International Journal
for Applied Science
Personal Care Detergents Specialities

Reprint
from
4-2007

C.H. Baehr, W. Koehl:

Soluble Silicates – Highly Versatile and Safe

C.H. Baehr, W. Koehl*

Soluble Silicates – Highly Versatile and Safe

Keywords: Soluble silicates, waterglass, risk assessment, HERA project

Abstract

Soluble silicates are a major class of synthetic chemicals, surpassed in volume only by commodity acids and bases. Also known as waterglass, they represent a highly versatile group of compounds. Due to their many advantageous properties they are used in many different applications and industries.
In an effort to assess product safety and provide more transparency to consumers, a HERA risk assessment on the environment and human health was carried out. For the major application of soluble silicates, anthropogenic emissions to the environment and human exposure were estimated. Respective hazards were assessed, drawing together all available animal and human data. Quantitative measures of potential risk were derived and the class of compounds demonstrated to be environmentally friendly and safe.

Fig. 1 Silicate production

Fig. 2 Cooling of heated waterglass

Introduction

Soluble silicates belong to one of the oldest anthropogenic classes of chemicals. First accounts of manmade silicate date back to the third millennium BC. The technique of making silicates was further developed in Egypt around 1500 BC and by the Phoenicians, who became the greatest silicate makers of the ancient world.
Nowadays silicate products are manufactured and marketed in several forms and used in a wide range of different applications. Largest quantities of soluble silicates are used in the production of detergents, soaps and cleaners, followed by pulp and paper applications, water treatment, soil stabilisation and coatings. Considering the large volumes marketed, manufacturers want to ensure that products are environmentally friendly and safe for consumer use.
The risk posed by soluble silicates was assessed for use in the largest single application, i.e. detergents and cleaners, and comprehensive safety information, beyond hazard evaluation, generated (CEES HERA, 2005). In a first step potential environmental emissions were estimated and specific scenarios developed to calculate human exposure. Derived exposure levels were then combined with available animal and human hazard data. Thus, potential risk was quantified in an integrated approach.

Fig. 3 Silicate lumps

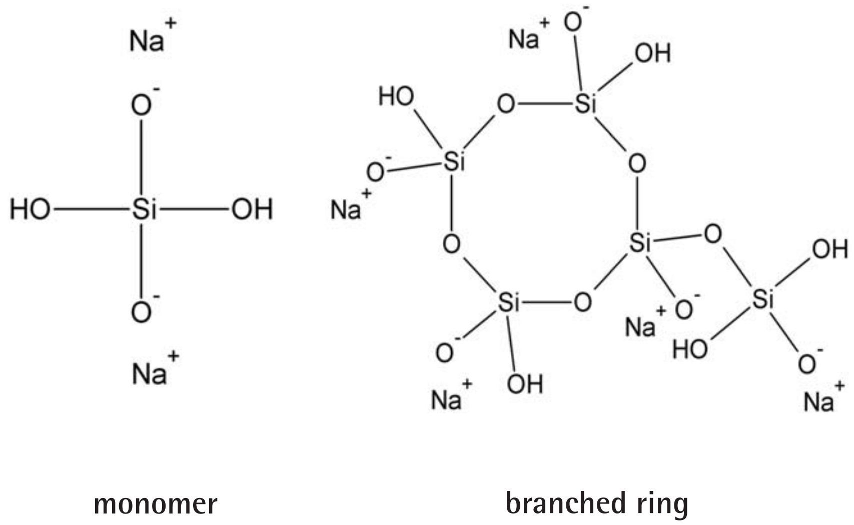

Fig. 4 Sodium silicate species

Soluble silicates definition and production

Raw materials for the production of silicates are quartz sand (or other sources, such as silica rich soils), alkali carbonates, such as soda ash (Na_2CO_3) or potash (K_2CO_3) and alkali hydroxides (e.g. NaOH, KOH, LiOH). Highest production volumes, representing approximately 90% of the total soluble silicate production, are reached for sodium silicate products in the form of lumps, liquor, hydrothermal liquor, powder or crystals. **Fig. 1** and **2** show soluble silicate production. **Fig. 3** shows the finished product in form of glass lumps.

