

PHILADELPHIA ELECTRIC COMPANY

2301 MARKET STREET

P.O. BOX 8699

PHILADELPHIA, PA. 19101

(215) 841-4000

2850559570

March 22, 1985

Mr. Richard Hinkle
Chief, Facilities Section
Department of Environmental Resources
1875 New Hope Street
Norristown, PA 19401

RE: Limerick Generating Station NPDES Permit PA 0051926

Dear Mr. Hinkle:

Please disregard our letter of January 7, 1985, concerning the subject permit.

This is to request a minor change to the subject permit and to request approval to use three chemical substances in the Limerick Unit #1 cooling water system.

We hereby request that the temperature monitoring of the Perkiomen Creek as specified in "Other Requirements" A and N of the subject permit be deleted. As discussed with you and Mr. J. P. Ridolfi of your staff previously, on November 2, 1984, water from the Perkiomen Creek will be used as a secondary source of water for the Limerick cooling towers. The Perkiomen Creek is approximately six (6) miles from the surge tank and the surge tank is about a half mile from the cooling towers. Due to this long pumping distance, temperature monitoring would have no meaning or relation to the temperature of the cooling tower blowdown discharged to the Schuylkill River.

In accordance with Section 92.7 "Reporting of New or Increased Discharges," of the Departments' Rules and Regulations, and pursuant to "Other Requirements" item E of the subject NPDES permit, we hereby request permission to use three chemical products for cooling water treatment at Limerick Generating Station, discharge point 001 (combined discharges). The three chemical products are: NALCO 1336 (tolyltriazole (TTL) corrosion inhibitor for copper), NALCO 1370 (polyacrylate scale inhibitor) and NALCO 2513 (sodium silicate corrosion inhibitor for steel). These NALCO products will be evaluated during a testing program as a means to control scale and corrosion in the Unit #1 cooling water system. Use of these chemical products is not expected to violate effluent limitations specified in the subject NPDES permit.

The NALCO 1336 (TTL) will be used and tested as a means to control copper corrosion in the condenser cooling water system. We intend to use 20 ppm active TTL into the condenser cooling water system for an initial three week period. The concentration of this product can be controlled to a discharge concentration acceptable to the Department. After the initial period, a concentration up to 5 ppm active TTL will be maintained in the cooling water system.

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PDR ADDOCK 05000352
P PDR

Cool
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The NALCO 1370 (polyacrylate) will be used and tested as a means to control scale in the cooling water system. We intend to maintain a concentration up to 3 ppm active polyacrylate in the cooling water system.

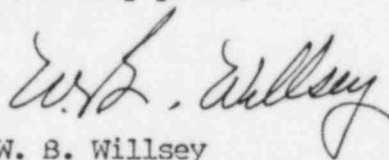
The NALCO 2513 (sodium silicate) will be used and tested as a means to control steel corrosion in the service water system. We intend to use a concentration up to 60 ppm SiO₂ above background in the cooling water system during an initial four week period. After the initial period, a concentration up to 30 ppm SiO₂ above background will be maintained in the cooling water system.

The concentration of these chemical products in the cooling tower blowdown discharge is expected to be the same as stated above. As submitted in our NPDES permit application, the Unit #1 cooling tower blowdown rate is expected to be 7.02 million gallons per day.

Attached is more information on the three NALCO products. The methodology used to obtain the aquatic toxicity of the NALCO 1336 and 1370 was based on the procedures for static bioassay, as described in Methods of Acute Toxicity Tests with Fish, Macroinvertebrates and Amphibians, and Standard Methods For Examination of Water and Waste Water. Aquatic toxicity for sodium silicate is indicated on pages 65 and 66 of Health, Safety, and Environmental Aspects of Soluble Silicates attached. The NALCO 2513 product is essentially the same material as discussed in the attached reference. Confidential information, such as the chemical formula for these chemical products will be or has been sent to you directly from the NALCO Chemical Company.

If you have any questions or concerns, please call David W. Mobraaten at (215) 841-5679.

Sincerely yours, ✓



W. B. Willsey
Director
Environmental Affairs

DWM:mas
Attachment

cc: J. A. Feola, DER w/ att.
J. P. Ridolfi, DER w/ att.

✓
NRC, Director, ONRR
Washington, DC w/ att.

NRC, Administrator, OIE
King of Prussia w/ att.

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Utility
ChemicalsProduct
Bulletin

REF-2210

2850500590

U-1336



SURE-COOL™ 1336

COPPER CORROSION INHIBITOR

Product Benefits

- Helps maximize turbine condenser efficiency
- Helps extend condenser tube life
- Can reduce maintenance costs

Principal Uses

SURE-COOL 1336 is an organic film-forming corrosion inhibitor formulated to protect copper and

copper alloy metals in utility cooling water systems.

