APR 24 2002

The PQ Corporation

Corporate Headquarters
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April 22, 2002

Mr. Robert Pooler
National Organic Standards Board
Agricultural Marketing Specialist
USDA/AMS/TM/NOP
Room 2510-So., Ag Stop 0268
P.O. Box 96456
Washington, D.C. 20090-6456

Dear Mr. Pooler,

This petition is submitted by PQ Corporation to add potassium silicate to the National List of Substances Allowed and Prohibited in Organic Production and Handling. If any questions arise during the review of this petition, please feel free to call me.

ITEM A

We are petitioning potassium silicate to be included in the category:

Synthetic Substances Allowed for Use in Organic Crop Production

ITEM B

1. The substance's common name is ***Potassium Silicate.***

2. The manufacturer is:

PQ Corporation
P.O. Box 840
Valley Forge, PA 19482
800-944-7411

3. The intended use of potassium silicate is for ***plant disease control*** and as ***plant or soil amendment***.

4. Potassium silicate may be used with a variety of crops including:

rice
wheat
barley
sugar cane
tomatoes
beans
cucurbits
strawberries
grapes
roses
turfgrass
ornamentals

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Potassium silicate may be applied either as a nutrient solution that will provide approximately 100 ppm SiO_2 or as a foliar spray that will provide approximately 100-2000 ppm SiO_2. The application rate may be approximately 10-65 gallons per acre.

5. Manufacturing Procedure:

Potassium silicate is manufactured by combining high purity silica sand and potassium carbonate (both mined materials) and heating to about 1900-2300°F. The potassium carbonate and silicon dioxide fuse to form a molten potassium silicate glass with the evolution of carbon dioxide gas. This glass can either be 1) cooled and ground into a powder or 2) it may be dissolved in water to form a potassium silicate solution. The solution may subsequently be spray dried to form hydrous powder granules of potassium silicate.

6. Summary of Previous Reviews by State or Private Certification Programs: Not available.

7. EPA, FDA, and State Regulatory Authority Registrations: Potassium silicate is considered by the FDA to be interchangeable with sodium silicate for food use [see Attachment A]. Sodium silicate has GRAS (Generally Recognized as Safe) status for a number of food-related uses. The basis for its GRAS status is documented in SCOGS-61 “Evaluation of the Health Aspects of Certain Silicates as Food Ingredients” attached hereto as Attachment B. The FDA, therefore, considers potassium silicate to also have GRAS status.

The EPA’s Lead and Copper Rule authorizes sodium silicate as one of four treatment options for controlling corrosion in potable water systems.

** Furthermore, sodium silicate is on the National List of Substances Allowed and Prohibited in Organic Production and Handling as a floating agent for postharvest handling (Section 205.601 (l) (2)).**

8. CAS number: 1312-76-1

Product Labels: See Attachment C

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9. Physical Properties and Chemical Mode of Action:

Potassium silicate in a solid form is readily soluble in water. Dissolving the solid into water creates a solution with an alkaline pH. In liquid potassium silicates, a variety of silicate species are present in solution. These consist of silica tetrahedra (i.e., $Si(OH)_4$-based units) that may be single monomer units or dimers or polymers, all with potassium ions in loose association. As the solutions are diluted, as they will be to make foliar sprays and nutrient solutions, the number of monomers increases at the expense of the larger units. Therefore, potassium silicate solutions at use concentration provide soluble silica predominantly as $Si(OH)_4$, the form that can be absorbed by plants.

Research has shown that $Si(OH)_4$ units accumulate and polymerize at infection sites in the cell walls of leaves and xylem vessels. In monocots it was proposed that this accumulation of silicon provided a mechanical barrier to disease.

Potassium silicate is commonly used in hydroponic solutions for growing cucumbers. Research relating to that use indicates that silicon "likely plays an active role in disease resistance by being able to stimulate the defense mechanisms, namely phytoalexins, of cucumbers in reply to fungal attack." ["Silicon and Disease Resistance in Dicotyledons" by Fawe *et al.*, pp.159-169 in Silicon in Agriculture, ed. by L.E. Datnoff,G.H. Snyder, and G.H. Korndorfer, Elsevier, 2001.] In dicots, then, silicon seems to be a natural activator of the plant's defenses, bolstering its own immune system.

Other beneficial effects of silicon on plants have been observed including: greater yields, enhanced soil fertility, increased photosynthesis, improved plant architecture, regulated evapotranspiration, increased tolerance to toxic elements, and reduced frost damage. In general, silicon provided in its soluble $Si(OH)_4$ form lessens the effects of abiotic and biotic stresses.

a) Chemical interactions with other substances: Potassium silicate will react in two ways. First, the silicate species will react with any multivalent metal cation (i.e., in solution) such as Ca^{2+} and Mg^{2+} and form a metal silicate compound. Secondly, acidification lowers the solubility of silica and can result in formation of a silica gel. In cases where it is desirable to lower the pH of a potassium silicate solution for use on alkali sensitive plant species, substances such as compost tea and citric acid have been used successfully.

b) Toxicity and environmental persistence: Potassium silicate is not a Toxic Chemical under SARA Title III Section 313. Potassium silicate is completely soluble in water and yields potassium ions and silica that is indistinguishable from natural dissolved silica.

c) Environmental impacts from its use or manufacture: Carbon dioxide is a by-product of the manufacturing process. PQ operates a furnace that minimizes CO_2 emissions by careful oxygen control. CO_2 emissions fall below the limits required by the Commonwealth of Pennsylvania.

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d) Effects on human health: As an eye irritant there is no data for potassium silicate; however, chemically similar sodium silicate is regarded as an eye irritant. Potassium silicate produces no irritation to intact skin but well-defined irritation to abraded skin. Dust and spray mist are considered irritating to respiratory tract. Sodium silicate dissolves in the lungs and is rapidly eliminated in the urine. Ingestion may cause irritation to mouth, esophagus and stomach as well as vomiting and diarrhea.

For additional information, see MSDS in Attachment D and Attachment E, "Health, Safety, and Environmental Aspects of Soluble Silicates."

e) Effects on soil organisms, crops, or livestock: Studies on waste potassium silicate-based drilling fluids for the petroleum industry showed no negative impact on either seed germination or earthworm survival. [See Attachment F "Silicate Based Drilling Fluids: A Highly Inhibitive Mud System Offering HS&E Benefits Over traditional Oil Based Muds" by M. McDonald *et al.*, presented at the 2002 Amer. Assoc. of Drilling Eng. Technical Conference, Houston, TX]

10. MSDS: See Attachment D

Substance Report from National Institute of Environmental Health Studies: It appears there are no studies in the database that are relevant to potassium silicate.

11. Research Information:

Silicon has been used in plant disease control for centuries. ["Soluble Silicon: Its Role in Crop and Disease management of Greenhouse Crops" by Bélanger *et al.*, Plant Disease, April 1995, pp. 329-336.] The earliest investigations were done in the 1920's and 30's. Silica slags have commonly been used in the Orient as a silica source to control rice blast disease. ["Slag as an Internal Preventative Chemical for Rice Blast Disease" by H. Suzuki and K. Shigematsu, Plant Protection, 6:294-297, 1952 (Japanese); "Effect of Calcium Silicate Application to the Rice Fields on Resistance for Blast Disease and on Growth and Yields of Rice," by K. Nakagawa and Y. Kobayashi, Ann. Rept. Plant Prot. North Japan 7:34-35 (Japanese)]

PQ has recently sponsored two studies on potassium silicate to control powdery mildew. These are summarized below.

- Wine Grapes: Vineland Agricultural Research Station, Ontario, Canada

In 2001, a trial was conducted by Dr. Wendy McFadden-Smith, associate professor at Brock University (Niagara Falls, Ontario). As stated in her final report:

> *The experiment was conducted on five-to six-vine plots replicated four times in a randomized complete block design in a mature research vineyard. Sprays were applied with a tunnel sprayer at 1380 kPa at a rate of 500 L per ha pre-bloom*

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> *and 1000 L per ha post-bloom. All treatments provided significant control compared with the unsprayed check at early veraison. Good to excellent control of pre-harvest fruit infection was provided by QRD131, QRD132, Nutrol, Prudent Plus and AgSil and rotations of Kumulus with Nova (200 or 280 g), Flint (3 or 5 applications), Sovran and BAS500. The protective activity of the QRD formulations, Nutrol, Prudent Plus and AgSil was not sufficient to maintain control of late season powdery mildew infections for the 7 wk interval between the final spray and Oct disease evaluations. There was no significant increase in control of powdery mildew on leaves or fruit by increasing the rate of Nova or increasing the number of Flint applications. No phytotoxicity was observed in any treatment.*

The potassium silicate used in the case was PQ's AgSil™25 at a dose of 630 ppm and 1260 ppm SiO_2. In addition, AgSil™ 25 appeared to out perform the mono potassium phosphate (Nutrol) and bacillus subtilis (Serenade), products that are considered to be "green" along with potassium silicate.

• Watermelon: Earthwise Organics, Harrlingen, TX
Also in 2001, a trial was conducted on melons by Thomas Harr in Hidalgo County, Texas. In this case, the cooperating farmer requested that the spray solution be buffered to a pH of +/- 6.5 and combined with a foliar feed material. This was achieved by combining 1% potassium silicate AgSil™ 21 with 1% *Compost Tea*, an acidifying, proprietary foliar spray solution. This mixture was applied to the treated blocks in 3 separate treatments in May and June of 2001. At time of treatment watermelon plants were mature, about 2 weeks from first harvest. Some pressure from powdery and downy mildew was being experienced in the immediate vicinity, and other watermelon farmers were applying preventative applications of fungicides. The cooperating farmer used a broad spectrum fungicide, *Mankocide*, on all fields throughout the trial. He considered the trialed products successful in that he was not forced to use high-cost, narrow spectrum fungicides on the trial area. The farmer observed that five days after first application, the watermelons in the treated area looked healthier overall; they exhibited reduced vine dieback and better color and vigor as compared to the control. These observations continued through the trial period.

1991 data from our European affiliate shows increases in yield by 4.6% and average fruit weight of cucumbers by 4.6% with nutrient solution of 0.81 mmol/l Si from potassium metasilicate (SiO_2/K_2O mole ratio of 1).

Numerous studies have been published in the literature. See Attachment G for Bibliography and abstracts.

There are no contrasting opinions to our view that potassium silicate should be included on the National List.

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12. Petition Justification Statement:

Currently the National List lacks any substances that provide soluble silicon for soil amendment (except as micronutrients) or plant disease control. The importance of silicon for nutrition and its effectiveness for controlling diseases such as powdery mildew, pythium root rot, and rice blast are well established. Reducing the occurrence of diseases encountered in organic farming will enhance the growth, yield, and nutritional value of organic crops, and consequently, the success of organic farming in the U.S.

Potassium silicate should be an allowed synthetic substance on the National List because it provides a soluble, readily absorbed form of silicon [$Si(OH)_4$] as well as potassium, a primary nutrient. There are no nonsynthetic substances that could be used in place of the manufactured products. In addition, solutions of the manufactured potassium silicates are appropriate for both foliar spray and nutrient solution applications.

If you have any questions, please contact me at 610-651-4353.

Sincerely,

Judy LaRosa Thompson

Judy LaRosa Thompson, Ph.D.
Senior Technical Service Representative
Industrial Chemicals Division

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ATTACHMENT A

FDA Letter Stating Potassium Silicate is Interchangeable with Sodium Silicate

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DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION
WASHINGTON, D.C. 20204

June 8, 1978

Mr. Walter L. Schleyer
PQ Corporation
P. O. Box 258
Lafayette Hill, PA 19444

Dear Mr. Schleyer:

This will acknowledge the receipt of your letter of May 16, 1978 to Dr. Corbin Miles regarding certain silicates.

We have asked the Select Committee on GRAS Substances to include the direct food use of sodium silicate in its final review. However, this review will be limited to the use of sodium silicate in canned potable water as a corrosion inhibiting agent. Since the regulation of municipal and well water supplies are beyond the scope of the GRAS review, the other uses you cited will not be considered at this time. Additionally, there is no evidence available to us that sodium silicate has been used in egg preservation before 1958 or that a prior sanction on this practice was ever granted. This use will, therefore, not be considered.

We are of the opinion that potassium silicate and sodium silicate can be used interchangeably. Therefore, we plan to propose potassium silicate for the same uses as sodium silicate in the regulations.

As you know, for each substance that is regulated as a GRAS ingredient for direct food use, a food grade specification is required. If you have any information which will aid us in establishing the identities and specifications of potassium and sodium silicate, we would appreciate your making the data available to us.

Finally, sodium metasilicate is the subject of a separate monograph and will be re-evaluated by the Select Committee in the near future. It is therefore excluded from our present review of silicates.

We appreciate your interest in silicates. Please contact us if you have any new information or questions on these substances.

Sincerely,

Helen M Chao

Helen M. Chao, Ph.D.
GRAS Review Branch
Division of Food and Color Additives
Bureau of Foods

ATTACHMENT B

SCOGS-61: "Evaluation of the Health Aspects of Certain Silicates as Food Ingredients"

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LIFE SCIENCES RESEARCH OFFICE

SCOGS-61

EVALUATION OF THE HEALTH ASPECTS OF CERTAIN SILICATES AS FOOD INGREDIENTS

1979

Prepared for

Bureau of Foods
Food and Drug Administration
Department of Health, Education, and Welfare
Washington, D.C.

Contract No. FDA 223-75-2004

LIFE SCIENCES RESEARCH OFFICE
FEDERATION OF AMERICAN SOCIETIES
FOR EXPERIMENTAL BIOLOGY
9650 Rockville Pike
Bethesda, Maryland 20014

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Life Sciences Research Office
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NOTICE

This report is one of a series concerning the health aspects of using the Generally Recognized as Safe (GRAS) or prior sanctioned food substances as food ingredients, being made by the Federation of American Societies for Experimental Biology (FASEB) under contract no. 223-75-2004 with the Food and Drug Administration (FDA), U.S. Department of Health, Education, and Welfare. The Federation recognizes that the safety of GRAS substances is of national significance, and that its resources are particularly suited to marshalling the opinions of knowledgeable scientists to assist in these evaluations. The Life Sciences Research Office (LSRO), established by FASEB in 1962 to make scientific assessments in the biomedical sciences, is conducting these studies.

Qualified scientists were selected as consultants to review and evaluate the available information on each of the GRAS substances. These scientists, designated the Select Committee on GRAS Substances, were chosen for their experience and judgment with due consideration for balance and breadth in the appropriate professional disciplines. The Select Committee's evaluations are being made independently of FDA or any other group, governmental or nongovernmental. The Select Committee accepts responsibility for the content of each report. Members of the Select Committee who have contributed to this report are named in Section VII.

Tentative reports are made available to the public for review in the Office of the Hearing Clerk, Food and Drug Administration, after announcement in the Federal Register, and opportunity is provided for any interested person to appear before the Select Committee at a public hearing to make oral presentation of data, information, and views on the substances covered by the report. The data, information, and views presented at the hearing are considered by the Select Committee in reaching its final conclusions. Reports are approved by the Select Committee and the Director of LSRO, and subsequently reviewed and approved by the LSRO Advisory Committee (which consists of representatives of each constituent society of FASEB) under authority delegated by the Executive Committee of the Federation Board. Upon completion of these review procedures the reports are approved and transmitted to FDA by the Executive Director of FASEB.

While this is a report of the Federation of American Societies for Experimental Biology, it does not necessarily reflect the opinion of all of the individual members of its constituent societies.

Kenneth D. Fisher

Kenneth D. Fisher, Ph.D., Director
Life Sciences Research Office
FASEB

CONTENTS

I. INTRODUCTION

This report concerns the health aspects of using certain silicates as food ingredients. It has been based partly on the information contained in a scientific literature review (monograph) furnished by FDA (1), which summarizes the world's scientific literature from 1920 through 1973.* To assure completeness and currency as of the date of this report, this information has been supplemented by searches of over 30 scientific and statistical reference sources and compendia that are generally available; use of new, relevant books and reviews and the literature citations contained in them; consideration of current literature citations obtained through computer retrieval systems of the National Library of Medicine; searches for relevant data in the files of FDA; and by the combined knowledge and experience of members of the Select Committee and the LSRO staff. In addition, announcement was made in the Federal Register on April 21, 1978 (43 FR 17055) that opportunity would be provided for any interested person to appear before the Select Committee at a public hearing to make oral presentation of data, information, and views on the health aspects of using aluminum calcium silicate, calcium silicate, magnesium silicate, sodium calcium aluminosilicate, tricalcium silicate, silica aerogel, talc, sodium metasilicate, sodium zinc metasilicate, and methyl polysilicones as food ingredients; diatomaceous earth, silicon dioxides, sodium silicate, and talc as substances migrating to foods from paper and paperboard packaging materials; and sodium silicate and talc as substances migrating to foods from cotton and cotton fabrics packaging materials; or, in lieu of an oral hearing presentation, to submit a written statement. One company, the PQ Corporation, Lafayette Hill, Pennsylvania, submitted a written statement in lieu of an oral hearing presentation. No other requests were received and a hearing was not held.

As indicated in the Food, Drug, and Cosmetic Act [21 USC 321 (s)], GRAS substances are exempt from the premarketing clearance that is required for food additives. It is stated in the Act and in the Code of Federal Regulations (2) [21 CFR 170.3 and 170.30] that GRAS means general recognition of safety by experts qualified by scientific training and experience to evaluate the safety of substances on the basis of scientific data derived from published literature. These sections of the Code also indicate that expert judgment is to be based on the evaluation of results of credible toxicological testing or, for those substances used in food prior to January 1, 1958, on a reasoned judgment founded in experience with common food use, and is to take into account reasonably anticipated patterns of consumption, cumulative effects in

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*The document (PB-228 554/2) is available from the National Technical Information Service, U.S. Department of Commerce, P.O. Box 1553, Springfield, Virginia 22161.

the diet, and safety factors appropriate for the utilization of animal experimentation data. FDA (2) recognizes further [21 CFR 170.30] that it is impossible to provide assurance that any substance is absolutely safe for human consumption.

The Select Committee on GRAS Substances of LSRO is making its evaluations of these substances in full recognition of the foregoing provisions. In reaching its conclusions on safety, the Committee, in accordance with FDA's guidelines, is relying primarily on the absence of substantive evidence of, or reasonable grounds to suspect, a significant risk to the public health. While the Committee realizes that a conclusion based on such reasoned judgment is expected even in instances where the available information is qualitatively or quantitatively limited, it recognizes that there can be instances where, in the judgment of the Committee, there are insufficient data upon which to base a conclusion. The Committee is aware that its conclusions will need to be reviewed as new or better information becomes available.

In this context, the LSRO Select Committee on GRAS Substances has reviewed the available information on certain silicates and submits its interpretation and assessment in this report, which is intended for the use of FDA in determining the future status of these substances under the Federal Food, Drug, and Cosmetic Act.

II. BACKGROUND INFORMATION

Silicon in the form of silicon dioxide (sand and quartz) and as silicates (salts of the various silicic acids) occurs abundantly in nature, comprising about 25 percent of the earth's crust. Common silicate minerals include feldspar, mica, kaolin, talc, asbestos, perlite, and zeolites. The silicates are used in industrial products such as glass, pottery, cement, wallboard, and insulating and packaging materials. Sodium and potassium silicates are used in water purification systems, oil refining processes, and home and industrial cleaning agents. Silicates and silicon dioxide are present in practically all plants and animals and natural waters (3,4). Between 10 and 200 mg silicon as silicon dioxide is present in 100 g dry weight of normal human tissues. The lungs and lymph nodes in older adults may have levels several times this amount (3).

GRAS silicon compounds may be used in foods as anticaking agents, multiple purpose food substances, and as substances migrating to foods from paper, paperboard, cotton, and cotton fabrics. Other uses of silicon compounds in connection with foods include refining agents, release agents, filtering aids, corrosion preventatives in water, chewing gum base, washing agents for fruits and vegetables, and fillers in cross-linked polyester resins for use in contact with food surfaces.

The Code of Federal Regulations (2) lists the following silicon compounds as GRAS:

Anticaking agents:
- Aluminum calcium silicate (2 percent tolerance in table salt) [21 CFR 182.2122]
- Calcium silicate (2 percent tolerance in table salt and 5 percent in baking powder) [21 CFR 182.2227]
- Magnesium silicate (2 percent tolerance in table salt) [21 CFR 182.2437]
- Sodium aluminosilicate (2 percent tolerance*) [21 CFR 182.2727]
- Sodium calcium aluminosilicate, hydrated (2 percent tolerance*) [21 CFR 182.2729]
- Tricalcium silicate (2 percent tolerance in table salt) [21 CFR 182.2906]

Multiple purpose GRAS food substances:
- Silica aerogel (finely powdered microcellular silica foam having a minimum silica content of 89.5 percent), as a component of antifoaming agents [21 CFR 182.1711]; also called silicon dioxide and hydrated silica

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*Specific food not listed in Code of Federal Regulations.

Substances migrating to food from paper and paperboard products used in food packaging [21 CFR 182.90]:
- Diatomaceous earth filler
- Silicon dioxides
- Sodium silicate
- Talc

Substances migrating to food from cotton and cotton fabrics used in dry food packaging [21 CFR 182.70]:
- Sodium silicate
- Talc

Silicon dioxide is regulated separately (2) for use as an anticaking agent, a stabilizer in beer production, and an adsorbent for dl-tocopherol acetate and pantothenyl alcohol in tableted foods for special dietary use [21 CFR 172.480]. Talc, when used as a coating for rice, is considered GRAS by prior sanction (5), and diatomaceous earth is considered GRAS but unpublished (6).

Other unpublished GRAS uses of certain silicates include: talc in chewing gum base (7) and as a filler in cross-linked polyester resins for use on food contact surfaces (8); sodium silicate or potassium silicate at concentrations not greater than 100 ppm as a corrosion preventative in potable water (9); and diatomaceous earth for use as a filteraid (10,11). All the silicon compounds indicated above, whether published, unpublished, or regulated, are considered in this report. Table I summarizes the information in the foregoing paragraphs and adds information on other authorized uses of silicon compounds in, or in connection with, foods.

Sodium metasilicate, sodium zinc metasilicate, and methyl polysilicones will be evaluated in future reports of the Select Committee. Kaolin and bentonite are clays containing aluminum silicate salts; they are evaluated in another report of the Select Committee, and will not be considered here (17).

The Food Chemicals Codex (18,19,20) provides food grade specifications for the silicates indicated in Table II. No food grade specifications are given for aluminum calcium silicate, potassium silicate, sodium silicate, or talc; however, food grade specifications for sodium silicate and potassium silicate have been submitted to FDA for consideration (21). The silicates listed in Table II are insoluble in water except calcium silicate, which is very slightly soluble, and perlite, which is slightly soluble in cold water. The only silicon compounds being considered in this report that are significantly soluble in water are potassium and sodium silicates.

