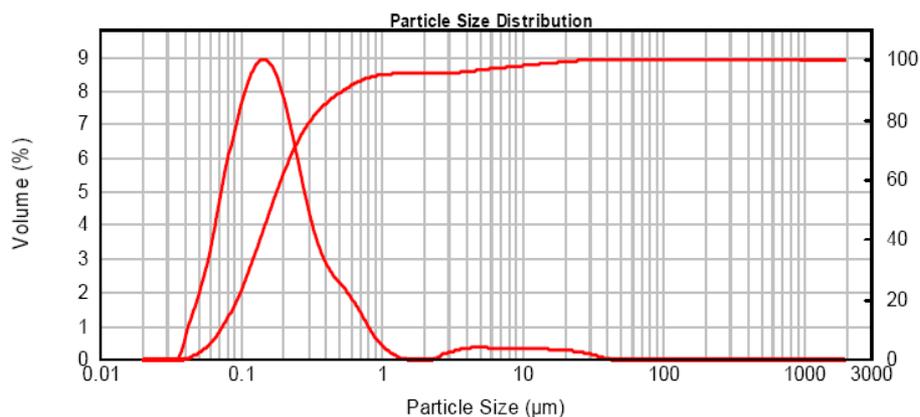
Figure 5 – Particle size distribution of 5 % microsilica in water after ultrasonic treatment. Malvern Mastersizer 2000.

TEM investigations

As the particle size distribution in Figure 5 indicates, the primary particles of microsilica are in the submicron range. Transmission Electron Microscopy (TEM) is the most suitable local probe to investigate such ultrafine clearly illustrates the ideal spherical particle shape of microsilica. The primary particle size of microsilica is between 20 nm and 1 µm, with most of the particles being 150-200 nm in diameter. Due to physical interaction (e.g. van-der-Waals interaction), submicron particles tend to agglomerate. According to the definition in ISO 14887, microsilica forms to the largest extend agglomerates (an assembly of particles which are loosely attached to each other) and only few aggregates (assembly of particles rigidly joined together). Figure 6 shows furthermore that microsilica is amorphous, because no diffraction reflexes are present – only a diffuse halo.
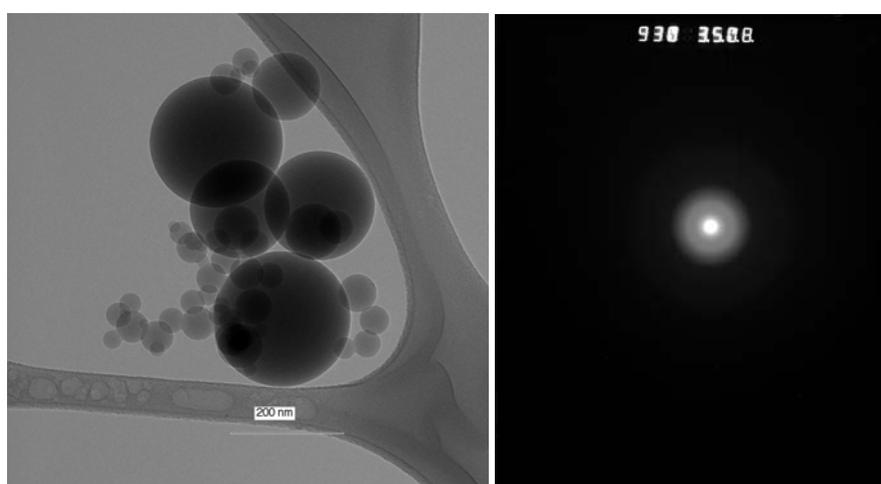
Figure 6 – Agglomerate of microsilica (left), electron diffraction pattern of microsilica (right) Philips CM 30, field emission gun, 300 kV (LaB$_6$ filament).

Extractable organic matter

Microsilica is formed during the silicon or ferrosilicon production process by reducing quartz with carbonaceous material such as coal, coke, wood chips and electrode material in an electrical arc furnace. During this combustion process, volatile organic compounds can form, such as aliphatic and polycyclic aromatic hydrocarbons (PAH). Due to the relatively high specific surface area, microsilica acts as a scavenger, and trace amounts of these organic molecules can be physisorbed to some extend on the microsilica surface.