General Description

SURE-COOL 1336 is an organic liquid copper corrosion inhibitor. It is designed to supplement other chemical treatments used in utility open recirculating systems that contain copper or copper alloys.

Form	Liquid
Color	Red
Odor	Organic
Density	9.9 lb/gal
pH (1% Solution)	10.5 - 11.0
Freeze Point	-10°F
Freeze-Thaw Recovery	Complete
Flash Point (PMCC)	None
Viscosity (@ 60°F)	55 cp

Application

SURE-COOL 1336 should be fed directly from the drum or bulk storage tank to a location in the system where it will be uniformly mixed and thoroughly distributed. It should be fed continuously to maintain optimum product activity.

The specific dosage of SURE-COOL 1336 will vary depending upon the operating characteristics of your system, the water chemistry, and the

severity of problems encountered. Your Nalco representative can recommend the optimum dosage necessary to ensure maximum program performance for your system.

SURE-COOL 1336 is noncorrosive to materials normally used in feeding systems. For specific feeding and material compatibility instructions, consult your Nalco representative.

Shipping

SURE-COOL 1336 is available in bulk quantities or in 55-gallon, non-returnable steel drums weighing approximately 555 pounds net.

The product is shipped from the nearest manufacturing or warehousing facility.

(Continued on Reverse Side)

NALCO CHEMICAL COMPANY UTILITY CHEMICALS

2901 BUTTERFIELD ROAD □ OAK BROOK, ILLINOIS 60521

SUBSIDIARIES IN ARGENTINA, AUSTRIA, BRAZIL, CHILE, COLOMBIA, ECUADOR, FINLAND, FRANCE, HOLLAND, HONG KONG, ITALY, PHILIPPINES, SAUDI ARABIA, SPAIN, SWEDEN, VENEZUELA AND WEST GERMANY • AFFILIATES IN AUSTRALIA, CANADA, JAPAN, MEXICO, SINGAPORE, SOUTH AFRICA, TAIWAN, UNITED KINGDOM, AND THE UNITED STATES



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2850559570

REF ID: A600590 2850500590



Handling and Storage

SURE-COOL 1336 is an alkaline corrosive material and should be handled with extreme caution. Do not get in eyes, on skin, or on clothing. Goggles or face shield are recommended for handling. In case of contact, immediately flush with large amounts of water for at least

15 minutes; for eyes, also get medical attention. Do not take internally. Keep out of reach of children.

Recommended in-plant storage limit is one year.

SECTION 1 - PRODUCT IDENTIFICATION

2850559570

2850500590

Trade Name Nalco Sure-Cool 1336

Formula No. _____

Synonyms An aqueous blend of a triazole saltChemical Family Organic

SECTION 2 - HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT		%
Product is alkaline		

MATERIAL SAFETY DATA SH

Product Nalco Sure-Cool 1336

SECTION 3 - PHYSICAL PROPERTIES

Boiling Point, 760 MM HG	2250F	Melting Point	-
Specific Gravity (H ₂ O=1)	1.19 @ 600F	Vapor Pressure	
Vapor Density (Air=1)		Solubility in H ₂ O, % By Wt.	Completely
% Volatiles By Vol.		Dynamic VISCOSITY	56 cps @ 600F
Appearance and Odor	Reddish brown liquid pH (1% sol'n) = 12.5		

SECTION 4 - FLAMMABILITY AND EXPLOSIVE PROPERTIES

Flash Point (Test Method)	> 2250F		
Flammable Limits in Air, % By Vol.	Lower		Upper
Extinguishing Media	Water fog, dry chemical, alcohol foam		
Special Fire Fighting Procedures	Wear air supplied breathing apparatus in enclosed areas.		
Unusual Fire and Explosion Hazard	None		

SECTION 5 - HEALTH HAZARD DATA

Threshold Limit Value	None established for the product.		
Effects of Overexposure	May cause eye and skin irritation.		
EMERGENCY AND FIRST AID PROCEDURES			
Eyes	Immediately flood with water for at least 15 minutes. Call a physician at once.		
Skin	Immediately flush with water for at least 15 minutes. Call a physician at once.		
Ingestion	Do not induce vomiting. Give large amounts of water. Call a physician.		
Inhalation			

NALCO CHEMICAL COMPANY
2901 BUTTERFIELD ROAD • OAK BROOK, ILLINOIS 60052-1

SECTION 6 - REACTIVITY DATA

Stability: Stable ☒ Unstable ☐ Conditions to Avoid

Materials to Avoid Strong acids, organic

Hazardous Decomposition Products

Hazardous Polymerization: Will Not Occur ☒ May Occur ☐ Conditions to Avoid

SECTION 7 - SPILL OR LEAK PROCEDURES

Steps to Take in Case Material is Released or Spilled Dilute with water. Neutralize with a weak acid and contain with absorbent material.