The Select Committee has been requested to review the health aspects of perlite, a non-GRAS, naturally-occurring silicates mixture, when used as a filtering aid in the processing of foods for human use (22). Perlite is a natural volcanic glass that, when crushed and expanded by heat, forms a low-density

TABLE I

Silicon Compounds Authorized for Use in Foods

Compound	Uses in foods	Reference
GRAS Substances:		
Aluminum calcium silicate	anticaking agent	21 CFR 182.2122
Calcium silicate	do	21 CFR 182.2227
Magnesium silicate	do	21 CFR 182.2437
Sodium aluminosilicate	do	21 CFR 182.2727
Sodium calcium aluminosilicate, hydrated	do	21 CFR 182.2729
Tricalcium silicate	do	21 CFR 182.2906
Silica aerogel (silicon dioxide; hydrated silica)	antifoaming agent	21 CFR 182.1711
Diatomaceous earth Silicon dioxide Sodium silicate Talc	substances migrating to food from paper and paperboard packaging materials	21 CFR 182.90
Sodium silicate Talc	substances migrating to food from cotton and cotton fabrics used in dry food packaging	21 CFR 182.70
GRAS by Prior Sanction:		
Talc	coating for rice	(5)
GRAS but not Published:		
Diatomaceous earth	filtering aid	(12)
Potassium silicate	corrosion preventative, water	(9)
Sodium silicate	corrosion preventative, water	(9,13-16)
Talc	in chewing gum base	(7)
	filler in food packaging	(8)

TABLE I (continued)

Compound	Uses in foods	Reference
Other authorized food uses:		
Silicon dioxide	adjuvant in microcapsules for flavoring oils	21 CFR 172.230
Silicon dioxide	anticaking agent; brewing stabilizer; special adsorbent	21 CFR 172.480
Silicon dioxide	defoaming agent	21 CFR 173.340
Aluminum and potassium silicate (mica)	pigments and colorants in resinous and polymeric coatings	21 CFR 175.300
Aluminum silicate (China clay)		
Calcium silicate	do	
Diatomaceous earth	do	
Magnesium silicate (talc)	do	
Silica	do	
Silica	defoaming agent in coatings	21 CFR 176.200
Silica	defoaming agent in the manufacture of paper and paperboard	21 CFR 176.210
Aluminum silicate	in coatings on cellophane used for packaging foods	21 CFR 177.1200
Silica		
Sodium silicate		
Aluminum silicate	filler for rubber articles used repeatedly in connection with foods	21 CFR 177.2600
Silica		

TABLE II

Food Chemicals Codex Specifications of Silicates (18-20)

Substance	Composition	Limits of Impurities, ppm			
		Arsenic	Fluoride	Heavy metals as lead	Lead
Calcium silicate	CaO^a, SiO$_2$^{a}, H$_2$O^a	≯3	≯50	≯40	≯10
Diatomaceous silica	Loss on drying ≯10%; loss on ignition ≯7%; nonsiliceous substances[b] ≯25% for natural powders	≯10			≯10
Magnesium silicate	≮15% MgO; ≮67% SiO$_2$ (on anhydrous basis) ≯10% H$_2$O	≯3	≯20	≯40	≯10
Silicon dioxide (silica aerogel; hydrated silica)	≮90% SiO$_2$ (silica aerogel) ≮89% SiO$_2$ (hydrated silica) ≯6% loss on drying (hydrated silica) ≯6% loss on ignition	≯3		≯30	≯10
Sodium silicoaluminate (sodium aluminosilicate)	≮66% SiO$_2$; ≯71% after drying ≮9% Al$_2$O$_3$; ≯13% after drying ≮4%Na$_2$O; ≯7% after drying ≯8% loss on drying; loss on ignition ≮8%--≯11%	≯3		≯10	
Perlite	Fused sodium potassium aluminum silicate	≯10			≯10

[a] Not more than the percentage stated or range claimed by vendor.

[b] For calcined or flux-calcined powders ≯3% loss on drying and ≯2% loss on ignition.

material (20). Corn syrup, cornstarch, and sugar refining, brewing, cola beverage and fruit juice manufacturing are examples of food industries that use perlite filteraids. The percent solubility of food grade perlite was reported as 0.044 in water, 0.036 and 0.13 in hydrochloric acid solution at pH 5 and pH 3, respectively, and 0.046 and 0.054 in pH 9 solutions of ammonium hydroxide and sodium hydroxide (23).

Table III lists the concentrations of mineral extractives of 8 samples of perlite filteraid derived from three different ore sources in the United States (24). The analyses from which the data for Table III were obtained were performed on water extracts of 20 g of each filteraid sample in 200 ml water at 96°C for 8 h. The extract was filtered through a 0.45 µm millipore filter prior to analysis. Because one of the New Mexico B samples showed a concentration of cadmium of 0.48 ppm, analysis of an aliquot of the same sample was repeated at a different laboratory. No cadmium was detected (25). Lead and arsenic concentrations from 20 g perlite samples extracted in 200 ml water at pH 6.5, hydrochloric acid solutions at pH 3 and 5, ammonium hydroxide and sodium hydroxide solutions at pH 9, were less than 0.01 ppm, which was the limit of detectability of the analytic method used (24). Chemical analyses of samples of commercial, food grade diatomaceous earth filteraid materials are shown in Table IV (26).

Talc is a basic magnesium silicate $Mg_3Si_4O_{10}(OH)_2$. It occurs as a metamorphic mineral often associated with serpentine or tremolite. These are types of magnesium silicates, certain forms of which are economically important as asbestos (29,30). Asbestos fibers have been detected in some commercial samples of talc and in samples of talc-coated rice, but a regulatory method for analyzing talc samples for asbestos content had not been adopted as of July, 1977 (31,32) and this appears to remain the current status. Asbestos occurs in the drinking water of many U.S. communities in mean concentrations ranging from 7 thousand to 39.3 million fibers per liter, and in the air of some urban areas in average concentrations ranging from 0.09 to 70 nanograms per cubic meter (33).

TABLE III

Water Extractives[a] of Perlite Filteraids Derived from Ores from Three Sources (24)

	Range of concentrations in ppm New Mexico A (2 samples)	 New Mexico B (2 samples)	 Arizona (4 samples)
Na	32.0 - 46.0	30.0 - 47.0	19.0 - 21.0
Si	4.6 - 12.0	12.0 - 20.0	28.0 - 39.0
K	1.8 - 3.3	3.2 - 10.0	1.0 - 1.7
Al	0.18 - 0.45	0.066 - 0.34	0.97 - 1.6
Ca	0.082 - 0.32	0.059 - 0.26	0.48 - 0.96
Li	0.046 - 0.11	0.016 - 0.019	--[b]
Mg	0.034 - 0.037	0.037 - 0.084	0.030 - 0.063
Cd	--[b]	--[b] - 0.48[c]	--[d]
Sn	0.0088- 0.017	0.12 - 0.55	--[b] - 0.013
B	0.025 - 0.13	0.087 - 0.18	0.15 - 0.32
Fe	0.020 - 0.041	0.017 - 0.048	0.047 - 0.32
Mn	0.0047- 0.0047	0.0084- 0.029	--[b] - 0.0091
Pb	--[b] - 0.018	--[b] - 0.059	--[b] - 0.12
Ga	0.0085- 0.012	0.0072- 0.012	0.018 - 0.12
Ni	0.014 - 0.017	0.0029- 0.046	0.0026- 0.0096
Mo	0.014 - 0.026	0.055 - 0.066	0.019 - 0.027
V	0.0029- 0.011	0.013 - 0.023	--[b] - 0.0051
Cu	0.028 - 0.043	0.024 - 0.22	0.0028- 0.0051
Ag	0.0014- 0.0016	0.0007- 0.0018	--[b]
Zn	--[b]	--[b] - 0.78	--[b]
Ti	--[b] - --[e]	--[b]	0.0022- 0.0049
Sr	--[b] - --[e]	--[b]	--[b]
Cr	0.0088- 0.014	0.0042- 0.014	0.0025- 0.0037
Zr	--[b]	--[b]	--[b] - 0.0023
other elements	nil	nil	nil

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[a] 20 g perlite filteraid in 200 ml water at 96°C for 8 h followed by filtration through a 0.45 μm millipore filter.

[b] None detected.

[c] No cadmium detected in a separate analysis by a different laboratory (see text, page 8) (25).

[d] Not analyzed.

[e] Trace.

TABLE IV

Analyses of Food Grade Diatomaceous Earth Filteraids (26-28)

A. Composition, percent by weight

	Sample 1 (26)	Sample 2 (27)	Sample 3 (27)[a]
SiO_2	88.6	88.0	92.0
Al_2O_3	4.3	0.75	0.9
Fe_2O_3	1.34	1.5	1.5
TiO_2	0.20	--	--
CaO	0.48	0.35	0.35
MgO	0.60	0.35	0.35
Na_2O	3.49	--	--
K_2O	0.72	--	--
$Na_2O + K_2O$	--	0.85	2.4
Cd	--	not detected	not detected
As	--	0.00001 to 0.00004	0.00001 to 0.00004
Pb	--	0.00001 to 0.00004	0.00001 to 0.00004

B. Extraction analysis, ppm[b]

	Atomic Absorption Spectrophotometry	
	Sample 4 (28)	Sample 5 (28)
Sb	0.05	0.05
Bi	0.1	0.1
Cd	0.030	0.030
Cu	0.03	0.03
Pb	0.00005	0.0002
Mo	4.949	2.146
Se[c]	0.01	0.01
Ag	0.005	0.005
Sn	0.2	0.2
Zn	0.214	0.236

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[a] Mean values of 3 samples.

[b] Done in accordance with Food Chemicals Codex method for arsenic (20).

[c] Colorimetric method.

III. CONSUMER EXPOSURE DATA

A subcommittee of the National Research Council (NRC) (6) surveyed manufacturers by questionnaire concerning the addition of GRAS substances to foods and estimated the possible average daily intake of these substances by persons in various age groups. Based on information supplied by those manufacturers who reported adding the substance to at least one food product in each food category, a weighted mean was calculated for the usual and maximal percentage addition of the substance to food products in the food categories. Weighted means of the usual level of addition of the several silicate compounds to food categories are shown in Table V. Many foods within these categories probably do not contain added silicates.

The NRC survey listed synonyms for three of the GRAS silicon compounds as follows: calcium silicate (tricalcium silicate); magnesium silicate (magnesium trisilicate); and silica aerogel (silica, silicon dioxide). Consequently, the quantities shown in Tables V, VI, and VII may include some of these synonymous compounds.

The NRC subcommittee (6) calculated possible average daily intakes (Table VI) based on Market Research Corporation of America data on the mean frequency of eating foods by food category, U.S. Department of Agriculture data on mean portion size of foods in these categories, and the assumption that all food products within a category contain the substance at the level shown in Table V. Such an assumption is likely to lead to overestimates of intake, and the NRC subcommittee has recognized that in most cases its calculations of possible intakes are overstated, often by a considerable margin. In the case of silicates, it appears that overestimations may also have occurred through errors of reporting data included in Table V. For example, the relatively high concentrations of aluminum sodium silicate and of calcium silicate in the categories baked goods, baking mixes, and dairy product analogs, and the high concentration of aluminum sodium silicate in the category soups, and soup mixes, may pertain to dry mixes and not to the foods as consumed. Furthermore, it should be noted that a manufacturer is likely to use only one anticaking agent in a product. Thus, if a product contains one silicate, it is unlikely to contain another.

An alternative calculation of per capita daily intakes can be made from annual poundage data provided in the NRC reports (6,34) on five silicates used in foods (Table VII). Such disappearance data are likely to be somewhat in excess of per capita consumption. Nevertheless, the data in Table VII suggest considerably lower per capita intakes than those presented in Table VI. The Select Committee considers the data in Table VII to be more reasonable estimates of average intakes. Table VII also provides estimates of the relative amounts of each compound used in 1970

TABLE V

Level of Addition of Silicates to Foods by Food Category (6)

Food category	Aluminum sodium silicate (Sodium alumino-silicate)	Calcium silicate (Tricalcium silicate)	Magnesium silicate (Magnesium trisilicate)	Silica aerogel (Silica, Silicon dioxide)	Sodium calcium aluminosilicate, hydrated
	Weighted mean percent				
Baked goods, baking mixes	0.68	0.16	<0.01	0.03	
Breakfast cereals	< 0.01			0.01	
Grain products, such as pastas or rice dishes	0.04	0.05	<0.01	0.08	
Fats and oils	0.04	0.19			
Milk, milk products	0.04			0.05	
Frozen dairy desserts, mixes	< 0.01				
Meat products	< 0.01	0.01		0.01	<0.01
Poultry products	0.01	0.01		0.01	<0.01
Fish products	< 0.01	0.02		0.01	
Condiments, relishes, salt substitutes	0.17				
Candy, soft		0.01	<0.01		
Sweet sauces, toppings, syrups	0.39				
Gelatins, puddings, fillings	0.03				
Soups, soup mixes	0.42	0.03		0.02	<0.01
Snack foods	0.63	0.13		< 0.01	<0.01
Beverages, nonalcoholic	0.08	<0.01		0.04	
Nuts, nut products		<0.01			
Gravies, sauces	0.06	0.03		0.05	
Dairy products analogs	0.88	0.49			
Hard candy				0.01	
Seasonings and flavors	0.54	0.30		0.41	

Levels of addition of silicates are the weighted means of the levels reported by manufacturers as their usual addition to one or more products in a food category. For discussion of weighted mean, see text, also Section X and Exhibit 59 of reference 6. Blanks in the table mean that the substance is not added to the foods indicated.

TABLE VI

Possible Average Daily Intake of Added Silicates by Individuals Over 2 Years of Age (6)

Substance	Intake (mg)
Aluminum sodium silicate	1250
Calcium silicate (tricalcium silicate)	300
Magnesium silicate (magnesium trisilicate)	2
Silica aerogel (silica; silicon dioxide)	150
Sodium calcium aluminosilicate, hydrate	1

TABLE VII

Quantities of Certain GRAS Silicon Compounds Added Annually to Foods and Corresponding Calculated Per Capita Daily "Intake"

Substance	Relative amounts used[a] 1975/1970	Total used (1975) kg	Per capita daily intake[b] mg
Aluminum sodium silicate	0.70	1,400,000	18
Calcium silicate (tricalcium silicate)	0.48	260,000	3
Magnesium silicate (magnesium trisilicate)	1.0[c]	36,000[c]	0.5[c]
Silica aerogel (silica; silicon dioxide)	4.0	38,000	0.5
Sodium calcium aluminum silicate, hydrate	--[d]	25[c]	0.01[c]

[a] Based on reports from those respondents to the National Research Council survey who submitted information for both 1970 and 1975 (34).

[b] Based on total consumption in 1975 and a U.S. population of 215 million.

[c] The relative amounts compared for magnesium silicate (magnesium trisilicate) in the second column are for the years 1970/1960. The total usage of magnesium silicate (magnesium trisilicate) and sodium calcium aluminum silicate, hydrate in the third column is for the year 1970. The per capita daily intake for both substances in the fourth column is based on a population of 205 million. Insufficient data were received in the 1975 resurvey to justify calculations.

[d] No data were reported for 1960 or 1975.

and 1975 in those foods where comparable figures are available and indicates trends in use in foods of several silicates over a recent 5-year period. Data on the use of silica aerogel as a multiple purpose GRAS food substance (component of antifoaming agents) are included in the table. Although there is little change in the relative amounts of the silicates used in the 5 years, the use of silica aerogel during that period increased approximately four-fold.

About 50,000,000 kg of perlite filteraids and between 145,000,000 and 172,000,000 kg of diatomaceous earth filteraids are estimated to be used annually for food processing in the United States (28,35). Based upon these figures, the approximate daily per capita amounts of perlite and diatomaceous earth filteraids used in this country are 0.7 and 2 g, respectively. It is emphasized that these are not consumer exposure values. For example, a representative amount of perlite filteraid needed to process 100 gallons of corn syrup (equivalent to 950 pounds of syrup) is 4 pounds (28). Crude hypothetical examples of possible per capita consumption of some of the water extractives of perlite filteraids, based on (a) the data in Table III; (b) the arbitrary assumption that the entire food use of perlite filteraids involves only aqueous feed liquors; and (c) an assumption that all feed liquors are exposed to the perlite at 96°C for 8 h, are: sodium, 2.63 mg; potassium, 0.43 mg; silicon, 2.17 mg; lead, 8 µg (lead was undetectable in some samples). These hypothetical intakes are small compared to those resulting from natural occurrence of these elements in foods.

Typical use levels of diatomaceous earth filteraids in the food industry are shown in Table VIII. In beer production, for example, representative use of diatomaceous earth filteraids would be 150 pounds of filteraid (about 1000 ft^2 of filter, 1/8 inch thick) on stream for about 5 h at a filtration rate of 500 to 1000 gallons per minute (primary step), and for 10 h at a rate of 1000 gallons per minute (polish step). Thus, in the primary step, the exposure of the feed liquor is between 1000 and 2000 gallons per pound of diatomaceous earth and 4000 gallons per pound in the polish step (36). In addition, dry powdered diatomaceous earth is added to the beer at levels of 0.1 to 0.2 percent as body feed. A rule in the beer industry is to use about 0.33 pounds of filteraid per barrel of beer (31.5 U.S. gallons).

A hypothetical estimated daily per capita consumption of silicon dioxide, the most abundant acid extractable of diatomaceous earth filteraids, is about 50 µg, based upon data from a composite sample indicating that the silicon dioxide in an acid extract was 0.0218 percent by weight of filteraid (26), and upon the arbitrary assumption that all foods filtered through diatomaceous earth filteraids are acidic aqueous feed liquors. However, the data in Table VIII indicate that not all feed liquors so filtered are acidic solutions or mixtures. It is understood that

TABLE VIII

Typical Uses of Diatomaceous Earth Filteraids in the Food Industry

(Based upon information in reference 35)

Product filtered	Type[a] filteraid used	Typical amount of body feed[b]
Alginates	FC	1 - 1.5%
Apple cider	all	0.25 - 1.5%
Beer		
primary step	C, FC	0.2 - 0.35 lb/bbl
polish step	C	0.05 - 0.1 lb/bbl
Beet sugar		
(standard liquor)	FC	0.1 - 0.5 lb/ton beets
Refined cane sugar		
washed sugar	C, FC	0.15 - 0.8%[c]
affination sugar[d]	FC	0.5 - 2.0%[c]
Cottonseed oil	FC	0.1 - 0.3%
hydrogenated	N	0.05 - 0.5%
Gelatin	FC,C	0.1 - 2.0%
Glucose syrup	N, C, FC	12 - 28 lb/1000 gal
Grape juice	FC	0.2 - 2.0%
Pectin (citrus)	C, FC	1.0 - 3.0%
Soya oil	FC	0.1 - 0.8%
Vinegar	N, C	0.1 - 0.25%
Potable water	FC	1 - 5 parts/part turbidity[e]
Wine		
rough step	FC	10 - 25 lb/1000 gal
polish step	C	2 - 5 lb/1000 gal

[a] N=natural; C=calcined; FC=flux-calcined [Calcining converts part of the amorphous silica to crystalline form, mostly cristobalite, and permits enlarging and controlling particle size. In flux-calcining, a flux, such as 6 percent by weight of soda ash, is added to the diatomaceous earth. In use, any residual soluble alkali is removed during prewash with water (36)].

[b] Quantity of diatomaceous earth added to the liquid being filtered, expressed as percent by weight except as otherwise noted.

[c] Based on brix, a measure of sugar concentrations.

[d] Treatment of raw sugar crystals with sugar syrup to remove adhering film of molasses.

[e] A measure of suspended solids.

the brewing industry considers 5 ppm the upper limit for mineral extractives in beer; further that centrifugation is replacing primary filtration (36).

No manufacturer surveyed by NRC (6,34) reported the use in foods of aluminum calcium silicate. No estimates are available of the amounts of diatomaceous earth, silicon dioxide, and sodium silicate that might enter food by abrasion or migration from paper and cotton packaging materials.

Because of the ubiquitous distribution of silicates in water, soils, and plant and animal tissues, diets free of silicates are not easily prepared. It would be difficult to estimate accurately the daily intake of silicates as natural constituents in foods. However, Baumann (37) reported the silicon content (as silicon dioxide) of raw potatoes at 10.1 mg per kg, Brötchen (rolls) at 28.5 mg per kg, and milk and beer at 2.1 and 131 mg per liter, respectively. In general, the city water of Europe and America contains from 2 to 7 mg silicon per liter (3). Examples of concentrations of sodium silicate when used as a corrosion inhibitor in potable water are 100 ppm (23 mg silicon per liter) in canned emergency drinking water and 8 ppm (1.8 mg silicon per liter) in municipal or domestic water supplies (38).

Talc is used in the coating of rice and also may be used in chewing gum base and as a filler in food packaging (Table I). Four companies reported that talc was used in production of chewing gum in the NAS/NRC survey of industry, but information on the amount retained in the gum was not provided (6). In 1974/1975, about 115 million lb of milled rice were talc coated, excluding shipments to Alaska, Hawaii, and U.S. territories (39). This represents a per capita annual consumption of about 0.5 lb. Coated rice is preferred by certain population groups in Hawaii, New York, and California (32). Nearly all rice consumed in Hawaii is talc coated, and shipments in 1974/1975 totaled about 58 million pounds or about 35 kg per capita. Per capita distributions of rice, coated and uncoated, for the same year in New York and California were about 4 and 5 kg, respectively. Individuals within these populations, particularly in the latter two states, probably consume much greater quantities of coated rice than the per capita value. Assuming that 1 percent by weight of a 1:1 talc-glucose coating is applied to rice (40) and that the coating was not removed before cooking, per capita consumption of talc in Hawaii would have been about 0.5 g per day. However, washing milled rice before cooking is reported to be a common practice of many Americans, especially those who consume large quantities of rice (32). Indeed, Food Inspection Decision No. 67, issued April 15, 1907 pursuant to the Food and Drugs Act of 1906, ruled that each package of coated rice must be labeled with instructions for washing which, if followed, would remove the talc-glucose coating. Hence, per capita consumption of talc from coated rice is probably much less than 0.5 g per day in those populations that consume the largest quantities of coated rice.

Experiments with dry packaged and shipped salt in direct and continuous contact with uncoated paper containing up to 6 percent tremolitic asbestos showed that less than 0.01 ppb asbestos migrated into the salt (31). In view of the abrasive properties of salt compared to most other dry foods and the relatively high asbestos content of the test paper compared with that expected in talc-filled paper or paperboard, the test result would represent a maximum migration value.

IV. BIOLOGICAL STUDIES

In recent years, silicon has been classified as an essential trace element in the chicken (41), and evidence for a silicon deficiency state in rats has been presented (42). Silicon is presumed to participate in bone calcification and it may be a component of collagen and the polysaccharides of the connective tissues (43). It is not known whether dietary silicon is essential for human nutritional needs.

Absorption and excretion

Both soluble and insoluble silicates are present in a wide variety of foods. The absorbability of ingested silicon compounds varies directly with their solubility in water; however, the degree of absorption of insoluble silicon compounds is not clearly established (44). Available evidence suggests that ingested silica derived from sodium silicate is indistinguishable from the dissolved silica of natural waters. At or below 120 ppm of silicon dioxide, aqueous solutions of sodium silicate contain only monomeric silica as the stable species (45), and this equilibrium condition should prevail because concentrated forms of sodium silicate depolymerize rapidly when they are diluted with water (46). Various investigators have suggested that insoluble silicates may be partially converted to soluble forms by hydrochloric acid and other digestive secretions (44,47,48). Monomeric silicic acid is rapidly absorbed from the gut and distributed throughout the extracellular fluid (37). Enteral administration of silicates to experimental animals results in increased urinary silicate output above basal levels, but no significant variation in blood levels (49,50). Levels of blood and urinary silicates in guinea pigs given various inorganic silicates in the diet and parenterally, suggested to Sauer and his associates (50) that the urinary excretion of silica is limited by restricted absorption from the gut; the kidneys can excrete much larger amounts of silica than are normally absorbed; and the absorption of ingested silica is limited by its solubility in the contents of the alimentary canal. Urinary excretion of silicic acid, a normal constituent of human urine, varies from 10 to 30 mg per day (51). The absorbability of ingested silicon dioxides appears to be slight (44). Studies of the effects of feeding various silicon compounds to laboratory animals have generally shown the substances to be innocuous under the test conditions; no signs or symptoms suggesting interference with absorption of other dietary components have been documented. Phillips _et al._ (52) reported that approximately 95 percent of single doses of tritium-labeled talc administered orally to rats and guinea pigs was excreted in the feces within 4 days. Based upon all parameters of their study, the authors concluded that talc, administered orally to rats, guinea pigs and mice, remains in the gastrointestinal tract and is completely eliminated within 3 to 4 days.

