

C E E S

Centre Européen

d'Etude des Silicates

SOLUBLE SILICATES

Chemical, toxicological, ecological and legal aspects
of production, transport, handling and application

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Chemistry making a world of difference

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1. INTRODUCTION

Soluble silicate glasses, powders and liquids are among the largest volume synthetic chemicals, surpassed in volume only by commodity acids and bases. They also represent one of the oldest anthropogenic classes of chemicals; there are strong indications that e.g. sodium silicates have been produced by the old Egyptians more than 5000 years ago melting mixtures of quartz sand and naturally occurring sodium carbonate.

2. CHEMICAL AND PHYSICAL CONSTITUTION

2.1 Chemical compositions

Soluble silicates, especially sodium, potassium and lithium silicates are generally not distinct stoichiometric chemical substances (with a specific chemical formula and molecular weight), but rather glasses or aqueous solutions of glasses, resulting from combinations of alkali metal oxide and silica in varying proportions.

The general formula for soluble alkali silicates is



where M is Na, K or Li, and x is the molar ratio (MR), defining the number of moles silica (SiO_2) per mole of alkali metal oxide (M_2O).

In industry it is common practice to indicate the weight ratio (WR) $SiO_2 : M_2O$ is more common which is derived from the MR by the following relations:

Sodium silicates:	MR = 1.032 WR
Potassium silicates:	MR = 1.566 WR
Lithium silicates:	MR = 0.5 WR

All of the above soluble silicates are alkaline substances (pH values of the concentrated products being usually between 10 and 13). The alkalinity of the products increases as the MR or WR is reduced.

2.2 Physical forms

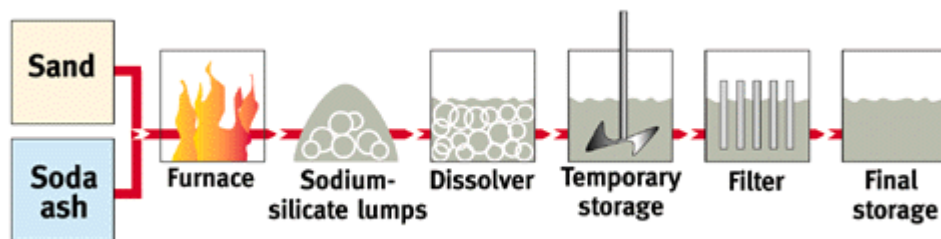
Soluble silicates are produced and marketed as glass lumps, ground glass, aqueous solutions or dried powders. The physical, chemical, toxicological and eco-toxicological

behaviour of these products is strongly dependent on the MR/WR $\text{SiO}_2:\text{M}_2\text{O}$, as this controls the degree of alkalinity of individual products.

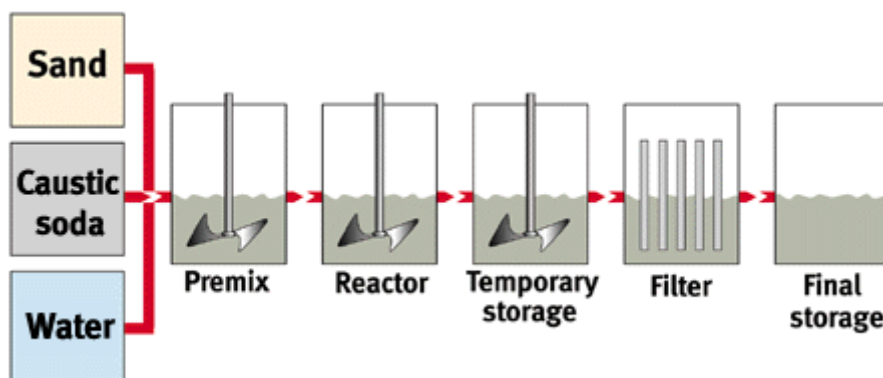
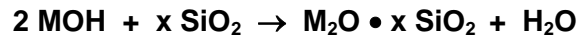
3. PRODUCTION AND RAW MATERIALS

3.1 Production routes

- a) Sodium and potassium silicate glasses (lumps) are produced by the direct fusion of precisely measured portions of pure silica sand (SiO_2) and soda ash (Na_2CO_3) or potash (K_2CO_3) in oil, gas or electrically fired furnaces at temperatures above 1000°C according to the following reaction:



- b) Solutions of soluble silicates (“waterglass”) may be produced either by dissolving the soluble silicate lumps in water at elevated temperatures (and partly at elevated pressure) or for certain qualities also by hydrothermally dissolving a reactive silica source (mainly silica sand) in the respective alkali hydroxide solution according to the equation:



In general, solutions are subsequently filtered and adjusted to yield products to a particular specification.

