

**SIDS INITIAL ASSESSMENT PROFILE**

<b>CAS No.</b>	1344-09-8 6834-92-0 10213-79-3 13517-24-3 1312-76-1
<b>Chemical Name</b>	Silicic acid, sodium salt Silicic acid (H <sub>2</sub> SiO <sub>3</sub> ), disodium salt Silicic acid (H <sub>2</sub> SiO <sub>3</sub> ), disodium salt, pentahydrate Silicic acid (H <sub>2</sub> SiO <sub>3</sub> ), disodium salt, nonahydrate Silicic acid, potassium salt
<b>Structural Formula</b>	<b>M<sub>2</sub>O • n SiO<sub>2</sub></b> (M = Na or K; n = molar ratio, defining the number of moles SiO <sub>2</sub> per mole of M <sub>2</sub> O; a molar ratio of 1 designates metasilicates, <b>M<sub>2</sub>SiO<sub>3</sub></b> )

**SUMMARY CONCLUSIONS OF THE SIAR****Category Rationale**

The soluble silicates are structurally very similar. Silicon-oxide tetrahedra as the basic structural units are linked with each other via Si-O-Si bonds resulting in an infinite three-dimensional network. The negative charge of unshared oxygen atoms is balanced by the presence of sodium or potassium cations which are randomly spaced in the interstices. The extent to which balancing alkali ions are present in a given silicate is defined by the molar ratio SiO<sub>2</sub>/M<sub>2</sub>O (M = Na or K). The higher the molar ratio, the less sodium or potassium ions are present in the silica network and consequently the less alkaline the silicates are. Whereas the sodium and potassium salts have an amorphous three-dimensional structure, the disodium salts (= metasilicate) are crystalline with penta- and nonahydrate differing from the anhydrous form only by their water of crystallisation. Once in aqueous solution, all soluble silicates are subject to the same molecular speciation resulting in a mixture of monomeric tetrahedral ions, oligomeric linear or cyclic silicate ions and polysilicate ions. At environmental pH values the soluble silicates are present as poorly soluble amorphous silica and monomeric silicic acid. The biological properties of soluble silicates are mainly governed by their intrinsic alkalinity. Based on the available data the members of the soluble silicates category exhibit a similar toxicological profile.

**Human Health**

The limited toxicokinetic studies on rats, cats, dogs and guinea pigs all showed that the excretion of silicon with the urine was markedly increased after ingestion of silicates. The excretion rate was independent of the doses applied indicating that the limiting factor is the rate of production of soluble or absorbable silicon in the gastrointestinal tract.

The oral LD<sub>50</sub> in rats was 1152 – 5700 mg/kg bw depending on the molar ratio of the silicate species, i.e. toxicity decreases with increasing molar SiO<sub>2</sub>:M<sub>2</sub>O ratio. Clinical signs included apathy, staggering gait, tonic cramps, dyspnoea, cyanosis, piloerection and signs of abdominal discomfort.

Sodium and potassium silicates can be irritating to corrosive to the skin of rabbits, depending on their molar ratio and concentration. The nature of the counterion (Na<sup>+</sup> or K<sup>+</sup>) has no influence as sodium and potassium silicates behave

similarly with respect to skin irritation. Any effects on the skin decrease with increasing molar ratio, superimposed by increasing irritancy with increasing concentrations. At concentrations of 35 % and 29 % (highest tested concentrations) potassium silicates with molar ratios of 3.4 and 3.9 were only slightly, and not irritating to the eyes of rabbits, respectively. Results from non-validated *in vitro* assays indicate that the severity of eye effects is inversely correlated with the molar ratio, with corrosive effects found in the enucleated rabbit eye test after exposure to disodium silicate powder with a molar ratio of 1.0.

In a mouse local lymph node assay, sodium metasilicate was not sensitising. In humans, a single case of contact urticaria elicited by sodium silicate is reported.

Soluble silicates have been tested in a number of repeated dose studies with exposures ranging from 28 to 180 days. The NOAELs (90d) of sodium metasilicate were 227 - 237 mg/kg bw/d for rats and 260 - 284 mg/kg bw/d for mice (highest tested dose levels, respectively). Sodium silicate had a NOAEL (180d) of 159 mg/kg bw/d for rats (highest tested dose). In mice the LOAEL (90 d) of sodium metasilicate was 716 - 892 mg/kg bw/d with reduction of pituitary glands weight in female mice as adverse effect. Adverse effects in rats, dogs and turkeys were polydipsia, polyuria and soft stools, reduction of blood plasma Ca and Mg levels, and of liver Zn concentrations, gross cortical lesions of the kidneys or increased blood plasma P and decreased Cu at doses above 1000 mg/kg bw/d.