The determination of silicon in biological material is difficult, and prior to about 1955, much of the experimental work on silicon content of tissues was conducted with methods that are now known to be nonspecific (53). Reported values for silicon concentration in the blood and tissues have varied by factors of 10 to 100 by the different analytical methods (54). Thus it is impossible to interpret the significance of many of the earlier papers reporting changes in tissue levels of silicon with age, diseases, and various treatments.

Acute toxicity

Although silicates vary considerably in physical properties and solubility in aqueous solvents, most of the silicates added to foods as anticaking and antifoaming agents are insoluble in water and relatively inert. With few exceptions, the available acute toxicity data were derived from tests in which the silicon compounds were administered intravenously, intraperitoneally, subcutaneously, or intratracheally. Such parenteral experience is not generally relevant to the evaluation of oral toxicity. For example, evidence that pulmonary damage follows the aspiration of certain silicates is of little significance with respect to the toxicity of silicates used as food additives. Reports of acute toxicity of silicates in man such as fatalities following aspiration of talcum powder (55,56) and talc embolism from the intravenous injection of crushed drug tablets containing talc are evidence of particulate damage by other than oral routes of administration (56).

According to unpublished reports available to the Joint Food and Agriculture Organization/World Health Organization Committee on Food Additives (49), the oral LD_{50} of sodium silicate in rats is >3 g per kg body weight. The acute oral LD_{50} of sodium silicoaluminate in rats is 1.05 g per kg (57), and 10 g per kg for perlite (23,58).

Colloidal silicic acid given intragastrically to three dogs in single doses of 25, 30, and 50 ml (equivalent to 416, 500, and 833 mg per kg body weight in a 6 kg animal) resulted in "general indisposition" and tachypnea "a short time" after administration of the compound, refusal to eat and bloody diarrhea on the second day, and death on the third day (59). The gastric and intestinal mucous membranes were "strongly hyperemic" and the gastric mucosa showed scattered hemorrhagic spots. Lungs, heart, liver, spleen, and kidneys were "very congested" and showed spotty fatty degeneration. The cause of death was not stated. A fourth dog, given a total of 7.5 g colloidal silicic acid orally for 4 days in divided doses (equivalent to approximately 312 mg per kg body weight per day in a 6 kg animal) remained "in good health" but had "abundant" diarrhea on the fourth day. Another dog, given intragastric doses of approximately 15 mg per kg body weight of colloidal silicic acid daily for 9 days tolerated the substance well.

In man, the estimated oral lethal doses are >15 g per kg body weight for silica (silicon dioxide) and magnesium trisilicate and between 0.5 and 5 g per kg for sodium silicate (49). Except for the foregoing information on sodium silicate, sodium silicoaluminate, silicon dioxide, perlite, and magnesium trisilicate, no data on the acute oral toxicity of the silicates under consideration in this review are available.

Short-term studies

Weanling rats fed a diet containing diatomaceous earth at a level of 5 percent (estimated intake varied from about 12 g per kg body weight per day at the start to about 5 g per kg at the end of the experiment) for 90 days gained weight more rapidly than controls and showed no pathological changes in their tissues. Silica accumulation in liver, kidney, and spleen was considered negligible (60). In another study in weanling rats, various silica preparations of different particle sizes were fed as 10 percent of the diet (estimated to be about 14 g per kg body weight per day at the start and 6 g per kg at the end of the experiment) for 3 months (61). Histologic examinations showed no lesions in the gastrointestinal tract, liver, spleen, pancreas, adrenals, and mesenteric lymph nodes.

Several unpublished reports on short-term effects of feeding rats silicates and silicon dioxide for 3 months also revealed no adverse effects on growth rate or tissue pathology (49). Newberne and Wilson (62) fed rats silicon dioxide, aluminum silicate, sodium silicate, or magnesium trisilicate for 4 wk at 0.8 g per kg body weight per day (as silicon dioxide). A few animals receiving magnesium trisilicate or sodium silicate demonstrated polydipsia, polyuria, and soft stools, no gross or microscopic renal lesions were found. Young beagles of both sexes were given the above-named compounds daily for 4 wk at the level of 0.8 g per kg body weight. Seven of the eight females and all of the eight males fed sodium silicate and all of the nine males and nine females fed magnesium trisilicate showed gross and microscopic renal damage including inflammatory changes; no renal lesions were observed in animals fed silicon dioxide or aluminum silicate (62).

Special studies

Sodium silicoaluminate. No evidence of teratogenicity was observed after oral administration of sodium silicoaluminate at levels up to 1600 mg per kg per day to pregnant mice (day 6 through day 15 of gestation); to pregnant rats (day 6 through day 15 of gestation); to pregnant hamsters (day 6 through day 10 of gestation); or to pregnant rabbits (day 6 through day 18 of gestation) (63). No structural defects were found in chick embryos injected with an aqueous suspension of sodium aluminosilicate into the yolk (up to 97 mg per kg) and into the air cell (up to 210 mg per kg) at 0 and 96 h. At levels of 50 mg per kg or above, there was a significantly higher mortality rate by both routes of administration, and at 25 mg per kg the increase in mortality rate was noted when the compound was given at the start of embryonic development (64).

Sodium silicoaluminate did not induce mutations in host-mediated assays with Salmonella typhimurium and Saccharomyces cerevisiae or in a dominant lethal assay in which male rats were given (by gastric intubation) 4.25, 42.5, or 425 mg per kg sodium silicoaluminate daily for 5 days prior to mating (57).

Calcium silicate. No evidence of teratogenicity was observed when hydrated calcium silicate was administered orally in daily doses up to 1600 mg per kg to pregnant mice and rats on days 6 through 15, to pregnant hamsters on days 6 through 10, and to pregnant rabbits on days 6 through 18 of gestation (65). No structural defects were found in chick embryos injected with a suspension of a glycerol-alcohol mixture containing hydrated calcium silicate into the yolks at 0 or 96 h, or into the air cells at 96 h at levels up to 100 mg per kg (66). Hydrated calcium silicate did not induce mutations in host-mediated assays with S. typhimurium and S. cerevisiae, nor did it produce significant aberrations in the bone marrow metaphase chromosomes of rats when given in vivo, or abnormal changes in anaphase chromosomes of human embryonic lung cells in tissue culture (67).

Silica aerogel (silicon dioxide). No evidence of teratogenicity was found in the evaluation of orally administered silica aerogel given daily at levels up to 1600 mg per kg to pregnant hamsters and pregnant rabbits, and at levels up to 1340 mg per kg to pregnant mice and up to 1350 mg per kg to pregnant rats (68). The schedule of administration of the compound was the same as noted for sodium silicoaluminate. No structural defects were found in chick embryos given an aqueous suspension of silica aerogel by injection into the yolks at 0 and 96 h, and into the albumen at 0 and 96 h at doses up to 200 mg per kg by both routes. At levels of 10 mg per kg or higher in the yolks and 20 mg per kg or higher in the albumen, there was significant embryotoxicity (69). Silica aerogel did not induce mutations in the host-mediated assay with S. typhimurium or S. cerevisiae, or in the dominant lethal assay in rats at 1.4, 14, and 140 mg per kg, suspended in saline and given by oral intubation (70). In addition, cytogenetic tests with rat bone marrow metaphase chromosomes and human embryonic lung cells in tissue culture showed no significant chromosomal aberrations.

Talc. No evidence of teratogenicity was observed when talc was administered by oral intubation in daily doses up to 1600 mg per kg to pregnant mice and rats; at levels up to 1200 mg per kg to pregnant hamsters; and up to 900 mg per kg to pregnant rabbits (71). The schedule of administration of the compound was the same as noted for sodium silicoaluminate.

Talc, suspended in a mixture of equal parts of glycerol and sterile water, was tested for teratogenic effects in chick embryos via the air cell at 0 h, the albumen at 96 h, and the yolk at 0 and 96 h (72). No evidence of teratogenicity was obtained, but some embryotoxic effect was noted at doses of 100 mg per kg, or higher. Talc did not induce mutations in the host-mediated assay with S. typhimurium or S. cerevisiae, or in the dominant lethal assay in rats at 30, 300, and 3000 mg per kg suspended in saline and given by oral intubation (73). In addition, cytogeneticic tests with rat bone marrow metaphase chromosomes and human embryonic lung tissue culture cells showed no significant chromosomal aberrations.

Asbestos in talc. An attempt was made to correlate the higher incidence of gastric carcinoma among Japanese men with a preference for polished rice treated with talc and a possible association with asbestos fibers in the talc (74). Asbestos fibers in the talc-coated rice have been identified by electron microscopy (75). However, it has been ascertained that talc-coated rice has never been sold in Japan (76), and the notion of a causal relationship between talc-coated rice and stomach cancer was thought to have little scientific support (75).

Several workers have investigated the ability of ingested asbestos fibers to penetrate tissues in rats. Gross et al. (77) reported results of independent investigations conducted in three laboratories. In the first laboratory, suspensions of 400 mg of finely ground amosite or taconite mine tailings in 1 ml water were administered to groups of 10 rats. Two treated rats from each series and one control animal were killed 1, 2, 7, 14, and 21 days after treatment. Portions of various tissues were fixed for microscopic examination and 1 to 5 g portions were digested in 5 percent sodium hypochlorite until the solution was cleared, centrifuged, and the sediment was then examined in the electron microscope for the presence of fibers. In only one of 10 rats gavaged with taconite were fibers found in a digest of tissues other than those of the gastrointestinal tract. In the digest of lung tissue from this animal, three fibers were found. Except for one rat whose esophagus had been perforated, none gavaged with amosite had fibers in the digest of tissues outside the gastrointestinal tract. No digest of tissues from the gastrointestinal tract of rats of either group killed after the 48 h period contained fibers.

In another study conducted in the first laboratory (77), ground amosite and taconite tailings were incorporated into oleomargarine at 10 and 20 percent concentrations, respectively. Rats deprived of all other food than the oleomargarine admixture for 6 days consumed 2.2 to 5 g amosite and 6.0 to 10 g taconite in this period. Two rats from each group were killed 1, 2, 3, 4, and

5 weeks after the dust feeding was completed. Tissues were collected and treated as described above. Electron microscopic study of sections of the intestinal wall revealed no fibers. Digest of the mesentery of an amosite-fed rat contained a chrysotile fiber and similar digests of mesentery from two other amosite-fed rats contained two fibers each. A single fiber was found in the digest of mesenteric tissues of one taconite tailings-fed rat.

In the second laboratory, crocidolite or chrysotile asbestos was sieved to a fiber length no greater than 100 µm and was incorporated in butter at concentrations of 0.2 or 0.4 percent (77). Rats were given a single dose of either 20 or 40 mg crocidolite and killed 7 to 19 days later; others were fed 10 mg crocidolite or chrysotile once weekly for 16 weeks, then sacrificed. Tissues were examined by optical microscopy after sectioning and after ashing. Neither penetration of the gastrointestinal mucosa nor transmigration of optically visible fibers was detected.

In the third laboratory (77), 10 mg of ground chrysotile or crocidolite were fed weekly in butter to groups of 12 rats. Examination by light and transmission electron microscopy of tissue sections from animals killed 1 and 3 months after start of ingestion gave no evidence of penetration of asbestos fibers.

Westlake _et al_. (78) fed a semipurified diet containing 6 percent chrysotile (about 1.2 g daily) asbestos dust or 6 percent cellulose to female Wistar rats. Two rats were killed after 3 months and sections of their colons examined by electron microscopy. Another rat was killed 3 days after asbestos had been eliminated from the diet. The colon, mesenteric nodes, and spleen were prepared for electron microscopy. Chrysotile particles, 0.5 to 1 µm in length, were detected in intercellular and interstitial locations of the colonic epithelium. Entrance of particles appeared to be through the goblet cells; some appeared to be penetrating the cell membrane at the base of the goblet cells. Fibers were also found in the lamina propria in both interstitial substance and smooth muscle cells. Possible contamination of tissue sections with surface fibers present in the gastrointestinal tract concerned the investigators. Fewer intracellular asbestos fibers were present in tissues from animals examined after elimination of asbestos from the diet had resulted in feces free of fiber.

Bolton and Davis (79) fed male SPF Han rats, initially 10 weeks old, chrysotile, crocidolite, or amosite asbestos in a margarine formulation as an _ad libitum_ supplement to a standard laboratory diet. Average weekly asbestos consumption was 250 to 300 mg per rat. Two rats were fed asbestos 1 yr and, after 1 mo on a diet free from asbestos, were killed, gastrointestinal tract removed, washed, muffle ashed, ash acid washed, and aliquots taken for electron microscopy. Only one possible asbestos fiber was found in a total of 180 preparations of gut residue from the two animals. In another study, gut tissues from rats fed chrysotile, crocidolite, or amosite were examined at 2 wk, 3 mo, 6 mo, and 1 yr after start of ingestion. Histological examination of tissue sections by light and electron microscopy showed no pathological changes and there was no evidence of penetration of asbestos fibers into the tissues.

The investigators noted that the quantity of asbestos ingested by rats in this study (about 40 mg per day or 100 mg per kg) was about 50,000 times the ingestion maximum for severely occupationally exposed workers calculated from exposure data.

Storeygard and Brown (80) injected 4 to 5 ml of a suspension of amosite asbestos fibers (about 9.4 x 10^9 fibers per ml, ranging from 0.5 to 25 µm in length and 0.12 to 1.8 µm in diameter) via cannula into an isolated segment of rat jejunum <u>in vivo</u>. One hour later, the cannula system was flushed with saline, the rats killed, jejunum segment detached, and sections fixed. Examination of the mucosa from the five rats exposed to amosite fibers showed some fibers penetrating (but only part of the fiber length embedded) the epithelial surface in three of them. An occasional fiber was found enmeshed within the interstices of the lamina propria.

In a long-term feeding study, groups of 28 to 35 SPF rats (Wistar strain) were fed once weekly for 18 wk 10 mg of North West crocidolite asbestos or Transvaal crocidolite (77). Animals were allowed to survive until they became ill or died a natural death. All tissues suspected of neoplastic change were examined histologically. No lesion of any kind was seen that could be related to the ingested asbestos. Smith (81) fed 45 hamsters diets throughout life containing 1 percent chrysotile or amosite asbestos (about 1 g per kg body weight). No gastric neoplasms were observed.

Gibel <u>et al</u>. (82) fed groups of 25 male and 25 female Wistar rats, 10 wk of age, commercial rat chow to which asbestos filter material (52.6 percent chrysotile asbestos, nature of remainder not stated), or talc ("customary standard quality") was added in amounts to provide 20 mg (50 mg per kg) per day. Twelve malignant tumors were observed among 42 asbestos-treated animals after an average of 441 d on the diet: 1 lung carcinoma, 4 kidney carcinomas, 3 reticulum cell carcinomas, and 4 liver carcinomas. Seven benign tumors including 1 lung adenoma, 2 cholangiomas, 2 stomach papillomas, and 2 mammary fibroadenomas were also observed. Two liver cell carcinomas and 5 mammary fibroadenomas occurred in 49 untreated controls. Three liver carcinomas and four mammary fibroadenomas were observed among 45 talc-treated rats after an average of 649 d on the diet.

In 1975, the Commissioner of Food and Drugs concluded that, on the basis of available test data, the asbestos content of talc used in the manufacture of food- or drug-contact paper and paperboard does not represent a potential contaminant of packaged food or drugs (31). The Food and Drug Administration is sponsoring a program to develop a practical assay method for asbestos fibers and the National Institute of Environmental Health and Safety is supporting toxicological studies of orally administered asbestos with rats and hamsters (31,83).

Diatomaceous earth. From the ages of 30 to 75 days through their lifespan, rats of the Sherman strain fed a diet of 95 percent rice and 5 percent kieselguhr (estimated to be about 4.1 g per kg body weight per day at the start and 2.5 g per kg at the end of the experiment) showed a high incidence of papilloma of the forestomach described as epithelial hyperplasia and hyperkeratosis without evidence of malignant change (84). Rats fed a diet of polished rice also had a high incidence of papilloma of the forestomach, but significantly less than those fed rice and diatomaceous earth together. The sex of the rats was not indicated in the report. However, Wistar rats of both sexes fed 5 percent diatomaceous earth in their diet (estimated intake varied from about 12 g per kg body weight per day at the start to 5 g per kg at the end of the experiment) for over 90 days at another laboratory demonstrated no pathologic changes (60).

Magnesium trisilicate. Magnesium trisilicate has been administered to patients for many years as an antacid in the treatment of peptic ulcer and other disorders associated with epigastric distress. Patients may ingest several grams per day for many years without serious adverse effects. However, occasional reports of patients with urinary calculi containing silica have appeared; prolonged use of magnesium trisilicate as an antacid was a common feature in the histories of these patients who, as of 1964, numbered nine cases recorded in the world literature (85-87). No renal malignancies were noted within this group of patients and renal parenchymal damage was not observed. In 1962, Herring reported finding no silica stones among 10,000 urinary calculi analyzed by crystallography and x-ray diffraction (88). Magnesium trisilicate and magnesium aluminosilicate are listed among the acceptable antacid product ingredients by the Advisory Review Panel on Over-the-Counter Drugs (89). In its review, the Panel took note of the rare occurrence of silica stones in patients taking magnesium trisilicate for prolonged periods of time. Marković and Arambasić (90) fed adult guinea pigs drinking water containing a suspension of finely divided silicon dioxide (ground quartz), particle size 1 to 3 μm, at 50 mg per liter and at 250 mg per liter (6 and 30 mg per kg body weight). After 4 to 6 wk, interstitial nephritis with hyaline tubular cast formation and parenchymal atrophic changes were noted. The authors suggested that the nephrotoxicity was caused by the release of silicic acid which reacted with the renal proteins at an acid pH. Marković suggested an association exists between endemic (Balkan) nephropathy and malignant tumors of the upper urinary tract in Bulgaria, Yugoslavia, and Romania and the silica content of the drinking water (91). The suggestion is of interest but requires further study, particularly in view of the unknown etiology of Balkan nephropathy (92).

FAO/WHO reports on silicates

In 1969, a FAO/WHO report (93) set no limit, within good manufacturing practice, for the acceptable daily intake of silicon dioxide, silica aerogel, hydrated silica, silicic acid, dehydrated silica gel, aluminum silicate, magnesium silicate (including talc and magnesium trisilicate) and sodium aluminosilicate. In 1970, the FAO/WHO Joint Committee on Food Additives (94) recommended that a microscopic test be developed to identify asbestos fibers in talc and kaolin (hydrated aluminum silicate), and in 1974 the FAO/WHO Committee again set no limit for the daily intake of silicon dioxide and the other silicates listed above, except for magnesium silicate and talc (49). Magnesium silicate and talc were temporarily not limited, with the expectation that further work would elucidate the reported kidney damage in dogs fed magnesium silicate (62) and a satisfactory method for estimating asbestos-like particles in talc and magnesium silicate would be developed (49).

Reactions to parenteral silicates

The Select Committee is aware of the extensive literature on the potential toxicity of inspired silicate particles. In addition, fibrous nodular lesions in the peritoneum caused by talc dust from surgical gloves and the intentional use of talc to induce adhesions of the visceral and parietal surfaces of the pleural cavities in treating pneumothorax are well documented examples of the tissue reactions to talc as a foreign material. Pneumoconiosis from chronic inhalation of silicate dust represents a similar tissue response. The pathological changes in reactions to silicates have recently been reviewed (95). The postulated relationships between mesothelial cell proliferation in response to silicates and chronic exposure to asbestos particles and the development of lung neoplasms (which is assumed to involve a lag period of 15 to 20 yr) remain controversial; however, the chronic inflammatory reaction to silicates is not disputed.

Gardner and Cummings (96) found that silica particles 1 to 3 μm in diameter injected intravenously into rabbits in divided doses over several weeks were localized in the liver. They produced a nodular cirrhosis and marked interstitial fibrosis. Larger particles (6 to 12 μm) were localized in lymph nodes and the spleen, and the largest particles injected (10 to 12 μm) were filtered out during pulmonary circulation. Persorption of ingested silicon carbide crystals has been demonstrated in dogs (97); however, it is not known whether silicate particles of the sizes encountered through dust inhalation penetrate the gastrointestinal tract as intact material when swallowed.

V. OPINION

Silicon dioxide and various silicates occur abundantly in the earth's crust, are present in practically all natural waters, animals, and plants, and are part of the normal human diet. The question of whether or not silicon is an essential human nutrient remains unresolved. Silicon compounds consumed as added food ingredients contribute only a minor proportion of the total dietary silicon intake. The estimated possible human intake of sodium aluminosilicate, the predominant silicate added to foods in this country, is approximately 0.3 mg per kg body weight per day. Silicon compounds that are GRAS for use as direct food ingredients, except potassium and sodium silicates, are insoluble or very slightly soluble in water and appear to be biologically inert. The water-soluble silicates are also of low acute toxicity.

The acute oral LD_{50} in rats of sodium aluminosilicate is >1 g per kg. No significant tissue accumulation, pathology, or toxicity has been reported from the ingestion of those insoluble or very slightly soluble GRAS silicon compounds for which data are available. Of the five substances that were reported as added to foods in the NRC survey, biologic effects and safety data are available for all except sodium calcium aluminosilicate, and there is no reason to suspect that the toxicity of the latter would differ from those for which there are data.

The results of two studies (1967 and 1970) in which various silicon compounds were fed to laboratory animals for 1 mo at a level of 0.8 g per kg body weight (as silicon dioxide) and for 3 mo at levels of 6 to 30 mg per kg body weight suggest there may be a species-related susceptibility to renal damage from ingestion of sodium silicate, magnesium trisilicate, and finely ground quartz. No substantiating reports of these effects have appeared. Magnesium trisilicate was recognized as safe for prolonged use in human ingestion in large amounts as a component of antacid preparations by the Advisory Review Panel on Over-the-Counter Drugs, and the available evidence on the acute toxicity of sodium silicate indicates that it is low.

Consumption data are lacking for aluminum calcium silicate and tricalcium silicate, two compounds that are listed as GRAS for use as anticaking agents. However, their use in keeping with good manufacturing practice and in currently regulated amounts would be of the same order of magnitude as the other GRAS silicates.

In addition, the Select Committee has limited information on the amounts of talc that are currently used in foods. However, a major food use of talc is in the coating of rice. Assuming package label statements are ignored and coated rice is not washed prior to cooking and no other losses occur, maximum per capita intake of talc from this source appears to be 0.5 g per day. With respect to paper and cotton food-packaging products, the possibility is remote that biologically significant amounts of talc, diatomaceous earth, or sodium silicate migrate to foods from packaging materials containing these substances.