- c) Amorphous silicate powders are made by drying aqueous solutions by means of spray or drum dryers. These products may then be further treated in order to modify powder properties, e.g. particle size, bulk density.
- d) Crystalline alkali silicate powders of a specific composition but containing different amounts of water of crystallisation can be produced by various routes; e.g. sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$) is normally produced by blending sodium silicate solutions and additional caustic soda (NaOH) to achieve a mother liquor with WR $\text{SiO}_2 : \text{Na}_2\text{O} = 1.0$, from which the final product is crystallised

The products are then separated, sieved and processed as required.

3.2 Raw materials

The main raw materials for the production of soluble silicates are quartz sand (or other silica sources), alkali carbonates (e.g. soda ash Na_2CO_3 , potash K_2CO_3), alkali hydroxides (e.g. NaOH , KOH , LiOH), water and fuels / energy, (e.g. oil, gas, electricity). Filter aids (mostly from natural sources) may also be used.

3.3 Life Cycle Inventories (impact on nature and resources)

For the most common sodium silicate products (sodium silicate 3,3 WR furnace lumps, sodium silicate 3,3 WR furnace route liquor, sodium silicate 2,0 WR hydrothermal liquor, sodium silicate 2,0 WR hydrated powder, sodium metasilicate pentahydrate), which represent more than 90 % of total soluble silicate production (sodium and potassium silicates total production in 2001 is 741.426 m.T. SiO_2 equivalent), Life Cycle Inventories (LCI) have been prepared on behalf of CEES by EMPA (Swiss Federal Laboratories for Materials Testing and Research), St. Gall in 1997 (EMPA Report No. 241). Copies of the report are available either directly from EMPA or from CEFIC or from any of the supporting CEES members.

These LCI's give averaged figures (based on measured values) for the consumption of raw materials, water and energy and for emissions to air and water along with solid waste generation for the production of the five most common commercially available sodium silicate products. Data were supplied by twelve West European silicate producers and were based on 1995 production figures.

A short version of this LCI study highlighting the key findings has been published in the International Journal of Life Cycle Analyses (Int. J LCA 4(4), p.207-212, 1999).

4. MAIN APPLICATIONS AND USES OF SOLUBLE SILICATES

Typical application fields and uses of soluble silicate products are as follows:

- Chemical industry (as raw materials for syntheses e.g. precipitated silica, zeolites, catalysts etc.)
- Detergent industry (as alkali, buffering agents, corrosion inhibitors)
- Pulp and paper industries
- Adhesives (e.g. tube winding, foil lamination, etc.)
- Textile processing
- Soil grouting
- Water and waste water treatment
- Oil reclamation
- Mineral ore flotation
- Inorganic binders for e.g.
 - Paints, plasters, special coating materials
 - Briquetting and agglomeration
 - Refractory and insulation materials
 - Foundry moulds and cores
 - Welding rods

In serving these industries more than 760 000 tons (calculated as SiO_2) of soluble silicates are produced in Western Europe (based on 2010 data).

5. REGULATORY STATUS OF SOLUBLE SILICATES

5.1 Product registration

Sodium, potassium and lithium silicates are Existing Chemical Substances according to EU regulations.

Identification numbers are as follows:-

	EINECS No.	CAS No.
Sodium silicates $\text{Na}_2\text{O} \cdot x \text{SiO}_2$	215-687-4	1344-09-8
Disodium metasilicate, anhydrous Na_2SiO_3	229-912-9	6834-92-0
Disodium metasilicate pentahydrate $\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$		10213-79-3
Disodium metasilicate nonahydrate $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$		13517-24-3
Potassium silicates $\text{K}_2\text{O} \cdot x \text{SiO}_2$	215-199-1	1312-76-1
Lithium silicates $\text{Li}_2\text{O} \cdot x \text{SiO}_2$	235-730-0	12627-14-4

In compliance with Council Regulation (EEC) No. 793/93 on Existing Chemicals, CEES members compiled as IUCLID data sets all published and internal data covering the chemical, physical, toxicological and ecotoxicological properties of sodium silicates, potassium silicates and anhydrous sodium metasilicate. (IUCLID = International Uniform Chemicals Information Data Base.) These were used as a starting point for the preparation of registration dossiers for these materials in accordance with REACH Regulation (EC) No. 1907/2006.

Soluble silicates are also listed in the national inventories of many countries; e.g. TSCA (USA), AICS (Australia), DSL (Canada), MITI/ENCS (Japan), ECL (Korea), SEPA/IECSC (China), PICCS (Philippines), ERMA/HSNO (New Zealand).