Soluble (alkali) silicates such as sodium, potassium and lithium silicates are combinations of silica and alkali metal oxides in varying proportions. They do not follow a distinct stoichiometric chemistry and can not be assigned a specific chemical formula or molecular weight **(Fig. 4).** The general formula for soluble alkali silicates is:

$$M_2OxSiO_2$$

where M is sodium (Na), potassium (K) or lithium (Li) and x is the molar ratio, defining the number of moles of silica per mole of alkali metal oxide. More common in practical use is the weight ratio which can be obtained by dividing of the molar ratio by 1.032 (for Na_2O), by 1.568 (for K_2O) and by 0.497 (for Li_2O). Besides the ratio, the concentration determines a product's characteristics and allows distinguishing one product from another.

The pH-value of the concentrated product is usually in the range of 10-13. The fraction of silicate in solution is rapidly reduced when the pH drops to a value of 9. Below a pH-value of 9 only a small, but constant amount of silicate remains in solution.

Applications

Soluble silicates are extremely versatile ingredients as well as economical and effective. Their use in many different applications is due to the compounds' multifunctional properties, including its capacity for alkaline buffering, surface modification (corrosion prevention) and metal-binding. The main application, in terms of metric tonnes, is the production of detergents, soaps and cleaners.

In detergent products, soluble silicates are incorporated into liquid detergents, powders, tablets and bars. They provide extra benefit from metal cleaning to textile processing, washing of industrial equipment, to laundering and cleaning household dishes. Generally, silicates are used in combination with soaps, wetting agents, surfactants, bleaches, enzymes and various other ingredients. The value of silicates in detergency has been established through decades of research on the principles of cleaning.

The beneficial properties of silicates for detergency are their low interfacial tension, good emulsifying and suspending powers, reserve alkalinity for neutralising or saponifying soil materials and high buffering power. Corrosive alkali is moderated, so that sensitive metals or the enamel of porcelain are saved from corrosion. Introduction of strong acidic soils can be buffered effectively, avoiding a drop-off in pH and consequent loss in cleaning action. Silicates stabilize the bleach system by complexing metal ions and thus damaging effects on textiles are prevented. Finally, silicates increase the effectiveness of surfactants or soaps, by lowering the interfacial tension.

Soluble silicates regulatory status

Sodium, potassium and lithium silicates are Existing Chemical Substances according to current EU regulations **(Table 1).** In compliance with EU Directive 793/93 on Existing Chemicals, all relevant information on sodium silicates, potassium sili-

cates and anhydrous sodium metasilicate has been published in the International Uniform Chemicals Information Data Base (IUCLID), including physical-chemical, toxicological and ecotoxicological endpoints. Further, soluble silicates are also listed in many national inventories, e.g. TSCA (USA), AICS (Australia), DCS/DSL (Canada), MITI/ENCS-No. 1-508 (Japan) and ECL-No. KE-31002 (Korea).
Additionally, product registration exists for several specific applications. For example, in several countries sodium silicates are registered for drinking water treatment and allowed in food contact materials. Or, in some countries alkali silicates are registered as cleaning products for the food and drink industry or, for sodium and potassium silicates, for use in cosmetics. In the United States, silicates are either registered as generally regarded as safe (GRAS) or as food additives.