Perlite, a naturally occurring polysilicate substance, has an oral LD_{50} in the rat of >10 g per kg body weight. Estimates of the maximum quantities of minerals that might be extracted from perlite and diatomaceous earth used as filteraids in food processing indicate no hazard to public health.

There are no food grade specifications for aluminum calcium silicate, sodium calcium aluminosilicate, and talc. Such specifications for the substances used in foods are desirable. Specifications for food grade talc should limit the content of asbestos fibers even though the potential hazard of ingested asbestos is not clearly established. The Food and Drug Administration is sponsoring the development of an assay method for asbestos fibers. An upper limit for cadmium should be added to the specifications for food-grade perlite, and consideration should be given to the need for limitation of cadium content of other silicates.

In the light of all of the foregoing, the Select Committee concludes that:

> It is essential to establish food-grade specifications for aluminum calcium silicate, sodium calcium aluminosilicate, and talc, with provision for an upper limit of asbestos fibers in talc.
>
> There is no evidence in the available information on aluminum calcium silicate, calcium silicate, magnesium silicate, potassium silicate, sodium silicate, sodium aluminosilicate, sodium calcium aluminosilicate, tricalcium silicate, silica aerogel, and talc that demonstrates or suggests reasonable grounds to suspect a hazard to the public when they are used at levels that are now current or that might reasonably be expected in the future.

There is no evidence in the available information on diatomaceous earth, silicon dioxides, sodium silicate, and talc that demonstrates or suggests reasonable grounds to suspect a hazard to the public when they are used as ingredients of paper and paperboard products used in food packaging in accordance with current practice.

There is no evidence in the available information on sodium silicate and talc that demonstrates or suggests reasonable grounds to suspect a hazard to the public when they are used as ingredients of cotton and cotton fabrics used in dry food packaging in accordance with current practice.

There is no evidence in the available information on diatomaceous earth and perlite that demonstrates or suggests reasonable grounds to suspect a hazard to the public when they are used as filteraids in food processing at levels that are now current or that might reasonably be expected in the future.

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Report submitted by:

July 20, 1979
Date

George W. Irving, Jr.
George W. Irving, Jr., Chairman
Select Committee on GRAS Substances

ATTACHMENT C

Product Labels

Judy Thompson
PQ Corporation
Valley Forge, PA
610-651-4353
Judy.Thompson@PQCorp.com

The PQ Corporation

AgSil™ 21

POTASSIUM SILICATE

GRADE: 0-0-12.5

GUARANTEED ANALYSIS:
Soluble Potash (K_2O) 12.5%

Derived from Potassium Silicate

F1253

Information regarding the contents and levels of metals in this product is available on the Internet at http://www.wa.gov/agr

Manufactured by:
PQ Corporation
P.O. Box 840
Valley Forge, PA 19482-0840

NET WEIGHT: 630 lbs. / 286.3 kg.

CONTAINS POTASSIUM SILICATE and WATER
CAS REGISTRY Nos. 1312-76-1, 7732-18-5

WARNING!
CAUSES EYE AND SKIN IRRITATION.
Avoid contact with eyes, skin and clothing. Wash thoroughly after handling.

FIRST AID:
In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing or shoes. Call a physician. Wash clothing before reuse. Thoroughly clear shoes before reuse.

SPILLAGE:
Contain and/or absorb spill with inert material (e.g., sand, vermiculite), then place in a suitable container. Do not flush to sewer or allow to enter waterways. Use appropriate Personal Protective Equipment (PPE).

Before using, read Material Safety Data Sheet (MSDS) for this chemical

FOR AGRICULTURAL USE ONLY

[honeycomb pattern]
Size: 11 x 8.5
Ink: PMS purple + black

0402

The PQ Corporation

AgSil™ 25

POTASSIUM SILICATE

GRADE: 0-0-8.1

GUARANTEED ANALYSIS:
Soluble Potash (K_2O) 8.1%

Derived from Potassium Silicate

F1253

Information regarding the contents and levels of metals in this product is available on the Internet at http://www.wa.gov/agr

Manufactured by:
PQ Corporation
P.O. Box 840
Valley Forge, PA 19482-0840

NET WEIGHT:

[honeycomb pattern]
Size: 11 x 8.5
Ink: PMS purple + black

CONTAINS POTASSIUM SILICATE and WATER
CAS REGISTRY Nos. 1312-76-1, 7732-18-5

WARNING!
CAUSES EYE AND SKIN IRRITATION.
Avoid contact with eyes, skin and clothing. Wash thoroughly after handling.

FIRST AID:
In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing or shoes. Call a physician. Wash clothing before reuse. Thoroughly clear shoes before reuse.

SPILLAGE:
Contain and/or absorb spill with inert material (e.g., sand, vermiculite), then place in a suitable container. Do not flush to sewer or allow to enter waterways. Use appropriate Personal Protective Equipment (PPE).

Before using, read Material Safety Data Sheet (MSDS) for this chemical

FOR AGRICULTURAL USE ONLY

0402

The PQ Corporation

AgSil™ 25H

HYDROUS POTASSIUM SILICATE

GRADE: 0-0-22.7

GUARANTEED ANALYSIS:
Soluble Potash (K_2O)................................ 22.7%

Derived from Potassium Silicate

F 1253
Information regarding the contents and levels of metals in this product is available on the Internet at http://www.wa.gov/agr

Manufactured by:
PQ Corporation
P.O. Box 840
Valley Forge, PA 19482-0840

NET WT.:

[PQ honeycomb pattern in PMS purple]

Ink: PMS purple + black
Size: 11 x 8.5

CONTAINS POTASSIUM SILICATE and WATER
CAS REGISTRY Nos. 1312-76-1, 7732-18-5

WARNING!
CAUSES EYE AND SKIN IRRITATION.
Avoid contact with eyes, skin and clothing. Wash thoroughly after handling.
FIRST AID:
In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing or shoes. Call a physician. Wash clothing before reuse. Thoroughly clear shoes before reuse.

SPILLAGE:
Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment.

Before using, read Material Safety Data Sheet (MSDS) for this chemical.

FOR AGRICULTURAL USE ONLY

0402

The PQ Corporation

AgSil™ 25A

POTASSIUM SILICATE

GRADE: 0-0-28

GUARANTEED ANALYSIS:
Soluble Potash (K_2O) 28%

Derived from Potassium Silicate

F1253

Information regarding the contents and levels of metals in this product is available on the Internet at http://www.wa.gov/agr

Manufactured by:
PQ Corporation
P.O. Box 840
Valley Forge, PA 19482-0840

NET WEIGHT:

[honeycomb pattern]
Size: 11 x 8.5
Ink: PMS purple + black

CONTAINS POTASSIUM SILICATE
CAS REGISTRY No. 1312-76-1

WARNING!
CAUSES EYE AND SKIN IRRITATION.
Avoid contact with eyes, skin and clothing. Wash thoroughly after handling.

FIRST AID:
In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing or shoes. Call a physician. Wash clothing before reuse. Thoroughly clear shoes before reuse.

SPILLAGE:
Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE).

Before using, read Material Safety Data Sheet (MSDS) for this chemical

FOR AGRICULTURAL USE ONLY

0402

The PQ Corporation

AgSil™ 25F

POTASSIUM SILICATE

GRADE: 0-0-27.8

GUARANTEED ANALYSIS:

Soluble Potash (K_2O) 27.8%

Derived from Potassium Silicate

F1253

Information regarding the contents and levels of metals in this product is available on the Internet at http://www.wa.gov/agr

Manufactured by:
PQ Corporation
P.O. Box 840
Valley Forge, PA 19482-0840

NET WEIGHT:

[honeycomb pattern]
Size: 11 x 8.5
Ink: PMS purple + black

CONTAINS POTASSIUM SILICATE
CAS REGISTRY No. 1312-76-1

WARNING!
CAUSES EYE AND SKIN IRRITATION.
Avoid contact with eyes, skin and clothing. Wash thoroughly after handling.

FIRST AID:
In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing or shoes. Call a physician. Wash clothing before reuse. Thoroughly clear shoes before reuse.

SPILLAGE:
Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE).

Before using, read Material Safety Data Sheet (MSDS) for this chemical

FOR AGRICULTURAL USE ONLY

0402

ATTACHMENT D

MSDS

Judy Thompson
PQ Corporation
Valley Forge, PA
610-651-4353
Judy.Thompson@PQCorp.com

Trade Name: **AgSil™ 21 Potassium Silicate Solution**
Date Prepared: **08/15/01**
Page: **1 of 5**

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name:	**AgSil™ 21 potassium silicate solution**
Product description:	**A 2.18 weight ratio potassium silicate, 39.2% solution in water**
Manufacturer:	**PQ Corporation** **P. O. Box 840** **Valley Forge, PA USA** **Phone number: 610-651-4200** **Fax number: 610-651-4504**
In case of emergency call:	**1 610-651-4200**
For customer service call:	**1 610-651-4330**

2. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical and Common Name	*CAS Registry Number*	*Wt. %*	*OSHA PEL*	*ACGIH TLV*
Water	**7732-18-5**	**68.8%**	**Not Established**	**Not Established**
Silicic acid, potassium salt; Potassium silicate	**1312-76-1**	**39.2%**	**Not Established**	**Not Established**

3. HAZARDS IDENTIFICATION

Emergency Overview:	**Clear to hazy, colorless, odorless, thick liquid. Causes eye, skin, and digestive tract irritation. Spray mist causes irritation to respiratory tract. High pH is harmful to aquatic life. Noncombustible. Spills are slippery. Reacts with acids, ammonium salts, reactive metals and some organics.**
Eye contact:	**Causes irritation.**
Skin contact:	**Causes irritation.**
Inhalation:	**Spray mist irritating to respiratory tract.**
Ingestion:	**May cause irritation to mouth, esophagus, and stomach.**
Chronic hazards:	**No known chronic hazards. Not listed by NTP, IARC or OSHA as a carcinogen.**
Physical hazards:	**Dries to form glass film which can easily cut skin. Spilled material is very slippery. Can etch glass if not promptly removed.**

4. FIRST AID MEASURES

Eye:	**In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention.**
Skin:	**In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Get medical attention.**

Inhalation: **Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.**

Ingestion: **If swallowed, DO NOT induce vomiting. Get medical attention immediately. If victim is fully conscious, give a cupful of water. Never give anything by mouth to an unconscious person.**

5. FIRE FIGHTING MEASURES

Flammable limits: **This material is noncombustible.**

Extinguishing Media: **This material is compatible with all extinguishing media**

Hazards to fire-fighters: **See Section 3 for information on hazards when this material is present in the area of a fire.**

Fire-fighting equipment: **The following protective equipment for fire fighters is recommended when this material is present in the area of a fire: chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots.**

6. ACCIDENTAL RELEASE MEASURES

Personal protection: **Wear chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots. See section 8.**

Environmental Hazards: **Sinks and mixes with water. High pH of this material is harmful to aquatic life, see Section 12. Only water will evaporate from a spill of this material.**

Small spill cleanup: **Mop up and neutralize liquid, then discharge to sewer in accordance with federal, state and local regulations or permits.**

Large spill cleanup: **Keep unnecessary people away; isolate hazard area and deny entry. Do not touch or walk through spilled material. Stop leak if you can do so without risk. Prevent runoff from entering into storm sewers and ditches which lead to natural waterways. Isolate, dike and store discharged material, if possible. Use sand or earth to contain spilled material. If containment is impossible, neutralize contaminated area and flush with large quantities of water.**

CERCLA RQ: **There is no CERCLA Reportable Quantity for this material. If a spill goes off site, notification of state and local authorities is recommended.**

7. HANDLING AND STORAGE

Handling: **Avoid contact with eyes, skin and clothing. Avoid breathing spray mist. Keep container closed. Promptly clean residue from closures with cloth dampened with water. Promptly clean up spills.**

Storage: **Keep containers closed. Store in clean steel or plastic containers. Separate from acids, reactive metals, and ammonium salts. Storage temperature 0-95° C. Loading temperature 45-95 ° C. Do not store in aluminum, fiberglass, copper, brass, zinc or galvanized containers.**

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls:	**Use with adequate ventilation. Keep containers closed. Safety shower and eyewash fountain should be within direct access.**
Respiratory protection:	**Use a NIOSH-approved dust and mist respirator where spray mist occurs. Observe OSHA regulations for respirator use (29 C.F.R. §1910.134)**
Skin protection:	**Wear body-covering protective clothing and gloves.**
Eye protection:	**Wear chemical goggles.**

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance:	**Thick liquid.**
Color:	**Clear to hazy white.**
Odor:	**Odorless or musty odor.**
pH:	**11.7**
Specific gravity:	**1.39 g/cm_3 (20°C), 40.4° Bé, 11.56 lbs/gal**
Solubility in water:	**Miscible.**

10. STABILITY AND REACTIVITY

Stability:	**This material is stable under all conditions of use and storage.**
Conditions to avoid:	**None.**
Materials to avoid:	**Gels and generates heat when mixed with acid. May react with ammonium salts resulting in evolution of ammonia gas. Flammable hydrogen gas may be produced on contact with aluminum, tin, lead, and zinc.**
Hazardous decomposition products:	**Hydrogen.**

11. TOXICOLOGICAL INFORMATION

Acute Data:	**This material has not been tested for primary eye irritation. However, on the basis of its similarity to sodium silicate solutions in composition and alkalinity it is regarded as an eye irritant.** **When tested for primary skin irritation potential, similar potassium silicate solution produced no irritation to intact skin, but well defined irritation to abraded skin. Human experience confirms that irritation occurs when potassium silicates get on clothes at the collar, cuffs or other areas where abrasion may occur.** **The acute oral toxicity of this product has not been tested. When chemically similar sodium silicates were tested on a 100% solids basis, their single dose acute oral LD_{50} in rats ranged from 1500 mg/kg to 3200 mg/kg. The acute oral lethality resulted from nonspecific causes. This product contains approximately 39.2% potassium silicate.**
Subchronic Data:	**The subchronic toxicity of this material has not been tested. In a study of rats fed chemically similar sodium silicate in drinking water for three**

months, at 200, 600 and 1800 ppm, changes were reported in the blood chemistry of some animals, but no specific changes to the organs of the animals due to potassium silicate administration were observed in any of the dosage groups. Another study reported adverse effects to the kidneys of dogs fed potassium silicate in their diet at 2.4g/kg/day for 4 weeks, whereas rats fed the same dosage did not develop any treatment-related effects. Decreased numbers of births and survival to weaning was reported for rats fed sodium silicate in their drinking water at 600 and 1200 ppm.

Special Studies: **The mutagenic potential of this material has not been tested. Chemically similar sodium silicate was not mutagenic to the bacterium E. Coli when tested in a mutagenicity bioassay. There are no known reports of carcinogenicity of potassium silicates. Frequent ingestion over extended periods of time of gram quantities of silicates is associated with the formation kidney stones and other siliceous urinary calculi in humans. Potassium silicate is not listed by IARC, NTP or OSHA as a carcinogen.**

12. ECOLOGICAL INFORMATION

Ecotoxicity: **The ecotoxicity of potassium silicate has not been tested. The following data is reported for chemically similar sodium silicates on a 100% solids basis: A 96 hour median tolerance for fish (Gambusia affnis) of 2320 ppm; a 96 hour median tolerance for water fleas (Daphnia magna) of 247 ppm; a 96 hour median tolerance for snail eggs (Lymnea) of 632 ppm; and a 96 hour median tolerance for Amphipoda of 160 ppm. This product contains approximately 39.2% potassium silicate.**

Environmental Fate: **This material is not persistent in aquatic systems, but its high pH when undiluted or unneutralized is acutely harmful to aquatic life. Diluted material rapidly depolymerizes to yield dissolved silica in a form that is indistinguishable from natural dissolved silica. It does not contribute to BOD. This material does not bioaccumulate except in species that use silica as a structural material such as diatoms and siliceous sponges. Where abnormally low natural silica concentrations exist (less than 0.1 ppm), dissolved silica may be a limiting nutrient for diatoms and a few other aquatic algal species. However, the addition of excess dissolved silica over the limiting concentration will not stimulate the growth of diatom populations; their growth rate is independent of silica concentration once the limiting concentration is exceeded. Neither silica nor potassium will appreciably bioconcentrate up the food chain.**

Physical/Chemical: **Sinks and mixes with water. Only water will evaporate from this material.**

13. DISPOSAL CONSIDERATIONS

Classification: **Disposed material is not a RCRA Hazardous waste.**

Disposal Method: **Neutralize with dilute acid and landfill solids in accordance with federal, state and local regulations. Flush neutral liquid to sewer accordance with federal, state and local regulations and permits.**

14. TRANSPORT INFORMATION

DOT UN Status:	**This material is not regulated hazardous material for transportation.**

15. REGULATORY INFORMATION

CERCLA:	**No CERCLA Reportable Quantity has been established for this material.**
SARA TITLE III:	**Not an Extremely Hazardous Substance under §302 Not a Toxic Chemical under §313. Hazard Categories under §§311/312: Acute**
TSCA:	**All ingredients of this material are listed on the TSCA inventory.**
FDA:	**Potassium silicate is regarded as GRAS (Generally Recognized As Safe) as a corrosion preventative in potable water.**

16. OTHER INFORMATION

Prepared by:	**John G. Blumberg**
Supercedes revision of:	**08/06/01**

THE INFORMATION ON THIS SAFETY DATA SHEET IS BELIEVED TO BE ACCURATE AND IT IS THE BEST INFORMATION AVAILABLE TO PQ CORPORATION THIS DOCUMENT IS INTENDED ONLY AS A GUIDE TO THE APPROPRIATE PRECAUTIONS FOR HANDLING A CHEMICAL BY A PERSON TRAINED IN CHEMICAL HANDLING. PQ CORPORATION MAKES NO WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY, EXPRESS OR IMPLIED WITH RESPECT TO SUCH INFORMATION OR THE PRODUCT TO WHICH IT RELATES, AND WE ASSUME NO LIABILITY RESULTING FROM THE USE OR HANDLING OF THE PRODUCT TO WHICH THIS SAFETY DATA SHEET RELATES. USERS AND HANDLERS OF THIS PRODUCT SHOULD MAKE THEIR OWN INVESTIGATIONS TO DETERMINE THE SUITABILITY OF THE INFORMATION PROVIDED HEREIN FOR THEIR OWN PURPOSES.

The PQ Corporation

MSDS

MATERIAL SAFETY DATA SHEET

Trade Name: **AgSil™ 25 Potassium Silicate Solution**
Date Prepared: **08/15/01**

Page: **1 of 5**

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name:	**AgSil™ 25 Potassium silicate solution**
Product description:	**A 2.50 weight ratio potassium silicate, 29.1% solution in water**
Manufacturer:	**PQ Corporation P. O. Box 840 Valley Forge, PA USA Phone number: 610-651-4200 Fax number: 610-651-4504**
In case of emergency call:	**1 610-651-4200**
For customer service call:	**1 610-651-4330**

2. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical and Common Name	*CAS Registry Number*	*Wt. %*	*OSHA PEL*	*ACGIH TLV*
Water	**7732-18-5**	**70.9%**	**Not Established**	**Not Established**
Silicic acid, potassium salt; Potassium silicate	**1312-76-1**	**29.1%**	**Not Established**	**Not Established**

3. HAZARDS IDENTIFICATION

Emergency Overview:	**Clear to hazy, colorless, odorless, thick liquid. Causes eye, skin, and digestive tract irritation. Spray mist causes irritation to respiratory tract. High pH is harmful to aquatic life. Noncombustible. Spills are slippery. Reacts with acids, ammonium salts, reactive metals and some organics.**
Eye contact:	**Causes irritation.**
Skin contact:	**Causes irritation.**
Inhalation:	**Spray mist irritating to respiratory tract.**
Ingestion:	**May cause irritation to mouth, esophagus, and stomach.**
Chronic hazards:	**No known chronic hazards. Not listed by NTP, IARC or OSHA as a carcinogen.**
Physical hazards:	**Dries to form glass film which can easily cut skin. Spilled material is very slippery. Can etch glass if not promptly removed.**

4. FIRST AID MEASURES

Eye:	**In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention.**
Skin:	**In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Get medical attention.**

Inhalation:	**Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.**
Ingestion:	**If swallowed, DO NOT induce vomiting. Get medical attention immediately. If victim is fully conscious, give a cupful of water. Never give anything by mouth to an unconscious person.**

5. FIRE FIGHTING MEASURES

Flammable limits:	**This material is noncombustible.**
Extinguishing Media:	**This material is compatible with all extinguishing media**
Hazards to fire-fighters:	**See Section 3 for information on hazards when this material is present in the area of a fire.**
Fire-fighting equipment:	**The following protective equipment for fire fighters is recommended when this material is present in the area of a fire: chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots.**

6. ACCIDENTAL RELEASE MEASURES

Personal protection:	**Wear chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots. See section 8.**
Environmental Hazards:	**Sinks and mixes with water. High pH of this material is harmful to aquatic life, see Section 12. Only water will evaporate from a spill of this material.**
Small spill cleanup:	**Mop up and neutralize liquid, then discharge to sewer in accordance with federal, state and local regulations or permits.**
Large spill cleanup:	**Keep unnecessary people away; isolate hazard area and deny entry. Do not touch or walk through spilled material. Stop leak if you can do so without risk. Prevent runoff from entering into storm sewers and ditches which lead to natural waterways. Isolate, dike and store discharged material, if possible. Use sand or earth to contain spilled material. If containment is impossible, neutralize contaminated area and flush with large quantities of water.**
CERCLA RQ:	**There is no CERCLA Reportable Quantity for this material. If a spill goes off site, notification of state and local authorities is recommended.**

7. HANDLING AND STORAGE

Handling:	**Avoid contact with eyes, skin and clothing. Avoid breathing spray mist. Keep container closed. Promptly clean residue from closures with cloth dampened with water. Promptly clean up spills.**
Storage:	**Keep containers closed. Store in clean steel or plastic containers. Separate from acids, reactive metals, and ammonium salts. Storage temperature 0-95° C. Loading temperature 45-95 ° C. Do not store in aluminum, fiberglass, copper, brass, zinc or galvanized containers.**

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls:	**Use with adequate ventilation. Keep containers closed. Safety shower and eyewash fountain should be within direct access.**
Respiratory protection:	**Use a NIOSH-approved dust and mist respirator where spray mist occurs. Observe OSHA regulations for respirator use (29 C.F.R. §1910.134)**
Skin protection:	**Wear body-covering protective clothing and gloves.**
Eye protection:	**Wear chemical goggles.**

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance:	**Thick liquid.**
Color:	**Clear to hazy white.**
Odor:	**Odorless or musty odor.**
pH:	**11.3**
Specific gravity:	**1.26 g/cm$_3$ (20°C), 29.8° Bé, 10.50 lbs/gal**
Solubility in water:	**Miscible.**

10. STABILITY AND REACTIVITY

Stability:	**This material is stable under all conditions of use and storage.**
Conditions to avoid:	**None.**
Materials to avoid:	**Gels and generates heat when mixed with acid. May react with ammonium salts resulting in evolution of ammonia gas. Flammable hydrogen gas may be produced on contact with aluminum, tin, lead, and zinc.**
Hazardous decomposition products:	**Hydrogen.**

11. TOXICOLOGICAL INFORMATION

Acute Data:	**This material has not been tested for primary eye irritation. However, on the basis of its similarity to sodium silicate solutions in composition and alkalinity it is regarded as an eye irritant.** **When tested for primary skin irritation potential, similar potassium silicate solution produced no irritation to intact skin, but well defined irritation to abraded skin. Human experience confirms that irritation occurs when potassium silicates get on clothes at the collar, cuffs or other areas where abrasion may occur.** **The acute oral toxicity of this product has not been tested. When chemically similar sodium silicates were tested on a 100% solids basis, their single dose acute oral LD$_{50}$ in rats ranged from 1500 mg/kg to 3200 mg/kg. The acute oral lethality resulted from nonspecific causes. This product contains approximately 29.1% potassium silicate.**
Subchronic Data:	**The subchronic toxicity of this material has not been tested. In a study of rats fed chemically similar sodium silicate in drinking water for three**

months, at 200, 600 and 1800 ppm, changes were reported in the blood chemistry of some animals, but no specific changes to the organs of the animals due to potassium silicate administration were observed in any of the dosage groups. Another study reported adverse effects to the kidneys of dogs fed potassium silicate in their diet at 2.4g/kg/day for 4 weeks, whereas rats fed the same dosage did not develop any treatment-related effects. Decreased numbers of births and survival to weaning was reported for rats fed sodium silicate in their drinking water at 600 and 1200 ppm.