5.2 Classification according to EU Regulations

As explained previously, the classification of soluble silicates depends on the molar ratio of individual products. Specific Material Safety Data Sheets (MSDS) should always be consulted.

The classification of the different groups of soluble silicates is not related to their pH value, but is based on reports of skin and eye irritation tests which have been performed and documented in the past.

A direct relation between pH value and corrosive or irritant properties does not exist. As an example, a 0.4 % aqueous solution of caustic soda (NaOH) showing a pH value of ca. 13.0 is not classified as dangerous (neither corrosive nor irritant) according to EU classification and labelling regulations (CLP).

Full details of classifications for soluble silicates, including pictograms and recommended P-phrases are given in the Annex to this brochure, however a short summary is given in the tables below.

DSD/DPD: With respect to EU Directives 67/548/EC (Dangerous substances) and 91/155/EC (Dangerous preparations) including relevant amendments (respectively 2001/59/EC and 2001/60/EC), sodium (and potassium) silicates are classified as follows:

Molar ratio SiO ₂ : M ₂ O	Classification	
	Lumps/Powders	Solutions
< / = 1.6	Corrosive R34, 37 S22, 26, 36/37/39, 45	Corrosive R34 S26, 36/37/39, 45
> 1.6, < / = 2.6	Irritant R37/38, 41 S22, 26, 36/37/39	Irritant R38, 41 S26, 36/37/39
> 2.6, < / = 3.2	Irritant R36/37/38 S22, 26	Irritant R36/38 S26
>3.2	Powders: Irritant R36/37/38 S22, 26 Lumps: Not classified as dangerous S26	Solutions of >40% solids: Irritant R36/38 S26 Solutions of <40% solids Not classified as dangerous S26

Classification of Sodium Metasilicate (according to Annex 1, Dir 67/548/EC): R34, 37, S(1/2), S13, 24/25, 36/37/39, 45. Annex I index number 014-010-00-8.

GHS/CLP: With respect to Regulation (EC) No. 1272/2008 (CLP) and its amendments, sodium (and potassium) silicates are classified as follows:

Molar ratio SiO ₂ : M ₂ O	Classification	
	Lumps/Powders	Solutions
< / = 1.6	Danger Skin Corr. 1B/Eye Dam. 1 H314 STOT SE 3 H335 Met. Corr. 1 H290	Danger Skin Corr. 1B/Eye Dam. 1 H314 Met. Corr. 1 H290
> 1.6, < / = 2.6	Danger Skin Irrit. 2 H315 Eye Dam. 1 H318 STOT SE 3 H335	Danger Skin Irrit. 2 H315 Eye Dam. 1 H318
> 2.6, < / = 3.2	Warning Skin Irrit. 2 H315 Eye Irrit. 2 H319 STOT SE 3 H335	Warning Skin Irrit. 2 H315 Eye Irrit. 2 H319
>3.2	Powders: Warning Skin Irrit. 2 H315 Eye Irrit. 2 H319 STOT SE 3 H335 Lumps: Not classified as dangerous	Solutions of >40% solids: Warning Skin Irrit. 2 H315 Eye Irrit. 2 H319 Solutions of <40% solids: Not classified as dangerous

Classification of Sodium Metasilicate (according to Annex VI, Reg (EC) No. 1272/2008 and CEES recommendations): Danger Skin Corr. 1B/Eye Dam. 1 H314, STOT SE 3 H335, Met. Corr. 1 H290. Annex VI index number 014-010-00-8.

The use of harmonised H Phrases, pictograms and signal words as shown above is mandatory. Recommendations on the use of P Phrases for these products are given in the annex to this brochure.

Appropriate hazard communication and assessment of risks and safety remains the sole responsibility of each company.

5.3 Transport regulations

Only those soluble silicates that are classified as corrosive (molar ratio $\leq 1,6$) are subject to the UN dangerous goods transport recommendations. (Section 14 of the relevant MSDS should be consulted.)

For metasilicates ($\text{Na}_2\text{SiO}_3 \cdot x \text{H}_2\text{O}$ / $x = 0$ or 5 or 9; $\text{MR}=1.0$) the following classifications are applicable:-

ADR / RID: Class 8 / packaging group III – UN No. 3253

6. HANDLING AND STORAGE

6.1 General information and advice

All the soluble silicates, even those that are not classified as Dangerous Substances, are alkaline chemicals. Therefore contact with eyes, skin and clothes should be avoided and the usual procedures for handling all chemicals should be followed.

Usually the pH values of soluble silicate solutions are in a range between about 11.0 (e.g. $\text{MR} > 3.2$) and 13.0 (e.g. $\text{MR} 1.0$ – alkali metasilicates);

A lot of “every day materials” like soda ash, Portland or Aluminate cements, lime wash, lime based construction mortars show pH values in the same range.