Substance	CAS No.	EINECS No.
Sodium silicates $Na_2O * xSiO_2$	1344-09-8	215-687-4
Disodium metasilicate, anhydrous Na_2SiO_3	6834-92-0	229-912-9
Disodium metasilicate, pentahydrate $Na_2SiO_3 * 5\ H_2O$	10213-79-3	229-912-9
Disodium metasilicate, nonahydrate $Na_2SiO_3 * 9\ H_2O$	13517-24-3	229-912-9
Potassium silicates $K_2O * xSiO_2$	1312-76-1	215-199-1
Lithium silicates $Li_2O * xSiO_2$	12627-14-4	235-730-0

Table 1 Silicates Registered in the EU

HERA to increase product safety

In an effort to assess product safety and provide greater transparency on potential risks to the consumer, posed by ingredients of products for home use, the makers of household cleaning products (AISE) and the chemical industry (Cefic) carried out a voluntary human and environmental risk assessment, as part of the human and environmental risk assessment (HERA) project (HERA, 2005).
The project provides necessary data to downstream producers and consumers for each to make informed decisions on products and use, and can serve as a model of how producers and downstream users can efficiently work together to e.g. fulfil the upcoming REACH requirements.
Up-to-date information can be found on the CEES website URL:
http://www.cees-silicates.org

Classification of soluble silicates

Based on their physical and chemical properties, toxicological and ecotoxicological behaviour, soluble silicates are generally considered safe, low risk chemicals.
The hazard classification of silicates is dependent on the molar ratio of the individual product. The higher the proportion of alkali metal oxide the more likely are irritation and corrosion to skin, eyes and, in case of powders, respiratory system. The only silicate classified as corrosive, in Annex 1 of the European dangerous substances directive 67/548/EC, is sodium metasilicate.

■ Environmental risk assessment

The environmental risk assessment was carried out according to the principles of the HERA guidance document and respective EU Technical Guidance Document (HERA, 2002; EU TGD, 2003). The risk characterisation is based on a detergent-relevant exposure assessment and on an effects evaluation considering all available ecotoxicological data. In addition, anthropogenic silicate emissions were assessed in the context of natural silicate flux.

Environmental fate

Released into the environment, pH and concentration lead to a dynamic polymerisation-depolymerisation equilibrium, with speciation into a variety of mono-, oligo-, and polymeric anions and amorphous silica. All soluble silicates exhibit very low vapour pressure and partitioning into the atmosphere is rather unlikely. They are moderately to highly soluble in water and practically insoluble in organic solvents, so partitioning into lipophilic compartments is also not relevant (CEES HERA, 2005).
As soon as soluble silicates reach the hydrosphere, they are diluted and de-polymerise rapidly to give molecular species indistinguishable from natural dissolved silica, such as H_4SiO_4 or SiO_2 (aq.). Based on their chemical structures and inorganic nature, they do not undergo biodegradation and they do not photodegrade. Notably, the silicates do not contribute to the chemical or biological oxygen demand (COD or BOD) of a water body.

Anthropogenic sources of soluble silicates

In Western Europe, total anthropogenic soluble silicate emissions range from 88 ktons to 121 ktons SiO_2/year (*van Dokkum*, 2004). The main application areas correspond to main emission sources: highest emissions result from detergent use, followed by pulp and paper production and waste water treatment, with 65 to 76, 21 to 43 and 2 ktons SiO_2 per year, respectively. Estimations of the total anthropogenic input average 4% of the total dissolved silica flux. Thus, considered in the context of natural silicate flux, the impact of manmade SiO_2 is rather low.

Environmental effects assessment

Based on the European Union System for the Evaluation of Substances (EUSES) calculations, emissions of soluble silicate are highest for the aquatic compartment. Emissions into the terrestrial compartment are negligible, based on the moderate to high water solubility and low octanol-water partitioning coefficients.
The effects assessment for soluble silicates thus concentrated on the aquatic environment. Effects of soluble silicates here are mainly governed by their intrinsic alkalinity. However, as most ecosystems are slightly acidic or alkaline naturally and buffer capacity is relatively high, potential effects of increased alkalinity are considered minimal. Further, a decrease in pH does not only lead to reduced effects of alkalinity, but also reduces bioavailability, as precipitation of amorphous silica increases at pH values below 11. Toxicity observed in laboratory settings is thus only relevant to those test systems and generally not transferable to intact ecosystems.
Nevertheless, numerous aquatic experiments, using a variety of species of fish, invertebrate and algae, assessing various types of soluble silicates, all revealed effect concentrations above the limit concentration (100 mg/L) for classification and labelling. Most comprehensive data was available for fish and thus, effect concentrations were extrapolated from observed toxicity in this species. Finally, no adverse effects of soluble silicates to micro-organisms of sewage treatment plants were recorded. In conclusion, the hazard assessment showed that soluble silicates can be considered to be of low toxicity to the aquatic environmental compartment.

