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June 26, 2006

Mr. Robert Pooler
Mr. Arthur Neal
National Organic Standards Board
Agricultural Marketing Specialist
USDA/AMS/TM/NOP
Room 4008-So., Ag Stop 0268
1400 Independence Ave, SW
Washington, D.C. 20250

Dear Mr. Pooler and Mr. Neal,

This document is submitted by PQ Corporation and serves as a revised petition to add **Aqueous Potassium Silicate** as an allowed substance to the National List of Substances Allowed and Prohibited in Organic Production and Handling.

Besides providing more information about mode of action, efficacy, and including the latest research on soluble silicon, there are two important differences between this and the original petition that we had submitted back in 2002. The first is that we are now calling the substance "Aqueous Potassium Silicate" instead of "Potassium Silicate." This should distinguish it from fly ash and slag by-product silicates that also could possibly be called potassium silicate.

The second is regarding the end uses. This petition has added Insecticide/Miticide uses and has limited the Soil/Plant Amendment use to hydroponic applications only.

If any questions arise during the review of this petition, please feel free to contact me at Judy.Thompson@pqcorp.com or 610-651-4353.

Best Regards,

Judy LaRosa Thompson

Judy LaRosa Thompson, Ph.D.
Development Chemist/Project Manager
Industrial Chemicals Division
PQ Corporation

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ITEM A

PQ Corporation is petitioning Aqueous 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 **Aqueous Potassium Silicate**

2. The manufacturer is:

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

3. The intended use of Aqueous Potassium Silicate is for:

- **Plant Disease Control** 205.601 (i)
- **Insecticide/Miticide** 205.601 (e)
- **Plant Amendment** (for hydroponic use) 205.601 (j)

4. Examples of crop use for Aqueous Potassium Silicate include but are not limited to those listed below. Pesticide applications would defer to EPA label for detailed list of crops, uses, and application methods.

- Application rates of approximately 1300 – 2600 ppm SiO_2/acre as a foliar spray; 100-250 ppm SiO_2 in hydroponic solutions; and soil drench using a 1300 – 2600 ppm SiO_2 solution. All should be in accordance with EPA label specifications.

Plant Disease Control:

- Powdery Mildew: grapes, cucurbits, ornamentals
- Botrytis: blueberry
- Root diseases such as pythium, fusarium crown and root rot: cucurbits, peppers
- Turf diseases including dollar spot, gray leaf spot, brown patch, and powdery mildew

Insecticide/Miticide:

- For suppression of mites: pome fruit, nut crops, stone fruit, grapes, beans
- For suppression of whiteflies, aphids, and other soft-bodied insects: lettuce, beans, ornamentals

Plant Amendment

- Application rate as a nutrient solution for hydroponic production is 100-250 ppm SiO_2 or as desired for K_2O supplementation.
- Example crops include cucurbits, tomato, strawberry, ornamentals

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5. Manufacturing Procedure:

- In the U.S., soluble potassium silicate is manufactured by combining mined, high purity silica sand (SiO_2) and potassium carbonate (K_2CO_3) (derived from mined potassium chloride) such that the $SiO_2/K_2O = 2.5$ (by weight) and heating to 1900-2300°F. The potassium carbonate and silicon dioxide fuse to form a molten potassium silicate with the evolution of carbon dioxide gas. The molten potassium silicate is dissolved in water to form the aqueous potassium silicate having a 2.5 SiO_2/K_2O weight ratio, or it can be cooled to form potassium silicate glass which is later dissolved in water to form a 2.5 ratio aqueous potassium silicate.

- Aqueous potassium silicate having a 2.1 SiO_2/K_2O weight ratio is made by starting with a 2.5 ratio liquid, adding KOH (derived from mined KCl), and evaporating water to increase the solids content.

- The components of aqueous potassium silicate are simply K_2O, SiO_2, and water. Aqueous potassium silicate solutions are described by the weight ratio of SiO_2 to K_2O (SiO_2/K_2O) and the percent solids (i.e., % solids = % SiO_2 + % K_2O). Typical solutions have a ratio of 2.1-2.5 and solids of 29-39%.

- To clarify, the PQ product used for pesticide applications (disease control and insecticide/miticide) is Sil-MATRIX™ which is a 2.5 SiO_2/K_2O ratio, 29% solids product. The product used as a plant amendment in hydroponic nutrient solutions is AgSil®21 having a 2.1 SiO_2/K_2O ratio and 39% solids.

6. Summary of Previous Reviews by State or Private Certification Programs:

- Not applicable

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. In addition, the EPA's Lead and Copper Rule authorizes sodium silicate as one of four treatment options for controlling corrosion in potable water systems.

- Potassium Silicate is on List 4B of the EPA List of Other (Inert) Pesticide Ingredients. List 4B contains "inerts which have sufficient data to substantiate they can be used safely in pesticide products."

- PQ Corporation has registered Potassium Silicate as an active ingredient with the EPA. The Biochemical Classification Committee of the Biopesticides & Pollution Prevention

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Division (BPPD) classified Potassium Silicate as a Biochemical Pesticide. This decision was based on research showing that the substance acts as an SAR-inducer in plants (i.e., promotes Systemic Acquired Resistance type response in plants). Furthermore, the BPPD granted potassium silicate a Tolerance Exemption. The EPA Registration number for the Technical Potassium Silicate is 82100-2 and the number for the end use product Sil-MATRIX™ aqueous potassium silicate is 82100-1.

- Sil-MATRIX™ is currently registered as a biopesticide in WA, ID, HI, with registrations pending in OR, AZ, and CA. Additional state registrations will be forthcoming.

- The Arizona Department of Environmental Quality recently granted Sil-MATRIX™ aqueous potassium silicate a waiver from the requirement to submit groundwater protection data. [See Attachment C] The reasoning was based on the ubiquitous nature of potassium silicate with the conclusion that it "will not have a negative impact on the environment or constitute a threat to groundwater quality."

- AgSil® 21 is registered as a fertilizer in several states including CA, FL, IL, MA, NY, OR, TX, and WA.

- In addition, sodium silicate is allowed as a floating agent for fruit flotation according to Section 205.601 (l) (2) of the National List. Sodium silicate is manufactured via the same glass making and dissolution processes as potassium silicate.

8. <u>CAS number for Water</u>: 7732-18-5
<u>CAS number for Potassium Silicate</u>: 1312-76-1

<u>Product Labels</u>: See Attachment D

*****Proposed Sil-MATRIX™ label change:** At the time of EPA registration there were no data regarding toxicity to honeybees. As a result, the EPA required a "Toxic to Honeybee" statement on the Sil-MATRIX label. However, testing has recently been completed that shows there is no toxicity to honeybees. See Attachment E. This label change is pending EPA approval.

9. <u>Physical Properties and Chemical Mode of Action:</u>
Potassium silicate glass is readily soluble in water. Dissolving the glass into water creates a solution with an alkaline pH 11.3-11.7 for most commercially available products. In aqueous potassium silicates, a variety of silicate species are present. 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 are for the uses petitioned here), the number of monomers increases at the expense

of the larger units. Therefore, potassium silicate solutions at use concentrations provide soluble silica predominantly as $Si(OH)_4$, the form that can be absorbed by plants.

It should be noted that the method of application of aqueous potassium silicates can be either foliar spray, soil drench, or root application (as in a hydroponic nutrient solution). Some plants will absorb soluble silicon (i.e., $Si(OH)_4$) readily as a foliar spray while others will gain greater benefit from root application [Liang, 2005]. All application methods should be available to the grower.

Soluble silicon for agriculture has been studied for the last several decades. Initial research on the mode of action for pest control indicated that soluble silicon as $Si(OH)_4$ units accumulate and polymerize at infection sites in the cell walls of leaves and xylem vessels. So it was proposed that this accumulation of silicon provided a mechanical barrier to disease. (In fact, potassium silicate is commonly used in turf fertilizer to improve physical properties such as leaf erectness and turgidity.)

More recent work indicates that soluble silicon plays an active role in disease and insect resistance. It has been noted that plants utilize soluble silicon as part of their defense mechanisms whether it is supplemented or not, but that supplementation enhances the defense response system. For example, in a study on powdery mildew and grapes, Reynolds [1996] compared sulfur and potassium silicate treatments and noted the following:

> *Scanning electron microscopy and energy dispersive X-ray analysis of the control and Kumulus S-treated berries showed large quantities of Si deposited near infection sites and hyphae, suggesting that grape berries may utilize endogenous Si to help fight disease. This suggests that exogenously applied silicates may act to augment the activity of their endogenous counterparts. At appropriate application intervals and concentration, potassium silicate has potential as an alternative spray material to sulfur for powdery mildew control, because: (1) material cost is lower; (2) risk of* H_2S *in wines is reduced; and (3) it would potentially fall within guidelines for "organic" winegrowers as a natural substance.*

Datnoff [2005] summarized recent research as follows:

> *Research also points to the role of Si* in planta *as being active, and this suggests that the element might amplify the response for inducing defense reactions to plant diseases. Silicon has been demonstrated to stimulate chitinase activity and rapid activation of peroxidases and polyphenoxidases after fungal infection* [Chérif, 1994, for cucumber roots infected with *Pythium* spp. and amended with Aqueous Potassium Silicate]. *Glycosidically bound phenolics extracted from Si amended plants when subjected to acid or β-glucosidase hydrolysis displayed strong fungistatic activity. More recently, flavonoids and momilactone phytoalexins, low molecular weight compounds that have antifungal properties, were found to be produced in both dicots and monocots, respectively, fertilized with Si and challenge inoculated by the pathogen in comparison to non-fertilized plants also challenge inoculated by the pathogen. These antifungal compounds appear to be playing an active role in plant*

disease suppression [Fawe, 1998, for cucumber infected with powdery mildew and amended with Aqueous Potassium Silicate; Rodrigues, 2004, for rice infected with rice blast and amended with calcium silicate].

Similarly Liang *et al.* [2005] found that root application of potassium metasilicate resulted in significantly enhancing the activity of pathogenesis-related proteins such as peroxidase, polyphenoxidase, and chitinase in cucumbers under the condition of powdery mildew inoculation; but interestingly, there was no effect when there was no pathogen inoculation. This observation indicates that the plant utilizes soluble silicon on an as needed basis.

In addition, Dann and Muir [2002] documented that peas grown in Si-amended soil had significantly greater activities of chitinase and β-1,3-glucanase in leaf extracts compared to controls. Other work by Smith *et al.* [2005] on banana indicates that soil drench applications of potassium silicate reduced the occurrence of fusarium wilt in banana because it "significantly up-regulated the expression of putative defense genes."

In addition to disease control we are documenting the efficacy of aqueous potassium silicate (i.e., Sil-MATRIX^{TM}) to suppress mites and insects such as whitefly. For soil and foliar applications, whiteflies showed a strong preference for untreated control plants. Furthermore, while aqueous potassium silicate provides good knockdown of mites and soft-bodied insects, it does not tend to eradicate beneficials. See Section 11 below for trial results.

As in the disease literature, there is more information coming to light about how soluble silicon provides host-plant resistance, via non-preference and antibiosis (Basagli *et al.*, 2003; Correa *et al.*, 2005), to insect and other herbivore attack. For example Correa *et al.* (2005) suggests that silicon induces the synthesis of defense chemicals which then affected whitefly preference for oviposition, expanded the developmental period, and increased nymphal mortality. Contact with the pest is not always necessary as evidenced by insect suppression when Si is applied as a soil application (e.g., Table 5 below) or by hydroponic nutrient solution. However, contact with the pest probably supplies additional suppression of mites and insects perhaps due to desiccation.

Other beneficial effects of soluble silicon for various 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: Aqueous potassium silicate can react in two ways. First, the silicate species will react with any multivalent metal cations (i.e., in solution) such as Ca^{2+} and Mg^{2+} and form a metal silicate complex or 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

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for use on alkali sensitive plant species, substances such as compost tea and citric acid have been used successfully when the silicate is diluted first.

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 are indistinguishable from potassium and silica from natural sources.

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.

Using aqueous potassium silicate in organic crop production should not have negative environmental effects because of the ubiquitous nature of the components – K_2O, SiO_2, and water.

d) Effects on human health: Potassium silicate is mildly irritating to the eyes. Potassium silicate is slightly irritating to intact skin but produces well-defined irritation to abraded skin. It is dermally non-toxic at 5,000 mg/kg. Potassium silicate dust and spray mist are considered irritating to respiratory tract. (See Section 10 below for toxicology testing results.) Potassium 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 F and Attachment G, "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 H "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. Safety Information

- See Attachment F for both Sil-MATRIX™ and AgSil® 21 MSDS.

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

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- Toxicology Testing for Sil-MATRIX^{TM} Aqueous Potassium Silicate (2.5 SiO_2/K_2O, 29% solids):

Study	EPA Guideline	Result	Category	Comment
Acute Oral	81-1	> 5 g/kg	IV	
Acute Dermal	81-2	> 5 g/kg	IV	
Acute Inhalation	81-3	> 2.06 mg/L	IV	
Acute Eye Irritation	81-4	Score = 12	III	
Acute Dermal Irritation	81-5	Slight	IV	Clears in 72 hrs
Acute Dermal Sensitization	81-6	Not Sensitizing		

- As a result of the toxicology testing, the signal word for the Sil-MATRIX label is "Caution." The REI is 4 hours and the PHI is 0 days.

11. Research Information:
The role of Si (soluble silicon) in agriculture has been studied for decades but has received increasing attention in the last 10 years. Its importance for rice and sugarcane production has led to Si being recognized as an essential nutrient in Japan and Brazil. Its commercial importance for crop production in the US and other countries (for example potassium metasilicate is used in European hydroponic production and various slag by-products are used in Asia and South America), has led to a global awareness of its benefits to plant health as well as a drive to discover exactly how it is utilized by plants. The many beneficial effects provided by soluble Si have been demonstrated over the years as documented in a substantial body of scientific literature. [See Bibliography in Attachment I]

Focusing now specifically on Aqueous Potassium Silicate, PQ trials have shown that applied as a preventative agent, aqueous potassium silicate can decrease a plant's susceptibility to disease. It is important to note that potassium silicate is a preventative "fungicide;" it is not curative and will not eradicate fungi. In fact, the Si must be mobile within the plant's system in order to participate and enhance the defense chemical reactions that occur during fungal and insect attack. To commercialize this feature of our product, PQ has conducted significant trial work, and the results show that under low to heavy disease pressure, Aqueous Potassium Silicate reduces the incidence and severity of, for example, powdery mildew. It is especially effective when used in an Integrated Pest Management Program, either as a replacement or in combination with other fungicides including sulfur and potassium bicarbonate. See Tables 1-3 below for examples of control of powdery mildew and botrytis.

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Table 1. Aqueous Potassium Silicate Alone and as Pre-Bloom Sulfur-Replacement for Suppression of Powdery Mildew on Grapes
[Aqueous Potassium Silicate applied foliarly at 1300ppm SiO_2 per acre per application]

Treatment	Trial 1		Trial 2		Trial 3	
	% Inc.	% Sev.	% Inc.	% Sev.	% Inc.	% Sev.
UTC	**82.5 a**	**22.05 a**	**100.0 a**	**49.0 a**	**73.8 a**	**27.8 a**
Potassium Silicate w/surfactant	**40.5 b**	**4.75 b**	**75.5 b**	**9.5 b**	**11.3 b**	**1.7 b**
Pot. Sil. pre-bloom, Abound/Rally	**0.5 c**	**0.005 b**	**16.0 c**	**0.45 c**	**0.0 c**	**0.0 b**
Sulfur pre-bloom, Abound/Rally	**0.0 c**	**0.0 b**	**10.5 c**	**0.10 c**	**0.0 c**	**0.0 b**

% Incidence – Percent of grape bunches inspected with presence of powdery mildew.
% Severity – Severity of infestation on each grape bunch inspected (or leaf if specified).
Trial 1 – Attaway (2004), Chardonnay, Ukiah, CA.
Trial 2 – Kukas (2004), Thompson seedless, Dinuba, CA.
Trial 3 – West (2004), Chardonnay, Walnut Grove, CA.