Waste Disposal Method Consult local, state and federal regulations for appropriate disposal.

SECTION 8 - SPECIAL PROTECTION INFORMATION

Type of Respiratory Protection Required None

Ventilation: Local Exhaust ☐ Mechanical (General) ☐ Special (Specify) Other (Specify)

Protective Gloves Rubber, gauntlets Eye Protection Goggles, face shield

Other Protective Equipment Eye wash fountain, apron

SECTION 9 - SPECIAL PRECAUTIONS

Handling and Storage Precaution Do not take internally. Do not contact eyes, skin or clothing. Remove and launder contaminated clothing before reuse.

Other Precautions None

Prepared By

Title

Corporate Toxicologist

Date

3/3/52



2850559570

2850500590

AQUATIC TOXICITY SUMMARYSURE COOL 1336

The acute 96 hour static LC_{50} of Sure Cool 1336 for the Rainbow Trout and Bluegill Sunfish was found to be 23.7 and 191.2 mg/L (ppm) respectively.

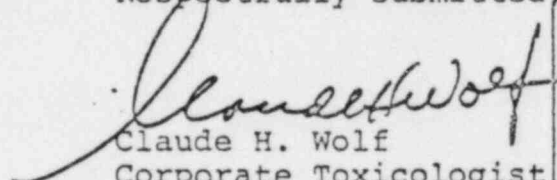
Corresponding 24 and 48 hour LC_{50} 's for Trout were 42.1 and 26.6 mg/L, respectively.

For Bluegill Sunfish the 24 and 48 hour LC_{50} values were both greater than 320 mg/L.

The 96 hour observable no effect concentrations for Rainbow Trout and Bluegill Sunfish were 10 and 56 mg/L, respectively.

ESTIMATED TOXICITY RATING = Moderately Toxic

Respectfully submitted,


Claude H. Wolf
Corporate Toxicologist
UCC/SHW11/TT50S/3/29/79



SURE-COOL™ 1370

MANGANESE STABILIZER/ DISPERSANT

U-1370

Product Benefits

- Helps maximize turbine condenser efficiency
- Can extend condenser tube life
- Helps reduce maintenance costs
- Minimizes handling costs and problems

Principal Uses

- Stabilizes soluble manganese and iron
- Helps inhibit calcium carbonate, calcium phosphate, and calcium sulfate scale
- Disperses mud, silt, particulate iron, and other suspended solids

General Description

SURE-COOL 1370 is a liquid polymeric dispersant and scale inhibitor for once-through and recirculating cooling water systems. This product is particularly effective at stabilizing soluble manganese and iron, thus eliminating deposits on heat exchange surfaces.

SURE-COOL 1370 is an effective dispersant for mud, silt, particulate iron, and other suspended solids. Its ability to inhibit calcium phosphate and calcium carbonate crystal growth helps provide protection from scale formation during mild pH upsets due to loss of acid feed.

SURE-COOL 1370 is designed to help prevent calcium phosphate, calcium carbonate, or calcium sulfate deposition in systems that are supersaturated with respect to calcium carbonate, calcium phosphate, or calcium sulfate.

SURE-COOL 1370 is compatible with other Nalco cooling water treatments, including chlorine, at the recommended dosages in the cooling water.

SURE-COOL 1370 is specially formulated to allow year-round storage in uninsulated tanks.

Form	Liquid
Color	Light brown
Odor	Slight organic
Density	10.2 lb/gal
pH (Neat)	13
Freeze Point	-12° F
Freeze-Thaw Recovery	Complete
Flash Point (PMCC)	None
Viscosity (@ 60° F)	13 cp
(@ 0° F)	95 cp
(@ -5° F)	108 cp
(@ -10° F)	117 cp

Shipping

SURE-COOL 1370 is available in bulk quantities or in 55-gallon, non-returnable steel drums weighing approximately 560 pounds net.

The product is shipped from the nearest manufacturing or warehousing facility.