Special Studies: **The mutagenic potential of this material has not been tested. Chemically similar sodium silicate was not mutagenic to the bacterium E. Coli when tested in a mutagenicity bioassay. There are no known reports of carcinogenicity of potassium silicates. Frequent ingestion over extended periods of time of gram quantities of silicates is associated with the formation kidney stones and other siliceous urinary calculi in humans. Potassium silicate is not listed by IARC, NTP or OSHA as a carcinogen.**

12. ECOLOGICAL INFORMATION

Ecotoxicity: **The ecotoxicity of potassium silicate has not been tested. The following data is reported for chemically similar sodium silicates on a 100% solids basis: A 96 hour median tolerance for fish (Gambusia affnis) of 2320 ppm; a 96 hour median tolerance for water fleas (Daphnia magna) of 247 ppm; a 96 hour median tolerance for snail eggs (Lymnea) of 632 ppm; and a 96 hour median tolerance for Amphipoda of 160 ppm. This product contains approximately 29.1% potassium silicate.**

Environmental Fate: **This material is not persistent in aquatic systems, but its high pH when undiluted or unneutralized is acutely harmful to aquatic life. Diluted material rapidly depolymerizes to yield dissolved silica in a form that is indistinguishable from natural dissolved silica. It does not contribute to BOD. This material does not bioaccumulate except in species that use silica as a structural material such as diatoms and siliceous sponges. Where abnormally low natural silica concentrations exist (less than 0.1 ppm), dissolved silica may be a limiting nutrient for diatoms and a few other aquatic algal species. However, the addition of excess dissolved silica over the limiting concentration will not stimulate the growth of diatom populations; their growth rate is independent of silica concentration once the limiting concentration is exceeded. Neither silica nor potassium will appreciably bioconcentrate up the food chain.**

Physical/Chemical: **Sinks and mixes with water. Only water will evaporate from this material.**

13. DISPOSAL CONSIDERATIONS

Classification: **Disposed material is not a RCRA hazardous waste.**

Disposal Method: **Neutralize and landfill solids in accordance with federal, state and local regulations. Flush neutral liquid to sewer accordance with federal, state and local regulations and permits.**

14. TRANSPORT INFORMATION

DOT UN Status:	**This material is not regulated hazardous material for transportation.**

15. REGULATORY INFORMATION

CERCLA:	**No CERCLA Reportable Quantity has been established for this material.**
SARA TITLE III:	**Not an Extremely Hazardous Substance under §302 Not a Toxic Chemical under §313. Hazard Categories under §§311/312: Acute**
TSCA:	**All ingredients of this material are listed on the TSCA inventory.**
FDA:	**Potassium silicate is regarded as GRAS (Generally Recognized As Safe) as a corrosion preventative in potable water.**

16. OTHER INFORMATION

Prepared by:	**John G. Blumberg**
Supercedes revision of:	**07/30/01**

THE INFORMATION ON THIS SAFETY DATA SHEET IS BELIEVED TO BE ACCURATE AND IT IS THE BEST INFORMATION AVAILABLE TO PQ CORPORATION THIS DOCUMENT IS INTENDED ONLY AS A GUIDE TO THE APPROPRIATE PRECAUTIONS FOR HANDLING A CHEMICAL BY A PERSON TRAINED IN CHEMICAL HANDLING. PQ CORPORATION MAKES NO WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY, EXPRESS OR IMPLIED WITH RESPECT TO SUCH INFORMATION OR THE PRODUCT TO WHICH IT RELATES, AND WE ASSUME NO LIABILITY RESULTING FROM THE USE OR HANDLING OF THE PRODUCT TO WHICH THIS SAFETY DATA SHEET RELATES. USERS AND HANDLERS OF THIS PRODUCT SHOULD MAKE THEIR OWN INVESTIGATIONS TO DETERMINE THE SUITABILITY OF THE INFORMATION PROVIDED HEREIN FOR THEIR OWN PURPOSES.

The PQ Corporation

MSDS

MATERIAL SAFETY DATA SHEET

Trade Name:	**AgSil™ 25H Potassium Silicate**
Date Prepared:	**08/15/01**

Page: **1 of 5**

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name:	**AgSil™ 25H Potassium Silicate**
Product description:	**A 2.5 weight ratio hydrous potassium silicate powder**
Manufacturer:	**PQ Corporation** **P. O. Box 840** **Valley Forge, PA USA** **Phone number: 610-651-4200** **Fax number: 610-651-4504**
In case of emergency call:	**1 610-651-4200**
For customer service call:	**1 610-651-4330**

2. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical and Common Name	*CAS Registry Number*	*Wt. %*	*OSHA PEL*	*ACGIH TLV*
Silicic acid, potassium salt; Potassium silicate	**1312-76-1**	**~85%**	**Not Established**	**Not Established**
Water	**7732-18-5**	**~15%**	**Not Established**	**Not Established**

3. HAZARDS IDENTIFICATION

Emergency Overview:	**White, odorless, powder. Causes eye and skin irritation. May cause irritation to respiratory tract, and digestive tract. High pH is harmful to aquatic life. Noncombustible. Reacts with acids and some organics.**
Eye contact:	**Causes irritation.**
Skin contact:	**Causes irritation.**
Inhalation:	**May cause irritation to respiratory tract.**
Ingestion:	**May cause irritation to mouth, esophagus, and stomach.**
Chronic hazards:	**No known chronic hazards. Not listed by NTP, IARC or OSHA as a carcinogen.**
Physical hazards:	**Can etch glass if not promptly removed.**

4. FIRST AID MEASURES

Eye:	**In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Call a physician.**
Skin:	**In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Call a physician. Wash clothing before reuse. Thoroughly clean shoes before reuse.**
Inhalation:	**Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.**

Ingestion:	**If swallowed, DO NOT induce vomiting. Get medical attention immediately. If victim is fully conscious, give a cupful of water. Never give anything by mouth to an unconscious person.**

5. FIRE FIGHTING MEASURES

Flammable limits:	**This material is noncombustible.**
Extinguishing Media:	**This material is compatible with all extinguishing media**
Hazards to fire-fighters:	**See Section 3 for information on hazards when this material is present in the area of a fire.**
Fire-fighting equipment:	**The following protective equipment for fire fighters is recommended when this material is present in the area of a fire: chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots.**

6. ACCIDENTAL RELEASE MEASURES

Personal protection:	**Wear chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots, NIOSH-approved dust respirator where dust occurs. See section 8.**
Environmental Hazards:	**Sinks and mixes with water. High pH of this material is harmful to aquatic life, see Section 12.**
Small spill cleanup:	**Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8.**
Large spill cleanup:	**Keep unnecessary people away; isolate hazard area and deny entry. Do not touch or walk through spilled material. Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8. In case of contact with water, prevent runoff from entering into storm sewers and ditches which lead to natural waterways. Neutralize contaminated area and flush with large quantities of water. Comply with applicable environmental regulations.**
CERCLA RQ:	**There is no CERCLA Reportable Quantity for this material. If a spill goes off site, notification of state and local authorities is recommended.**

7. HANDLING AND STORAGE

Handling:	**Avoid contact with eyes, skin and clothing. Avoid breathing dust. Keep container closed. Promptly clean up spills.**
Storage:	**Keep containers closed. Store in clean steel or plastic containers. Separate from acids, reactive metals, and ammonium salts. Do not store in aluminum, fiberglass, copper, brass, zinc or galvanized containers.**

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls: **Use with adequate ventilation. Keep containers closed. Safety shower and eyewash fountain should be within direct access.**
Respiratory protection: **Use a NIOSH-approved dust respirator where dust occurs. Observe OSHA regulations for respirator use (29 C.F.R. §1910.134)**
Skin protection: **Wear body-covering protective clothing and gloves.**
Eye protection: **Wear chemical goggles.**

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance: **Powder.**
Color: **White.**
Odor: **Odorless.**
pH (aqueous solutions): **Approximately 11.3**
Bulk density: **Approximately.43 lbs/ft^3 untamped.**
Solubility in water: **Soluble in all proportions.**

10. STABILITY AND REACTIVITY

Stability: **This material is stable under all conditions of use and storage.**
Conditions to avoid: **None.**
Materials to avoid: **Generates heat when mixed with acid. May react with ammonium salt solutions resulting in evolution of ammonia gas. Flammable hydrogen gas may be produced on contact with aluminum, tin, lead, and zinc.**
Hazardous decomposition products: **Hydrogen.**

11. TOXICOLOGICAL INFORMATION

Acute Data: **This material has not been tested for primary eye irritation. However, on the basis of its similarity to sodium silicates in composition and alkalinity it is regarded as an eye irritant.**

This material has not been tested for primary skin irritation potential. However, on the basis of its similarity to sodium silicates in composition and alkalinity it is regarded as a skin irritant. Human experience confirms that irritation occurs when potassium silicates get on clothes at the collar, cuffs or other areas where abrasion may occur.

The acute oral toxicity of this product has not been tested. When chemically similar sodium silicates were tested on a 100% solids basis, their single dose acute oral LD$_{50}$ in rats ranged from 1500 mg/kg to 3200 mg/kg. The acute oral lethality resulted from nonspecific causes.

Subchronic Data: **In a study of rats fed chemically sodium silicate in drinking water for three months, at 200, 600 and 1800 ppm, changes were reported in the blood chemistry of some animals, but no specific changes to the organs of the animals due to sodium silicate administration were observed in any of the dosage groups. Another study reported adverse effects to the kidneys of dogs fed sodium silicate in their diet at 2.4g/kg/day for 4 weeks, whereas rats fed the same dosage did not develop any treatment-related**

effects. Decreased numbers of births and survival to weaning was reported for rats fed sodium silicate in their drinking water at 600 and 1200 ppm.

Special Studies: **The mutagenic potential of this material has not been tested. Chemically similar sodium silicate was not mutagenic to the bacterium E. Coli when tested in a mutagenicity bioassay. There are no known reports of carcinogenicity of potassium silicates. Frequent ingestion over extended periods of time of gram quantities of silicates is associated with the formation kidney stones and other siliceous urinary calculi in humans. Potassium silicate is not listed by IARC, NTP or OSHA as a carcinogen.**

12. ECOLOGICAL INFORMATION

Eco toxicity: **The ecotoxicity of potassium silicate has not been tested. The following data is reported for chemically similar sodium silicates on a 100% solids basis: A 96 hour median tolerance for fish (Gambusia affnis) of 2320 ppm; a 96 hour median tolerance for water fleas (Daphnia magna) of 247 ppm; a 96 hour median tolerance for snail eggs (Lymnea) of 632 ppm; and a 96 hour median tolerance for Amphipoda of 160 ppm.**

Environmental Fate: **This material is not persistent in aquatic systems, but its high pH when undiluted or unneutralized is acutely harmful to aquatic life. Diluted material rapidly depolymerizes to yield dissolved silica in a form that is indistinguishable from natural dissolved silica. It does not contribute to BOD. This material does not bioaccumulate except in species that use silica as a structural material such as diatoms and siliceous sponges. Where abnormally low natural silica concentrations exist (less than 0.1 ppm), dissolved silica may be a limiting nutrient for diatoms and a few other aquatic algal species. However, the addition of excess dissolved silica over the limiting concentration will not stimulate the growth of diatom populations; their growth rate is independent of silica concentration once the limiting concentration is exceeded. Neither silica nor potassium will appreciably bioconcentrate up the food chain.**

Physical/Chemical: **Sinks and mixes with water. Only water will evaporate from this material.**

13. DISPOSAL CONSIDERATIONS

Classification: **Disposed material is not a RCRA Hazardous waste.**

Disposal Method: **Neutralize and landfill solids in accordance with federal, state and local regulations. Flush neutral liquid to sewer accordance with federal, state and local regulations and permits.**

14. TRANSPORT INFORMATION

DOT UN Status: **This material is not regulated hazardous material for transportation.**

15. REGULATORY INFORMATION

CERCLA: **No CERCLA Reportable Quantity has been established for this material.**
SARA TITLE III: **Not an Extremely Hazardous Substance under §302 Not a Toxic Chemical under §313. Hazard Categories under §§311/312: Acute**
TSCA: **All ingredients of this material are listed on the TSCA inventory.**
FDA: **Potassium silicate is regarded as GRAS (Generally Recognized As Safe) as a corrosion preventative in potable water.**

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16. OTHER INFORMATION

Prepared by: **John G. Blumberg**
Supercedes revision of: **07/03/01**

THE INFORMATION ON THIS SAFETY DATA SHEET IS BELIEVED TO BE ACCURATE AND IT IS THE BEST INFORMATION AVAILABLE TO PQ CORPORATION THIS DOCUMENT IS INTENDED ONLY AS A GUIDE TO THE APPROPRIATE PRECAUTIONS FOR HANDLING A CHEMICAL BY A PERSON TRAINED IN CHEMICAL HANDLING. PQ CORPORATION MAKES NO WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY, EXPRESS OR IMPLIED WITH RESPECT TO SUCH INFORMATION OR THE PRODUCT TO WHICH IT RELATES, AND WE ASSUME NO LIABILITY RESULTING FROM THE USE OR HANDLING OF THE PRODUCT TO WHICH THIS SAFETY DATA SHEET RELATES. USERS AND HANDLERS OF THIS PRODUCT SHOULD MAKE THEIR OWN INVESTIGATIONS TO DETERMINE THE SUITABILITY OF THE INFORMATION PROVIDED HEREIN FOR THEIR OWN PURPOSES.

The PQ Corporation

MSDS

MATERIAL SAFETY DATA SHEET

Trade Name: **AgSil™ 25A Potassium Silicate**
Date Prepared: **08/15/01**

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name:	**AgSil™ 25A Potassium Silicate**
Product description:	**A 2.5 weight ratio potassium silicate**
Manufacturer:	**PQ Corporation** **P. O. Box 840** **Valley Forge, PA USA** **Phone number: 610-651-4200** **Fax number: 610-651-4504**
In case of emergency call:	**1 610-651-4200**
For customer service call:	**1 610-651-4330**

2. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical and Common Name	*CAS Registry Number*	*Wt. %*	*OSHA PEL*	*ACGIH TLV*
Silicic acid, potassium salt; Potassium silicate	**1312-76-1**	**~100%**	**Not Established**	**Not Established**

3. HAZARDS IDENTIFICATION

Emergency Overview:	**White, odorless, powder. Causes eye, skin, and digestive tract irritation. Dust causes irritation to respiratory tract. High pH is harmful to aquatic life. Noncombustible. Reacts with acids and some organics.**
Eye contact:	**Causes irritation.**
Skin contact:	**Causes irritation.**
Inhalation:	**Dust irritating to respiratory tract.**
Ingestion:	**May cause irritation to mouth, esophagus, and stomach.**
Chronic hazards:	**No known chronic hazards. Not listed by NTP, IARC or OSHA as a carcinogen.**
Physical hazards:	**Can etch glass if not promptly removed.**

4. FIRST AID MEASURES

Eye:	**In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention.**
Skin:	**In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Get medical attention.**
Inhalation:	**Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.**

Ingestion:	**If swallowed, DO NOT induce vomiting. Get medical attention immediately. If victim is fully conscious, give a cupful of water. Never give anything by mouth to an unconscious person.**

5. FIRE FIGHTING MEASURES

Flammable limits:	**This material is noncombustible.**
Extinguishing Media:	**This material is compatible with all extinguishing media**
Hazards to fire-fighters:	**See Section 3 for information on hazards when this material is present in the area of a fire.**
Fire-fighting equipment:	**The following protective equipment for fire fighters is recommended when this material is present in the area of a fire: chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots.**

6. ACCIDENTAL RELEASE MEASURES

Personal protection:	**Wear chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots, NIOSH-approved dust respirator where dust occurs. See section 8.**
Environmental Hazards:	**Sinks and mixes with water. High pH of this material is harmful to aquatic life, see Section 12.**
Small spill cleanup:	**Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8.**
Large spill cleanup:	**Keep unnecessary people away; isolate hazard area and deny entry. Do not touch or walk through spilled material. Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8. In case of contact with water, prevent runoff from entering into storm sewers and ditches which lead to natural waterways. Neutralize contaminated area and flush with large quantities of water. Comply with applicable environmental regulations.**
CERCLA RQ:	**There is no CERCLA Reportable Quantity for this material. If a spill goes off site, notification of state and local authorities is recommended.**

7. HANDLING AND STORAGE

Handling:	**Avoid contact with eyes, skin and clothing. Avoid breathing dust. Keep container closed. Promptly clean up spills.**
Storage:	**Keep containers closed. Store in clean steel or plastic containers. Separate from acids, reactive metals, and ammonium salts. Do not store in aluminum, fiberglass, copper, brass, zinc or galvanized containers.**

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls: **Use with adequate ventilation. Keep containers closed. Safety shower and eyewash fountain should be within direct access.**
Respiratory protection: **Use a NIOSH-approved dust respirator where dust occurs. Observe OSHA regulations for respirator use (29 C.F.R. §1910.134)**
Skin protection: **Wear body-covering protective clothing and gloves.**
Eye protection: **Wear chemical goggles.**

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9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance: **Powder.**
Color: **White.**
Odor: **Odorless.**
PH (aqueous solutions): **Approximately 11.3**
Bulk density: **Approximately. 57 lbs/ft^3**
Solubility in water: **Soluble in all proportions.**

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10. STABILITY AND REACTIVITY

Stability: **This material is stable under all conditions of use and storage.**
Conditions to avoid: **None.**
Materials to avoid: **Generates heat when mixed with acid. May react with ammonium salt solutions resulting in evolution of ammonia gas. Flammable hydrogen gas may be produced on contact with aluminum, tin, lead, and zinc.**
Hazardous decomposition products: **Hydrogen.**

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11. TOXICOLOGICAL INFORMATION

Acute Data: **This material has not been tested for primary eye irritation. However, on the basis of its similarity to sodium silicates in composition and alkalinity it is regarded as an eye irritant.**

This material has not been tested for primary skin irritation potential. However, on the basis of its similarity to sodium silicates in composition and alkalinity it is regarded as a skin irritant. Human experience confirms that irritation occurs when potassium silicates get on clothes at the collar, cuffs or other areas where abrasion may occur.

The acute oral toxicity of this product has not been tested. When chemically similar sodium silicates were tested on a 100% solids basis, their single dose acute oral LD_{50} in rats ranged from 1500 mg/kg to 3200 mg/kg. The acute oral lethality resulted from nonspecific causes.

Subchronic Data: **In a study of rats fed chemically sodium silicate in drinking water for three months, at 200, 600 and 1800 ppm, changes were reported in the blood chemistry of some animals, but no specific changes to the organs of the animals due to sodium silicate administration were observed in any of the dosage groups. Another study reported adverse effects to the kidneys of dogs fed sodium silicate in their diet at 2.4g/kg/day for 4 weeks, whereas rats fed the same dosage did not develop any treatment-related**

effects. Decreased numbers of births and survival to weaning was reported for rats fed sodium silicate in their drinking water at 600 and 1200 ppm.