Table 2. Aqueous Potassium Silicate Alone and Tank-Mixed with Potassium Bicarbonate or Sulfur for Suppression of Powdery Mildew on Grapes
[Aqueous Potassium Silicate applied foliarly at 2000ppm SiO_2 per acre per application]

Treatment	Trial 1		Trial 2			
	% Inc. Cluster	% Sev. Cluster	% Inc. Leaf	% Sev. Leaf	% Inc. Cluster	% Sev. Cluster
UTC	**53 a**	**17.05 a**	**100 a**	**63.6 a**	**100 a**	**85.1 a**
Potassium Silicate	**30 b**	**5.6 ab**	**100 a**	**43.5 b**	**100 a**	**79.7 a**
Pot. Silicate w/surfactant	**1 b**	**1.65 b**	**98 ab**	**30.3 bc**	**100 a**	**71.6 a**
Potassium Bicarbonate w/surf	**24 b**	**5.85 ab**	**95 ab**	**26.0 bcd**	**100 a**	**74.2 a**
Pot. Sil./Pot. Bicarb./ surfactant (tank mix)	**12 b**	**1.95 b**	**83 bc**	**11.6 cde**	**88 ab**	**28.2 b**
Wettable Sulfur	**9 b**	**1 b**	**75 c**	**3.9 e**	**75 b**	**7.9 b**
Pot. Sil./Sulfur (tank mix)	**3 b**	**0.2 b**	**85 abc**	**9.8 cde**	**100 a**	**25.8 b**

Trial 1 – Monterey AgResources (2005), Ruby Reds, Traver, CA
Trial 2 – Calkin (2005), Pinot Noir, Corvalis, OR

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Table 3. Aqueous Potassium Silicate for Suppression of Botrytis in Blueberry
[Aqueous Potassium Silicate applied foliarly at 2600ppm SiO_2 per acre per application]

Treatment	Avg. Number Diseased Blossoms 7DAA5*	Avg. Number Diseased Blossoms 13DAA6
1. Potassium Silicate	**14.8 bc**	**26.5 b**
2. Potassium Silicate with surfactant	**20.5 bc**	**28.3 b**
3. Potassium Bicarbonate	**30.0 ab**	**34.8 b**
4. Elevate	**3.5 c**	**7.5 c**
5. Potassium Silicate w/surfactant alternated with Elevate	**4.5 c**	**10.0 c**
6. UTC	**44.0 a**	**64.0 a**

Kukas (2005), Emerald Blueberry, Visalia, CA.
* "7DAA5" is 7 days after application 5

In addition to disease control, we are documenting the efficacy of Aqueous Potassium Silicate to suppress mites and insects such as whitefly and aphid. For soil and foliar applications, whiteflies showed a strong preference for untreated control plants. Furthermore, while Aqueous Potassium Silicate provides a good knockdown of mites and soft-bodied insects it does not tend to eradicate beneficials/predators. See Tables 4-7 below.

Table 4. Aqueous Potassium Silicate for Suppression of European Red Mites on Apple [Aqueous Potassium Silicate applied foliarly at 1300ppm SiO_2 per acre per application except as noted.]

Treatment	European Red Mite Motiles			Predator Mites		
	8DAA*	14DAA	22DAA	8DAA	14DAA	22DAA
UTC	**152.0 a**	**54.5 a**	**60.5 a**	**1.8 a**	**0.8 a**	**0.5 a**
Potassium Silicate w/surf	**131.5 ab**	**45.3 ab**	**25.5 b**	**1.8 a**	**0.0 a**	**0.8 a**
Potassium Silicate w/surf, 2600ppm SiO_2	**105.3 bc**	**61.0 a**	**30.0 b**	**2.0 a**	**0.3 a**	**2.0 a**
Pot. Sil. w/surf., 2 applications	**102.8 bc**	**[6DAA2] 53.0 a**	**[14DAA2] 31.0 b**	**0.0 a**	**[6DAA2] 0.0 a**	**[14DAA2] 1.0 a**
JMS Stylet Oil	**82.0 c**	**44.5 ab**	**52.3 a**	**0.0 a**	**0.0 a**	**1.0 a**

Calkin (2005), Sweet Home, OR
"8DAA" is 8 days after application

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Table 5. Aqueous Potassium Silicate for Suppression of Aphids on Lettuce

Treatment	0DAA	3DAA	7DAA	7DAA2	14DAA2
UTC	12.50 a	17.00 a	23.33 a	14.33 a	10.07 a
Pot. Sil., soil drench, 1300 ppm SiO_2	18.00 a	13.00 b	12.33 b	8.08 b	8.04 a
Pot. Sil., soil drench, 2600ppm SiO_2	11.23 a	6.27 c	6.78 bc	7.44 bc	8.30 a
Pot. Sil. w/surf, foliar spray, 1300 ppm SiO_2	19.25 a	1.00 d	1.67 c	3.42 c	2.82 a
Pot. Sil. w/surf, foliar spray, 2600ppm SiO_2	13.00 a	0.50 d	1.50 c	3.17 c	3.28 a
Pyrethrin	19.50 a	0.42 d	1.75 c	3.42 c	2.96 a

Bio-Research (2006), Romaine lettuce, greenhouse

Table 6. Aqueous Potassium Silicate for Suppression of Two-Spotted Mites on Strawberry [Aqueous Potassium Silicate applied foliarly at 2000 ppm SiO_2 per acre per application]

Treatment	Two-Spot Mites			Predatory Mites		
	1DAA	4DAA	7DAA	1DAA	4DAA	7DAA
UTC	11.2 a	7.92 a	28.76 a	0.7 a	1.04 a	0.72 a
Potassium Silicate	7 a	0.44 b	5.48 b	1.1 a	0.04 b	0.32 a

Beem (2004),Woodland, CA.

Table 7. Aqueous Potassium Silicate for Suppression of Two-Spotted Mites on Grape [Aqueous Potassium Silicate applied foliarly]

Treatment	2DAA	7DAA	3DAA2	6DAA2	3DAA3	7DAA3
UTC	2.53 a	24.1 a	20.4 a	15.9 a	17.3 a	1.43 a
Wettable Sulfur	2.00 a	5.83 b	3.80 b	2.03 b	3.33 b	0.17 a
Pot. Silicate w/surfactant [1300 ppm SiO_2/acre]	2.50 a	7.41 b	3.67 b	2.87 b	4.07 b	1.40 a
Pot. Silicate w/surfactant [2000 ppm SiO_2/acre]	5.67 a	8.03 b	3.40 b	1.53 b	6.00 b	1.33 a

Beem (2005), Syrah, El Dorado, CA.

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12. Petition Justification Statement:

As a source of soluble silicon $Si(OH)_4$, Aqueous Potassium Silicate is used by plants to help resist biotic and abiotic stresses. Plants accumulate silica in epidermal tissue which improves physical strength, and the soluble silicon helps to amplify pathogenesis-induced host defense responses. Silicon is used by plants whether supplemented or not, but evidence points to significantly enhanced resistance to fungal diseases as well as mite and insect attack when soluble potassium silicate is applied either as foliar spray, a soil drench, or added to a hydroponic nutrient solution. Interestingly, the effect that soluble silicon has on amplifying the defense chemical response seems to occur only when there is a pathogen attack. So the plant uses the aqueous potassium silicate on an as needed basis; the substance works along with the plant to defend itself. In addition, potassium silicate appears to have a contact effect as a miticide/ insecticide.

There are no nonsynthetic substances that could be used in place of the manufactured product for pesticide purposes. There is no natural source of aqueous potassium silicate or soluble potassium silicate. While some natural silicates (e.g., glauconite or clays) may have a significant silica content, it is not necessarily plant-available silica. Furthermore, the soluble silica (i.e., plant available) content of these materials is insufficient to provide the control of fungal diseases and suppression of mites and insects, especially compared to synthetic aqueous potassium silicate. Providing the plant with additional soluble silica via foliar spray, soil application, or nutrient solution, enhances the plant's natural defense system, bolstering it to combat pathogen attack more effectively.

Allowing Aqueous Potassium Silicate – the components of which are ubiquitous in nature – for Organic Production will provide a much needed alternative pesticide. Reducing the occurrence of diseases encountered in organic growing will enhance the growth, yield, and nutritional value of organic crops, and consequently, the success of organic production in the U.S.

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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
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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
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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 filler in food packaging	(7) (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_2O[a]	≯3	≯50	≯40	≯10
Diatomaceous silica	Loss on drying ≯10%; loss on ignition ≯7%; nonsiliceous substances ≯25% for natural powders[b]	≯10			≯10
Magnesium silicate	≮15% MgO; ≮67% SiO_2 (on anhydrous basis) ≯10% H_2O	≯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_2O_3; ≯13% after drying ≮4%Na_2O; ≯7% after drying ≯8% loss on drying; loss on ignition ≮3%--≯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 36°C for 3 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	0.0025- 0.011	0.015 - 0.025	--[e] - 0.0031
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 85°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 aluminosilicate)	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 product 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 50 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

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[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 (26)].

[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 and 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 _in vivo_. 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 _et al_. (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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25. Letter dated December 7, 1978, from J.B. Gilmour, Grefco Inc., Torrance, Calif., to J. Talbot, Federation of American Societies for Experimental Biology, Bethesda, Md.

26. Letter dated September 22, 1978, from T.M. Jackson, Johns-Manville Sales Corporation, Denver, to J.M. Talbot, Federation of American Societies for Experimental Biology, Bethesda, Md.

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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

Letter from Arizona Department of Environmental Quality

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ARIZONA DEPARTMENT
OF
ENVIRONMENTAL QUALITY

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Janet Napolitano
Governor

Stephen A. Owens
Director

Notice of Approval of Waiver

June 14, 2006

Mr. Robert C. Ehn
Regulatory Agent/Consultant
Ag-Chem Consulting LLC
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Re: Pesticide Active Ingredient POTASSIUM SILICATE – Approval of Waiver for Submittal of Groundwater Protection Data for Registration of SIL-MATRIX

Dear Mr. Ehn:

The Arizona Department of Environmental Quality (ADEQ) received on May 31, 2006 your request on behalf of PQ Corporation for a waiver of groundwater protection data for the registration of **Potassium Silicate**, an active ingredient in agricultural-use pesticide **SIL-MATRIX**. ADEQ has completed its review of your correspondence and the product chemistry document you submitted in support of your request.

ADEQ agrees with your explanation that Potassium Silicate is one of the most abundant, naturally-occurring compounds on the earth's surface, and its agriculture use as an active ingredient in SIL-MATRIX will not have a negative impact on the environment or constitute a threat to groundwater quality.

ADEQ has therefore determined that the active ingredient Potassium Silicate be granted a waiver from data call-in requirements of A.R.S. §49-302(A) of the Pesticide Contamination Prevention Program of the EQA, and the new rules R18-6-102C. Potassium Silicate is approved without restriction as an active ingredient for agricultural-use pesticides in Arizona.

You may register agricultural pesticide products containing Potassium Silicate with the Arizona Department of Agriculture. Please, accept my congratulations!

If you have any questions regarding this correspondence, please do not hesitate to contact me at (602) 771-4552 or by email at mao@azdeq.gov.

Sincerely,

Moses A. Olade, Ph.D
Pesticides Program Coordinator
Water Quality Division

cc: Jack Peterson, ESD, Arizona Department of Agriculture
Gary Christian, ESD, Arizona Department of Agriculture

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ATTACHMENT D

Product Label

*****Proposed label changes:** At the time of EPA registration there was no data regarding toxicity to honeybees. As a result, the EPA required a “Toxic to Honeybee” statement on the Sil-MATRIX label. However, testing has been completed that shows there is no toxicity to honeybees. See Attachment E. This label change is pending EPA approval.

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

SiI-MATRIX™

FUNGICIDE/MITICIDE/INSECTICIDE

For use on vegetables, fruits, nuts, vine crops, field crops, ornamentals and turf for control of fungal diseases, and suppression of spider mites, whiteflies and other insects

ACTIVE INGREDIENT:	
Potassium silicate	29%
OTHER INGREDIENTS:	71%
Total	100%

EPA Reg. No. 82100-1 EPA Est. No. 82100-PA-001
Net Weight XX lbs

KEEP OUT OF REACH OF CHILDREN
CAUTION
PRECAUCION

Si usted no entiende la etiqueta, busque a alguien para que se la explique a usted en detalle. (If you do not understand the label, find someone to explain it to you in detail.)

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

PRECAUTIONARY STATEMENTS

HAZARDS TO HUMANS AND DOMESTIC ANIMALS

CAUTION

Causes moderate eye irritation. Slightly irritating to the skin. Avoid contact with eyes, skin, or clothing. Wash thoroughly with soap and water after handling.

FIRST AID

IF IN EYES: Hold eye open and rinse slowly and gently with water for 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye. Call a poison control center or doctor for treatment advice.

IF ON SKIN: Take off contaminated clothing. Rinse skin with plenty of water for 15-20 minutes. Call a poison control center or doctor for treatment advice.

HOT LINE NUMBER: Have the product container or label with you when calling a poison control center or doctor, or going for treatment. You may also contact 1-866-359-5667 day or night, for emergency medical treatment information.

PERSONAL PROTECTIVE EQUIPMENT (PPE)

Applicators and other handlers must wear:

- Long-sleeved shirt and long pants
- Shoes and socks.

Follow manufacturer's instructions for cleaning/ maintaining PPE. If no such instructions exist for washables, use detergent and hot water. Keep and wash PPE separately from other laundry.

USER SAFETY RECOMMENDATONS:

Users should:

- Wash hands before eating, drinking, chewing gum, using tobacco or using the toilet.
- Remove clothing immediately if pesticide gets inside.
- Remove PPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change into clean clothing.

ENVIRONMENTAL HAZARDS:

Toxic to Honey Bees. This product is toxic to bees exposed to direct treatment or residues on blooming crops or weeds. Do not apply this product if bees are visiting the treatment area.

This product is for terrestrial uses, do not apply directly to water, or to areas where surface water is present or to intertidal areas below the mean high water mark. Do not contaminate water when cleaning equipment or disposing of equipment wash water or rinsate.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System (NPDES) permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA.

In the event of an in-transit environmental release or spill of this product, that may endanger the environment, call 1-800-424-9300.

DIRECTIONS FOR USE

AGRICULTURAL USE REQUIREMENTS

Use this product only in accordance with its labeling and with the Worker Protection Standard, 40 CFR Part 170. This standard contains requirements for the protection of agricultural workers on farms, forests, nurseries, and contains requirements for training, decontamination, notification, and emergency assistance. It also contains specific instructions and exceptions pertaining to the statements on this label about personal protective equipment (PPE), and restricted-entry interval. The requirements in this box only apply to uses of this product that are covered by the Worker Protection Standard.

Do not enter or allow worker entry into treated areas during the restricted entry interval (REI) of 4 hour.

PPE required for early entry to treated areas that is permitted under the Worker Protection Standard and that involves contact with anything that has been treated, such as plants, soil, or water is:

- Coveralls
- Chemical-resistant gloves made of any waterproof material
- Shoes and socks

NON-AGRICULTURAL USE REQUIREMENTS

The requirements in this box apply to uses of this product that are NOT within the scope of the Worker Protection Standard for agricultural pesticides (40 CFR Part 170). The WPS applies when this product is used to produce agricultural plants on farms, forests, nurseries, or greenhouses.
Keep unprotected persons out of treated area until sprays have dried.

It is a violation of Federal law to use this product in a manner inconsistent with its labeling. Do not apply this product in a way that will contact workers or other persons, either directly or through drift. For any requirements specific to your State or Tribe, consult the agency responsible for pesticide regulation. This product must not be used when honey bees are present or actively foraging.