6.2 Materials

For storage no aluminium, light alloy, galvanised steel and glass receptacles or pipes should be used. On contact with aluminium or light alloys hydrogen gas may be evolved. Steel, stainless steel and alkali stable plastic materials (e.g. HDPE) are generally appropriate.

6.3 Exposure limits

No occupational exposure limits have been established for soluble silicates. In animal studies, soluble silicate solutions lead to slight general toxicity when applied at high doses via oral uptake. Several animal species were tested and the most relevant no-observed-adverse-effect level from these studies was selected under REACH to derive both dermal and inhalation DNELs (derived no effect levels) of 1.49 mg/kg/d and 5.61 mg/m³, respectively. These values may be used to assess workplace exposure, however, they do not account for the local irritating effects of some soluble silicates on skin and the respiratory tract. Hence, aerosol formation should be avoided in the case of liquid formulations and for corrosive soluble silicates ($\text{MR} \leq 1.6$), the exposure limit for sodium hydroxide of 1 mg/m³ should be considered as a guidance value. For solid silicates or preparations, the dust limit according to national regulations (typically between 3-10 mg/m³, depending on particle size) may apply.

6.4 Fire precautions

- Soluble silicates are inorganic substances. They are not combustible, self-igniting or explosive.
- Soluble silicates have no oxidising properties.
- No dangerous decomposition products are known in case of fire or thermal heating.

6.5 Water hazard regulations

According to German Regulations on Water Hazard Alkali Silicates have been classified in Class 1 (= slightly hazardous to water) due to their alkalinity.

Sodium silicate glass lumps with molar ratio $\text{SiO}_2 : \text{Na}_2\text{O} > 3.2$ are not subject to water hazard regulations.

6.6 Edible fats and oils

Sodium silicate solutions are strongly basic and barely soluble in edible fats and oils. When used as a previous cargo to edible fats and oils it has to be transported as a solution, to enable effective transfer and tank cleaning. In its Scientific Opinion on the evaluation of the substances listed in the annex to Commission Directive 96/3/EC as acceptable previous cargoes for edible fats and oils, EFSA Panel on Contaminants in the Food Chain has concluded that sodium silicate solution meets the criteria for acceptability as a previous cargo for edible fats and oils. There are no reactions of concern with edible fats and oils, nor are any anticipated impurities likely to be present at levels of toxicological concern.

7. WASTE DISPOSAL

European Waste Catalogue (EWC) No. 060299 (alternatively 200115, especially for solid products).

For further information local regulations and MSDS guidelines should be consulted.

8. HAZARDS TO THE ENVIRONMENT AND HUMAN HEALTH

Under the OECD High Production Volume Chemicals Programme, a comprehensive hazard and initial risk assessment was performed for soluble silicates. Some important aspects of the OECD assessment are described under this section. For further detail it is referred to the published document on the website of the United Nations Environmental Programme (UNEP Chemicals 2006).

8.1 ECOLOGICAL ISSUES

8.1.1 pH value

Untreated soluble silicate solutions are generally alkaline (pH values > 9) and therefore neutralisation should be carried out before discharging to water/effluent systems. Once neutralised, no adverse effects on aquatic biosystems are to be expected.

8.1.2 Water solubility

- 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 > 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. Above a pH of 11 - 12 stable solutions of monomeric and polymeric silicate ions exist. The soluble content rapidly decreases when the pH is lowered to 9. Below pH 9 only a small proportion is present as soluble monomeric silicate ions, the majority existing as insoluble amorphous silica gel.

8.1.3 Partition coefficient / bioaccumulation potential

Soluble silicates are totally insoluble in n-octanol (as for most other organic solvents). The Oil/Water partition coefficient of these substances (as normally determined with n-octanol/water) is therefore not applicable or relevant. Soluble silicates have no bioaccumulation potential.

8.1.4 Biodegradability, chemical or biochemical oxygen demand (COD, BOD)

Soluble silicates are inorganic substances and therefore not amenable to biodegradation. In view of their chemical structure and inorganic nature, they are also not expected to be photodegraded. The substances have no COD or BOD impact on effluents.

In a simulation test, the elimination and influence of spray-dried sodium silicate (MR 2.1) on the biological activity of a model sewage treatment plant was determined. Continuous dosing of 25 mg sodium silicate/l had no adverse effects on the operation of the model sewage treatment plant. Elimination was only marginal; 90 - 100 % was detected in the effluent of the model sewage plant.