Special Studies: **The mutagenic potential of this material has not been tested. Chemically similar sodium silicate was not mutagenic to the bacterium E. Coli when tested in a mutagenicity bioassay. There are no known reports of carcinogenicity of potassium silicates. Frequent ingestion over extended periods of time of gram quantities of silicates is associated with the formation kidney stones and other siliceous urinary calculi in humans. Potassium silicate is not listed by IARC, NTP or OSHA as a carcinogen.**

12. ECOLOGICAL INFORMATION

Eco toxicity: **The ecotoxicity of potassium silicate has not been tested. The following data is reported for chemically similar sodium silicates on a 100% solids basis: A 96 hour median tolerance for fish (Gambusia affnis) of 2320 ppm; a 96 hour median tolerance for water fleas (Daphnia magna) of 247 ppm; a 96 hour median tolerance for snail eggs (Lymnea) of 632 ppm; and a 96 hour median tolerance for Amphipoda of 160 ppm.**

Environmental Fate: **This material is not persistent in aquatic systems, but its high pH when undiluted or unneutralized is acutely harmful to aquatic life. Diluted material rapidly depolymerizes to yield dissolved silica in a form that is indistinguishable from natural dissolved silica. It does not contribute to BOD. This material does not bioaccumulate except in species that use silica as a structural material such as diatoms and siliceous sponges. Where abnormally low natural silica concentrations exist (less than 0.1 ppm), dissolved silica may be a limiting nutrient for diatoms and a few other aquatic algal species. However, the addition of excess dissolved silica over the limiting concentration will not stimulate the growth of diatom populations; their growth rate is independent of silica concentration once the limiting concentration is exceeded. Neither silica nor potassium will appreciably bioconcentrate up the food chain.**

Physical/Chemical: **Sinks and mixes with water. Only water will evaporate from this material.**

13. DISPOSAL CONSIDERATIONS

Classification: **Disposed material is not a RCRA hazardous waste.**

Disposal Method: **Neutralize and landfill solids in accordance with federal, state and local regulations. Flush neutral liquid to sewer accordance with federal, state and local regulations and permits.**

14. TRANSPORT INFORMATION

DOT UN Status: **This material is not regulated hazardous material for transportation.**

15. REGULATORY INFORMATION

CERCLA:	**No CERCLA Reportable Quantity has been established for this material.**
SARA TITLE III:	**Not an Extremely Hazardous Substance under §302 Not a Toxic Chemical under §313. Hazard Categories under §§311/312: Acute**
TSCA:	**All ingredients of this material are listed on the TSCA inventory.**
FDA:	**Potassium silicate is regarded as GRAS (Generally Recognized As Safe) as a corrosion preventative in potable water.**

16. OTHER INFORMATION

Prepared by:	**John G. Blumberg**
Supercedes revision of:	**07/30/01**

The PQ Corporation

MSDS

MATERIAL SAFETY DATA SHEET

Trade Name: **AgSil™ 25F Potassium Silicate**
Date Prepared: **08/15/01**

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name:	**AgSil™ 25F Potassium Silicate**
Product description:	**A 2.5 weight ratio potassium silicate**
Manufacturer:	**PQ Corporation** **P. O. Box 840** **Valley Forge, PA USA** **Phone number: 610-651-4200** **Fax number: 610-651-4504**
In case of emergency call:	**1 610-651-4200**
For customer service call:	**1 610-651-4330**

2. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical and Common Name	*CAS Registry Number*	*Wt. %*	*OSHA PEL*	*ACGIH TLV*
Silicic acid, potassium salt; Potassium silicate	**1312-76-1**	**~100%**	**Not Established**	**Not Established**

3. HAZARDS IDENTIFICATION

Emergency Overview:	**White, odorless, flakes. Causes eye, skin, and digestive tract irritation. Dust causes irritation to respiratory tract. High pH is harmful to aquatic life. Noncombustible. Reacts with acids and some organics.**
Eye contact:	**Causes irritation.**
Skin contact:	**Causes irritation.**
Inhalation:	**Dust irritating to respiratory tract.**
Ingestion:	**May cause irritation to mouth, esophagus, and stomach.**
Chronic hazards:	**No known chronic hazards. Not listed by NTP, IARC or OSHA as a carcinogen.**
Physical hazards:	**Can etch glass if not promptly removed.**

4. FIRST AID MEASURES

Eye:	**In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention.**
Skin:	**In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Get medical attention.**
Inhalation:	**Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.**

Ingestion:	**If swallowed, DO NOT induce vomiting. Get medical attention immediately. If victim is fully conscious, give a cupful of water. Never give anything by mouth to an unconscious person.**

5. FIRE FIGHTING MEASURES

Flammable limits:	**This material is noncombustible.**
Extinguishing Media:	**This material is compatible with all extinguishing media**
Hazards to fire-fighters:	**See Section 3 for information on hazards when this material is present in the area of a fire.**
Fire-fighting equipment:	**The following protective equipment for fire fighters is recommended when this material is present in the area of a fire: chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots.**

6. ACCIDENTAL RELEASE MEASURES

Personal protection:	**Wear chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots, NIOSH-approved dust respirator where dust occurs. See section 8.**
Environmental Hazards:	**Sinks and mixes with water. High pH of this material is harmful to aquatic life, see Section 12.**
Small spill cleanup:	**Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8.**
Large spill cleanup:	**Keep unnecessary people away; isolate hazard area and deny entry. Do not touch or walk through spilled material. Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8. In case of contact with water, prevent runoff from entering into storm sewers and ditches which lead to natural waterways. Neutralize contaminated area and flush with large quantities of water. Comply with applicable environmental regulations.**
CERCLA RQ:	**There is no CERCLA Reportable Quantity for this material. If a spill goes off site, notification of state and local authorities is recommended.**

7. HANDLING AND STORAGE

Handling:	**Avoid contact with eyes, skin and clothing. Avoid breathing dust. Keep container closed. Promptly clean up spills.**
Storage:	**Keep containers closed. Store in clean steel or plastic containers. Separate from acids, reactive metals, and ammonium salts. Do not store in aluminum, fiberglass, copper, brass, zinc or galvanized containers.**

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls:	**Use with adequate ventilation. Keep containers closed. Safety shower and eyewash fountain should be within direct access.**
Respiratory protection:	**Use a NIOSH-approved dust respirator where dust occurs. Observe OSHA regulations for respirator use (29 C.F.R. §1910.134)**
Skin protection:	**Wear body-covering protective clothing and gloves.**
Eye protection:	**Wear chemical goggles.**

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance:	**Glass flakes.**
Color:	**White.**
Odor:	**Odorless.**
pH (aqueous solutions):	**Approximately 11.3**
Bulk density:	**Approximately. 77 lbs/ft^3**
Solubility in water:	**Soluble in all proportions.**

10. STABILITY AND REACTIVITY

Stability:	**This material is stable under all conditions of use and storage.**
Conditions to avoid:	**None.**
Materials to avoid:	**Generates heat when mixed with acid. May react with ammonium salt solutions resulting in evolution of ammonia gas. Flammable hydrogen gas may be produced on contact with aluminum, tin, lead, and zinc.**
Hazardous decomposition products:	**Hydrogen.**

11. TOXICOLOGICAL INFORMATION

Acute Data:	**This material has not been tested for primary eye irritation. However, on the basis of its similarity to sodium silicates in composition and alkalinity it is regarded as an eye irritant.** **This material has not been tested for primary skin irritation potential. However, on the basis of its similarity to sodium silicates in composition and alkalinity it is regarded as a skin irritant. Human experience confirms that irritation occurs when potassium silicates get on clothes at the collar, cuffs or other areas where abrasion may occur.** **The acute oral toxicity of this product has not been tested. When chemically similar sodium silicates were tested on a 100% solids basis, their single dose acute oral LD$_{50}$ in rats ranged from 1500 mg/kg to 3200 mg/kg. The acute oral lethality resulted from nonspecific causes.**
Subchronic Data:	**In a study of rats fed chemically sodium silicate in drinking water for three months, at 200, 600 and 1800 ppm, changes were reported in the blood chemistry of some animals, but no specific changes to the organs of the animals due to sodium silicate administration were observed in any of the dosage groups. Another study reported adverse effects to the kidneys of dogs fed sodium silicate in their diet at 2.4g/kg/day for 4 weeks, whereas rats fed the same dosage did not develop any treatment-related**

	effects. Decreased numbers of births and survival to weaning was reported for rats fed sodium silicate in their drinking water at 600 and 1200 ppm.
Special Studies:	**The mutagenic potential of this material has not been tested. Chemically similar sodium silicate was not mutagenic to the bacterium E. Coli when tested in a mutagenicity bioassay. There are no known reports of carcinogenicity of potassium silicates. Frequent ingestion over extended periods of time of gram quantities of silicates is associated with the formation kidney stones and other siliceous urinary calculi in humans. Potassium silicate is not listed by IARC, NTP or OSHA as a carcinogen.**

12. ECOLOGICAL INFORMATION

Eco toxicity:	**The ecotoxicity of potassium silicate has not been tested. The following data is reported for chemically similar sodium silicates on a 100% solids basis: A 96 hour median tolerance for fish (Gambusia affnis) of 2320 ppm; a 96 hour median tolerance for water fleas (Daphnia magna) of 247 ppm; a 96 hour median tolerance for snail eggs (Lymnea) of 632 ppm; and a 96 hour median tolerance for Amphipoda of 160 ppm.**
Environmental Fate:	**This material is not persistent in aquatic systems, but its high pH when undiluted or unneutralized is acutely harmful to aquatic life. Diluted material rapidly depolymerizes to yield dissolved silica in a form that is indistinguishable from natural dissolved silica. It does not contribute to BOD. This material does not bioaccumulate except in species that use silica as a structural material such as diatoms and siliceous sponges. Where abnormally low natural silica concentrations exist (less than 0.1 ppm), dissolved silica may be a limiting nutrient for diatoms and a few other aquatic algal species. However, the addition of excess dissolved silica over the limiting concentration will not stimulate the growth of diatom populations; their growth rate is independent of silica concentration once the limiting concentration is exceeded. Neither silica nor potassium will appreciably bioconcentrate up the food chain.**
Physical/Chemical:	**Sinks and mixes with water. Only water will evaporate from this material.**

13. DISPOSAL CONSIDERATIONS

Classification:	**Disposed material is not a RCRA hazardous waste.**
Disposal Method:	**Neutralize and landfill solids in accordance with federal, state and local regulations. Flush neutral liquid to sewer accordance with federal, state and local regulations and permits.**

14. TRANSPORT INFORMATION

DOT UN Status:	**This material is not regulated hazardous material for transportation.**

15. REGULATORY INFORMATION

CERCLA:	**No CERCLA Reportable Quantity has been established for this material.**
SARA TITLE III:	**Not an Extremely Hazardous Substance under §302 Not a Toxic Chemical under §313. Hazard Categories under §§311/312: Acute**
TSCA:	**All ingredients of this material are listed on the TSCA inventory.**
FDA:	**Potassium silicate is regarded as GRAS (Generally Recognized As Safe) as a corrosion preventative in potable water.**

16. OTHER INFORMATION

Prepared by:	**John G. Blumberg**
Supercedes revision of:	**07/30/01**

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ATTACHMENT E

"Health, Safety, and Environmental Aspects of Soluble Silicates"

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Health, Safety, and Environmental Aspects of Soluble Silicates

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The alkalinity of soluble silicates is their primary hazard. Contact exposure effects can range from irritation to corrosion. Inhaled or ingested sodium silicates are rapidly eliminated in the urine. Trace quantities of dissolved silica are essential to nutrition, but if normal dietary amounts are exceeded, siliceous urinary calculi may result. Dissolved silica is a minor but ubiquitous constituent of the environment. When dissolved silica becomes depleted in natural waters, diatoms are displaced by species that accelerate eutrophication. Commercial soluble silicates rapidly depolymerize upon dilution to molecular species indistinguishable from natural dissolved silica.

Soluble silicates have been known since ancient times, but it was not until the middle of the 19th Century that soluble silicates were produced on a commercial scale. In 1877, a 46-page pamphlet(1) was sufficient to encompass most of the knowledge about soluble silicates then available. By 1928, over 400 pages were required for Vail's first American Chemical Society Monograph on the subject(2). This monograph contained information on the amelioration of the adverse environmental effects of emissions from the now abandoned sulfate process for soluble silicate production(3), the use of soluble silicates in aqueous effluent treatment(4), and a short chapter on the physiological effects of soluble silicates(5).

In recent years, there has been an increasing emphasis on biological testing for the quantitative determination of environmental and health effects of chemical products and processes. But since biological testing is both time consuming and expensive, those who fund this type of research, government, industry, labor or academic organizations, tend to give higher priority for testing to newer chemicals about which little is

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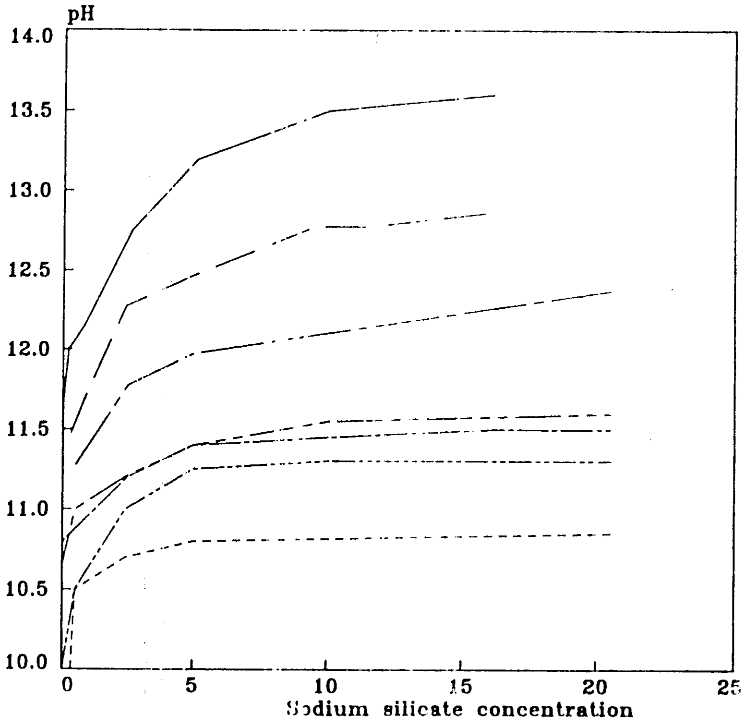

Figure 2. Concentration vs. pH. Key: – – –, 3.7; - - — - -, 3.2; — - —, 2.9; — – –, 2.5; — –, 2.0; — —, 1.6; and ——, 1.0 ratio.

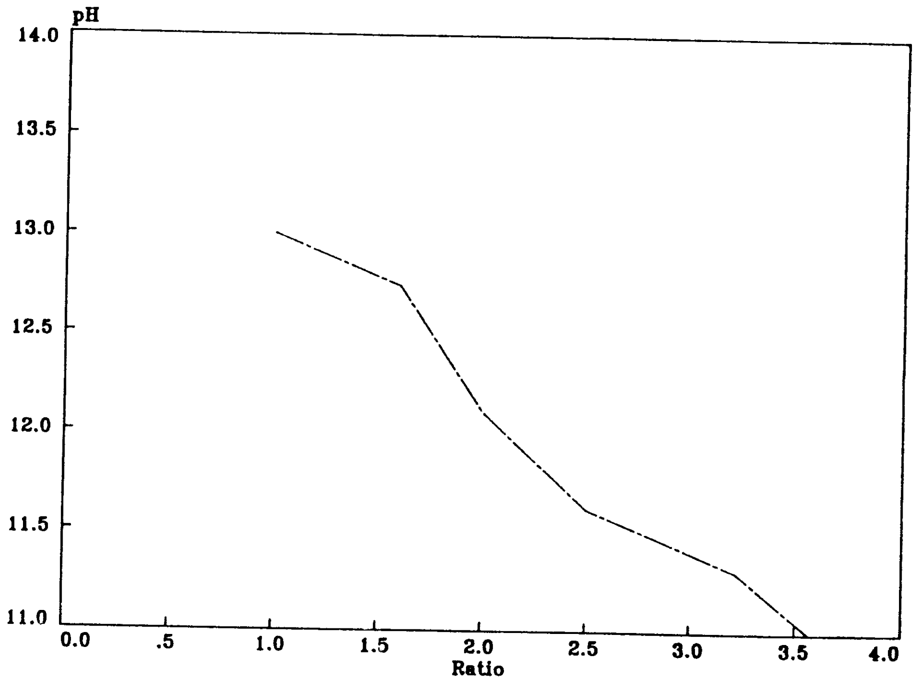

Figure 3. Ratio vs. pH.

tests using rabbits during the late 1960s and early 1970s. Initially a description of the findings upon macroscopic examination were the only results reported. Two samples of a 2.0 ratio sodium silicate powder (80% solids) and two samples of sodium metasilicate were tested at this time. "No lesions ..." and "submucosal edema" were noted in the animals exposed to 2.0 ratio sodium silicate, but "severe ulcer" and "active hyperemia" resulted from metasilicate exposure(12). In 1973, Bierbower,(13) reported on a series of similar tests, conducted under the auspices of the Consumer Product Safety Commission. Microscopic examination of the esophagus was used as the primary criterion for categorizing results as either "corrosive" or "negative." This data is summarized on Table II. The data indicate a correlation of hazard with ratio only at the extremes of ratio. In the intermediate range, the results for liquids vary with concentration (independent of pH which is virtually constant - see Figure 2), and the results for powders in this range are equivocal.

In man, the lethal oral dose of sodium silicates has been estimated as 0.5-5 g/kg(7). Ingestion of 200 ml of sodium silicate egg preserving solution (these solutions typically contain 5-36% of 3.2 SiO_2/Na_2O) caused severe vomiting, diarrhea and bleeding, elevated blood pressure, and renal damage, but was not fatal(14). In the past, sodium silicate has been administered orally for medicinal purposes in doses of 1 to 3 g/day without reported adverse effects(15), however, it is not presently known to be used as a drug.

In an early feeding study, King et al.(16) attempted to administer soluble silicates to dogs as 5% solutions, but found they had to preneutralize the solutions or the dogs invariably vomited them. Such soluble silica that was absorbed by the dogs from the neutralized solution was found to be quickly eliminated in the urine. The level of silica in the blood remained low and it was suggested that these animals have a low renal threshold for dissolved silica. Newberne and Wilson(17) succeeded in feeding dogs and rats sodium silicate incorporated into an semisynthetic diet at levels equivalent to 0.8 g SiO_2/kg/day. The only untoward clinical signs observed were polydipsia, polyuria, and soft stools. Renal lesions were observed in the dogs upon histopathological examination. Similar effects were not observed in the rats. Smith(18) studied the effects of 3.22 ratio sodium silicate added to the drinking water of rats at levels of 600 and 1200 mg/l. Two trials were conducted. The first, with a nutritionally adequate diet, lasted 180 days. The second, in which a diet inadequate for normal growth was provided, lasted 84 days. The rats used in the second trial were the offspring of those used in the control group of the first trial. Nitrogen and phosphorus retention was measured by assaying the diet and wastes for these elements. Weight gain and reproductive ability were recorded. Consumption of the water was

Table II. Esophageal Test (Oral, Rabbit)
Sodium Silicate

SiO2/Na20 wt. ratio	CONCENTRATION	RESULTS + = corrosive
3.2	5% w/v	–
3.2	10% w/v	–,–
2.9	10% w/v	–
2.9	15% w/v	+
2.9	Neat liq.(43%)	+
2.4	10% v/v	–
2.4	15% v/v	+
2.4	Neat pwd.	+,–
2.0	5% V/V	–
2.0	10% v/v	+,+
2.0	Neat pwd.	+,–
1.0	10% w/v	+,+
0.7	10% w/v	+

only noted by casual observation, but it was reported to be similar for all groups.

In the trial receiving an adequate diet, the male rats receiving sodium silicate at the 600 ppm SiO_2 level (about 790 ppm sodium silicate), experienced a 6% greater weight gain over controls receiving deionized H_2O. Females from this same group gained 5% less weight than the controls. At the higher level (about 1580 ppm sodium silicate) weight gains by both sexes did not differ significantly ($P = 0.05$) from controls. In the second trial, there was no significant difference in weight gain of the silicate treated versus the control animals at the lower level, although the males at the higher levels were 6% lighter than controls. The greatest variation in nitrogen retention was a 13% retention of urinary nitrogen in the first trial group at the lower level of silicate consumption - the same group that gained weight. The largest variation in phosphorus retention was a 9% increase in the second trial group that consumed silicate at the higher level, but it was not apparent whether this difference was due to the silicate treatment or the greater body size of these animals. The results of the study of the rats reproductive performance are given in Table III. It appears that of all the factors observed, the number of offspring to survive until weaning the is the only one to consistently correlate with increased silicate consumption. In view of the high mortality of the control offspring (only 35% survived), any additional stress might have produced the same effect. The author concludes that "soluble silica ... exerts biologically important effects on growth and reproductive performance,"(19) but it is not clear from his data whether there is an effect, and if there is, whether it can be attributed to the dissolved silica or the alkalinity of the drinking water.

Ito et al.(20), fed rats drinking water containing from 200 to 1800 ppm sodium silicate for 3 months. They reported an increase in serum alkaline phosphatase activity at a concentration of 1800 ppm in males, and an increase of serum glutamic-pyruvic transaminase activity at 200 and 600 ppm sodium silicate in females. A decrease in leukocyte count occurred in both sexes at 600 ppm. No specific change in the rats due to the sodium silicate was observed upon histopathological examination.

Benke and Osborne(21) studied the rate and extent of urinary excretion of silicon in rats after oral administration of single doses of several silicates, including a 2.4 ratio sodium silicate, to rats. Two trials were conducted: in the first trial, a dose of 40 mg/kg was administered, in the second trial the dose was 1000 mg/kg. At the 40 mg/kg level, 18.9% of the administered silicate was excreted in the urine, and elevated levels of Si in the urine were observed only in the first 24 hours after the oral dose. At the 1000 mg/kg level, 2.8% of the total administered silicate was excreted in the urine, and the data in Figure 4 were obtained for the rate of excretion. Benke

Table III. Reproductive Ability of Rats Fed Sodium Silicate in Drinking Water

	CONCENTRATION (as ppm SiO2)		
	0	600	1200
Matings	77	77	77
Litters	54	51	49
No. Born	517	346	414
No. Weaned	182	83	44
% Weaned	35	24	11
Difference as % of Controls			
Born		67	80
Weaned		46	24

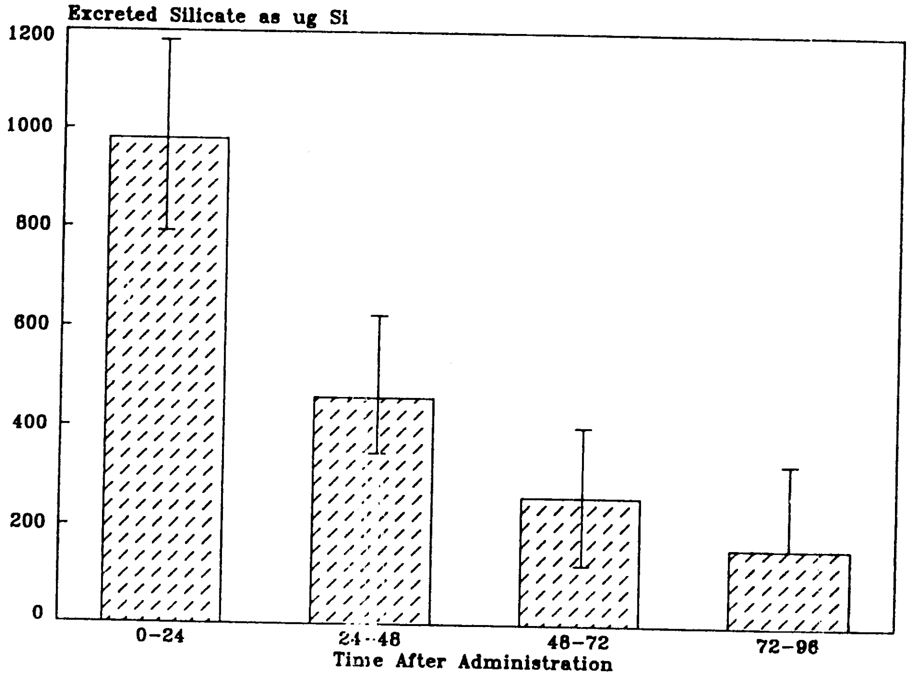

Figure 4. Urinary excretion of sodium silicate.

and Osborne calculated the urinary excretion half-life for ingested sodium silicate to be 24 hours.

Sauer et al.(22), measured the total silica eliminated (i.e., urinary and fecal SiO_2) by guinea pigs after oral administration of 1) a single dose of sodium metasilicate pentahydrate, equivalent to 80 mg SiO_2, and 2) four doses of sodium metasilicate pentahydrate, equivalent to 80 mg SiO_2, at 48 hr. intervals. Within 8 days, 60% of the silica administered as a single dose and 96% of the silica administered as multiple doses was excreted.

Although there are no reports in the scientific literature of chronic testing or carcinogenicity of sodium silicates, a number of studies on zeolite type A, which rapidly decomposes to amorphous aluminates and sodium silicate in the stomach and tissues, were recently reported(23). Among these studies was a lifetime feeding study in rats which concluded that chronic feeding of high doses (.001, .01 and .1% in diet) of type A zeolite did not produce cancer or chronic organ toxicity in rodents(24). It is also relevant to note that sodium silicates have had a long history of safe use in numerous food-related applications(25). Sodium silicate and potassium silicate are considered GRAS (Generally Recognized as Safe) by the U.S. FDA for addition to canned drinking water as a corrosion preventative at concentrations up to 100 ppm(26).

Skin Contact

Tests for the effects of skin contact of sodium silicates have been undertaken by both industry and governmental agencies. Since many soluble silicates are not stoichiometric compounds but rather can be prepared with variable SiO_2/Na_2O ratios, tests have been conducted at various points on the continuum of possible ratios, usually at points within the specifictions of commercial products.

Two similar experimental procedures have been used to quantify the skin contact effects of soluble silicates; both are based on the Draize method(27). The first is the protocol adopted by the U.S. Food and Drug Administration and Consumer Product Safety Commission for determining the contact hazard of substances under the Federal Hazardous Substances Act, and is specified in 16 C.F.R. §1500.41 et seq. The second, is the protocol adopted by the U.S. Department of Transportation for determining the contact hazard of substances under the Federal Hazardous Materials Transporation Act, and is specified in 49 C.F.R. §173.240.