STORAGE AND DISPOSAL

Storage: Keep pesticide in original container. Keep container tightly closed when not in use. Store product above 40°F. Do not store in aluminum, fiberglass, copper, brass, zinc, or galvanized containers. Protect from excessive heat. Store in a cool, dry place.
Pesticide Disposal: Wastes resulting from the use of this product may be disposed of on site or at an approved waste disposal facility.
Container Disposal: Do not reuse container. Completely empty container into application equipment. Prior to container disposal, rinse out the container three times with water and empty rinse water into application equipment. Then dispose of empty container in a sanitary landfill in accordance with federal, state, and local waste disposal regulations.

GENERAL USE INFORMATION

Sil-MATRIX™ is a broad spectrum preventative fungicide recommended for agricultural crops, fruits, nuts, vines, turf and ornamentals. Optimum disease control is obtained when the fungicide is applied on a regularly scheduled preventative spray program. Sil-MATRIX™ also provides suppression of mites, whiteflies and other insects. Optimum performance is achieved using a sufficient volume of water to insure complete coverage of all stems and foliage.

Sil-MATRIX™ has been evaluated for phytotoxicity and has a wide margin of safety on a variety of crops. However, since all combinations or sequences of pesticide applications including surfactants and adjuvants have not been tested, it is recommended that a small area be sprayed first to make certain that no phytotoxicity occurs.

Read the entire label before using Sil-MATRIX™. Consult your State Agricultural Experimental Station or Extension Service Specialist for additional information on application timing, rates and any additional requirements or restrictions.

MIXING INSTRUCTIONS:
Be sure the sprayer is clean and not contaminated with other materials prior to use.

When using an agitated spray tank fill tank 1/2 to 3/4 full with clean water and start agitation. Be certain that the agitation system is working properly. With the agitator running add the required amount of Sil-MATRIX™ to the tank. If tank mixing with other materials, add them to the tank and continue agitation. Continue filling tank with the remainder of the water. Agitate until mixed thoroughly and avoid excessive foaming. Mix as needed; do not store diluted material.

COMPATIBILITY:
Sil-MATRIX™ is compatible with most commonly used agricultural fungicides. If compatibility is in question, use the compatibility jar test before mixing a whole tank. Because of the wide variety of possible combinations that can be encountered, observe all precautions and limitations on the label of all products used in mixtures.

APPLICATION INSTRUCTIONS:
Sil-MATRIX™ is a broad spectrum pesticide for control of the fungal disease powdery mildew, and suppression of mites, whiteflies and other insects on vegetables, fruits, nuts, vine crops, agronomic crops, and ornamentals and for suppression of gray leaf spot, brown patch and dollar spot on turf.

Rate of application is variable according to pest pressure, timing of sprays and plant stage of growth. Use lower rates under light to moderate pest pressure; higher rates under heavy pest pressure and for mite suppression. Arid climates generally require higher rates.

For all crops, apply Sil-MATRIX™ at a volume to volume concentration of 0.5% to 1% spray solution, unless otherwise specified. For example, 2-4 quarts per 100 gallons of water. See Dilution Table for other volumes. Apply on a preventative schedule for disease control. Begin applications when environmental conditions are conducive to disease development. Repeat applications no sooner than every 7 days. When conditions are conducive for rapid disease development, it is recommended that Sil-MATRIX™ be used in a rotational program with other registered fungicides. For mite and insect suppression, begin applications when pests first appear and repeat applications as necessary to maintain suppression, but no sooner than every 7 days.

For maximum results, use a high analysis non-ionic surfactant such as No-Foam A at recommended label rates.

DILUTION TABLE FOR FOLIAR APPLICATIONS (20-250 gallons per acre)

Gallons Water	Quarts Sil-MATRIX™ 0.5% Sol.	Quarts Sil-MATRIX™ 0.75% Sol.	Quarts Sil-MATRIX™ 1% Sol.
20	0.4 quarts	0.6 quarts	0.8 quarts
40	0.8 quarts	1.2 quarts	1.6 quarts
50	1 quart	1.5 quarts	2 quarts
100	2 quarts	3 quarts	4 quarts
150	3 quarts	4.5 quarts	6 quarts
200	4 quarts	6 quarts	8 quarts
250	5 quarts	7.5 quarts	10 quarts

For fruit, nut and vine crops: apply 0.5 to 1% solution (2-4 quarts Sil-MATRIX™ /100 gal.) in 50 to 250 gallons finished spray per acre.
<u>Specific Use Restrictions</u>:
1. Apply up to the day of harvest (0 day PHI).
2. Do not apply more than 10 quarts per acre (7.5 lb ai/a) per application.
3. Do not apply more than 20 gallons per acre (60 lb ai/a) per season.
4. Do not make post harvest applications.

For vegetable crops and other agronomic crops: apply 0.5 to 1% solution (2-4 quarts Sil-MATRIX™ /100 gal.) at a minimum rate of 20 gallons finished spray per acre.
<u>Specific Use Restrictions</u>:
1. Apply up to the day of harvest (0 day PHI).
2. Do not apply more than 4 quarts per acre (3.0 lb ai/a) per application.
3. Do not apply more than 7 gallons per acre (21 lb ai/a) per season.
4. Do not make post harvest applications

For ornamental crops: apply 0.5 to 1% solution (2-4 quarts Sil-MATRIX™ /100 gal.) making sure to get good coverage of the foliage. Apply in 20 to 250 gallons of water per acre.
<u>Specific Use Restrictions</u>:
1. Do not apply more than 10 quarts per acre (7.5 lb ai/a) per application.
2. Do not apply more than 15 gallons per acre (45 lb ai/a) per season.

For turf use: apply 1 to 2% solution (4-8 quarts Sil-MATRIX™ /100 gal.) in a minimum of 40 gallons finished spray per acre.
<u>Specific Use Restrictions</u>:
1. Do not apply more than 8 quarts per acre (6.0 lb ai/a) per application.

2. Do not apply more than 10 gallons per acre (30 lb ai/a) per season.

Hydroponics: Sil-MATRIX™ may also be used in nutrient solutions for hydroponics growing to suppress powdery mildew, black spot, pythium, fusarium crown and root rot, and whiteflies, when concentrations of 100 to 250 ppm SiO_2 are maintained.

Specific Use Restrictions:

1. Apply up to the day of harvest (0 day PHI).
2. Do not exceed 250 ppm SiO_2 in nutrient solutions.
3. Do not make post harvest applications.

DISEASE MONITORING:

Sil-MATRIX™ is a broad spectrum, preventative fungicide. If not applied on a routine protectant spray schedule, observe plants for disease signs or symptoms. Fungicide application should be made, at the recommended label use rate and spray schedule, at the first sign of disease, report of disease in the area, or during environmental conditions favorable for disease development.

POME FRUIT, NUT CROPS, STONE FRUITS
(Including but not limited to)

Apples
Mayhaw
Apricot
Peach
Almond
Butternut
Chinquapin
Hickory
Crabapple
Pear
Cherry
Plum
Beech nut
Cashew
Brazil nut
Pecan
Loquat
Quince
Nectarine
Prune
Filbert
Chestnut
Macadamia
Walnut

BERRIES AND VINE CROPS
(Including but not limited to)

Blackberry
Loganberry
Grapes
Blueberry
Raspberry
Gooseberry
Strawberry

ROOT & BULB VEGETABLES
(Including but not limited to)

Beet, garden
Beet, sugar
Horseradish
Celeriac
Chervil
Ginger
Garlic
Onion
Chicory
Ginseng
Carrot
Radish
Potato
Sweet Potato
Leek
Shallot
Rutabaga
Salsify
Parsley root
Turnip
Cassava
Yam

LEAFY & BRASSICA VEGETABLES
(Including but not limited to)

Arugula
Fennel
Rhubarb
Broccoli
Celery
Parsley
Spinach
Brussels sprouts
Endive
Radicchio
Swiss chard
Cabbage
Cauliflower
Kohlrabi
Collards
Mustard Greens
Kale
Lettuce

LEGUME VEGETABLES
(Including but not limited to)

Beans
Lentil
Broad bean
Pea
Chickpea
Soybean

CUCURBIT & FRUITING VEGETABLES
(Including but not limited to)

Cucumber
Muskmelon
Eggplant
Gherkin
Squash
Pepper
Pumpkin
Watermelon
Tomato

CITRUS FRUITS
(Including but not limited to)

Grapefruit
Lemon
Tangerine
Orange
Mandarin
Lime
Pummelo

CEREAL GRAINS
(Including but not limited to)

Barley
Popcorn
Wheat
Wild rice
Oats
Corn
Millet
Sorghum
Rice
Rye

TURF & ORNAMENTALS
(Including but not limited to)
Broadleaf Shrubs & Trees

Andromeda
Azalea
Cherry Laurel
Eucalyptus
Flowering almond
Flowering peach
Flowering quince
Holly
Maple
Red-tip
Rhododendron
Sycamore
Ash
Buckeye
Crabapple
Euonymus
Lilac
Laurel
Poplar
Sequoia
Viburnum
Aspen
Camellia
Dogwood
Firethorn
Flowering cherry
Flowering plum
Hawthorn
Magnolia
Oak
Privet
Spirea
Walnut

FLOWERING PLANTS & BULBS

African violet
Chrysanthemum
Daisy
Hollyhock
Lily
Pansy
Poinsettia
Tulip
Begonia
Crocus
Geranium
Hydrangea
Marigold
Petunia
Rose
Zinnia
Carnation
Daffodil
Gladiolus
Iris
Narcissus
Phlox
Statice

FOLIAGE PLANTS

Aglaonema
Boston fern
Fatsia
Lipstick plant
Pachysandra
Philodendron
Zebra plant
Palm
Dracaena
Ficus
Ming aralias
Parlor palm
Prayer plant
Leatherleaf fern
Artenesia
Dumbcane
Ruffle fern
Oyster plant
Peperomia
Syngonium

ADDITIONAL CROPS

Artichoke
Coffee
Jojoba
Sesame
Asparagus
Cotton
Ornamental
Sunflower
Chayote
Hops
Turf grass
Tea

CONDITIONS OF SALE – Limited Warranty and Limitations of Liability and Remedies

Read the Conditions of Sale – Warranty and Limitations of Liability and Remedies before using this product. If the terms are not acceptable, return unopened container at once to the seller for full refund of purchase price paid.

The directions on this label are believed to be reliable and should be followed carefully. Insufficient control or suppression of pests and/or injury to the crop to which the product is applied may result from the occurrence of extraordinary or unusual weather conditions or the failure to follow the label directions or good application practices, all of which are beyond the control of PQ Corporation or the seller. PQ Corporation recommends that the user or grower test this product on a portion of the crop to determine suitability for the intended use. In addition, failure to follow label directions may cause injury to crops, animals, man or the environment.

PQ Corporation warrants that this product conforms to the chemical description on the label and is reasonably fit for the purposes stated on the label when used in strict accordance with the directions, subject to the factors noted above which are beyond the control of PQ Corporation. PQ Corporation makes no other warranties or representations of any kind, express or implied, concerning the product, including no implied warranty of merchantability or fitness for any particular purpose, and no such warranty shall be implied by law.

The exclusive remedy against PQ Corporation for any cause of action relating to the handling or use of this product shall be limited to, at PQ Corporation's election, one of the following:

1. Refund of purchase price paid by buyer or user for product bought, or
2. Replacement of amount of product used

To the extent allowed by law, PQ Corporation shall not be liable and any and all claims against PQ Corporation are waived for special, indirect, incidental, or consequential damages or expense of any nature, including, but not limited to, loss of profits or income. PQ Corporation and the seller offer this product, and the buyer and user accept it, subject to the foregoing conditions of sale and limitation of warranty, liability and remedies.

Sil-MATRIX^{TM} is a registered trademark of PQ Corporation.

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.

[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

ATTACHMENT E
Honeybee Toxicity Report

PQ Corporation

6/26/06

Judy LaRosa Thompson, Ph.D
Senior Technical Service Representative
610-651-4353
judy.thompson@pqcorp.com

The final report is not yet available ~~so~~ It ~~Will~~ will be sent ~~Send it~~ separately

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

ATTACHMENT F

MSDS

- Sil-MATRIX^{TM} Biopesticide for Disease Control and Insecticide/Miticide
- AgSil 21 as Plant Amendment for use in hydroponic nutrient solutions

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

PQ Corporation

MSDS
MATERIAL SAFETY DATA SHEET

Trade Name: **SIL-MATRIX Potassium Silicate Solution**

Date Prepared: **05/18/06** *Page:* **1 of 5**

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name:	**SILMATRIX™ Potassium silicate solution**
EPA registration number:	**82100-1**
Product description:	**A 2.50 weight ratio potassium silicate, 29.1% solution in water**
Manufacturer:	**PQ Corporation** **P. O. Box 840** **Valley Forge, PA 19482 USA**
Telephone:	**610-651-4200 800-944-7411**
For medical emergency call PROSAR:	**866-359-5667**
For transportation emergency Call CHEMTREC:	**800-424-9300**

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 moderate eye irritation, slightly irritating to the skin. 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 moderate irritation to the eyes.**
Skin contact:	**Causes slight irritation to the skin.**
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:	**IF IN EYES: Hold eye open and rinse slowly and gently with water for 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye. Call a poison control center or doctor for treatment advice.**

Skin:	**IF ON SKIN: Take off contaminated clothing. Rinse skin with plenty of water for 15-20 minutes. Call a poison control center or doctor for treatment advice.**
Inhalation:	**IF INHALED: 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:	**Toxic to Honey Bees. This product is toxic to bees exposed to direct treatment or residues on blooming crops or weeds. Do not apply this product if bees are visiting the treatment area.** **This product is for terrestrial uses, do not apply directly to water, or to areas where surface water is present or to intertidal areas below the mean high water mark. Do not contaminate water when cleaning equipment or disposing of equipment wash water or rinsate.** **Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System (NPDES) permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA.** **In the event of an in-transit environmental release or spill of this product, that may endanger the environment, call 1-800-424-9300.**
Small spill cleanup:	**Mop up and dispose 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: **Wash hands before eating, drinking, chewing gum, using tobacco or using the toilet. Remove clothing immediately if pesticide gets inside. Remove PPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change into clean clothing. 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. Wash thoroughly with soap and water after handling.**

Storage: **Keep pesticide in original container. Keep container tightly closed when not in use. Store product above 40°F. Do not store in aluminum, fiberglass, copper, brass, zinc, or galvanized containers. Protect from excessive heat. Store in a cool, dry place.**

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: **Applicators and other handlers must wear long-sleeved shirt and long pants, shoes and socks. PPE required for early entry to treated areas that is permitted under the Worker Protection Standard and that involves contact with anything that has been treated, such as plants, soil, or water is: Coveralls, Chemical-resistant gloves made of any waterproof material, Shoes and socks.**

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:	**When tested for primary irritation potential, this material caused moderate irritation to the eyes and was slightly irritating to the skin. Human experience indicates 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:	**Pesticide Disposal: Wastes resulting from the use of this product may be disposed of on site or at an approved waste disposal facility.** **Container Disposal: Do not reuse container. Completely empty container into application equipment. Prior to container disposal, rinse out the container three times with water and empty rinse water into application equipment. Then dispose of empty container in a sanitary landfill in accordance with federal, state, and local waste disposal regulations.**

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.**

16. OTHER INFORMATION

Prepared by:	**John G. Blumberg**
Supersedes revision of:	**01/11/06**

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.