The amount of extractable organic matter (EOM) depends on the raw materials, the furnace process parameters and the extraction parameters itself. As a result of a multitude of Soxhlet extractions, 0.5-70 ppm EOM could be detected by GC-MS on different microsilica grades.

Crystalline silica in amorphous silica fume

Crystalline silica (quartz) is the starting material for the production of amorphous silica fume. It is known from the quarry and mining industry that quartz lumps form airborne silica dust during handling. Small quartz particles may therefore be transported with the furnace off-gas, following bag house filtration, and end up in the microsilica bulk material.

The standard method for the quantification of quartz in bulk materials is X-ray diffraction (XRD). The detection limit of quartz in a matrix of amorphous silica fume is higher than in crystalline minerals, because the broad hump of the amorphous silica fume XRD pattern superimposes Bragg reflexes of quartz. In other

words: traces of crystalline silica might be hidden in the amorphous silica fume matrix. As a result, the detection limit of crystalline silica in silica fume, following the method of matrix flushing (CHUNG 1974), is only 0.3 %.

In the light of the classification of respirable crystalline silica (EN 481) from occupational sources as carcinogenic to human (IARC 1987), the U.S. Occupational Safety and Health Agency decided that any product containing more than 0.1 % crystalline silica has to be labeled to indicate a cancer hazard (OSHA 1993). As the detection limit of crystalline silica in silica fume is 0.3 %, labeling issues get difficult and inconsequent for silica fume. When it comes to low detection limits, alternative analytical techniques, such as IR-spectroscopy (BJØRSVIK 1991) or thermosonimetry (HEGGESTAD 1984) also fail.

That there really are quartz particles present in microsilica can be demonstrated by lightmicroscopic examination of the residue after wet screening on a 45 μm sieve, where the ultrafine silica fume matrix is removed. The transparent angular particles in Figure 7 have been identified as quartz. Traces of quartz in microsilica do not affect the properties in the final application, however, people are concerned about potential health risks.
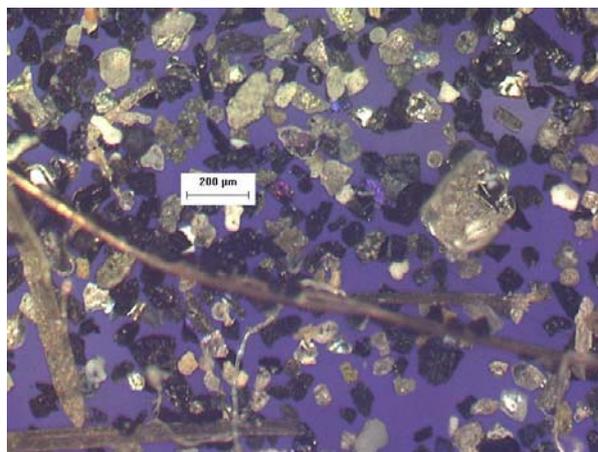
Figure 7 – Coarse fraction (> 45 μm) after screening microsilica. Optical micrograph using polarized light.

HEALTH, SAFETY AND ENVIRONMENT ASSESSMENT OF MICROSILICA

Heavy metals

Since natural raw materials like quartz, coal and wood chips are used in the silicon and ferrosilicon production, it is not surprising that the resulting microsilica is not chemically pure SiO_2 but contaminated with other elements, including traces of heavy metal oxides. Table 1 gives an overview over the heavy metal contaminants in microsilica as determined by X-Ray Fluorescence (XRF) analysis and compared to those in fly ash and cement (HANSEN 1992). The concentration is in the ppm [mg/kg] range and is below for example the official limit values for children's playgrounds in Germany or the RoHS regulation, which restricts the use of certain hazardous substances in electrical and electronic equipment (RoHS 2004).

Table 1 – Heavy metal contamination in microsilica.
*= German regulation for soil protection (BBodSchV 1998)

element	microsilica	fly ash	cement	German limit value for children's playground*	RoHS 2004
				ppm; [mg/kg]	
As	<10	58		25	
Pb	<1-335 (av. < 100)	97-932	70-132	200	100
Cd	<1-6	<1-16	2	10	10
Cr	<1-47	124-203	99-698	200	10
Ni	<1-39	113-145	<12-13	70	
Hg	<0.03-2.2	0.2-0.27		10	10

Because the heavy metal content of microsilica is very low, and these impurities have not been intentionally added but are present due to natural impurities of the raw materials below limits specified in applicable legislation, microsilica complies with certain company policies, which issue lists of banned substances to avoid contamination of their end products, and which might compromise safe disposal at down-stream users.