In the FHSA test, 0.5 g or 0.5 ml of the test substance is moistened with physiological saline and applied to the intact and abraded skin of rabbits for 24 hours. The site of contact is examined after 24 and 72 hours and the extent of irritation is ranked on a scale (Primary Irritation Index) of increasing severity of from 1 to 4. Corrosivity, i.e., nonreversible injury, is also noted. Tables IV. and V. list the values obtained for soluble silicates in a number of laboratories over the course of about 20 years. The PII values listed are the sum of intact and abraded scores unless otherwise noted. Too few determinations have been done to compute the standard error of the PII, but the subjective nature of the scaling system makes the inference reasonable that it is large enough to account for the otherwise anomalous values for 3.2 ratio at 80 and 36 percent, respectively.

It appears that the breakpoint between irritant and corrosive solid sodium silicates occurs between 2.0 and 2.4 ratio. Potassium silicates are evidently more irritating than sodium silicates of equivalent mole ratio. Perhaps this is the result of the greater aqueous solubility of potassium silicates.

Test Results

The DOT test differs from the FHSA test principally in that the exposure period is 4 hours instead of 24 hours, and dry substances are tested dry - they are not moistened with saline solution. Consequently, this test is less sensitive to small differences in the activity of compounds, but it provides a more realistic model of accidental human exposure. The data in Table VI. indicates that the breakpoint between irritant and corrosive liquid sodium silicates occurs between 1.6 and 1.8 ratio, but it is also probably influenced by the concentration of the solutions.

In industries using sodium silicates, dermatitis has been attributed to sodium silicate exposure(34). Where adequate protection of the hands is not undertaken, physical injury by projecting points of dried silicate is further aggravated by alkaline irritation(35). Workers within the soluble silicate industry have been reported to sustain burns from hot glass and dermatitis from alkaline materials.(36) In our experience, the most common type of accidents involve spilling or splashing silicates into shoes or getting it between the skin and clothing at the collar and cuffs where abrasion occurs.(37) Safety boots and gloves with gauntlets are recommended to avoid these types of exposure.

Eye Contact

The effects of eye contact with sodium silicates have been tested by industry and in government laboratories. The standard test for determining the hazard of eye contact is the FHSA Draize method specified in 16 C.F.R. §1500.42. The data in Table VII. indicates that at the ratios and concentrations tested, soluble silicates are irritating to the eyes, and severely irritating at high concentrations. A new test for assessment of eye contact effects is currently under development.

Table IV. FHSA Skin Contact Data
Sodium Silicate

SiO2/Na2O wt. ratio	CONC. wt.%	PII	CORROSIVITY + = corrosive	Ref.
3.2	99	4	–	28.
3.2	80	0	–	28.
3.2	36	3	–	28.
2.9	43	3	–	28.
2.5	37	3	–	28.
2.4	24	4	–	28.
2.0	99	8	+	28.
2.0	54	4	–	28.
2.0	8	>4*	–	29.
1.0	10	5.6*	+	29.
1.0	6	>8*	+	29.

* 2x average of intact and abraded score.

Table V. FHSA Skin Contact Data
Potassium Silicate

SiO2/K2O mol. ratio	CONC. wt.%	PII	CORROSIVITY + = corrosive	Ref.
3.45	29	0	–	28.
3.33	39	2	–	28.
2.5	85	8	–	30.

Table VI. DOT Skin Contact Data
Sodium Silicate

SiO2/Na2O wt. ratio	CONC. wt.%	PII	CORROSIVITY + = corrosive	Ref.
2.9	43	3.3	–	31.
2.5	37	0	–	31.
2.4	47	4.2	–	31.
2.0	44	4.2	–	31.
2.0	54	4.7	–	32.
1.8	38	3.2	–	32.
1.6	51	*	+	33.
1.0	99	*	–	33.
0.7	61	*	–	33.
0.5	90	*	+	33.

* not reported.

Table VII. FHSA Eye Contact Data
Soluble Silicates

SiO2/Na2O wt. ratio	CONC. wt.%	IRRITATION	Ref.
3.2	36	–	37.
2.9	43	+(severe)	37.
2.0	8	+	37.
2.0	44	+(severe)	37.
1.0	10	+	37.
1.0	6	+	37.
1.0	5	+	37.
1.0	3	+.	37.
0.7	6	+	37.
0.7	3	+	37.
2.5*	80	+(severe)	38.

* SiO2/K2O ratio

Inhalation

Michon, et al.(40), studied the silicon metabolism of rabbits after inhalation of a sodium silicate aerosol. They concluded that sodium silicate dissolves in the lungs and is rapidly eliminated in the urine.

Becking(41) summarized two inhalation studies of type A sodium zeolite which rapidly decomposes to sodium silicate and amorphous aluminates under physiological conditions. In the first study, hamsters were exposed to approximately 20 mg/m^3 of type A zeolite 3 days per week, 5 hours per day for 52 weeks. In the second study, Cynomolgus monkeys were exposed to 1 and 6 mg/m^2 of type A zeolite for 24 months, and 50 mg/m^3 type A zeolite for 12 months. No evidence of fibrosis was observed in the animals in either study.

ENVIRONMENTAL ASPECTS

Occurrence

Compounds of silicon and oxygen are the primary constituents of earth's land masses. Dissolved silica is a minor but ubiquitous constituent of earth's hydrosphere. Ground waters contain the highest concentrations of dissolved silica: the median value in the U.S. is 17 ppm(42). Of earth's surface waters, streams and rivers contain the most dissolved silica. The median value for streams in the U.S. is 14 ppm(43). For rivers, the worldwide mean concentration is 13 ppm(44). Lakes are reported to contain about 4 ppm(45), while the mean concentration of dissolved silica in the oceans is about 6 ppm(46). The median value for dissolved silica in the public water supplies of the 100 largest U.S. cities is 7.1 ppm(47).

Earth's biomass also contains appreciable soluble silica. Relatively large amounts of silica are absorbed from solution, concentrated, and precipitated by the siliceous sponges (Hyalospongiae) and the protozoan orders Radiolaria and Heilozoa, while the majority of species in the Animal Kingdom only contain dissolved silica in the parts per million range.(48) The precise amount of soluble silica found in plants is determined by both species and soil factors. Lower plants, such as grasses (Gramineae) are very rich in silica, wet-land varieties usually containing the highest concentrations(49). In general, legumes and dicotyledonous plants contain less soluble silica than monocotyledons.(50)

Infrared absorption studies have shown that most biogenic silica is present as gel or dissolved silica. However, emission spectroscopy studies have indicated that some of the soluble silica found in animals is bound to organic molecules, such as glycosaminoglycans, whose structure has yet to be identified(51).

Environmental Chemistry

The solubility of silica can be characterized by the following equilibria at 25°C. Monosilicic acid has been written $H_2SiO_2(OH)_2$, rather than $Si(OH)_4$ or H_4SiO_4 in order to emphasize its diabasic character, and the tendency of silicon, like other metalloids, to coordinate with hydroxo and oxo ligands.

$$\text{Quartz} + 2H_2O \longrightarrow H_2SiO_2(OH)_2 \qquad \log K = -3.7$$

$$\text{Amorphous silica} + 2H_2O \longrightarrow H_2SiO_2(OH)_2 \qquad \log K = -2.7$$

$$H_2SiO_2(OH)_2 \longrightarrow HSiO_2(OH)_2^- + H^+ \qquad \log K = -9.46$$

$$HSiO_2(OH)_2^- \longrightarrow SiO_2(OH)_2^{-2} + H^+ \qquad \log K = -12.56$$

$$4H_2SiO_2(OH)_2 \longrightarrow Si_4O_6(OH)_6^{-2} + 2H^+ + 4H_2O \qquad \log K = -12.57$$

Stumm(52) used these equilibria to construct the diagram in Figure 5 which describes the speciation of silica in aqueous solution. His data indicate that at normal environmental pH values (pH 9) dissolved silica exists exclusively as monosilicic acid. This conclusion is supported by the finding that soluble silica has a diffusion coefficient of 0.53 indicating a molecular size about equivalent to monosilicic acid(53).

Below about pH = 9.4 the solubility of amorphous silica is about 120 ppm(54). Quartz has a solubility of only about 6 ppm, but its rate of crystallization is so slow at ordinary temperatures and pressures that the solubility of amorphous silica represents the upper limit of dissolved silica concentration in natural waters.

Dissolved silica is supplied to the environment by chemical and biochemical weathering processes which involve the transfer of energy from biological systems to silicate minerals as well as ion substitution and chelate forming reactions which remove mineral lattice cations(55). The concentration of dissolved silica in natural waters is controlled by a buffering mechanism which is thought to involve the sorption and desorption of dissolved silica by soil particles and sediments(56, 57). The average silica weathering rate of watersheds is 20 kg/ha/hr(58). The processes of the natural silica cycle are depicted in Figure 6. Any soluble silica input to this natural cycle as a result of the production or use of commercial soluble silicates would be a trivial amount in view of the high flux of the natural silica cycle. Dissolved silica from commercial soluble silicates is indistinguishable from natural dissolved silica since depolymerization of polysilicate anions to monomeric dissolved silica occurs very rapidly when

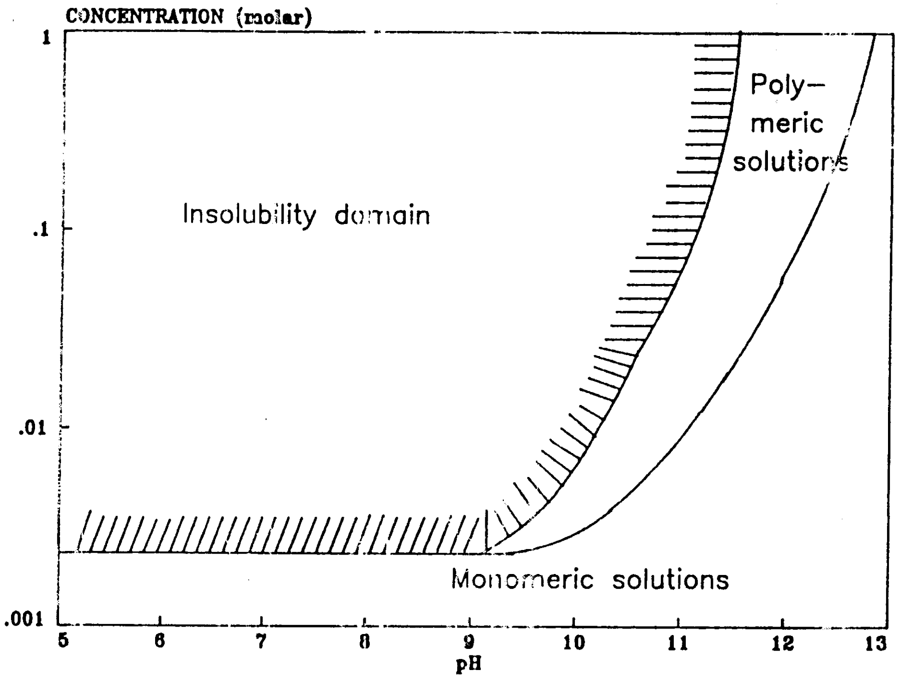

Figure 5. Soluble silicate speciation.

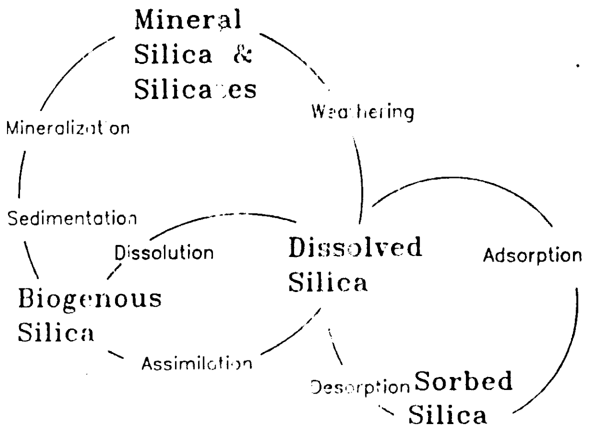

Figure 6. The natural silica cycle.

commercial soluble silicate solutions are diluted with water(59).

Aquatic Toxicity

Aquatic toxicity data is usually expressed in terms of the median tolerance limit. TLm, which is defined as that concentration of a substance that it lethal to 50 percent of the test population in an arbitrary time period. Table VIII. lists the TLm values obtained for sodium silicate.

Nutritional Aspects

The essential nature of silicon as a nutrient has long been recognized in primitive plant and animal species that utilize it in the form of silica as a structural material(60). Until recently, it had been thought that since the bone-cartilage system had evolved in animals and the cellulose-lignin system had evolved in plants silica had become obsolete; that the presence of silica in higher species was simply attributable to their contamination by the vast quantities of silica in the natural environment. In the past few years, however, a number of experiments have indicated that silicon is necessary, albeit in trace quantities, for the normal growth, development and functioning of a large variety of higher animals(61), and it is anticipated that silicon will become recognized as an essential nutrient for most if not all species.

The problems associated with "blooms" of algae which occur in eutrophic bodies of water have motivated much research into determining the limiting nutrients which control the growth of algal populations. It has been demonstrated that at concentrations of less than 0.1 ppm, silica is a limiting nutrient for diatoms(62), and a few other algal species(63). Thus, only in bodies of water which are orders of magnitude lower in silica concentration than normal environmental levels, could silica become a limiting factor to algal growth. The addition of excess soluble silica over the limiting concentration will not stimulate the growth of diatom populations; their growth rate is independent of silica concentration, once the limiting concentration is exceeded(64, 65).

It has been observed that when a body of water becomes eutrophic due to large inputs of phosphorus, diatom populations increase, and this results in a decline in the dissolved silica content of the water, especially the surface water(66). If this process continues until the available silica becomes depleted below the limiting concentration for diatoms, they are replaced by obnoxious green and blue-green algal species which have much lower requirements for silicon(67). Thus, it is beneficial to maintain an adequate supply of soluble silica in a phosphorus-rich body of water in order to promote diatoms as

Table VIII. Aquatic Toxicity Sodium Silicate

Animal	Time	Dose	Ref.
Annelids			
Negris grubei	28days	250g-at/l.	68.
Capitella capitata	28days	210g-at/l.	68.
Mosquitofish			
Gambusia affnis	24hr.	3200ppm	69.
" "	48hr.	2400ppm	69.
" "	96hr.	2320ppm	69.
Water flea			
Daphnia magna	96hr.	247ppm	70.
Snail eggs			
Lymnea	96hr.	632ppm	70.
Amphipoda	96hr.	160ppm	70.

the dominant algae. Sodium silicate has been reported to inhibit the growth of a troublesome species of blue-green algae(68).

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ATTACHMENT F

"Silicate Based Drilling Fluids: A Highly Inhibitive Mud System Offering HS&E Benefits Over traditional Oil Based Muds"

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ATTACHMENT F

“Silicate Based Drilling Fluids: A Highly Inhibitive Mud System Offering HS&E Benefits Over traditional Oil Based Muds”

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AADE XXXXX

Silicate Based Drilling Fluids: A Highly Inhibitive Mud System Offering HS&E Benefits Over Traditional Oil Based Muds

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This paper was prepared for presentation at the AADE 2002 Technology Conference "Drilling & Completion Fluids and Waste Management", held at the Radisson Astrodome Houston, Texas, April 2 - 3, 2002 in Houston, Texas. This conference was hosted by the Houston Chapter of the American Association of Drilling Engineers. The information presented in this paper does not reflect any position, claim or endorsement made or implied by the American Association of Drilling Engineers, their officers or members. Questions concerning the content of this paper should be directed to the individuals listed as author/s of this work.

Abstract

The past few years have witnessed a rapid growth in the use of sodium and potassium silicate based drilling fluids. The rise in North American popularity has followed from growing recognition within the oil and gas industry that soluble silicate based drilling fluids offer a combination of superior shale inhibition, cost savings and significant advantages with regard to Health Safety and Environment. A general overview will be presented of silicate chemistry, geographical areas using silicate muds and field performance. However, the focus of the paper will be the Health Safety and Environment implications of using silicate muds. Key areas to be discussed include the role of silicate in the health of marine and terrestrial plants and the corresponding results of toxicity tests on sodium and potassium silicate muds. Disposal options and cost will be discussed under current and future state regulations. Finally, health and safety will be discussed as it pertains to workers in contact with, or exposed to silicate muds

Introduction

Offshore and onland, operators in North America are increasingly having to deal with more stringent standards with regards to the disposal of drilling fluids and cuttings. Some of the regulatory changes in North America include:

- -increased restrictions on disposal of advanced gel chem systems
- -limits on admissible chloride levels
- -more stringent ROC limits on olefinic and ester based drilling fluids
- -oil and grease limits
- -new sediment toxicity test

Likewise, operators and contractors are facing higher standards with regards to employees being exposed to drilling fluids. The concern comes in the form of the effect of :

- -skin contact
- -inhalation of air borne drilling fluids
- -flammability and fire hazard
- -Slippery surfaces and footing

The HS&E issues regarding the use and disposal of drilling fluids and cuttings can become particularly challenging and costly in the pursuit to meet regulatory compliance. Therefore much research has gone into developing environmentally friendly drilling fluids that still meet the performance requirements of:

- -high level of shale inhibition
- -low cost
- -high ROP
- -ease of use
- -low depletion rate

It has been well documented that silicates meet the performance requirements of shale inhibition, low depletion rate and high ROP[1,2,3,4,5]. Until now, less attention has been given to the HS&E aspects of using sodium and potassium silicate drilling fluids.

1.0 Silicate Use in North America:

Silicate based drilling fluids have come full circle in North America. Silicate muds were first used in the 1930's to control "heaving shale" that plagued drillers along the Gulf Coast. These early wells proved that silicate based fluids could give oil-like levels of shale inhibition. Lack of strict environmental regulations meant that there was little economic incentive to develop these early silicate muds. Silicate muds were periodically assessed in subsequent years but did not make a commercial return to North America till 1999[5] . Silicate muds have seen the quickest growth in Western Canada. The growth in popularity can be partly attributed to silicate muds being able to meet the strict guidelines for landspreading of waste mud as outlined in Guide 50[6]. Formulation modifications and the recycling of potassium silicate based muds have further improved both the economics as well as the environmental performance.

In the United States, silicate muds are being used on a commercial scale in Oklahoma and Wyoming. Offshore use of silicate muds in the Gulf of Mexico has been ~~oradic to date

Potassium silicate muds are now being used in Mexico and are showing the potential to be used as a supplement to traditional oil based systems. More wells are expected to be drilled using silicate muds in 2002.

2.0 Silicate Chemistry

Soluble silicates are manufactured by the fusing of sand (SiO_2) with sodium or potassium carbonate (Na_2CO_3 or K_2CO_3) at 1100-1200°C. The resulting glass is dissolved with high-pressure steam to form a clear, slightly viscous liquid that is sometimes referred to as "waterglass". The most important property of soluble silicates is the weight ratio of SiO_2: K_2O (or Na_2O). For example, a "2.5" ratio potassium silicate has 2.5kgs of SiO_2 for every 1kg of K_2O. Silicates are commercially produced in a variety of ratio ranges. The selection of ratio of silicate to formulate a drilling fluid is based on a number of criteria that include ease of use, stability and shale inhibition. In the case of Western Canada, a high ratio potassium silicate is the ratio of choice.

Sodium (or potassium) silicates are unique in that they can undergo four very distinct types of chemical reactions[7]. These reactions have been defined as:

-gelation/polymerization
-precipitation
-hydration/de-hydration
-surface charge modification

The gelation and ppt reaction has been discussed as it pertains to shale inhibition but these reactions can be used to help in the disposal of silicate drilling fluids or more particularly cuttings covered with silicate drilling fluids.

3.0 Health and Safety Benefits

Soluble silicates are well-established industrial chemicals that have been used in a variety of environmentally sensitive and health sensitive applications such as water treatment, soil remediation, manufacturing of soap and the latter discussed application of agriculture. Silicates have been classified as GRAS or Generally Recognized As Safe by the FDA. It is the designation given to substances that are considered safe for direct or indirect additives to foods and in many industries is considered a blanket statement of the harmless and nontoxic nature of a substance.

The main hazard associated with soluble silicates derives from their alkalinity. Both sodium and potassium silicate products can range from moderately to strongly alkaline. A similar level of safety and handling ecautions should be exercised when working with silicates as with any other alkaline chemicals. Silicate may cause mild skin and eye irritation depending on the degree of alkalinity. It is recommended that personal protective equipment (PPE) and protective clothing be worn based on the degree of alkalinity of the silicate being handled. The inherent alkalinity of silicate drilling fluids has meant that biocides are generally not added to the drilling fluid. Furthermore, soluble silicates are established corrosion inhibitors thus eliminating the need to add corrosion inhibitors to the drilling fluid. The removal of biocides and corrosion inhibitors contributes to a reduction in mud costs and complements the health, safety and environmental benefits.

Soluble silicates are odorless, inorganic chemicals that produce no unpleasant fumes or VOC emissions. Because of this silicate based drilling fluids do not exhibit the distinctive odor associated with petroleum and synthetic drilling fluids. Silicate drilling fluids are also not as slick as oil muds. This helps to reduce slipping and falling hazards on an operating rig. The non-flammable nature of silicates further reduces the safety concerns associated with some drilling muds and makes silicate fluids less of a hazard to work with.

4.0 Agricultural

The use of soluble silicates in the agricultural industry provides data that supports the contention that silicates are not only benign but can be beneficial when applied directly to crops or to cultivated and natural lands supporting vegetation.

Therefore, the most effective and inexpensive disposal option for a drilling fluid is to discard at sea or to land spread. The soluble silica found in a silicate drilling fluid is identical to the material used in agriculture applications and delivers the same growth benefits.

Potassium silicate is an approved fertilizer in many countries including the USA. Crops primarily benefiting from the application of potassium silicate include; rice, grasses, wheat, barley, sugar cane, melons, grapes, beans, apples and other pome fruits, cucurbits, and ornamental plants. The application of potassium silicate is based on the need of plants for potassium but also the need for soluble silica, which is an essential micronutrient. Some of the benefits sited for soluble silica includes the following :[8,9,10,11]

1. Improves the structural strength of cell walls
2. Improves resistance to water stress
3. Improves resistance to fungal and other diseases
4. Higher tolerance to metals such as manganese, iron, phosphorous and aluminum (sequestration)
5. Increases plant growth rate and yield

Sodium silicate is used as a fertilizer in marine applications to help increase the growth of diatoms in seawater. The nutritional value of silica was established recently in North Sea region in a number of "sea arvesting" projects which involved addition of silicates for blue mussels, scallops and cod farming. MARICULT[12] a large-scale "marine cultivation" research and optimization program was funded by both, European Union and The Research Council of Norway. This program, implemented in 1996, has also recognized silica's nutritional value. . Similiar programs have been initiated in the USA (Oceanic Farming) and Japan (Marino Forum 21). High natural levels of silica can already be found in marine sediments. Dissolved silica from commercial soluble silicates is virtually indistinguishable from natural dissolved silica.

5.0 Disposal

Worldwide, various methods have been utilized for silicate drilling waste disposal including land spreading, land farming, solidification and burying for onshore disposal. In offshore drilling, spent silicate mud and associated cuttings have been typically discharged to the sea. The UK and Norwegian governments have awarded silicate the highest environmental rating of class E. Class E material such as silicates can be discharged to the sea at a maximum rate of 4750 tonnes/year/installation.

In Western Canada, a growing number of operators ave chosen potassium silicate based drilling fluids over other water based drilling technologies.