Trade Name: **AgSil™ 21 Potassium Silicate Solution**
Date Prepared: **03/05/05**

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**
In case of emergency call:	**1 610-651-4200**
For transportation emergency Call CHEMTREC:	**1 800-424-9300**

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 moderate eye irritation, slight skin irritation and digestive tract irritation. Spray mist causes irritation to respiratory tract. High pH of product is harmful to aquatic life. Noncombustible. Spills are slippery. Reacts with acids, ammonium salts, reactive metals and some organics.**
Eye contact:	**Causes moderate irritation to the eyes.**
Skin contact:	**Causes slight irritation to the skin.**
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.**

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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.**

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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: **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.**

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11. TOXICOLOGICAL INFORMATION

Acute Data: **When tested for primary irritation potential, this material caused moderate irritation to the eyes and slight irritation to the skin. Human experience indicates 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.

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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.

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13. DISPOSAL CONSIDERATIONS

Classification: Disposed material is not a RCRA Hazardous waste.
Disposal Method: Dispose in accordance with federal, state and local regulations and permits.

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14. TRANSPORT INFORMATION

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

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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**
Supersedes revision of:	**08/15/01**

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.

ATTACHMENT G

“Health, Safety, and Environmental Aspects of Soluble Silicates”

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4

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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known, rather than test established chemicals, such as soluble silicates, with which there has been over a century of human experience. Nevertheless, there has been a limited amount of biological testing conducted on soluble silicates by government, industry and academic scientists. There have also been several critical evaluations of the available information on soluble silicates by expert groups impaneled to assess to the environmental or health risks of various uses of these substances.

The objective of this review is to draw together and briefly discuss the available information on the health, safety and environmental aspects of the soluble silicates. The sources of information for this review include scientific publications, reports of regulatory bodies and government agencies, and the incidental records of a corporation which has manufactured soluble silicates for over 20 years(6).

HEALTH AND SAFETY ASPECTS

Ingestion

Oral LD_{50}, the dose level where 50% of an exposed population of rats will die within a specified time, is a useful expression of the approximate magnitude of toxicity of a substance. It also provides a standard measure of comparison among many substances. The LD_{50} values for sodium silicates in Table I and Figure 1 were compiled from the results of a number of studies. It should be noted that these studies were conducted at different times, and vary somewhat in their test conditions such as, length of observation period, and strain, number and sex distribution of the animals. Nevertheless, we believe the comparison is useful for the purpose of illustrating, in a general way, the influence of silicate composition on acute oral toxicity. Even a very closely controlled LD_{50} study would not yield data from which conclusions could be drawn with greater certainty unless a great number of animals were used. Thus, in the lethal range of sodium silicates, large doses are required, and the 95% confidence intervals are on the order of 0.5 g/kg.

The autopsy results for the reported studies, acute gastroenteritis, vascular congestion, mottled livers(8), were consistent with nonspecific causes of death, e.g., changes in pH of body fluids, shock, chemical irritation or corrosion of the viscera, etc. It appears that the SiO_2/Na_2O ratio of sodium silicates has a greater influence on their toxicity than their concentration. This relation is perhaps not unexpected when it is considered in light of the sodium silicate's property of yielding aqueous solutions of relatively constant pH over a range of concentrations, while at constant concentration, pH varies inversely with ratio (see Figures 2 and 3).

In an attempt to develop a more specific test for modeling ingestion hazard than oral LD_{50}, the FDA conducted a series of

Table I. Median Lethal Dose (Oral, Rat) Sodium Silicate

SiO2/Na20 wt. ratio	CONCENTRATION wt. percent	LD-50 g/kg	REFERENCE
-	-	>3	7.
3.2	36	3.2	8.
3	-	1.6-8.6	9.
2	-	1.3-2.1	9.
2.0	81	1.5-2.2	10.
2.0	81	1.6	11.
1.6	51	2.0-2.5	10.
1.0	39	0.6	11.
1.0	50	0.8	11.
0.7	61	1.5	10.
0.7	61	1.0	11.
0.5	90	0.5	10.

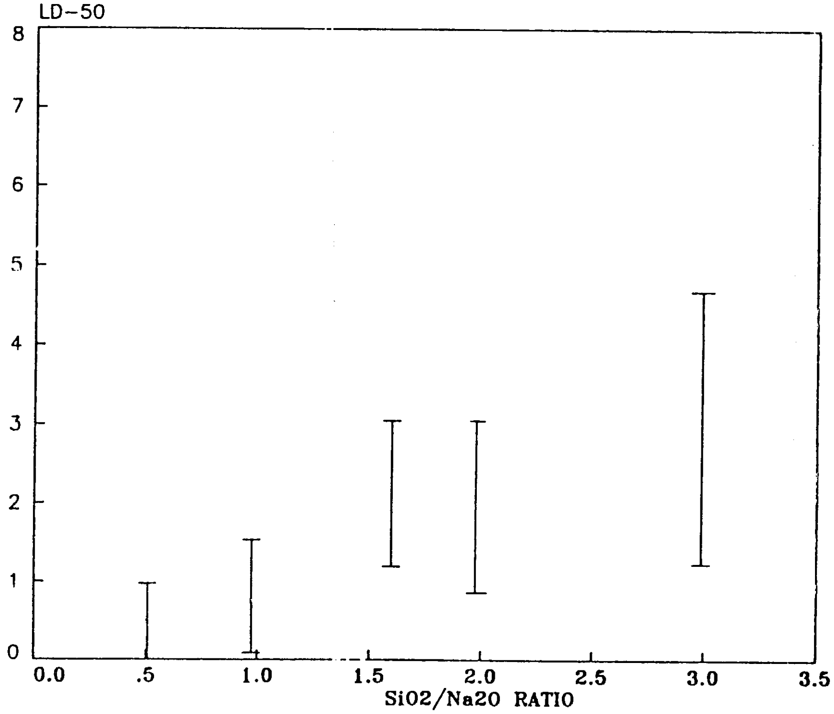

Figure 1. Ratio vs. LD_{50} sodium silicate.

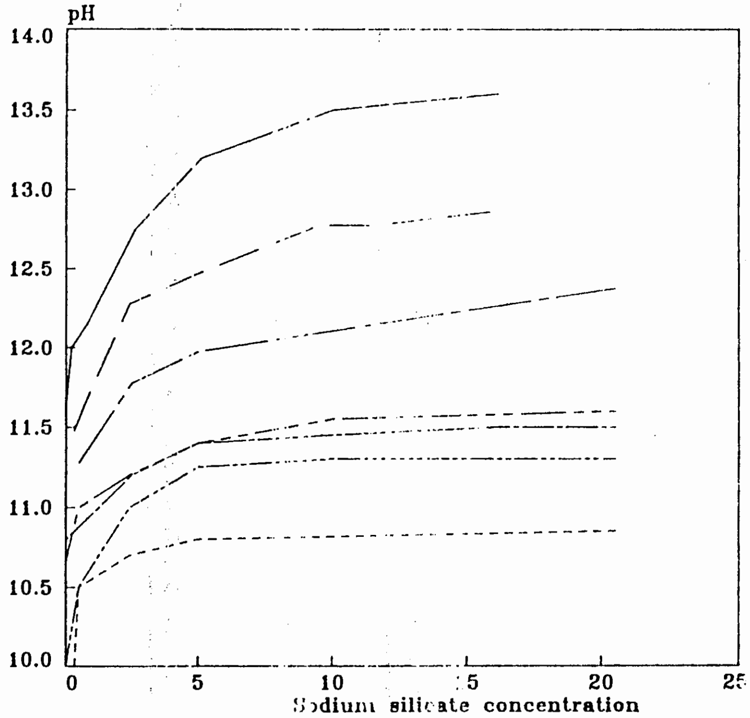

Figure 2. Concentration vs. pH. Key: – – –, 3.7; - - — - -, 3.2; — - —, 2.9; — – –, 2.5; — –, 2.0; — —, 1.6; and ——, 1.0 ratio.

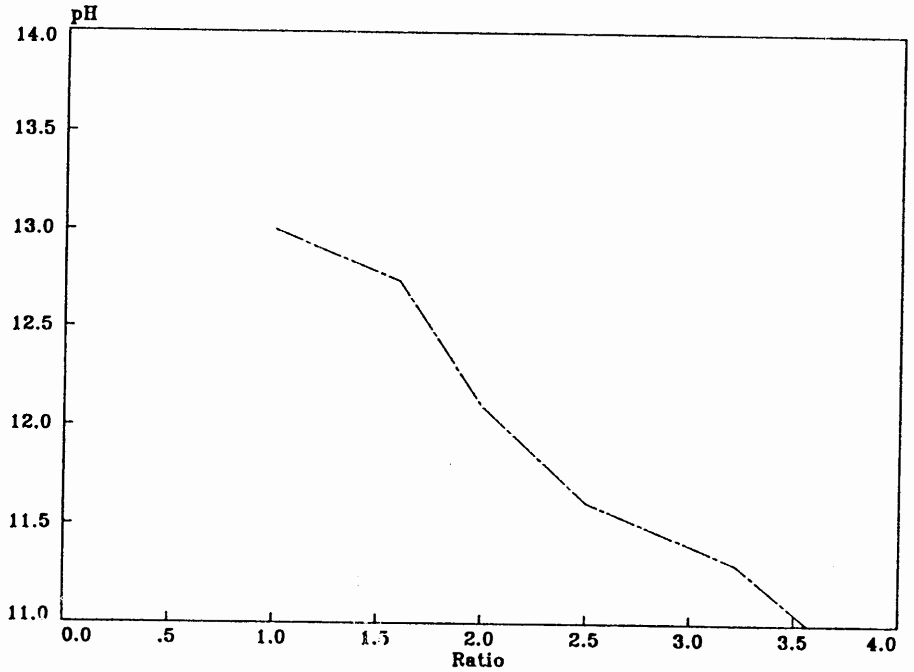

Figure 3. Ratio vs. pH.

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/Na2O 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	51	51	49
No. Born	517	346	414
No. Weaned	132	83	44
% Weaned	35	24	11
Difference as % of Controls			
Born		67	80
Weaned		46	24

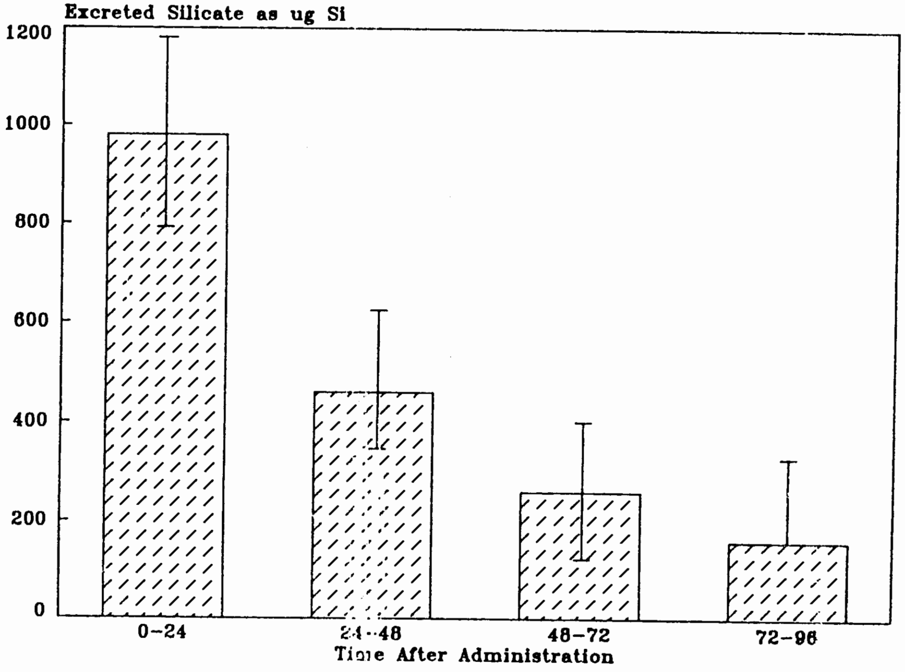

Figure 4. Urinary excretion of sodium silicate.

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	>3*	+	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	3	–	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

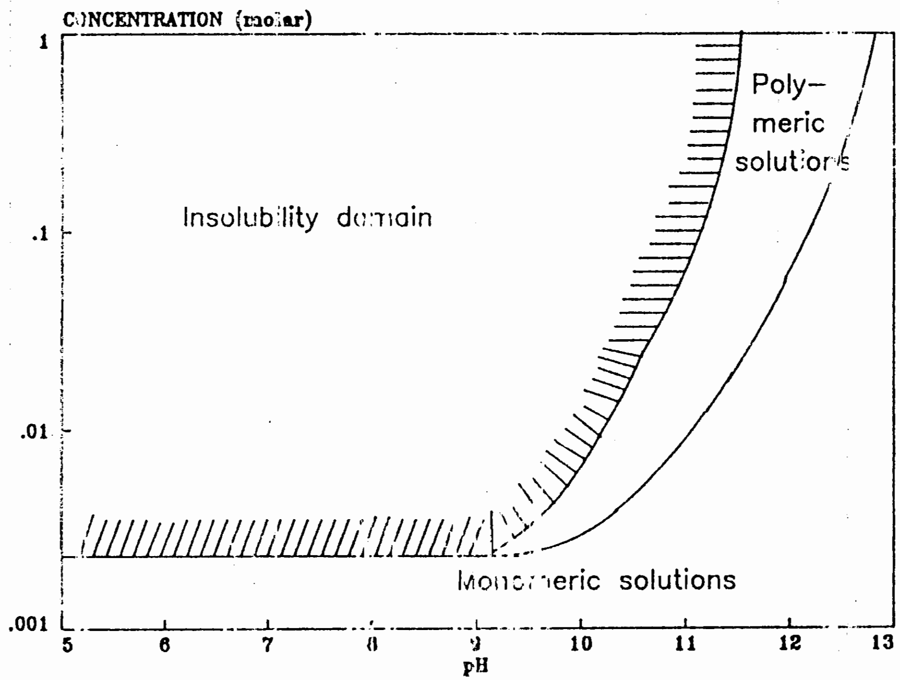

Figure 5. *Soluble silicate speciation.*

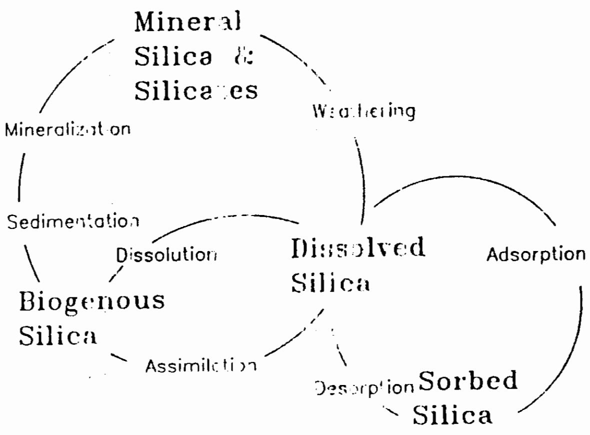

Figure 6. *The natural silica cycle.*

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.

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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 H

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

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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 sporadic 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 precautions 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 harvesting" 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 have 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.