No significant inhibition of respiration was observed at exposure concentrations up to 100 mg/l sodium metasilicate (MR 1.0, 100 % active matter) for microorganisms from active sludge.

8.1.5 Behaviour of soluble silicates in natural aquatic systems

Dissolved silica resulting from commercial soluble silicates is indistinguishable from naturally dissolved silica. Depending on pH values, reaction with naturally occurring dissolved polyvalent metals (e.g. Ca, Mg, Fe, Al) will result in insoluble silicates or amorphous silica being formed. These products occur in abundance in natural soils and rocks.

8.1.6 Emissions of soluble silicates in comparison to natural input

A study of the fate and possible effects of soluble silicates (waterglass) emissions to surface water which was performed by TNO (van Dokkum et al. 2002), gave no indication of significant adverse effects on aquatic systems. The amount of soluble silicate introduced into the environment must be seen in the context of the background input due to geochemical weathering processes of silicate minerals. For example, the total flux of dissolved silicate transported by rivers to the sea in Western Europe is estimated to be 5 Mtons SiO₂/year (van Dokkum et al. 2004). The anthropogenic contribution to this total flux is only 4 %. However, in a local situation, the contribution of anthropogenic sources may be significantly higher: when four paper plants were analysed for their contribution to the SiO₂ background concentration of the receiving waters, a local increase of ca. 10 - 40 % was estimated (van Dokkum et al. 2004).

8.2 ECOTOXICOLOGICAL DATA

Acute toxicity testing in fish, invertebrates and algae indicate a low order of toxicity: the soluble silicates exhibit aquatic toxicities in excess of 100 mg/l irrespective of molar ratio or metal cation. The aquatic toxicities of the penta- and nonahydrate forms are expected to be in the same range as those for the anhydrous disodium salt. In general, toxic or lethal effects against aquatic organisms are related to the alkalinity of the test solutions rather than to any direct influence of the silicate species.

The following results were obtained in acute tests:

Fish:

<i>Danio rerio</i>	LC50 (96 h) = 210 mg/l (Na, MR 1.0)
<i>Danio rerio</i>	LC50 (96 h) = 1108 mg/l (Na, MR 3.46)
<i>Oncorhynchus mykiss</i>	LC50 (96 h) = 260 - 310 mg/l (Na, MR 3.1)

Leuciscus idus LC50 (48 h) > 146 mg/l (K, MR 3.9- 4.1)

Invertebrates:

Daphnia magna EC50 (48 h) = 1700 mg/l (Na, MR 3.2)

Daphnia magna EC50 (24 h) > 146 mg/l (K, MR 3.9- 4.1)

Algae:

Scenedesmus subspicatus E_bC50 (72 h) = 207 mg/l

E_rC50 (72 h) > 345 mg/l (Na, MR 3.0)

Microorganisms:

Pseudomonas putida EC0 (18 h) = 348 mg/l (Na, MR 3.46)

EC0 (18 h) = 3480 mg/l (Na, MR 3.46)*

Pseudomonas putida EC0 (30 min) = 3454 mg/l (Na, MR 3.0)*

Pseudomonas putida EC0 (30 min) = 1000 mg/l (Na, MR 1.0)

activated sludge EC50 (3 h) = >100 mg/l (Na, MR 1.0)

* neutralized test solutions

8.3 TOXICOLOGICAL DATA

The toxicological properties of soluble silicates are mainly governed by their intrinsic alkalinity. At a given concentration the alkalinity of silicate solutions is inversely correlated with the ratio SiO₂/M₂O: the lower the ratio, the higher the alkalinity. A clear correlation exists between oral toxicity as well as skin and eye irritation and the molar ratio; the toxicity and irritation increasing with decreasing ratio.

For sodium and potassium silicates the data have shown that the nature of the alkali ion has no effect on the biological properties. For example, results obtained with sodium silicate can be extrapolated to potassium silicates of the same molar ratio, and vice versa.

8.3.1 Acute oral toxicity (e.g. OECD 401)

Toxicity decreases in rats with increasing molar ratio from LD₅₀ of 1152 mg/kg bw for molar ratio 1.0 to 5700 mg/kg bw for 2.25. The one solitary study on potassium silicate fits well into the toxicity pattern of the sodium silicates. The observed toxicological symptoms in acute oral toxicity studies are indicative of effects due to alkalinity.

The following LD₅₀ results were obtained in acute oral toxicity tests:

Molar Ratio	Na / K	LD ₅₀ /rat/oral
3.27	Na	5150 mg/kg bw
2.25	K	5700 mg/kg bw
2.0	Na	3400 mg/kg bw
1.0	Na	1152 – 1349 mg/kg bw

8.3.2 Skin Irritation

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⁺ or K⁺) 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.