*In vitro*, soluble silicates did not induce gene mutations in bacteria: sodium silicate was negative in an *E. coli* reverse mutation assay and sodium metasilicate exerted no mutagenic activity in *B. subtilis* and *S. typhimurium*. In a modern guideline study that was performed in accordance with OECD TG 473, an aqueous sodium silicate solution (36% active ingredient) induced no chromosomal aberrations in V79 cells, both in the absence and in the presence of metabolic activation. *In vivo*, sodium metasilicate did not induce chromosomal aberrations in bone marrow cells of mice in a study performed similarly to OECD TG 475, with the restriction that no information on the use of positive controls was available for this study. Although the reliability of this study can therefore not be fully evaluated, the negative result is corroborated by the fact that the chemical structure does not contain elements that raise concern for a genotoxic activity and by the negative results of genotoxicity tests with sodium silicate. For the group of soluble silicates under review here, it is therefore concluded that there is no evidence of a genotoxic potential.

There were no valid carcinogenicity studies available.

The available data on toxicity to reproduction are limited. In a 4-generation study, the total number of offspring born at 79 mg/kg bw/d was reduced to 67 % and of offspring weaned to 46 % of the control, respectively. Severe limitations of the study and intercurrent deaths, including controls, make it however difficult to draw any firm conclusions from this study. In mice, litter size and fertility index were unaffected at sodium metasilicate concentrations up to and including 200 mg/kg bw/d. No developmental effects were observed in mice up to and including 200 mg/kg bw/d. In repeat dose toxicity studies with rats, mice and dogs the macroscopic and microscopic examination of reproductive organs did not reveal treatment-related effects.

### Environment

Solid crystalline silicates have discrete melting points which depend on the content of crystallisation water: anhydrous sodium metasilicate melts at 1089 °C while sodium penta- and nonahydrate melt at 72 °C and 48 °C, respectively. Due to their glass nature, solid amorphous silicates do not have discrete melting points but rather flow points. Aqueous silicate solutions have a melting point only slightly lower than that of water.

The specific gravity or density of silicate solutions depends on the concentration (solids content), the temperature, and the silica to alkali ratio. Commercial silicate solutions have densities ranging from ca. 1.2 – 1.7 g/cm<sup>3</sup> at 20 °C. The vapour pressures that have been measured for three solid sodium silicates are extremely low: 0.0103 hPa at 1175 °C (MR 1.0, metasilicate), 0.0031 hPa at 1165 °C (MR 2.0) and 0.0016 hPa at 1172°C (MR 3.0). This indicates that the respective pressures at ambient temperature will be unmeasurably small.

Crystalline silicates like sodium metasilicate are readily soluble in water. Amorphous silicate glasses are only slightly attacked by water at ambient temperatures. They can be solubilised only at elevated temperature and pressure (ca. 150 °C and  $\geq 5$  bar). The solutions are infinitely dilutable with water. Silicate powders obtained by water

evaporation from silicate solutions are readily soluble in water. The water solubility depends on the pH and pH is elevated upon dissolution of soluble silicates. Above a pH of 11 - 12 stable solutions of monomeric and polymeric silicate ions exist. Solubility rapidly decreases when the pH is lowered to 9 leading to increasing precipitation of amorphous silica. Below pH 9 only a small proportion is present as soluble monomeric silicate ions, the majority existing as insoluble amorphous silica gel. Soluble silicates are insoluble in alcohols, like n-octanol, making determination of a log Kow not feasible.

As inorganic substances, soluble silicates are not amenable to photo- or biodegradation. Respiration of activated sludge is not inhibited at sodium metasilicate concentrations  $\geq 100$  mg/l. Continuous dosing of 25 mg sodium silicate/l has no adverse effects on the operation of a model sewage treatment plant simultaneously fed with easily degradable nutrients; no significant elimination occurred with  $>90\%$  detected in the effluent.

Acute toxicity testing in fish, invertebrates, and algae indicate a low order of toxicity with effect concentrations between 210 and 1700 mg/l. The following results were obtained in acute tests:

<i>Danio rerio</i>	LC <sub>50</sub> (96 h) = 210 mg/l (Na, MR 1.0)
<i>Danio rerio</i>	LC <sub>50</sub> (96 h) = 1108 mg/l (Na, MR 3.46)
<i>Oncorhynchus mykiss</i>	LC <sub>50</sub> (96 h) = 260 - 310 mg/l (Na, MR 3.1)
<i>Leuciscus idus</i>	LC <sub>50</sub> (48 h) > 146 mg/l (K, MR 3.9- 4.1)
<i>Daphnia magna</i>	EC <sub>50</sub> (48 h) = 1700 mg/l (Na, MR 3.2)
<i>Daphnia magna</i>	EC <sub>50</sub> (24 h) > 146 mg/l (K, MR 3.9- 4.1)
<i>Scenedesmus subspicatus</i>	EbC <sub>50</sub> (72 h) = 207 mg/l
	ErC <sub>50</sub> (72 h) > 345 mg/l (Na, MR 3.0)

No long-term tests are available for fish, invertebrates or algae.