Disposal 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 above the EPA allowable concentration of 30,000 ppm and 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

Oil 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

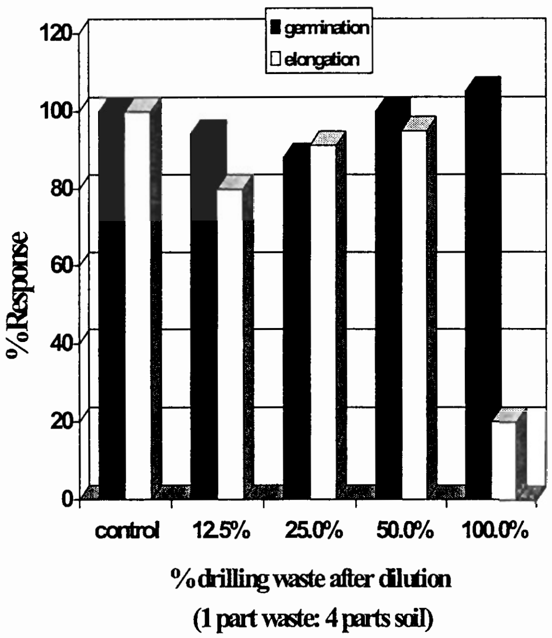


Figure 2 – Response of Cucumber Seeds to Increasing Levels of Waste Potassium Silicate Drilling Fluid

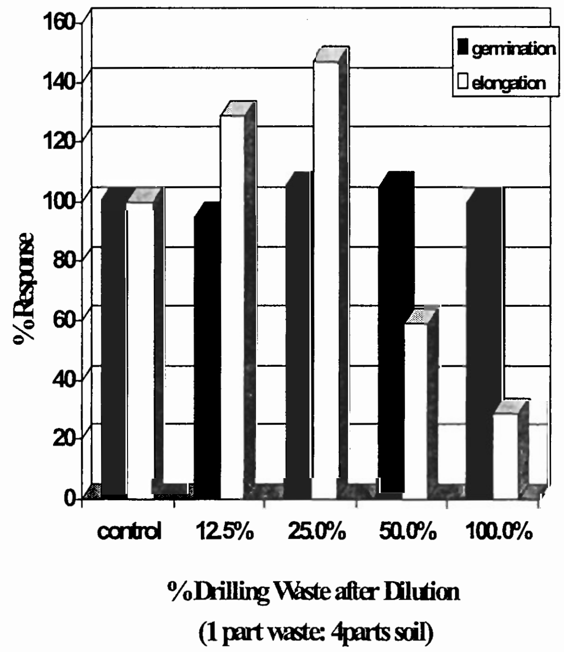
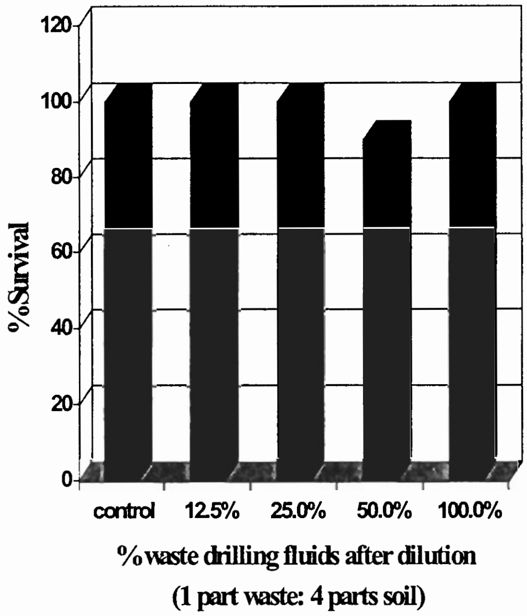


Figure 3 – Survival Rate of Earthworms in Soil Mixed with Waste Potassium Silicate Drilling Fluid



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 petri 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.

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

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 reduces 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

CADE/CAODC DRILLING CONFERENCE
October 23 & 24, 2001
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TITLE:	**Potassium Silicate Based Drilling Fluids: An Environmentally Friendly Drilling Fluid Providing Higher Rates of Penetration**	**PAPER NO. 2001-016**
AUTHOR(S):	**Rawlyk, Dave, Marquis Fluids** **McDonald, Michael, National Silicates**	**Page 1 of 11**

ABSTRACT

Recently potassium silicate based drilling fluids have been introduced in Western Canada as an environmentally progressive drilling fluid system. This paper will discuss the environmental aspects of using potassium silicate based drilling fluids. Beyond the environmental benefits of using the fluid, this paper will further discuss the field results showing near gauge hole and rates of penetration comparable to an oil system or invert system.

INTRODUCTION

Oil based drilling fluids have long been known to impart superior stability to unstable shale while providing high rates of penetration. However, in recent years, the health, safety and environmental problems associated with oil muds has lead many in our industry to realize that high performance water based mud alternatives must be developed. Even new synthetic and low toxicity oils present their own problems with environmental acceptability.

In recent years a growing number of E & P operators in Western Canada have explored viable alternatives to oil muds. The main motivations behind this are the ever-increasing mud and disposal costs. Disposal of the resultant waste effluent and subsequent restoration of the drilling location, to a condition acceptable to the local authorities is becoming an onerous expense. Beginning in 1998, Marquis Fluids has been working with and developing mud systems containing soluble silicates. The main purpose of this development effort is to offer an environmentally acceptable, cost-effective substitute for oil mud. The criteria for success of this new mud system was set as follows:

1. Equal borehole stability versus oil mud
2. Lower cost to build and maintain
3. Meet all current local criteria for on-site disposal
4. It should represent no health or safety hazards to rig personnel
5. It should require no major logistical or operation concessions

Soluble silicate mud systems meet all of these criteria within the scope of application in Western Canada.

HISTORY OF SILICATE DRILLING FLUIDS

The history, inhibition mechanisms and performance characteristics of silicate based drilling fluids have been well documented in recent years[1,2,3,4,5,6]. Since the re-introduction of silicate drilling fluids in the mid 90's, the typical silicate based drilling fluid formulation has been based on sodium silicate alone or in combination with a potassium salt. Given that silicate drilling fluids were re-introduced in the North Sea, it made economic and environmental sense to formulate a drilling fluid based on sodium silicate and potassium chloride. The idea of taking "an all in one approach" and using potassium silicate has been previously evaluated in the lab and the field. Results showed that potassium silicate made a superior drilling fluid[1,5,6] but there was little reason to pay a price premium for potassium silicate if the drilling fluid was to be used offshore.

Western Canada can arguably claim that it has become the first oil and gas producing region to commercialize potassium silicate drilling fluids. The initial premise for introducing potassium silicate into Western Canada was the following:

1. Cuttings and waste potassium silicate drilling fluids would be less expensive and easier to dispose of compared to alternative systems offering similar levels of inhibition.

2. Potassium silicate drilling fluids could be formulated to be less expensive on a per cubic metre basis than synthetic or natural oil mud

As this paper will discuss, field results have shown additional performance and cost benefits.

In 1998 Marquis Fluids began running mud systems on wells in the foothills and using silicate sweeps to stabilize friable, unstable shale with significant success – to the point that operators became interested in using soluble silicates in whole mud systems. Over the past 2.5 years Marquis Fluids, with the aid of National Silicates, and several operators began by developing drilling muds incorporating sodium silicate. These mud systems were very successful but it was felt that using potassium silicate would broaden the range of disposal options. At the time of writing this paper, Marquis Fluids has provided service and silicate technology on over 40 wells in Alberta and British Columbia.

POTASSIUM SILICATE: HEALTH AND SAFETY

Potassium silicates are manufactured by fusing sand (SiO_2) with potassium carbonate (K_2CO_3) at 1100-1200°C. The resulting glass is dissolved with high-pressure steam to form a clear, slightly viscous liquid. As would be expected of a material manufactured from sand, potash and water, potassium silicates are quite benign and therefore are not classified under the toxic and dangerous chemical group category. Furthermore, potassium silicates have no volatile organic compounds (VOC's), no odors and no flash point.

The potassium silicate products used for drilling fluid formulations typically have a pH of 11.3 and it is therefore recommended that gloves and safety glasses be worn when handling potassium silicate drilling fluids. Rig personnel working with potassium silicate drilling fluids have consistently expressed their preference with it over inverts or synthetic systems.

The inherent alkalinity of silicate drilling fluids means that biocides need not be added to the drilling fluid. Furthermore, soluble silicates are established corrosion inhibitors[7], 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.

POTASSIUM SILICATE: AGRICULTURE AND ENVIRONMENT

Potassium silicate is a recognized and registered fertilizer in various countries including the United States[8]. Liquid potassium silicate provides a soluble, readily available source of potassium. It is well established that potassium is a macro nutrient necessary for photosynthesis, osmotic regulation and activation of enzymes. Lesser-known are the benefits of soluble silica to plant life. There is a growing body of evidence that suggests silicon in the form of soluble silica plays an important and varied role in plant health. Some of the benefits sited for soluble silica include the following :[9,10,11,12]

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

The discussion on potassium silicate in agriculture applications is meant to show that both the cation and anion of potassium silicate are considered non-toxic and even beneficial when correctly applied to plants.

Although there is an extensive body of work on the interactions of potassium silicate with plants, there is very little data on the effects of potassium silicate based drilling fluids and plants. In order to establish safe disposal options meeting AEUB guidelines, an extensive biological study was completed to document the effects of spent potassium silicate muds. Testing was done in accordance with recommendations by Environment Canada (Keddy et al, 1993) as well as the American Society for Testing and Materials. These included seed germination and root elongation (barley and cucumber) as well as earthworm survival. Testing was done by HydroQual Laboratories in accordance to US-EPA protocols for short-term toxicity screening of hazardous waste (EPA 600/3-88-029).

Testing involved taking the waste potassium silicate drilling fluid and diluting to various concentrations. The diluted waste potassium silicate drilling fluid was mixed 1 to 4 with artificial soil. Cucumber (cucumis satvis) and barley (hordeum vulgare) were planted in petri dishes and scored on the 5th day for germination and root elongation. Figures 1, 2 and 3 in the appendix show the responses in comparison to the control.

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 at a dilution up to 25% with a negative impact at higher levels. Root elongation results for barley showed a minimal effect up to 50% dilution.

The specific grade of potassium silicate selected by Marquis Fluids was National Silicates' EcoDrill® 317. Table 1 shows the product specification for potassium silicate. A potassium silicate drilling fluid prepared with 10% v/v of EcoDrill® 317 would have 8,670 mg/L of potassium or roughly half the amount of potassium of what would be found in a drilling fluid prepared with potassium sulphate (Table 2).

OPERATIONAL PERFORMANCE: FIELD EXPERIENCE

General field results show that potassium silicate muds when properly managed can be formulated at a lower concentration than sodium silicate muds without loss of inhibitive characteristics. The physical properties of the potassium silicate would suggest higher ROP than a sodium silicate mud by virtue of the fact the SG of potassium silicate is considerably lower, 1.534 vs. 1.259 respectively. Because it is run at a lower concentration, a fresh mud formulated with 10% v/v potassium silicate would furnish a starting density of 1020-1030 kg/m^3 as opposed to 1120-1130 kg/m^3 with 20% v/v sodium silicate.

General Ferrier area:

In spite of drilling successful wells with a proprietary oil mud, Husky Energy (formerly Renaissance) chose a potassium silicate fluid with the hopes of achieving penetration rates comparable to an oil mud but also to reduce the impact of disposing the oil mud cuttings and waste. The first potassium silicate well was drilled vertically at 14-10-41-9 W5M to a depth of 2826 m and was subsequent to a directionally drilled oil mud hole located at 2-9-41-9 W5M to 3010 m Measured Depth (MD). A third hole, 10-32-40-9 W5M, was drilled directionally to 3002 mMD with re-used silicate mud from the 14-10 location. Typically, Husky drills the upper section with a motor using tri-cone bits (Table 6) to 1750-1850 m. Once into the Lea Park shale, a PDC is run with a motor to take advantage of the higher ROP usually associated with this type of bit. It is also typical of the area to have to weight up to some degree to control background gas in the Second White Specks formation.

2-9-41-9 W5M

This well was drilled with Husky's proprietary Pure Oil 2000 all oil drilling mud. Because Husky had drilled numerous wells with this system, it was their practice to not rely on daily mud service. Hence, in Table 3, the only mud properties displayed are Density, Funnel Viscosity and the High Temperature, High Pressure filtrate (HTHP). As this was to be a directional hole, the angle and azimuth were monitored passively after drilling out the shoe. Initially, additions of up to 35 m^3 per day of base oil were required to maintain volume and also contributed to maintaining a low mud density. A PDC was run at 1791 m with a motor and almost immediately, deviation became a problem increasing to 3° by 1979 m. In spite of control drilling, high ROP was still evident until the PDC was pulled at 2359 m. At this point, a tri-cone was run and drilled to kick off point at 2376 m. By 2370 m, the mud density had been increased to 1065 kg/m^3 and further to 1090 kg/m^3 by Total Depth (TD) to control background gas. The hole was kicked off to 9.1° by 2550 m with only a slight 10° change in azimuth. At 2775 m the motor was pulled and the remainder of the hole was drilled with a rotary string averaging a 2.9 m/hour ROP. No problems were encountered while logging or running casing.

14-10-41-9 W5M

As previous silicate experience dictated, this well was programmed to be drilled with a Potassium Silicate concentration of 8-10 % v/v. As evident in Table 4, the flow properties were initially maintained at a level that would be conducive to drilling at a high ROP. The silicate level was monitored on a daily basis and a depletion to 6.0% v/v by 773 m indicates the upper shales and clays to be somewhat reactive. For the most part, the silicate level was maintained in the prescribed range for the remainder of the hole. Two centrifuges were run to control the drilled solids at a minimum – in the 2-3% range. The first bit trip at 969 m was somewhat tight and was originally thought to be due to insufficient hole cleaning. Viscous sweeps consisting of base mud enhanced with a fibre and Xanthan gum for a Yield Point (YP) of 5 Pa was run with no increase in cuttings at the shaker. The YP was slowly increased as the hole was deepened and minor tight hole manifested itself only on the next two trips.

As per area operating practice, the density was allowed to increase to 1080 kg/m³, but through drilled solids rather than with barite additions. Background gas was noticeable after each trip from the Cardium formation (~2160 m) and also from the Second White Specks. This led to the eventual increase in mud density to 1120 kg/m³ by TD. As drilling continued, deviation impacted on the ROP during the PDC run, increasing to 3° by 2426 m which resulted in fanning the hole with only 3-4 daN on the bit. Drilling to TD was uneventful, as was logging and running casing.

10-32-40-9 W5M

Since the results of 14-10 were favourable, it was decided to continue the program on the 10-32 directional well. The one change made to the mud program was the potassium silicate concentration was to be maintained at 6-8% v/v as opposed to the 8-10% v/v on 14-10. This change was based on the exceptional caliper of 14-10 (Figure 5) and the resulting query whether reducing the concentration of potassium silicate would provide comparable hole gauge.

Once drilled out, the hole was displaced to the potassium silicate mud remaining from 14-10. A PDC on a motor was run and the deviation problems encountered on surface hole also plagued the main hole section through to kick off point (KOP). Although the bit was being fanned, ROP was comparable to that of the 2-9 invert and the 14-10 silicate. However, at ~1600 m it can be observed the ROP had reduced substantially (Figure 7), and can be attributed to the attempt to hold vertical and azimuth. The reduced ROP was also compounded by a density increase to 1180 kg/m³ at 2500 mMD and further to 1280 kg/m³ by 2755 m to control gas prior to and after trips. Eventually the density was increased to 1335 kg/m³ by TD at 3002 mMD. At ~2000 m, the hole was kicked off and angle built to a maximum of 19.6° at 2683 mMD. Angle was then allowed to drop and the last reported survey was 11° at 2980 mMD. Increased drag on trips was the product of several small doglegs resulting from difficulty holding angle and azimuth. The addition of Graphite helped to lessen the drag but at TD, solid beads and ground walnut were spotted as insurance for successful logging and to run casing.

Summary of Performance

In reviewing the ROP data in Table 6, and the Depth vs. Days curves in Figure 7, it is apparent that potassium silicate muds performed comparably to the oil mud. Though deviation problems slowed the 10-32 silicate, it performed just as well to ~1600 m. Even from under the shoe to 2500 m the average ROP was 10.7 m/hour on this hole. The 14-10 silicate at an average ROP of 11.6 m/hour showed a 5% increase in ROP over the 2-9 invert.