As there are only trace amounts of heavy metals present in microsilica in the form of oxides (ppm levels), the potential health risk is limited, and microsilica is not classified as health hazard.

Organic impurities

Microsilica is obtained from a complex reduction process, in which the formation and evaporation of volatile organic matter, e.g. polycyclic aromatic hydrocarbons (PAH) cannot be avoided. To assess the potential health hazard of these organic impurities one has to bear in mind that they are physisorbed on the microsilica surface and basically not soluble in water. Furthermore, the level of contamination must be put in perspective and compared to environmental background levels, as it is illustrated in Figure 8.
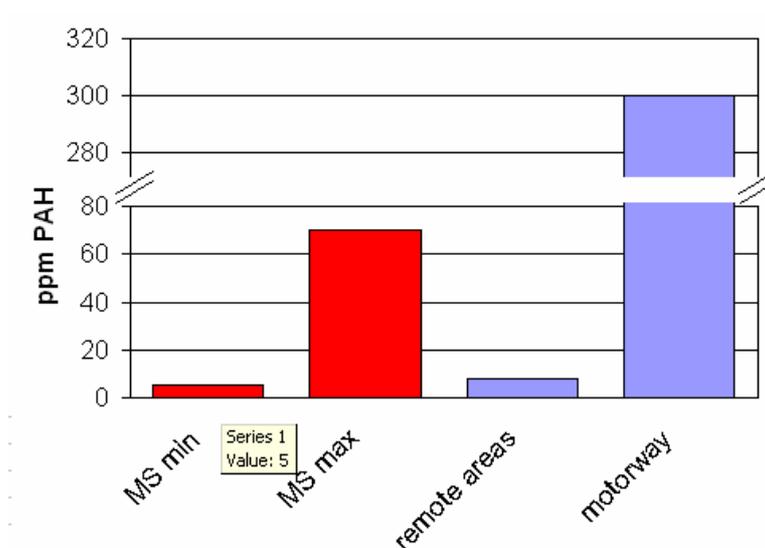
Figure 8 – Organic impurity levels on microsilica (MS) as compared to various background levels. PAH = polycyclic aromatic hydrocarbons.

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Environmental risk, Ecotox-tests

To study potential hazards of microsilica in an aquatic environment, a number of ecotox tests were carried out according to ISO 8692 and the OECD guideline 201-203. Test organisms were Corophium (fresh water shrimp), Skeletonema (sea water algae), Pseudokirchneriella (fresh water algae), Daphnia (fresh water flea), and Brachidanio (zebra fish). The results are displayed in Table 2 and will help to assess whether ppm levels of heavy metals and organic matter have any relevant toxicity to water organisms.

It was not possible to obtain a LC_{50} value (where 50 % of the animals die) for Corophium at the maximum test concentration of 50 g microsilica/kg sediment. The effect concentration EC_{50}, where 50 % of the organisms stop growing, was 4.2 g/l seawater for the algae Skeletonema. Also for the fresh water algae, the EC_{50} value after 72 hours was > 100 mg/l. Daphnia water fleas did not show any signs of mortality at the maximum test concentration of 1 g/l. In fresh water, Zebra fish were exposed to 100 mg microsilica/l water and did not show any signs of toxicity after 96 hours.

Table 2 – Results of biological tests

10 d LC_{50} (Corophium)	> 50 g/kg sediment
72 h EC_{50} (Skeletonema)	> 1000 mg/l seawater
72 h EC_{50} (Pseudokirchneriella)	> 100 mg/l fresh water
24 h EC_{50} (Daphnia)	> 100 mg/l fresh water
96 h LC_{50} (Brachidanio)	> 100 mg/l fresh water

The overall conclusion of the ecotox tests is that even high concentrations of microsilica do not have any acute toxicity to water organisms. These findings support the hypothesis that the level of inorganic and organic impurities is too low to show toxic effects, and that the impurities are basically not in a water soluble form, e.g. not bioavailable.