Environmental risk characterisation

The environmental risk characterisation brings together predicted environmental concentrations (PEC), derived for regional and local concentrations and predicted no effects concentrations (PNEC), derived from observed results in toxicity tests. The ratio of PEC/PNEC values describes the potential risk of environmental concentrations to cause effects in the environmental compartment assessed. The lower the ratio (i.e. < 1), the less risk is posed.
For each of the relevant compartments, the ratios for soluble silicates emitted from commercial use of detergents, on a regional and local basis, were far below 1 (0.07 for regional and 0.23 for local surface waters, respectively), indicating that there is no risk to organisms. The ratio for sewage treatment plants was again below 1, for estimated and measured real-life PEC values, with 0.67 and 0.80, respectively, again indicating that there is little to no effect.
In consequence, soluble silicates in detergents pose no risk to the environment. Further, in the context of natural silicate flux, the anthropogenic input of soluble silicates to the environment is considered negligible. Total anthropogenic input is approximately 4% when compared to natural background levels of SiO_2.

Human health risk assessment

As for the environmental risk assessment, the human health risk assessment is based on the principles of the HERA project and the EU Technical Guidance Document (HERA, 2002; EU TGD, 2003). The assessment integrates soluble silicate exposure and hazard assessment to derive the potential risk posed by soluble silicates used in household detergent and cleaning products. Endpoints were chosen accordingly.

Consumer exposure

Consumer exposure was estimated using specific exposure scenarios. The development of these scenarios focused on soluble silicates in commercial detergents and cleaners for consumer use. Different types of detergents, soaps and cleaning products were considered and all possible exposure routes taken into account. Accidental exposure was also included.
For each possible exposure scenario and each of the products of the consumer detergent category or type of application, total consumer exposure concentrations were calculated. Typically, detergent products are not used concurrently, so cumulative exposure was not considered. Considering oral, dermal and inhalative exposure, concentrations for all possible routes were summed, yielding the potentially highest dose.
The different scenarios for the dermal exposure route included direct contact during hand washing of laundry, wearing of pre-treated clothes, direct contact to laundry or automatic dishwasher, surface and toilet cleaning products and indirect contact to skin via cleaned clothes. For the oral exposure route, food and drinking water as well as potential residues on dinnerware were considered. For the inhalation route, exposure to dusts, powder forms and aerosols were included.
The calculation for soluble silicate exposure for each exposure scenario showed that the maximum dose or total body burden, summing all potential routes of exposure, was calculated to be 5.1 µg SiO_2/kg bw/day, with the highest doses becoming available through skin.
Accidental overexposure was considered separately, with two main uptake routes of concern: exposure to the eye and the oral route. Accidental exposure of detergents to the eye may occur through splashing of solutions or through powder dusts. Ingestion of detergents or solutions containing detergents was considered for accidental oral exposure. Notably, accidental exposure to detergents has never caused a fatality, at least for all recorded cases in Germany and Great Britain, even though the number of cases may well be in the thousands.

Human hazard assessment

First summaries on the safety of silicates were published as early as 1920 and a number of more recent reports are available. Most reports focus on sodium silicates, especially sodium metasilicate, whereas only few address potassium or other alkali silicates. However, the hazard characteristics of potassium silicates are expected to be very similar to those of sodium silicates.