(Continued on Reverse Side)

NALCO CHEMICAL COMPANY UTILITY CHEMICALS

2901 BUTTERFIELD ROAD □ OAK BROOK, ILLINOIS 60521

SUBSIDIARIES IN ARGENTINA, AUSTRIA, BRAZIL, CHILE, COLOMBIA, ECUADOR, FINLAND, FRANCE, HONG KONG, ITALY, JAPAN, KOREA, MALAYSIA, MEXICO, NETHERLANDS, PHILIPPINES, SAUDI ARABIA, SPAIN, SWEDEN, SWITZERLAND, TAIWAN, THAILAND, UNITED KINGDOM, U.S.A., U.S.S.R., VENEZUELA AND WEST GERMANY • AFFILIATES IN AUSTRALIA, CANADA, JAPAN, MEXICO, SINGAPORE, SOUTH AFRICA, TAIWAN, UNITED KINGDOM, AND THE UNITED STATES



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REFSEQNO 2850559570

2850559570



Application

SURE-COOL 1370 should be fed directly from the drum or bulk storage tank to a location in the system where it will be uniformly mixed and thoroughly distributed. It should be fed continuously to maintain optimum product activity. The specific dosage of SURE-COOL 1370 will vary depending upon the operating characteristics of your system, the water chemistry, and the severity of problems encountered.

Your Nalco representative will recommend the optimum dosage necessary to ensure maximum program performance for your system.

For specific feeding and material compatibility instructions, consult your Nalco representative.

Handling and Storage

SURE-COOL 1370 is an alkaline corrosive solution and should be handled with caution. Do not get in eyes, on skin, or on clothing. Goggles or face shield are recommended for handling. In case of contact, immediately flush with large amounts

of water for at least 15 minutes; for eyes, also get medical attention. Do not take internally. Keep out of reach of children.

Recommended in-plant storage limit is one year.

SECTION 1 - PRODUCT IDENTIFICATION

Trade Name Nalco Sure-Cool 13702850559570

Formula No. _____

Synonyms Polyacrylate solutionOrganic/
Inorganic

Chemical Family _____

SECTION 2 - HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%
Sodium hydroxide	11

SECTION 3 - PHYSICAL PROPERTIES

Boiling Point, 760 MM HG >100°C	Freeze Point -12°F
Specific Gravity (H ₂ O=1) 1.22 @ 60°F	Vapor Pressure
Vapor Density (Air=1)	Solubility in H ₂ O, % By WL Completely
% Volatiles By Vol.	Viscosity 13 cps @ 60°F, 95 cps @ 0°F
Appearance and Odor Light brown liquid, slight organic odor	pH (neat) = 13

SECTION 4 - FLAMMABILITY AND EXPLOSIVE PROPERTIES

Flash Point (Test Method) None (PMCC)			
Flammable Limits in Air, % By Vol.	Lower	Upper	
Extinguishing Media Not applicable			
Special Fire Fighting Procedures None			
Unusual Fire and Explosion Hazard None			

SECTION 5 - HEALTH HAZARD DATA

Threshold Limit Value None established for the product. Sodium hydroxide = 2 mg/m ³
Effects of Overexposure Corrosive. Causes burns to the eyes and skin.
EMERGENCY AND FIRST AID PROCEDURES
Eyes Immediately flood with water for 15 minutes. Call a physician.
Skin Flood with water for 15 minutes. Call a physician.
Ingestion Do not induce vomiting. Give large amounts of water. Call a physician.
Inhalation Remove to fresh air.



2850559570

SECTION 6 - REACTIVITY DATA

Stability: Stable ☒ Unstable ☐ Conditions to Avoid

REFCEQNO 850500590

Materials to Avoid Mild steel, aluminum, hypalon

Hazardous Decomposition Products None

Hazardous Polymerization: Will Not Occur ☒ May Occur ☐ Conditions to Avoid

SECTION 7 - SPILL OR LEAK PROCEDURES

Steps to Take in Case Material is Released or Spilled Rinse with water or neutralize with a mild acid.

Waste Disposal Method No special method. This product is regulated under RCRA (D002).

SECTION 8 - SPECIAL PROTECTION INFORMATION

Type of Respiratory Protection Required None normally required

Ventilation: Local Exhaust ☐ Mechanical (General) ☐ Special (Specify) _____ Other (Specify) _____

Protective Gloves Rubber Eye Protection Goggles

Other Protective Equipment None

SECTION 9 - SPECIAL PRECAUTIONS

Handling and Storage Precaution Treat as any alkaline material.

Other Precautions Do not take internally. Do not get in eyes, on skin or clothing.