In view of 1996 Guide 50 Drilling Waste Management Guidelines issued by the Alberta Energy and Utility Board (AEUB), a significant amount of study concerning environmentally sound disposal options for silicate based drilling fluids has been completed to date. The results of these studies have confirmed potassium silicate drilling wastes meet current requirements for safe disposal. One of the recommended on-site disposal methods for silicate drilling wastes is Mix-Bury-Cover, where drilling waste is incorporated into the subsoil in a ratio of at least three parts subsoil to one part drilling wastes. From the off-site disposal methods, clear fluids pump off and Mix-Bury-Cover method for disposal of drill solids and cuttings, is a viable and cost effective disposal option. Frequently, the choice of one disposal method over the other is determined by the method's suitability at the particular site.

As mentioned earlier in this paper, more stringent standards in regards to disposal have been imposed on all Advanced Gel Chem. Systems. As a result of tighter regulations, disposal approvals are mandatory for any land application involving these fluids. At present, operators are successfully obtaining approvals for disposal of potassium silicate drilling wastes.

isposal practices for silicate based drilling wastes in US are comparable to the previously discussed practices. Drilling wastes can be disposed by landfarming, landspreading, roadspreading, solidification and burying activities. Primary agencies with jurisdiction over drilling wastes disposal vary with each state. Disposal regulations also differ from state to state.

6.0 Toxicity Testing of Soluble Silicate Muds

Although there is an extensive body of work on the toxicity limits of potassium silicate and sodium silicate, it is important to measure the toxicity effects of silicate based drilling fluids in order to establish safe disposal options. Based on drilling waste management guidelines set out by the Alberta Energy Utility Board (AEUB) and American guidelines set out by the American Society for Testing and Materials (ASTM), the Environmental Protection Agency (EPA) and the Rail Road Commision (RRC) the following tests have been performed on soluble silicate muds:

- seed germination and root elongation (barley and cucumber)
- earthworm survival.
- Microtox
- Mysid shrimp testing

Figures 1,2,3 give a summary of the test results. At the concentrations tested, waste potassium silicate drilling fluids had no negative impact on either seed germination or earthworm survival. Root elongation testing for cucumbers showed an improvement in root length of cucumber at a dilution up to 25% with a negative impact at higher levels.

One of the essential criteria that must be satisfied prior to any drilling waste disposal is that the drilling waste has to pass a toxicity evaluation. In Western Canada, the evaluation of potential mud toxicity was conducted on marine luminescent groups of bacterium, *Photobacterium Phosphoreum*. Soluble Silicates and silicate drilling fluid waste have been rated as non-toxic and successfully passed the Microtox bioassay, the established drilling industry standard test for defining potential mud toxicity in Western Canada. The Microtox results correlate to LC50 concentrations. Table 1 contains Mircotox test results and protocol for the tested silicate drilling fluids.

In the Gulf of Mexico, Mysid shrimp toxicity is a critical parameter. Mysid shrimp are known to be extremely sensitive to free potassium ions so there are some concerns surrounding the use of potassium silicate mud in this ecosystem. Growth, fecundity and survival tests run on *Mysidopsis Bahia*
(EPA Method 1007.0) indicates that a neat solution of potassium silicate has an LC50 of 41,000 ppm. Since drilling fluids normally contain only about 10% silicate, the LC50 concentration should be approximately ten times higher for the drilling fluid itself if there were no

other factors contributing to toxicity. This would be well bove the EPA allowable concentration of 30,000 ppm nd more than double the level of 200,000 ppm that most operators set as a minimum to avoid compliance problems.

To test this assumption, two generic mud formulations were prepared using potassium silicate and tested on Mysid shrimp. Both muds were designed to match common formulations currently used in the Gulf of Mexico. Table 2 contains the 96-hour LC50 Bioassay Test results for both muds. Detailed mud formulations are presented in Table 3.

Mud formulation A was found to have an LC50 of 166,000 ppm. While this result is a slightly lower LC50 concentration than expected based on the neat silicate numbers it is explained by the presence of KOH in the formula. KOH contributed additional potassium ions to the system thereby slightly increasing the impact on Mysid shrimp. Mud formulation B, which contained no additional sources of potassium, had an LC50 concentration of approximately 600,000ppm, which was more in line with the anticipated results. Both potassium silicate drilling fluids tested exceed the EPA requirement by a substantial margin and as such would be acceptable for use in the Gulf of Mexico.

Conclusions

l based muds offer excellent shale inhibition but at an ever increasing HS&E cost. Silicate based muds offer the same degree of shale inhibition as oil based systems but with numerous HS&E advantages. Some of the key HS&E properties of silicate muds are as follows:

-soluble silicate can be disposed with negligible environmental impact
-soluble silicates are safe, non-toxic and have a GRAS rating
-silicates are non-volatile and contain no organics
-soluble silicates have agricultural applications including the use of potassium silicate as a fertilizer
-numerous environmentally sound disposal options exist for silicate based muds

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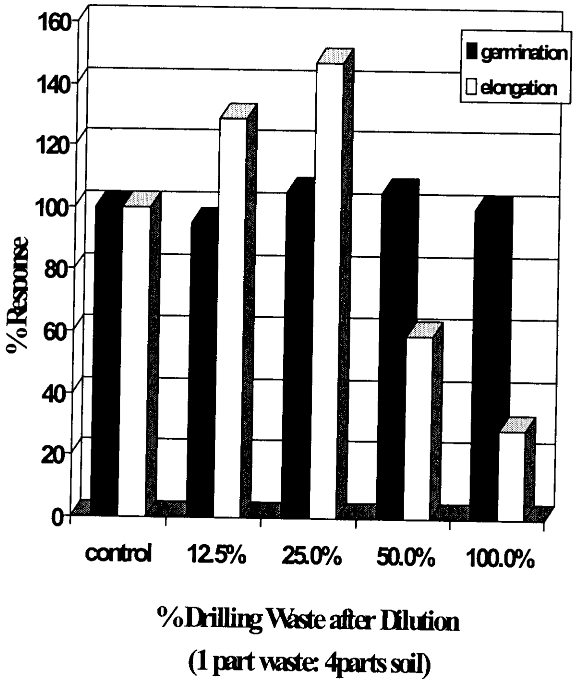


Figure1 – Response of Barley Seeds to Increasing Levels of Waste Potassium Silicate Drilling Fluid

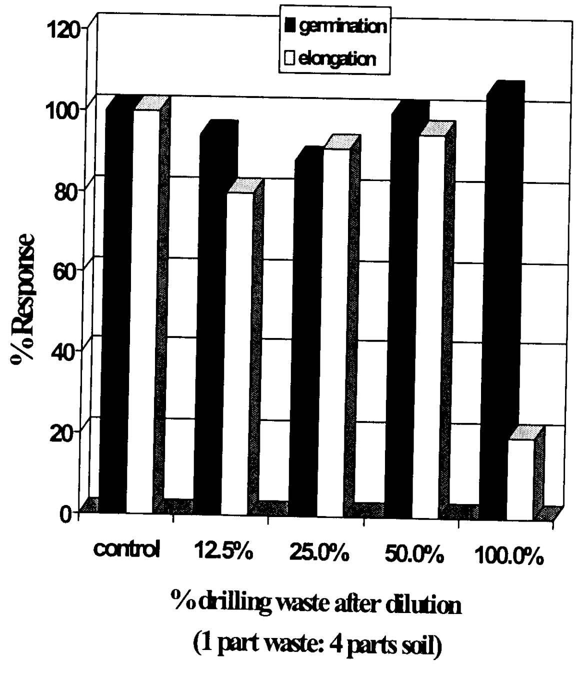
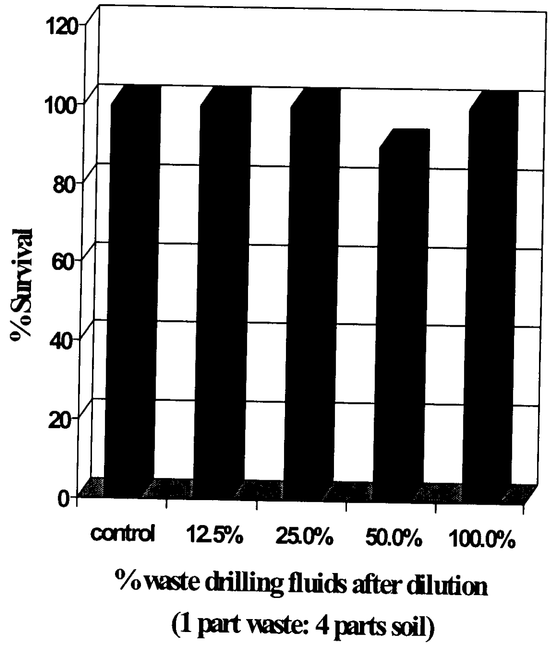


Figure 2 – Response of Cucumber Seeds to Increasing Levels of Waste Potassium Silicate Drilling Fluid

Figure 3 – Survival Rate of Earthworms in Soil Mixed with Waste Potassium Silicate Drilling Fluid



Testing Protocols

For Seed Germination, artificial soil was mixed with the appropriate sample dilution at a ratio of 1 part waste: 4 parts artificial soil. 30 grams of soil and sample were placed in a etri dish. Twenty seeds were added to the soil and covered by a 30g sand cap. Soil was hydrated with 7.5ml of de-ionized reverse osmosis water. Test was scored on the 5th day

For root elongation, a Whatman #3 filter paper was placed in a plastic petri dishes. The filter paper was hydrated with 3.5ml of the appropriate sample dilution after centrifugation. The controls were hydrated with deionized reverse osmosis water. The root lengths were scored on the 5th day.

Table 1- Microtox® Test Results

	Potassium Silicate concentration % by vol.	EC50(15) %
Potassium silicate drilling fluid waste(1)	12	>91
Potassium silicate drilling fluid waste(2)	10	100% with charcoal

The Microtox test is based on monitoring changes in the level of light emission from *Photobacterium Phosphoreum* bacterium cultures when challenged with a toxic substance or sample containing toxic materials. The Microtox endpoint is measured as the effective or inhibitory concentration of a test sample that duces light emission under defined conditions of time and temperature. Normally, it is expressed as EC50 (15), which is effective concentration of a sample that reduces light emission of the test organism by 50% over a 15-minute test period at 15°C.

Table 2 – 96 hour LC50 Definitive Bioassay Test Results on *Mysidopsis bahia;*
EPA, "Drilling Fluids Toxicity Test", 40 CFR; Part 435, Subpart A, Appendix 7

Drilling Fluid	Drilling Fluid Type	96 hour LC50	Pass or Fail
A	Silicate with 10% by vol Ecodrill 317	166,280 ppm	Pass
B	Generic 7 with 10% by vol Ecodrill 317	604,590 ppm	Pass

Table 3- Drilling Fluid Formulations

Additive	Drilling Fluid **A**	Drilling Fluid **B**
Seawater, bbl	0.79	-
Freshwater,bbl	-	0.79
Bentonite, ppb	-	20
Soda Ash, ppb	0.5	1
Lignosulfonate,ppb	-	4
Lignite,ppb	-	4
KOH, ppb	1.6	-
Caustic Soda, ppb	-	2
Xanthan Gum,ppb	0.75	-
PAC LV, ppb	5	0.5
Ecodrill 317,ppb	10% by vol	10% by vol
Barite, ppb	157.8	150

For the survival rate of earth worms, 200g of artificial soil was placed in a 474 ml plastic cup. Ten worms were randomly added to the soil. The soil was hydrated with 40 ml of the appropriate dilution of sample. The organisms were scored on day 7 and 14. Day 14 results are reported

Note: All tests were conducted at 23C with 16hrs of light followed by 8hrs of darkness

ATTACHMENT G

Bibliography

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"The Effects of Silicon Supplementation on Cucumber Fruit: Changes in Surface Characteristics"; Samuels, A.L. Glass, A.D.M.; Ehret, D.L.; Menzies, J.G.; Annals of Botany, Nov. 1993, Vol. 72(5), Page 433-440

Addition of silicate to hydroponic nutrient media has been shown to increase resistance of cucumber to powdery mildew. As a side effect of this treatment, the fruit surface developed an unusual dull appearance, or bloom. The effects of silicate supplementation on cucumber fruit were observed using scanning and transmission electron microscopy, energy-dispersive X-ray analysis, and colourimetric assays. Changes in the fruit trichome morphology occurred: trichomes from +Si fruit had a coarse outer appearance compared to -Si fruit where the trichomes were smooth. X-ray mapping showed high Si content in trichomes but not in the surrounding epidermis or fleshy mesocarp and endocarp tissues. Sections through the epidermal layer reveal that the silica is restricted to the trichomes, primarily in the epicuticular wax.

"Silicon Induced Resistance in Cucumber Plants Against Pythium Ultimum"; Cherif, M. Benhamou N.; Menzies, J.G.; Belanger, R.R.; Physiological and Molecular Plant Pathology, Doc. 1992. Vol. 41(6), Page 411-425

The effect of the amendment of nutrient solutions with soluble potassium silicate on the response of cucumber (cv. Corona) root and hypocotyl tissues infected by Pythium ultimum was examined by light and electron microscopy, and by energy dispersive X-ray analysis (EDX). Plants were grown in 0 or 1.7 mM Si-amended nutrient solutions, and root and hypocotyl samples were collected at different times after inoculation with P. ultimum. By 48 h after infection, striking differences in the markedly stimulated the accumulation of an electron-dense, phenolic-like material in infected host tissues, and significantly increased the percentage of cells filled with this material. Fungal hyphae colonizing occluded host cells were seriously damages and were often reduced to empty hyphal shells. Additionally, Si-treated cucumber plants responded to P. ultimum infection by forming electron-dense layers along primary and secondary cell walls, as well as over pit membranes of xylem vessels. EDX analysis failed to reveal the presence of silica deposits in P. ultimum-infected plants grown in Si-supplemented media. Our results suggest that a relationship exists between Si treatment, resistance to P. ultimum attack, and expression of plant defense mechanisms.

"Studies of Silicon Distribution in Wounded and Pythium Ultimum Infected Cucumber Plants"; Cherif, M.Menzies, J.G.; Benhamou, N; Belanger, R.R.; Physiological and Molecular Plant Pathology, Nov. 1992. Vol. 41(5), Page 371-385.

The objective of this study was to investigate the deposition of silicon (Si) in relation to the ability of Si to reduce the severity of Pythium ultimum infection on cucumber. Roots, hypocotyls and leaves of cucumber plants grown in nutrient solutions unamended or amended with 1.7 mM (100 ppm) potassium silicate were inoculated with P. ultimum or

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pierced with a sharp needle. At 24, 48 and 72 h after treatment, the plants were examined for Si distribution using scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) microanalysis. No Si was detected at sites of fungal penetration or in P. ultimum hyphae, regardless of the plant organ studies. Si was also absent from wounded roots and almost absent in wounded leaves and hypocotyls collected from plants maintained under high humidity in a growth chamber. By contrast, a specific and intense deposition of Si was found in cells surrounding the trichome hairs and in wounded leaves and hypocotyls of silicon amended plants. These results reinforce the idea that accumulation and polymerization of silica at fungal penetration sites or in epidermal cell walls has no role as a physical barrier against fungal attack. Thus Si deposition does not appear to be the mechanism by which fungal growth and penetration of plant tissues are hindered.

"Use of Potassium Silicate Amendments in Recirculating Nutrient Solutions to Suppress Pythium Ultimum on Long English Cucumber"; Cherif, M. Belanger, R.R.; Plant Disease, Oct, 1992, Vol. 76(10), Page 1008-1011.

"Wheat Leaf Silicification: An Inducible Defense Against Vertebrate Herbivores"; Grey, C.B.; Watkins, R.W.; Cowan, D.P.; Brighton Crop Protection Conference; Pests & Diseases, 1996. Vol. 3, Page 829-834.

It is proposed that systemic application of sodium silicate may significantly enhance the level of leaf silicification in winter wheat (Triticum vulgare cv. Mercia) and reduce the palatability of these plants for vertebrate herbivores such as the European rabbit (Oryctolagus cuniculus). Concn of sodium silicate above 1 p.p.m. significantly increased the level of leaf silicification when compared with the controls. Treated plants (100 and 250 p.p.m.) also had significantly higher levels of leaf silicates than cv Mercia grown in three geologically distinct locations around the UK. Scanning electron microscopy (SEM) showed that the treated plants also appeared to have a greater number of trichomes on the leaf tips when compared with the controls. Evidence is provided that leaf silicification is an inducible defense mechanism in wheat when has potential for use as a novel method of crop protection against vertebrate pests.

"Role of Silicon in the Management of Rice Blast"; Hooda, K.S.; Srivastava, M.P.; Indian Phytopathology, 1996, Vol. 49(1); Page 26-31

During 1992-93, the effect of different silicon sources (burnt rice husk at 200, 400, 600 q/ha. sodium silicate (AR) AT 1.25, 2.50 q/ha. Sodium silicate (AR) and commercial sodium silicate both at 1.0%) on rice blast (Pyricularia oryzae (Magnaporthe grisea) development in Haryana, India, was investigated. All applied sources reduced rice blast incidence. Burnt rice husk at 400 q/ha and 1% commercial sodium silicate spray were the most effective and economically viable. All treatments increased cellulose, hemicellulose, silica, total protein, total phenols, 1000-grain weight and yield of rice.

"Investigation of Glasshouse Structure, Growing Medium and Silicon Nutrition as Factors Affecting Disease Incidence in Cucumber Crops"; O'Neil, T.M.; Mededelingen van de Faculteit Landbouwwetenschappen, Rijksuniversiteit Gent, Vol. 56(2b); Page 359-367

Crop monitoring performed on glasshouse cucumbers in the Lee Valley, north of London, UK, in 1988-90 often showed considerable differences in the incidence of several diseases. There were no consistent differences in the incidence of aggressive stem lesions between crops in aluminum glasshouses and those in wooden glasshouses. Stem lesions caused by Botrytis cinerea were consistently more frequent in crops grown on rockwool slabs that in those grown on straw beds, and the concn of silicon in leaf and shoot tissue was lower in the former crops than in the latter. Twice-daily application of liquid potassium silicate through a separate set of drip lines to cucumbers grown on rockwool slabs significantly ($P<0.01$) reduced the incidence of stem lesions caused by Didymelia bryonise, and appeared to reduce that of those caused by B. cinerea. This paper was presented at the 43rd International Symposium on Crop Protection held in Ghent, Belgium on May 7, 1991. 7 ref.

"Silica Reduces Disease on Upland Rice in a High Rainfall Area"; Yamauchi, M.; Winslow, M.D. International Rice Research Newsletter, 1987, Vol. 12 (6), Page 22-23

All cultivars tested benefited from applications of sodium silicate (400 kg/ha). The greatest effect was in reducing grain discoloration and neck blast (Pyricularia oryzac).

"Foliar Applications of Potassium Silicate Reduce Severity of Powdery Mildew on Cucumber, Muskmelon, and Zucchini Squash"; Menzies, J. Bowen, P; Ehret, D; Glass, A.D.M.; Journal of the American Society for Horticultural Science, Nov. 1992 v. 117(6), Page 902-905.

The effect of soluble potassium silicate applied to cucumber (Cucumis sativus L.) muskmelon (C.melo L.) and zucchini squash (umis sativus L.) muskmelon (C. melo L.) and zucchini squash (Cucurbiga pepoL.) on the severity of powdery mildew was examined. Application methods included amending nutrient solutions to a concentration of 1.7 mM Si and foliar sprays containing 1.7, 8.5, 17, and 34 mM Si. Untreated plants and plants sprayed with distilled water were used as controls. The leaves of all plants were inoculated with known concentrations of conidia of Sphaerotheca fuliginea (Schlecht.:Fr.) Poll. (cucumber and muskmelon) or Erysiphe cichoracearum DC: Merat (zucchini squash) 1 day after the sprays were applied. Inoculated leaves on plants receiving the Si-amended nutrient solution or foliar sprays of greater than or equal to 17.9

mM Si developed fewer powdery mildew colonies than those on control plants. Results of a separate experiment that included a potassium spray, indicated that the active ingredient of the potassium silicate sprays appears to be Si. Experiments to test the persistence of Si foliar sprays on cucumber demonstrated that a 17 mM Si spray applied 7 days before inoculation with S. fullginea reduced mildew colony formation.

"Distribution of Silicon in Cucumber Leaves during infection by powdery mildew fungus (Sphaerotheca fuliginea)"; Samuels, A.L.; Glass, A.D.M.; Ehret, D.L.; Menzies, J.G.; Canadian Journal of Botany, 1991, Vol. 69(1), Page 140-146.

The distribution of silicon in the leaf epidermis of cucumber grown in hydropanic nutrient solutions supplemented with soluble silicates was examined by SEM and energy dispersive X-ray analysis. Silicon was found primarily in cells surrounding the bases of the trichome hairs. During infection by S. fuliginea, areas of host cell wall adjacent to the germinating hyphae showed altered surface morphology and high concn of silicon. Measurements of total hyphal length per colony showed the fungal colonies grown on silicate-treated plants were significantly smaller than fungal colonies grown on control Plants. In the colonies grown on silicate-treated plants were significantly smaller than fungal colonies grown on control plants. In the colonies grown on silicate-treated plants were significantly smaller than fungal colonies grown on control plants. In the colonies grown on silicate treated plants were significantly smaller than fungal colonies grown on control plants. In the early stages of infection the presence of high silica surrounding colonies was correlated with lower fungal growth.

"The Effects of Silicon on Cucumber Plants Grown in Recirculating Nutrient Solution"; Adapt, M.H.; Bedford, R.T.; Annals of Botany 1986, Vol. 58(3); Page 343-351.

Cucumber plants CV. Corona were grown in recirculating nutrient solution containing either 10 mg/litre SiO_2 (low Si) which was the level present in the water supply or with an additional 100 mg/litre SiO_2 (high Si). Silicate was depleted from the solution when cucumbers were grown, but accumulated when (in a smaller trial) tomatoes were grown. Major effects on cucumber leaves of added Si were: increased rigidity of the mature leaves which had a rougher texture and were held more horizontally; they were darker green and senescence was delayed. The mature high Si leaves acquired characteristics of leaves grown in a higher light intensity, i.e. they had shorter petioles and an increased fresh weight per unit area, dry weight per unit areas, chlorophyll content, ribulosebisphosphate carboxylase activity and soluble protein (all expressed per unit area of interveinal laminar tissue). Addition of Si did not affect the final leaf area of the mature leaves but root fresh weight and dry weight were increased. A pronounced effect of Si addition was the increased resistance to powdery mildew (Sphaerotheca fuliginea). Despite regular applications of fungicide, outbreaks of the fungal disease occurred on most of the mature leaves on the low Si plants, while the high Si plants remained almost free of symptoms. The addition of Si could be beneficial to cucumbers grown in areas where the local water supply is low in this element, especially when grown in recirculating solution or in a medium low in Si, e.g. peat.

"Effect of Silicon on the Growth of Cucumber Plant in Soil Culture"; Miyake, Y.; Takahashi, E.; Soil Science and Plant Nutrition, 1983, Vol. 29(4); Page 463-471.

In field experiments conducted in alluvial soils for 3 years, silicate fertilizers (700 or 1400 kg SiO2/ha/yr) promoted the growth and yield of cucumber plants, and reduced the damage caused by wilt disease. There were no deleterious effects associated with continuous cropping. However, successive applications of silicate fertilizer increased the soil pH and adversely affected plant growth. The application of large amounts of organic matter was effective in correcting the soil pH.

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