As a result of the low molar ratio, sodium metasilicate and its hydrates (MR 1.0) exhibit a higher alkalinity than the silicates of higher molar ratio. With the assumption that the primary hazard of soluble silicates is their alkalinity, it is expected that sodium metasilicate generally exhibits a higher toxicity than silicates of molar ratios 3 - 4. This is confirmed by toxicity data available for fish. Concerning invertebrate and algal toxicity, studies are available only for silicates of molar ratios 3-4 or of unknown ratio. Because of their higher alkalinity, the sodium metasilicates are expected to exhibit a higher daphnid and algal toxicity. The extent to which this toxicity will be increased should be similar to that observed for fish toxicity in *Danio rerio*. This would result in metasilicate toxicities in the same order of magnitude as observed for fish.

## Exposure

The worldwide production volume is approximately 3-4 million metric tons per year. In the year 2000, ca. 770,000 metric tons of sodium silicates and disodium metasilicates were produced in Western Europe with a total consumption of ca. 890,000 metric tons. Potassium silicates were produced at approximately 22,000 metric tons. Sodium silicates are used as raw materials for industrial products, like silicas or zeolites (51 %), in detergents and cleaners (21 %), pulp & paper production (15 %) and numerous other applications, including soil stabilization, TiO<sub>2</sub> production, refractories, ceramic binders, water treatment etc. (13 %). Applications for potassium silicates are the building industry (45 %), welding rods (19 %), detergents (16 %), molecular sieves (9 %), and miscellaneous uses (11 %).

About 50% of the combined sodium and potassium silicates production (460 ktons SiO<sub>2</sub>/year) is further processed to derivatives. Emissions to the environment may take place during production and processing, but no quantitative information is available. Another 10 % (ca. 80 - 90 ktons SiO<sub>2</sub>/year) go into direct uses which result in inclusion into or onto a matrix (e.g. refractories, TiO<sub>2</sub>, ceramic binders, welding rods, building industry). There is potential for release to the aqueous and terrestrial environment during production, processing and use, but no emission data are available. The remaining soluble silicates (ca. 40 % or 360 ktons SiO<sub>2</sub>/year) are used in applications with likely emissions into the hydro- and/or geosphere (e.g. detergents, pulp & paper, water/wastewater treatment and soil stabilization). Detergents (188 ktons SiO<sub>2</sub>/year) and pulp & paper (136 ktons SiO<sub>2</sub>/year) are the most important water-relevant applications and together make up about 90 % of the soluble silicates used in these application areas.

Once they reach the hydrosphere, they are diluted and depolymerize rapidly to give molecular species indistinguishable from natural dissolved silica ( $\text{H}_4\text{SiO}_4$  or  $\text{SiO}_2$  [aq.]) in the hydrosphere. Workers or professional users may be exposed to liquid or powder products. Since the primary hazard of soluble silicates is their alkalinity, precautions must be observed to prevent contact with clothes, skin and in particular with the eyes. Workers are recommended to wear protective equipment (safety gloves and glasses, dust masks when handling powders). Dust exposure should be limited to  $2 \text{ mg/m}^3$ , the limit concentration foreseen for caustic soda (NaOH) and potash (KOH).

Consumer exposure may occur primarily by contact with laundry or automatic dishwashing detergents and by ingestion of drinking water. Background exposure via the environment can be expected, as compounds of silicon and oxygen are the primary constituents of earth's landmasses, and an important compound in the biomass. Silicon is a ubiquitous constituent of foods.

### RECOMMENDATION

The chemicals in this category are currently of low priority for further work.

### RATIONALE FOR THE RECOMMENDATION AND NATURE OF FURTHER WORK RECOMMENDED

#### Human Health:

Soluble silicates possess properties indicating a hazard for human health (irritancy/corrosivity). In the Sponsor country, adequate risk reduction measures are in place (classification and labelling). No further work is recommended. In situations where this is not the case, risk assessment and, if necessary, risk reduction measures are recommended.

#### Environment:

Soluble silicates are currently of low priority for further work because of their low hazard profile.