Silicates are ubiquitously present in environment, in food and drinking water and have been used for decades in many different applications. Adverse systemic effects from use have never been reported. Acute, subacute and chronic toxicity are very low and soluble silicates are not carcinogenic, mutagenic or reproductive toxins.

Numerous animal studies have shown, that local effects, such as irritation or corrosion to skin and eyes/mucous tissues, are the predominant effects noted. Most human data is derived from accidental exposure cases and a few attempted suicides. In man, exposure of soluble silicates to skin and eye may also cause effects ranging from mild skin irritation to corrosion. In contrast to soluble silicates, powder forms generally do not produce effects to skin when in dry form.

Repeated dose oral toxicity studies with sodium silicate or sodium metasilicate, including subacute and chronic studies, have been conducted in rats, mice, dogs and turkeys. Overall, only mild effects were observed and no mortalities occurred. Again, noted systemic toxicity is most likely linked to local tissue damage. *In vitro* genetic toxicity tests on bacteria, using sodium silicate and sodium metasilicate, were all negative. In *in vivo* chromosomal aberration tests, using sodium metasilicate, no adverse effects were noted either, confirming the *in vitro* results.

Human health risk assessment

In human risk assessments margins of exposure (MOE) are used to quantitatively describe the risk posed by a chemical hazard. They are equal to the ratio of the no observed adverse effect level (NOAEL) and the predicted exposure level. Inherently MOEs account for a hazards uncertainty and variability and include inter- and intra-species variation. The MOE or ratio between exposure and systemic NOAEL was calculated to be 31,000. Based on the low exposure levels and the high MOE, soluble silicates in commercial detergents were judged to present no risk to human health systemically.

However, if not handled according to product specifications or if products are misused, adverse effects, mostly in form of locally confined mild tissue damage, may occur. This is especially true for liquid products containing high concentrations of soluble silicates with low molar ratios. If exposed areas are rinsed, initially high concentrations of soluble silicate are diluted and adverse effects greatly reduced. Typically, amounts accidentally ingested are small and generally limited by the taste of products, with little consequences to human health.

■ Conclusion

Soluble silicates are a major class of chemicals, with a wide range of applications in a number of different industry sectors. Generally, soluble silicates are classified as safe low risk chemicals, with regulatory approval existing for many applications. Currently, the major application is in detergents and cleaners for household use.

To assess product safety and provide greater transparency on potential risks to manufacturers and consumers, the makers of household cleaning products carried out a human and environmental risk assessment for soluble silicates, according to principles of the HERA project. The risk assessment used scientific tools and expert knowledge to determine the chemicals hazard profile and the likely exposure of people and environment.

Based on their chemical and physical properties and their toxicological and ecotoxicological profile, the risk assessment on soluble silicates concluded that this class of chemicals generally does not pose a risk to the environment and consumers, especially when viewed in context of natural silicate flux and human intake through food and drinking water. Soluble silicates have been used for many centuries, but fulfil tomorrow's requirements of being environmental friendly and safe.

References

(1) Human & Environmental Risk Assessment on ingredients of European household cleaning products: Risk Assessment of AISE chemicals for human health and the environment, Guidance Document, Methodology, 2002

(2) Soluble Silicates: Human & Environmental Risk Assessment on ingredients of European household cleaning products. Draft for Public Comment, 2005

(3) Technical Guidance Document (Parts I-IV) in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances, 1996

(4) *Van Dokkum HP, Hulskotte JHJ, Kramer KJM and Wilmot J*: Emission, Fate and Effects of Soluble Silicates (Waterglass) in the Aquatic Environment. Environ. Sci. Technol. 38, 515-521, 2004.

**Correspondence address:*
Dr. Werner Koehl
Scientific Consulting Company GmbH
Microforum Ring 1
55234 Wendelsheim
Germany
Email: werner.koehl@scc-gmbh.de

■