As demonstrated on Husky 2-9, any hole stability problems unique to this area of the Ferrier field can be overcome by the use of oil mud. Since there was no reaming or cleaning associated with instability evident on the two holes drilled with potassium silicate, it becomes apparent the silicates performed just as well if not better. The tight hole or perceived hole cleaning problem that was reported on 14-10 can be attributed to the excellent caliper that was obtained from use of the potassium silicate at 8-10% v/v as seen in Figure 5. Hole enlargement on 10-32 (Figure 6) is still acceptable and could be a result of rotating and sliding with the motor and bent sub while attempting to control angle and azimuth. The 2-9 caliper (Figure 4) also shows some enlargement that could be characteristic of this type of operation. However, based on numerous caliper comparisons, we have found inverts formulated with a calcium chloride brine phase to impart a 3-5% increase in hole diameter.

Potassium Silicate Drilling Fluids: Disposal

The Alberta Energy Utility Board has established the requirements for individual submission, review and approval process concerning disposal options for new drilling fluid systems that are not covered in the current Guide 50-Drilling Waste Management Disposal manual (October 1996).

Spent potassium silicate mud has been placed in the potassium based drilling waste category (e.g. potassium sulphate) and consequently the same or similar protocol can be applied for its safe disposal. Consistent with the AEUB requirements, the toxicity testing of the spent mud must be completed using the Microtox testing protocol. If mud is considered non-toxic, the potential impacts to the physical and chemical properties of the soil must be addressed. This involves soil salinity determinations such as: pH, EC, Ca, Mg, Na, Cl and SAR.

Potassium Silicate Drilling Fluids: Re-use

Both mud and disposal costs are partially mitigated by the re-use of potassium silicate muds. The inhibition mechanisms of potassium silicate drilling fluids helps prevent the build-up of drill solids, however as in any high performance drilling fluid, efficient solids removal equipment is paramount. The Ferrier experience showed that after being re-used once, the drill solids of the potassium silicate mud were in the range of 2-3%. It is expected potassium silicate muds could be re-used multiple times.

CONCLUSIONS

The documented field performance of potassium silicate drilling fluids has proven to be an excellent alternative to oil mud for various reasons, some readily apparent as described throughout the paper. Several advantages of potassium silicate muds versus oil muds and sodium silicate muds can be identified:

- Penetration rates comparable to or better than that of a low density oil mud.
- Very stable mud properties that can be easily modified for any situation be it hole cleaning or well control.
- In most cases provides better hole gauge than oil muds and better than the 8-10% overgauge by diameter typically observed with muds consisting of 18-20% v/v sodium silicate.
- Lower starting density than that of a sodium silicate mud consisting of 18-20% v/v.
- Muds formulated with potassium silicate can be superior to oil muds with respect to health, safety and environment.

ACKNOWLEDGMENTS

Marquis Fluids and National Silicates would like to thank Husky Energy for permission to publish the data shown and help prove the technology. Marquis Fluids also expresses its appreciation to Mr. Colin Logan for his contribution to the betterment of this paper. National Silicates wishes to thank Vicky Sidorkiewicz (National Silicates) for her work in the environmental testing of potassium silicate.

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APPENDIX

Table 1 - Typical physical properties of potassium silicate product used in formulating muds used at Ferrier

Product Name	Wt. Ratio $SiO_2:K_2O$	% K_2O	% SiO_2	% Solids	Density	pH	Viscosity centipoise
EcoDrill® 317	2.50	8.30	20.8	29.1	1.259	11.3	40

Table 2 - Comparison of a potassium levels in muds prepared with Potassium Silicate vs. Potassium Sulphate

Mud	Concentration	mg/L Potassium
Potassium Sulphate	4% wt/vol	17,960
Potassium Silicate	10% vol/vol	8,670

Table 3 - Husky Ferrier 02-09-41-9 W5M Mud Properties - Oil Mud
Note: Density increase was made to control background gas.

Depth (m)	Density (kg/m^3)	Funnel Vis (sec/L)	HTHP Filtrate (cm^3/30 min. @ 3500 kPa)
732	1005	92	25
1100	995	62	25
1307	970	56	15
1507	960	69	20
1710	945	55	25
1830	940	52	25
2003	950	55	11
2240	940	56	18
2371	1065	60	19
2475	1070	56	18
2615	1070	58	19
2738	1060	56	15
2775	1070	56	18
2847	1065	57	18
2884	1070	60	18
2905	1080	65	18
2955	1090	60	15
3003	1090	54	18
3010	1090	58	18

Table 4 - Husky Ferrier 14-10-41-9 W5M Mud Properties - Potassium Silicate Mud

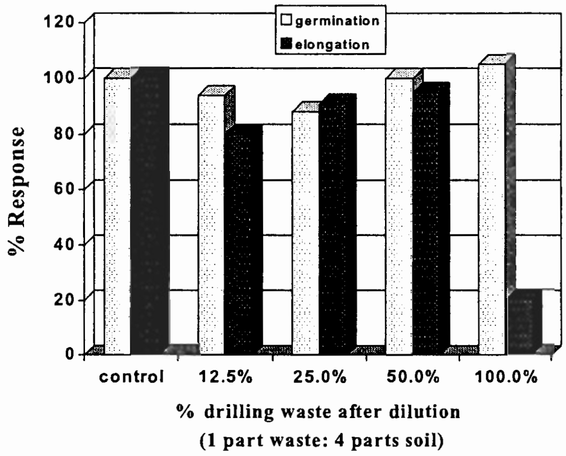
Depth (m)	Density (kg/m^3)	PV (mPa.s)	YP (Pa)	Filtrate (cm^3/30 min. @ 700 kPa)	Silicate (% v/v)
424	1035	2	3.35		12.5
773	1050	3	0.96	12.0	6.0
945	1060	3	0.96	11.0	7.7
1181	1060	2	1.92	8.5	7.1
1582	1060	9	2.87	9.5	8.5
1745	1055	9	1.92	8.0	8.1
2058	1080	10	4.79	8.5	9.5
2358	1080	10	7.18	7.5	8.3
2510	1080	10	6.22	7.5	7.2
2571	1085	10	5.75	7.5	7.0
2662	1090	12	7.18	7.5	7.2
2726	1110	11	8.62	8.0	8.0
2782	1120	12	7.18	8.0	8.0

Table 5 - Husky Ferrier 10-32-40-9 W5M Mud Properties - Potassium Silicate Mud

Note: A density increase was made at 2500 m to control background gas.

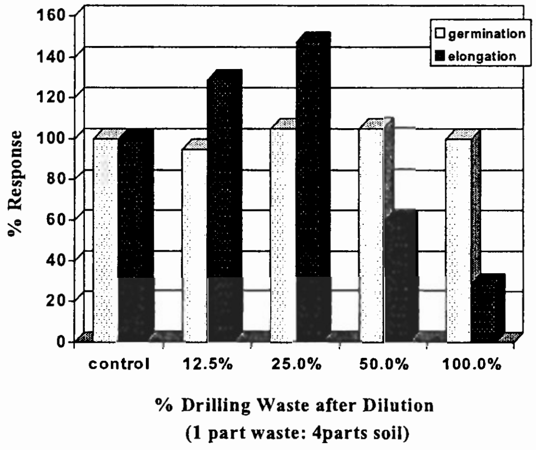
Depth (m)	Density (kg/m³)	PV (mPa.s)	YP (Pa)	Filtrate (cm³/30 min. @ 700 kPa)	Silicate (% v/v)
421	1060	8	2.87	19.0	9.0
803	1060	8	2.87	13.5	8.7
1274	1065	9	3.35	16.0	8.45
1342	1070	10	2.87	12.8	8.5
1500	1070	10	3.35	10.0	8.5
1654	1075	11	4.79	8.0	8.0
1726	1080	10	6.70	8.0	6.9
1829	1090	11	6.70	7.4	6.7
1874	1090	14	6.7	7.6	7.1
1984	1095	13	6.70	9.0	7.4
2066	1090	12	6.22	10.4	6.3
2188	1095	11	5.75	9.8	6.3
2308	1095	11	4.31	10.5	5.9
2364	1095	10	4.31	9.8	5.9
2457	1095	11	4.79	10.8	6.4
2500	1180	18	7.18	11.0	7.4
2535	1225	24	8.14	10.0	6.5
2602	1240	23	9.58	10.0	7.1
2672	1250	23	9.58	10.4	7.0
2755	1280	24	8.62	11.4	6.4
2867	1285	22	7.66	11.4	6.3
2901	1295	22	7.66	12.6	6.3
2942	1305	22	7.66	10.8	6.2
2966	1290	22	7.66	11.6	6.1
2984	1305	20	7.18	11.0	6.0
3002	1335	22	7.18	12.4	5.7

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



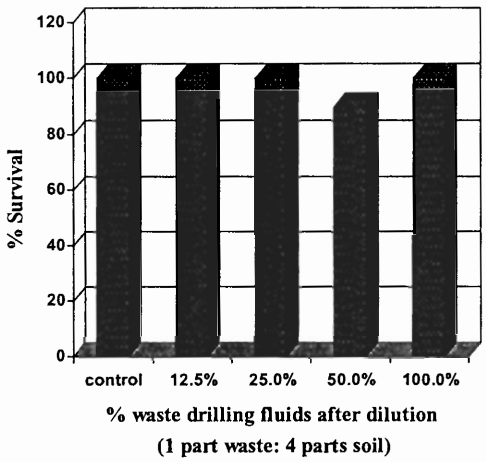
For Seed Germination, artificial soil was mixed with the appropriate sample dilution at a ratio of 1 part waste: 4 parts artificial soil. 30 grams of soil and sample were placed in a petri dish. Twenty seeds were added to the soil and covered by a 30g sand cap. Soil was hydrated with 7.5ml of de-ionized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

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



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.

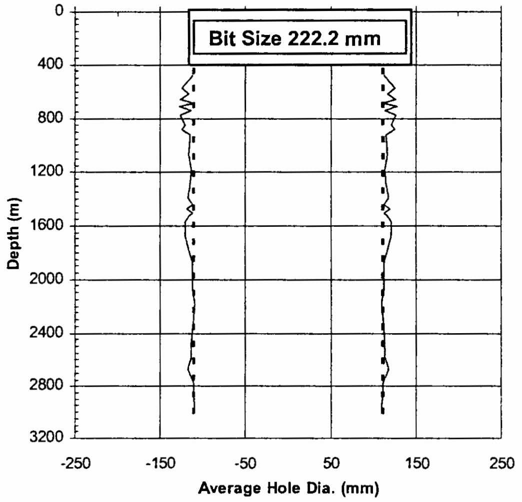
Figure 3 – Survival Rate of Earthworms in Soil Mixed with Waste Potassium Silicate Drilling Fluid



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.

Figure 4 – Caliper graph of Husky Ferrier 2-9-41-9 W5M using oil mud. Average Hole Diameter is 233 mm (4.86% over by dia., 8.86% over by volume).



\- - - - - - Bit Size
——— Hole Diameter

Figure 5 - Caliper graph of Husky Ferrier 14-10-41-9 W5M using Potassium Silicate mud. Average Hole Diameter is 225 mm (1.3% over by dia., 3.55% over by volume).

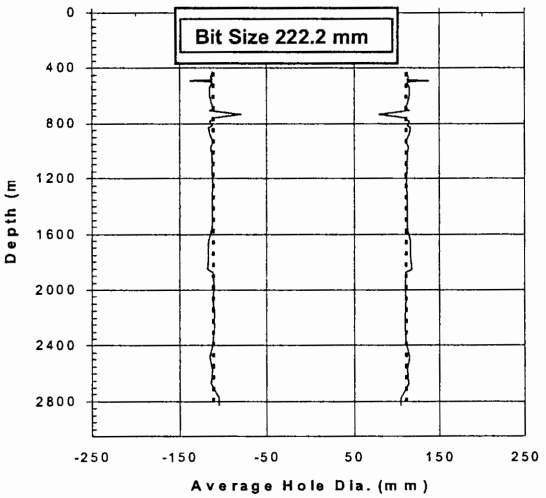


Figure 6 - Caliper graph of Husky Ferrier 10-32-40-9 W5M using Potassium Silicate Mud. Average Hole Diameter is 234mm (5.3% over by dia., 10.9% over by volume)

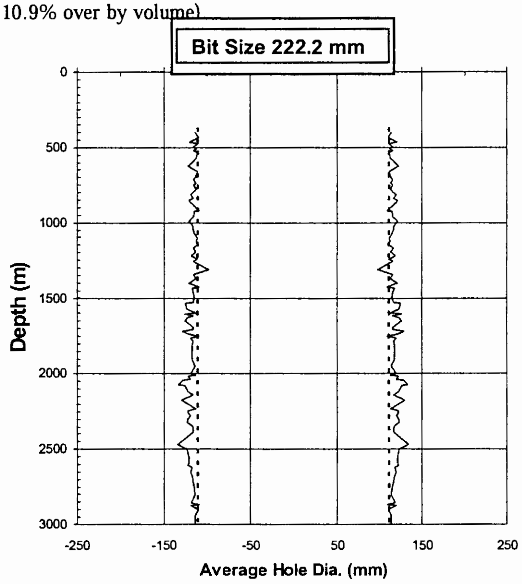
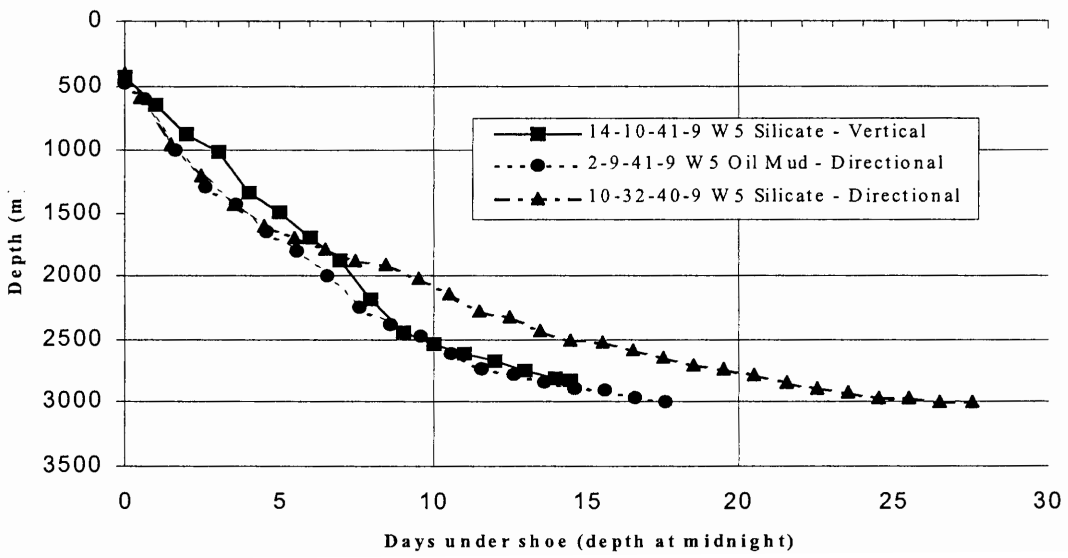
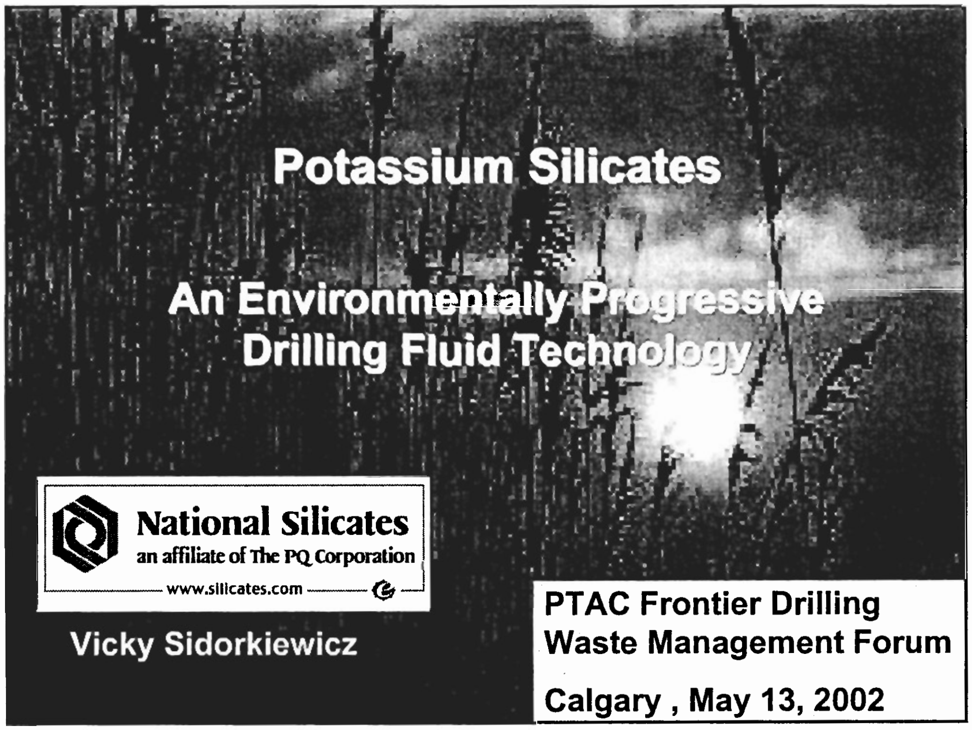