Crystalline silica

Respirable crystalline silica from occupational sources is an important issue, as it is causally associated with the deadly lung disease silicosis, and has been classified as class 1 carcinogenic to human by IARC. However, IARC noted that carcinogenicity of silica depends on its inherent characteristics and was not detected in all industrial circumstances studied. To protect the worker's health, occupational exposure limits have been issued world-wide.

Because the detection limit of crystalline silica in an amorphous silica matrix is 0.3 %, and thus not sufficient to address OSHA regulations (US Occupational Safety and Health Agency), labeling of products containing more than 0.1 % quartz is mandatory in the USA. Quartz as a product is not classified as carcinogenic in the European Union. Furthermore, it is not possible to measure the amount of respirable crystalline silica in bulk materials, because the term "respirable" presupposes that the material is airborne – and bulk materials are definitely not airborne.

Even more confusion is created when taking into account the recommended threshold limit values (TLV) for silica fume (2 mg/m^3) and respirable crystalline silica (0.05 mg/m^3) issued by the American Conference of Governmental Industrial Hygienists (ACGIH 2002). According to these values, one can add 2.5 % of crystalline silica to microsilica, and when keeping the TLV for silica fume, one will automatically stay below the TLV of respirable crystalline silica as well.

Taking into account this mismatch, the US Mine Safety and Health Administration (MSHA) calculates permissible exposure limits (PEL) of mixed dust according to the following equation:

$$PEL[mg/m^3] = \frac{10}{\%\ crystalline\ silica + 2}$$

For microsilica with a total, not necessarily respirable silica content of 0.3 %, the PEL would be 4 mg/m^3.

Finding crystalline silica in silica fume can be compared with searching for a needle in a haystack. The fact that quartz particles are only visible in the coarse fraction after wet sieving (Figure 7), indicates that the major mass and volume fraction of crystalline silica is actually larger than 45 μm and thus, not respirable (EN 481).

Traces of crystalline silica in microsilica do not seem to represent a health risk, neither for silicosis nor for lung cancer, due to the low levels and the large particle size.

Based on epidemiological studies, amorphous silicas do not have any relevant potential to induce fibrosis in workers with high occupational exposure to these substances (MERGET et al. 2002). Furthermore, Elkem workers exposed to microsilica have been monitored since 1970 with respect to respiratory diseases. No increased risk of silicosis or lung cancer caused by exposure to microsilica has been observed at any of the Elkem silicon and ferro-silicon plants in Norway (HOBBESLAND et al. 1997). These findings support the IARC classification of silica fume (Group 3, inadequate evidence).

Chronic obstructive pulmonary disease (COPD)

Any type of dust is potentially harmful for the respiratory system of humans, as the long history of pulmonary diseases reflect. Due to exposure control, the classic mineral dust-induced pneumoconioses (silicosis, asbetosis) decrease in frequency, and instead, obstructive airway diseases have emerged as the most prevalent category of occupational respiratory disorder (BALMES et al. 2003). Evidence has been obtained from epidemiological studies of workers exposed to respirable crystalline silica dust (average 0.1-0.2 mg/m^3) that there is an exposure-response relation for cumulative dust exposure and COPD, which is independent of radiological signs of silicosis (HNIZDO & VALLYATHAN 2003).

The International Agency for the promotion of silicon metal (AIS) published an extensive literature review of thermally generated silica fume (Galton-Fenzi 1998). The outcome was that COPD is suspected following long term exposure for concentrations of silica fume above recommended occupational exposure limits. Smoking habits are influential in this respect.

Evidence from this literature review suggests that an acute disease might occur when exposed to high levels of silica fume. However, upon cessation of exposure in many cases the symptoms and chest X-ray findings are resolved, which is in agreement with the findings of Merget (MERGET et al. 2002).

CONCLUSION

All evidence indicates that microsilica, silica fume (CAS-no. 69012-64-2), is not a hazardous substance. When applied as advised it is unlikely to acquire adverse lung diseases. There is insufficient evidence for the carcinogenicity of silica fume. Upon long term exposure to microsilica dust at concentrations above recommended occupational exposure limits (OEL) chronic obstructive pulmonary disease is suspected. Dust protection masks should therefore be worn when handling dry microsilica.

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