Irrespective of the counterion, silicates were found to be corrosive at molar ratios up to 1.6 and concentrations >50%. At molar ratios >1.6, silicates are irritating to the skin, while molar ratios >3.2 and concentrations <40% did not lead to irritative effects.

8.3.3 Eye Irritation

Only potassium silicates have been tested in OECD Guideline tests. 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 with sodium silicates 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 sodium metasilicate powder (molar ratio of 1.0).

8.3.4 Sensitisation

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.

8.3.5 Repeated Dose Toxicity

Soluble silicates have been tested in a number of repeated dose studies with exposures ranging from 28 to 180 days. The No Observed Adverse Effect Levels (NOAELs) determined revealed a low toxicity.

The NOAEL (90 d) of sodium metasilicate were 227 - 237 mg/kg bw/d for rats (highest tested dose level) and 260 - 284 mg/kg bw/d for mice. Sodium silicate had a NOAEL (180 d) of 159 mg/kg bw/d for rats (highest tested dose).

8.3.6 Mutagenicity

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, WR 3.3) induced no chromosomal aberrations in Chinese hamster V79 cells. *In vivo*, sodium metasilicate did not induce chromosomal aberrations in bone marrow cells of mice in a study performed similarly to OECD TG 476. From the available evidence it can be concluded that there is no evidence of a genotoxic potential for soluble silicates.

8.3.7 Carcinogenicity

The information available in the open literature does not indicate any potential for carcinogenicity. However, the informative value is very limited. Although no reliable carcinogenicity studies are available, a carcinogenic activity of soluble silicates is unlikely in view of the absence of any structural alerts for such a property.

8.3.8 Reproduction / developmental toxicity

In a developmental toxicity study, pregnant mice were administered 12.5, 50 or 200 mg/kg bw/d sodium metasilicate in aqueous solution from day 0 until 17/18 of gestation by daily gavage. Litter size and fertility index were unaffected at concentrations up to and including 200 mg/kg bw/d. Furthermore, no developmental effects were observed up to and including 200 mg/kg bw/d.

Also, in repeat dose toxicity studies with rats, mice and dogs the macroscopic and microscopic examination of reproductive organs did not reveal treatment-related effects.

In summary, no indications of reproductive effects for silicates have been reported.

9. PRODUCT REGISTRATION FOR SPECIAL APPLICATIONS

Soluble silicates have been registered for REACH with a wide variety of industrial, professional and consumer uses. A comprehensive list of identified uses can be found on the ECHA webpage:

<http://echa.europa.eu/de/information-on-chemicals/registered-substances;jsessionid=C976E3F5F316B60A4B28AEF989AA330E.live2>

The list below indicates specific application areas for soluble silicates. It is not exhaustive and is based on the current knowledge of the members. There may be additional specific national/regional requirements which should also be considered.

9.1 Drinking water treatment

Many natural waters already contain certain levels of silicates. Silicates are beneficial in that they can prevent the corrosion of water pipes, particularly for very soft water sources.

Examples of European and national regulations are:

- a) EC: According to the Drinking Water Directive 98/83/EC (amendment in preparation) and EN 1209 (Chemicals used for treatment of water intended for human consumption – Sodium silicate / September 2001) treatment with sodium silicate is allowed up to 15 mg SiO₂/l
- b) B: According to “Besluit van de Vlaamse regering van 13 december 2002 houdende reglementering inzake de kwaliteit en levering van water, bestemd voor menselijke consumptie” and “Belgisch Staatsblad /Moniteur Belge van 28/01/2003” treatment with sodium silicate is allowed up to 10 mg SiO₂/L.
- c) CH: CH: Verordnung des EDI vom 26. Juni 1995 über Fremd- und Inhaltsstoffe in Lebensmitteln (Fremd- und Inhaltsstoffverordnung, FIV) / Status October 2010 / (Sodium silicate is allowed up to 5mg/l calculated as Si).
- d) D: Trinkwasser-Aufbereitungsverordnung / 2007 – (15,0 mg/L SiO₂)
- e) N: Silicates approved as corrosion inhibitors and precipitation chemicals for drinking water
- f) E: According to the Real Decreto 140/2003 and the Orden SSI/304/2013 (Annex 1), in which sodium silicate is listed, soluble silicates can be used in drinking water treatment in compliance with EN 1209.
- g) SF (FIN): Silicates allowed as corrosion inhibitors and precipitation chemicals
- h) UK: Water Supply (water quality) Regulations - SI 3184/2000 - amended by SI 2734/2007.
List of approved water treatment products of the Drinking Water Inspectorate - sodium silicates are included in the list.
- i) USA: Sodium silicates approved as additives for drinking water up to 100 ppm
Select committee on GRAS substances – SCOGS-61, NT IS Pb 301-402/AS (1979)