Table 6 – Bit record and ROP data. ('M' denotes motor. M(90) denotes motor RPM)

	Make	Type	In	Out	ROP (m/hour)	Average WOB	RPM	Vertical Deviation
Location: 2-9-41-9 W5								
Bit #1	STC	F14T	476	1307	20.6	15.1	M+50	0.25
Bit #2	STC	F2H	1307	1791	11.2	14.7	120	0.75-1.25
Bit #3	Hycalog	DS146	1791	2359	21.4	4.3	M+40	1.25-3.2
Bit #4	RTC	HP44	2359	2775	7.0	15.5	M+40	3.2-9.1
Bit #5	RBI	C3LR	2775	2884	3.2	16.1	80	9.1-6.5
Bit #6	STC	F35	2884	3010	2.6	17.6	80	6
				Average	**11.0**			
Location: 14-10- 41-9 W5								
Bit #1	HC	GT1	424	969	14.4	10.2	120	1-2
Bit #2	RTC	HP44	969	1745	15.2	14.3	M+40	0.5-1
Bit #3	Hycalog	DS146	1745	2528	17.1	10.4	M+50	0.5-3
Bit #4	RBI	C3L	2528	2726	6.5	15.1	M(90)+50	1-1.5
Bit #5	RTC	62A	2726	2825	4.8	15.4	M(90)+50	0.5-1
				Average	**11.6**			
Location: 10-32-40-9 W5								
Bit #1	HGY	DS180	398	1276	22.2	4.4	M+40	2.25
Bit #2	RTC	HP44	1276	1693	9.6	11.5	M+50	2.50
Bit #3	HTC	GT09	1693	1874	5.5	11.0	110	2.50
Bit #4	Hycalog	DS149	1874	1994	9.9	3.7	M+20	2.00
Bit #5	RTC	HP44	1994	2314	7.0	12.2	M+20	10.80
Bit #6	HTC	GT18	2314	2500	10.0	15.0	M+40	18.70
Bit #7	STC	F2	2500	2707	3.8	15.2	M+40	19.60
Bit #8	SEC	X530	2707	2881	3.0	18.2	M+40	18.00
Bit #9	STC	F35	2881	2966	3.0	19.9	M+40	17.00
Bit #10	RTC	HP62	2966	2985	1.8	16.8	70	15.00
Bit #11	RBI	CLR	2985	3002	1.3	18.6	100	11.00
				Average	**7.0**			
				Average to 2500 m	**10.7**			

Figure 7 - Depth versus Days graph.





Potassium Silicates

An Environmentally Progressive Drilling Fluid Technology

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Vicky Sidorkiewicz

PTAC Frontier Drilling Waste Management Forum

Calgary , May 13, 2002

Overview

- Introduction
- Chemistry of Soluble Silicates
- Environment, Health and Safety Characteristics
- Toxicological Evaluations
- Agricultural and Farming Benefits
- Disposal Options
- Summary

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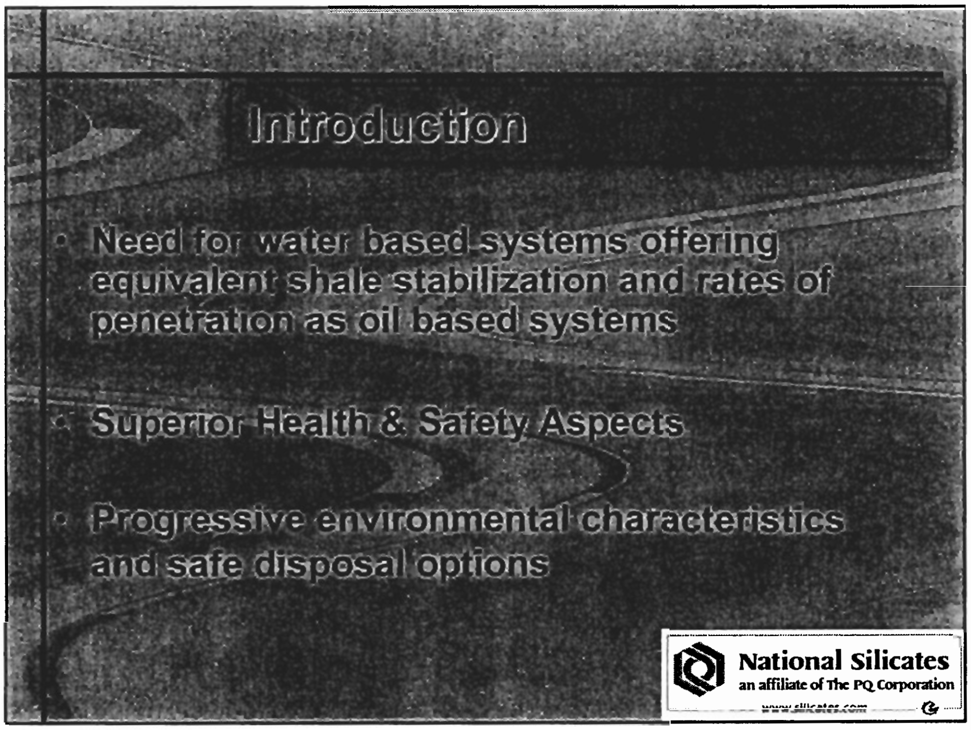

Introduction

- Need for water based systems offering equivalent shale stabilization and rates of penetration as oil based systems
- Superior Health & Safety Aspects
- Progressive environmental characteristics and safe disposal options

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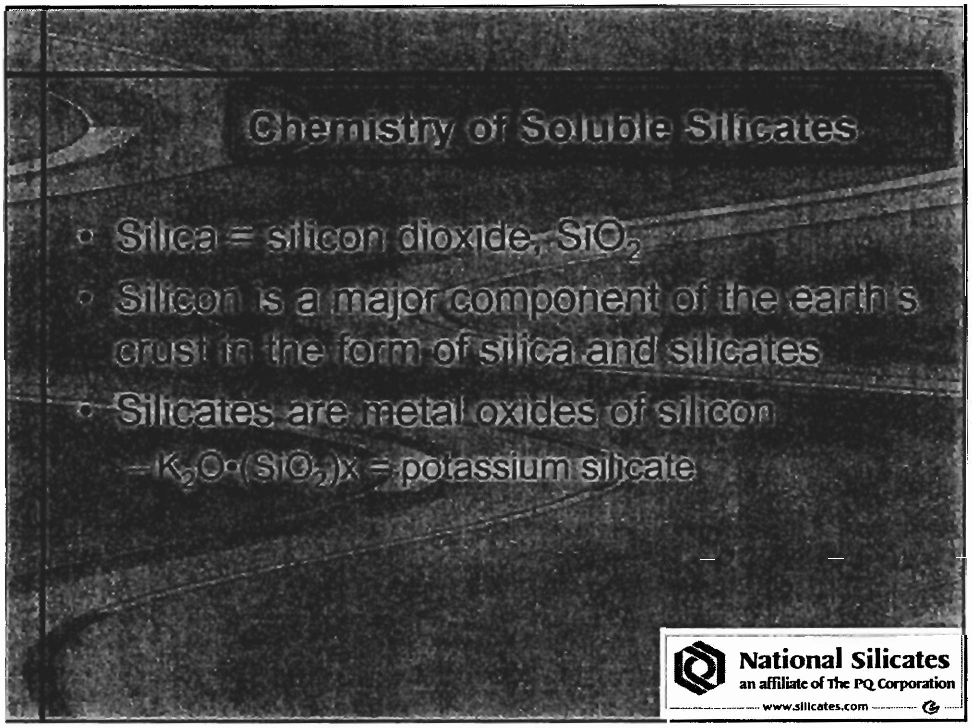

Chemistry of Soluble Silicates

- Silica = silicon dioxide, SiO_2
- Silicon is a major component of the earth's crust in the form of silica and silicates
- Silicates are metal oxides of silicon
  - $K_2O \cdot (SiO_2)x$ = potassium silicate

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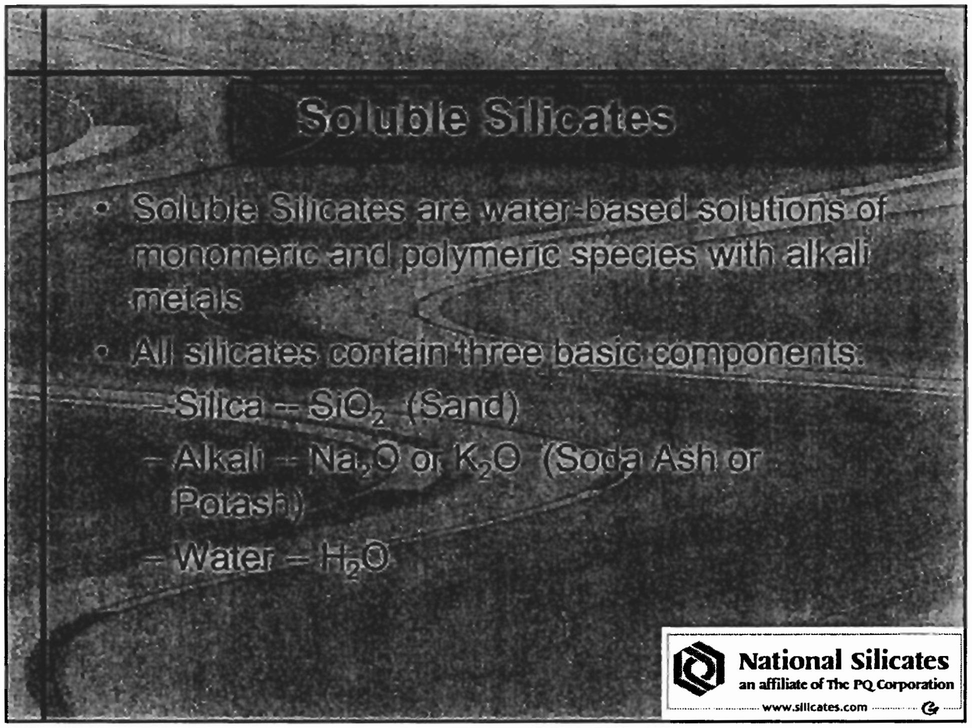

Soluble Silicates

- Soluble Silicates are water-based solutions of monomeric and polymeric species with alkali metals
- All silicates contain three basic components:
  - Silica – SiO_2 (Sand)
  - Alkali – Na_2O or K_2O (Soda Ash or Potash)
  - Water – H_2O

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Environment, Health & Safety Characteristics

- One of the safest, most benign industrial chemicals
- Stable, inorganic, non-toxic material
- Not Corrosive , non-flammable and contain no VOC s, non-carcinogenic
- HMIS rating
  - health rating -1 (slight)
  - flammability rating -0 (none)
  - reactivity rating - 0 (none)
  - contact rating - 2 (moderate due to pH)

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EH&S Continued

- Alkalinity of a silicate drilling fluid is very similar to a laundry soap(mild reactivity)
- Not TDG regulated, not a hazardous substance
- Not on the Alberta Industrial Waste ID and Management Options List
- Generally Recognized As Safe by USDA and FDA (GRAS List)
- Used in water treatment, soil remediation, agriculture etc

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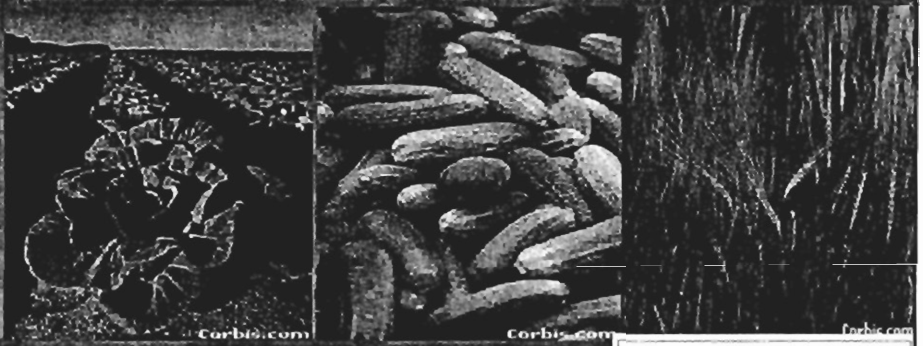
Toxicological Evaluation

- Terrestrial Toxicity Assessment

(Environment Canada Test Methods)



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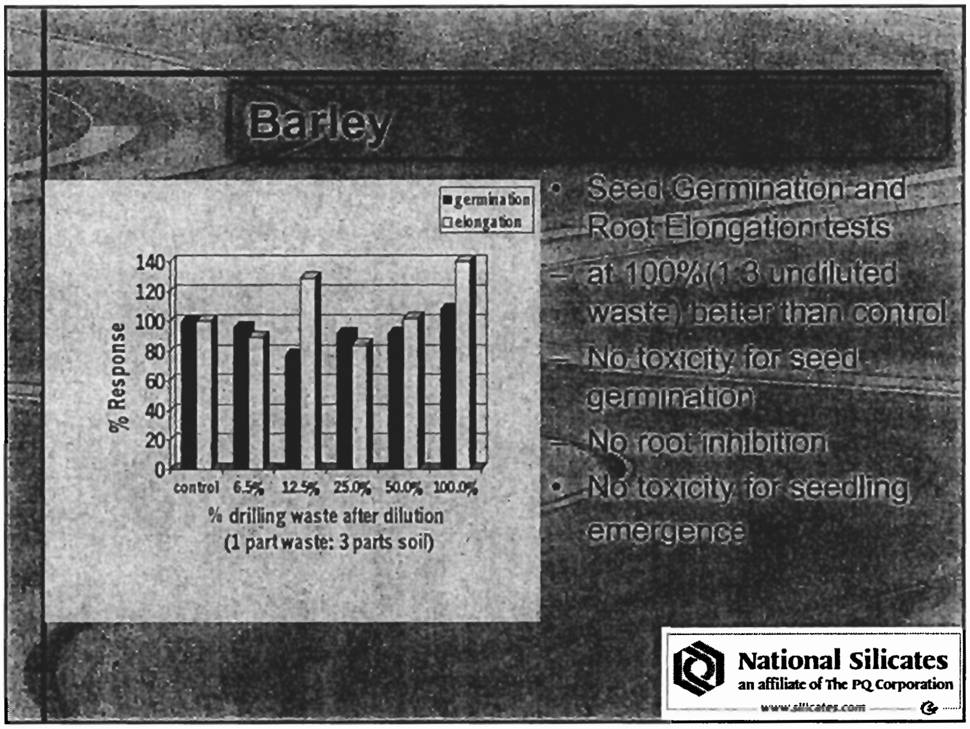