9.2 Use in cleaning products for the food/drinks industry

- a) CH: Alkali silicates (“Waschalkalien”) may be contained in cleaning agents for food and drink processing equipment. (Stoffverordnung StoV, Anhang 4.2, Abs. 23/29.11.1995)
- b) F: Alkali silicates (“silicates alcalins”) may be contained in cleaning agents for food and drink processing equipment. (Décret no. 73-138 du 12 Fevrier 19973 / Annexe I – Arrêté du 25 Septembre 1985, art 2 “Substances admises dans des produits de nettoyage” – Matériaux au contact des denrées alimentaires / Produits de nettoyage de ces matériaux.)

9.3 Pulp, paper and cardboard production

- a) B: Sodium silicate is listed as acceptable filler for paper & cardboard intended for contact with fatty or hydrated foodstuffs. Koninklijk Besluit / Arrêt Royal 11/5/1992
- b) D: Paper and board intended for contact with food and drink products. Alkali silicates may be used as raw materials or production auxiliaries. 36. Empfehlung des BgVV: Papiere, Kartons und Pappen für den Lebensmittelkontakt- A: Papierrohstoffe / B: Fabrikationshilfsstoffe – No. 8.
- c) NL: Potassium and sodium silicates are listed in VGB, 5e suppl. – Januari 1992 – Hoofdstuk II / 1 Papier en karton voor algemeen gebruik 1.2.2 f
- d) USA: FDA / CFR 21 part 176: Indirect Food Additives – Paper and Paper-board Components: Sodium silicate is listed among the substances generally regarded as safe (GRAS) with respect to migration from paper or paperboard to foods.

9.4 Use in plastics intended for foods/beverage applications

- a) EC: Silicic acid is listed as FCM Substance No. 417 under Ref. No 85680 in Annex I of Commission Regulation (EU) No. 10/2011 on plastic materials and articles intended to come into contact with food.
Article 6(3) states that “the following substances not included in the Union list are authorised subject to the rules set out in Articles 8, 9, 10, 11 and 12:
(a) salts (including double salts and acid salts) of aluminium, ammonium, barium, calcium, cobalt, copper, iron, lithium, magnesium, manganese, potassium, sodium, and zinc of authorised acids, phenols or alcohols”.
From this it follows that potassium and sodium salts of silicic acid are authorized as additives which may be used in the manufacture of plastic materials and articles which come into contact with food.
- b) D: Silicates including mixed silicates of sodium and potassium may be used as fillers for plastic articles in contact with food or beverages. 52. Empfehlung des BgVV: Füllstoffe für Bedarfsgegenstände aus Kunststoff
- c) UK: SI 2619/2012 The Materials and Articles in Contact with Food Regulations 2012.

9.5 Use as a cosmetics ingredient

- EC: Ingredients for cosmetics are controlled by the Cosmetics Regulation 1223/2009. Soluble silicates are not mentioned in any list either banning or controlling their use in cosmetics, so that they may be used at the manufacturers' discretion. The INCI inventory of ingredients (International Nomenclature on Cosmetic Ingredients) includes both sodium and potassium silicate in its listings.

10. SUMMARY

Soluble silicates are a major class of chemicals finding a wide range of applications in numerous industry sectors. Product regulatory approval exists in many of these areas.

Based on their chemical and physical properties and their toxicological / ecotoxicological behaviour, it can be seen that soluble soluble silicates are, in general, low risk products. Although certain soluble silicates are classified as dangerous substances, this in essence is a consequence of the alkalinity of this group of chemicals. Alkalinity increases with alkali metal oxide M_2O content, which means of course, that alkalinity will be higher for lower molar ratio (MR) $SiO_2 : M_2O$ products.

CEES member companies are committed to provide users of soluble silicates with technical data and information as required in order to ensure the safe handling, application and disposal of this environmentally acceptable group of industrial materials.

11. LITERATURE





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The Soluble Silicates brochure is regularly updated.
Please check our website (www.cees-silicates.eu) for the latest version.





Annex

SOLUBLE SILICATES: Classification and labelling according to the Regulation on classification, labelling and packaging of substances and mixtures (CLP) in comparison to the former EU dangerous substances and/or preparations Directives (DSD/DPD)

The classification of soluble silicates depends on the molar ratio (SiO₂:M₂O) of individual products, with M being Na or K. Specific Material Safety Data Sheets (MSDS) should always be consulted. The classification of the different groups of soluble silicates is not related to their pH value, but is based on reports of skin and eye irritation tests which have been performed and documented in the past. The following table gives the comparison between the former classification in line with EU Directives 67/548/EEC (dangerous substances) and 1999/45/EC (dangerous preparations) including relevant amendments (respectively 2001/59/EC and 2001/60/EC) and the most recent GHS classification (Regulation (EC) No. 1272/2008).