Barley

- Seed Germination and Root Elongation tests
  - at 100%(1:3 undiluted waste) better than control
  - No toxicity for seed germination
  - No root inhibition
- No toxicity for seedling emergence

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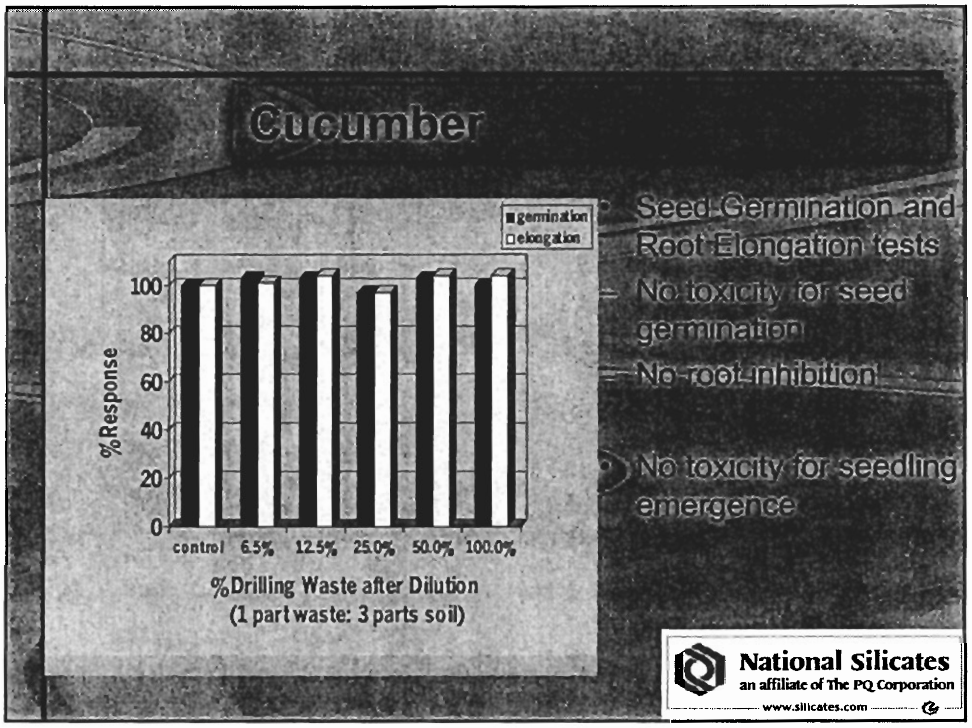

Cucumber

- Seed Germination and Root Elongation tests
  - No toxicity for seed germination
  - No root inhibition
- No toxicity for seedling emergence

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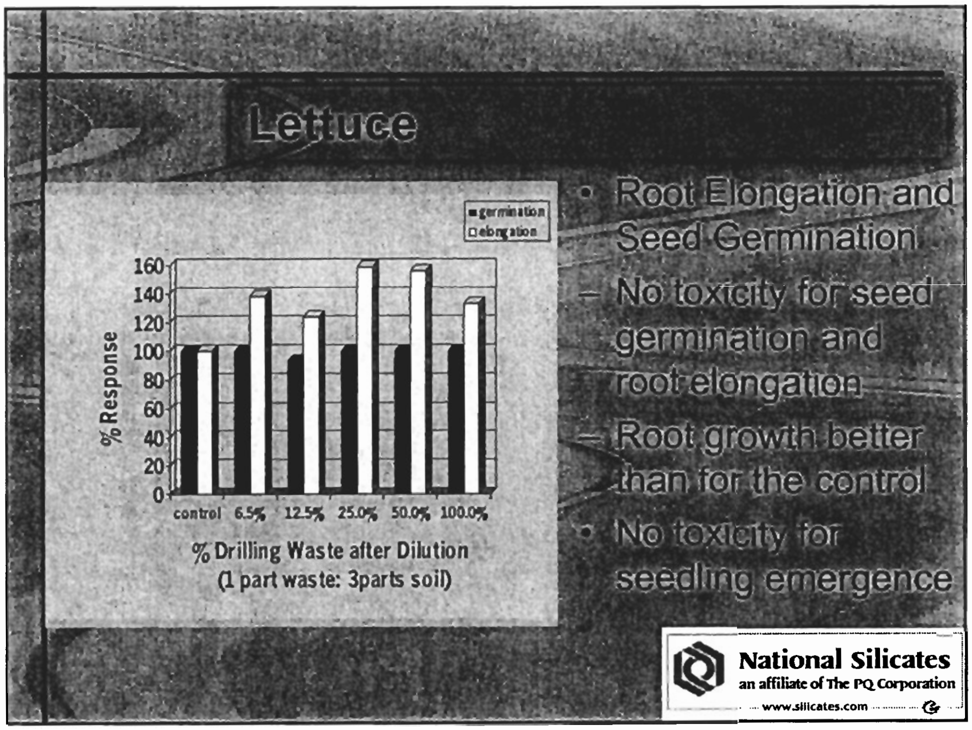

Lettuce

- Root Elongation and Seed Germination
  - No toxicity for seed germination and root elongation
  - Root growth better than for the control
- No toxicity for seedling emergence

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Earthworm Survival

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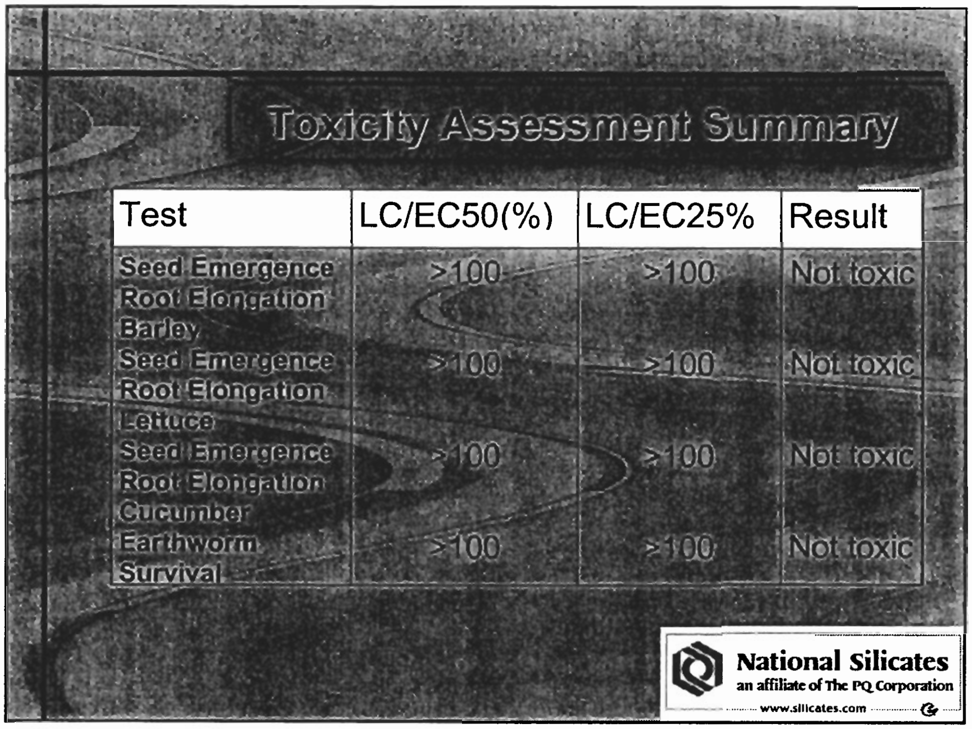

Toxicity Assessment Summary

Test	LC/EC50(%)	LC/EC25%	Result
Seed Emergence Root Elongation Barley	>100	>100	Not toxic
Seed Emergence Root Elongation Lettuce	>100	>100	Not toxic
Seed Emergence Root Elongation Cucumber	>100	>100	Not toxic
Earthworm Survival	>100	>100	Not toxic

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Agricultural Benefits

- Silica recognized as essential micronutrient
  - Reduces disease pressure
  - Increases growth and yield
  - Improves resistance to drought and climatic stress
  - Provides resistance to mineral toxicity
- Potassium provides additional growth and health benefits

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Potassium Silicates -Traditional Uses in Agriculture

Recognized fertilizer in various countries worldwide including USA

Traditional uses of potassium silicates

Australia & USA

⇒ Fruit floatation and binders for feed & fertilizers

Europe

⇒ Hydroponic fertilizer

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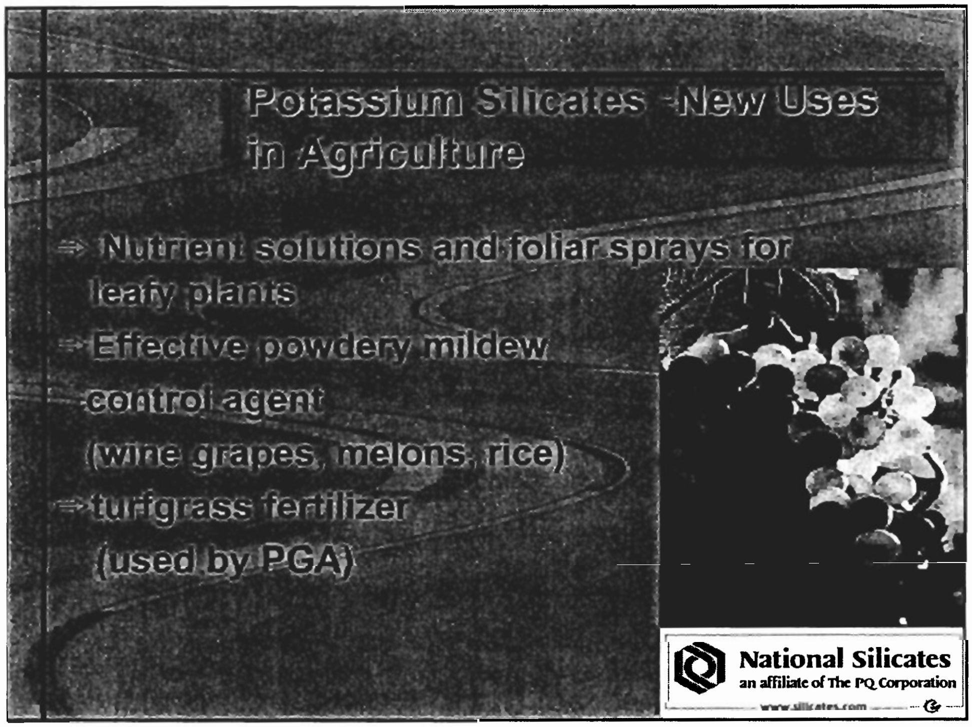

Potassium Silicates -New Uses in Agriculture

⇒ Nutrient solutions and foliar sprays for leafy plants

⇒ Effective powdery mildew control agent (wine grapes, melons, rice)

⇒ turfgrass fertilizer (used by PGA)

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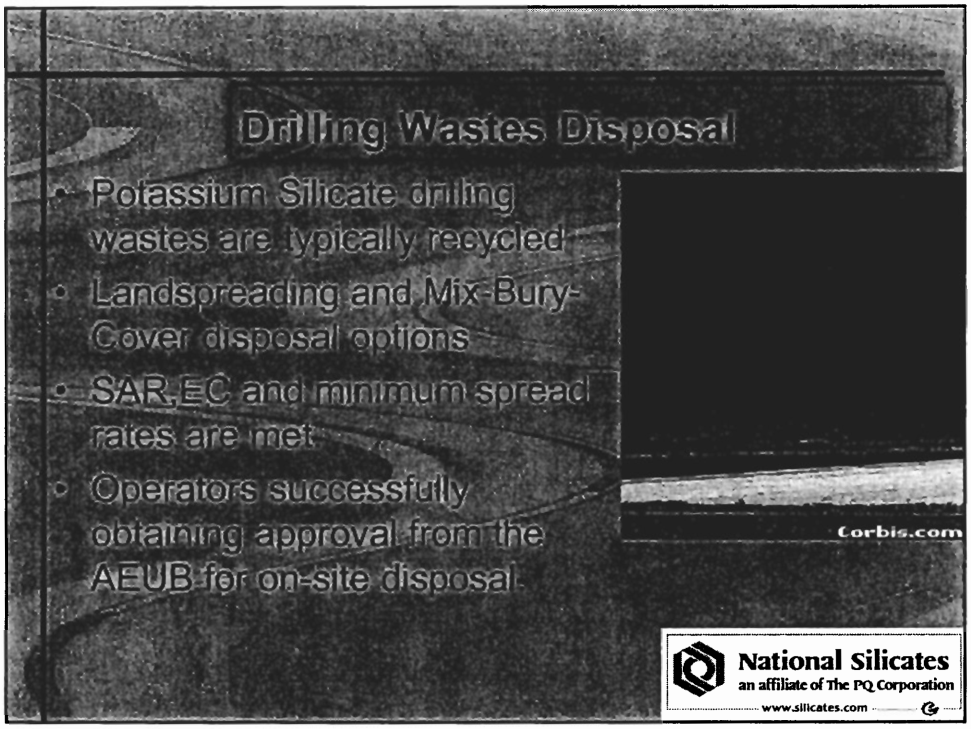

Drilling Wastes Disposal

- Potassium Silicate drilling wastes are typically recycled
- Landspreading and Mix-Bury-Cover disposal options
- SAR,EC and minimum spread rates are met
- Operators successfully obtaining approval from the AEUB for on-site disposal

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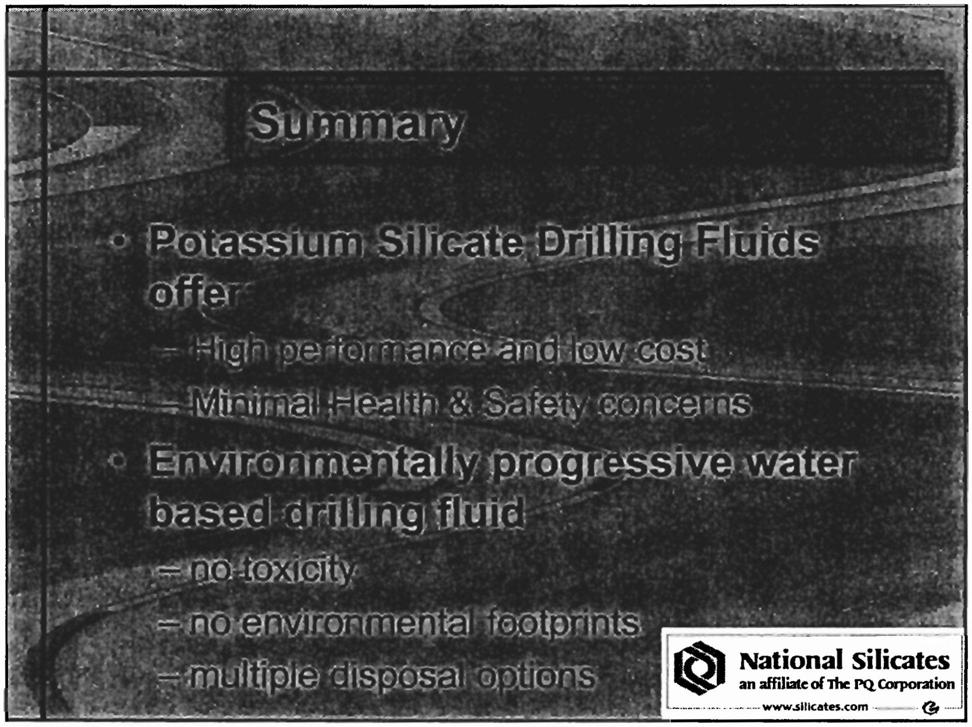

Summary

- Potassium Silicate Drilling Fluids offer
  - High performance and low cost
  - Minimal Health & Safety concerns
- Environmentally progressive water based drilling fluid
  - no toxicity
  - no environmental footprints
  - multiple disposal options

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ATTACHMENT I

Bibliography

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