Former legislation		CLP Regulation	
MR > 3.2			
Solid lump glass and aqueous solutions with solids <40% are not classified as dangerous			
MR > 2.6			
<i>Powders/lumps</i>			
<p>Xi</p>  <p>Irritant</p>	<p>R36/37/38 Irritating to eyes, respiratory system and skin</p>	 <p>Warning</p>	<p>Skin Irrit. 2 H315 Causes skin irritation Eye Irrit. 2 H319 Causes serious eye irritation STOT SE 3 H335 May cause respiratory irritation</p> <ul style="list-style-type: none"> • P261 - Avoid breathing dust. • P262 - Do not get in eyes, on skin, or on clothing. • P280 - Wear protective gloves/protective clothing/eye protection/face protection.. • P303+P361+P353 - IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. • P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
<i>Solutions</i>			
<p>Xi</p>  <p>Irritant</p>	<p>R36/38 Irritating to eyes and skin</p>	 <p>Warning</p>	<p>Skin Irrit. 2 H315 Causes skin irritation Eye Irrit. 2 H319 Causes serious eye irritation</p> <ul style="list-style-type: none"> • P262 - Do not get in eyes, on skin, or on clothing. • P280 - Wear protective gloves/protective clothing/eye protection/face protection. • P303+P361+P353 - IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. • P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

MR > 1.6 < / = 2.6			
<i>Powders/lumps</i>			
<p>Xi</p>  <p>Irritant</p>	<p>R37/38 Irritating to respiratory system and skin</p> <p>R41 Risk of serious damage to eye</p>	 <p>Danger</p>	<p>Skin Irrit. 2 H315 Causes skin irritation</p> <p>Eye Dam. 1 H318 Causes serious eye damage</p> <p>STOT SE 3 H335 May cause respiratory irritation</p> <ul style="list-style-type: none"> • P261 Avoid breathing dust. • P262 Do not get in eyes, on skin, or on clothing. • P280 Wear protective gloves/protective clothing/eye protection/face protection. • P303+P361+P353 IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. • P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
<i>Solutions</i>			
<p>Xi</p>  <p>Irritant</p>	<p>R38 Irritating to skin</p> <p>R41 Risk of serious damage to eye</p>	 <p>Danger</p>	<p>Skin Irrit. 2 H315 Causes skin irritation</p> <p>Eye Dam. 1 H318 Causes serious eye damage</p> <ul style="list-style-type: none"> • P262 Do not get in eyes, on skin, or on clothing. • P280 Wear protective gloves/protective clothing/eye protection/face protection. • P303+P361+P353 IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. • P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

MR \leq 1.6			
<i>Powders/lumps</i>			
 Corrosive	<p>R34 Causes burns R37 Irritating to respiratory system</p>	 Danger	<p>Skin Corr. 1B/Eye Dam. 1 H314 Causes severe skin burns and eye damage STOT SE 3 H335 May cause respiratory irritation Met. Corr. 1 H290: May be corrosive to metals</p> <ul style="list-style-type: none"> • P261 - Avoid breathing dust. • P262 - Do not get in eyes, on skin, or on clothing. • P280 - Wear protective gloves/protective clothing/eye protection/face protection. • P301+P330+P331 - IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. • P303+P361+P353 - IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. • P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. • P406 – Store in corrosive resistant/... container with a resistant inner liner.
<i>Solutions</i>			
 Corrosive	<p>R34 Causes burns</p>	 Danger	<p>Skin Corr. 1B/Eye Dam. 1 H314 Causes severe skin burns and eye damage Met. Corr. 1 H290: May be corrosive to metals</p> <ul style="list-style-type: none"> • P262 Do not get in eyes, on skin, or on clothing. • P280 Wear protective gloves/protective clothing/eye protection/face protection. • P301+P330+P331 IF SWALLOWED: rinse mouth. Do NOT induce vomiting. • P303+P361+P353 IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. • P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. • P406 – Store in corrosive resistant/... container with a resistant inner liner.

Whereas the use of harmonised H Phrases, pictograms and signal words as shown above is mandatory, the use of these P Phrases is recommended but not mandatory.

Appropriate hazard communication remains the sole responsibility of each company.

You will find more information about Soluble Silicates in our CEES brochure regularly updated and freely available on our website www.cees-silicates.eu