Prepared By

Title

Corporate
Toxicologist

Date

3/3/82



2850559370
REFSEQNO 2850500590

AQUATIC TOXICITY SUMMARY
SURE-COOL 1370

The acute 96 hour static LC_{50} of Sure-Cool 1370 for the Rainbow Trout and Bluegill Sunfish was found to be greater than 1000 mg/L (ppm) for both species.

Corresponding 24 and 48 hour LC_{50} 's for were also greater than 1000 mg/L.

Estimated Toxicity Rating = Essentially Non-Toxic

Respectfully submitted,

A handwritten signature in cursive script, appearing to read 'Claude H. Wolf'.

Claude H. Wolf

Corporate Toxicologist

July 7, 1982

ABC/EH&S237/B-2077

Corrosion Inhibitor

Nalco 2513 corrosion inhibitor is formulated in a convenient, easy to use liquid form for use in domestic and once-through cooling water systems.

Principal Uses

Nalco 2513 is a corrosion inhibitor formulated in convenient to handle liquid form. It is primarily used for domestic and once-through cooling water systems. Nalco 2513 is also used to provide corrosion protection in cooling systems.

General Description

Nalco 2513 is a liquid product with the following properties:

Color	Water white
Specific Gravity (@ 80°F)	1.39
Density	11.6 lb/gal
pH (Neat)	12
Viscosity (@ 68°F)	160 cp
Flash Point	None

Feeding

Nalco 2513 may be fed neat, directly from the drum, or in water dilutions of up to 5%. Dilutions are stable for up to one month. Longer storage of the diluted product is not recommended due to possible microbiological growth. Mild steel feeding and storage equipment is satisfactory.

Dosage

Normal dosages of Nalco 2513 will vary from 2 to 60 ppm depending upon the characteristics and operating conditions of the individual system. Your Nalco Representative will recommend optimum dosages for your system. For potable water the recommended dosage is 30 ppm.

Handling and Storage

Do not get in eyes, on skin or on clothing. Wear goggles or face shield when handling. In case of contact, wash skin with plenty of water. Do not take internally. For eye contact, flush with large amounts of water and get medical attention. Do not use eye wash solution.

Recommended in-plant storage is one year.

Shipping

Nalco 2513 is shipped in 15- and 55-gallon nonreturnable drums weighing approximately 174 and 638 pounds respectively.

Nalco Chemical Company
2901 Butterfield Road
Oak Brook, Illinois 60521

Trade Name Nalco 25 Formula No. 2850559570
 Synonyms An alkaline silicate solution
 Chemical Family Inorganic

SECTION 2 - HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%
Entire product is alkaline	

SECTION 3 - PHYSICAL PROPERTIES

Bolling Point, 760 MM HG	Melting Point
Specific Gravity (H ₂ O=1) 1.39 @ 68°F	Vapor Pressure
Vapor Density (Air=1)	Solubility in H ₂ O, % By Wt. Soluble
% Volatiles By Vol.	Viscosity 160 cps @ 68°F
Appearance and Odor Water white liquid, odorless	pH (neat) = 12.0

SECTION 4 - FLAMMABILITY AND EXPLOSIVE PROPERTIES

Flash Point (Test Method) Not applicable			
Flammable Limits in Air, % By Vol.	Lower	Upper	
Extinguishing Media Not applicable			
Special Fire Fighting Procedures None			
Unusual Fire and Explosion Hazard None			

SECTION 5 - HEALTH HAZARD DATA

Threshold Limit Value None established for the product.
Effects of Overexposure May cause severe irritation due to its alkalinity.
EMERGENCY AND FIRST AID PROCEDURES
Eyes Immediately flush with water for at least 15 minutes. Call a physician.
Skin Immediately flush with water for at least 15 minutes.
Ingestion Do not induce vomiting. Give large amounts of water. Call a physician.
Inhalation

SECTION 6 - REACTIVITY DATA

2850559570

Stability: Stable ☒ Unstable ☐ Conditions to Avoid Precipitation of inorganic salts when mixed with low pH solution

Materials to Avoid Acids, oxidizers

Hazardous Decomposition Products None

Hazardous Polymerization: Will Not Occur ☒ May Occur ☐ Conditions to Avoid

SECTION 7 - SPILL OR LEAK PROCEDURES

Steps to Take in Case Material is Released or Spilled Contain with absorbent material. Neutralize spill with weak acid.

Waste Disposal Method No special method. This product is not regulated under RCRA.

SECTION 8 - SPECIAL PROTECTION INFORMATION

Type of Respiratory Protection Required None normally required

Ventilation: Local Exhaust ☐; Mechanical (General) ☐; Special (Specify) Other (Specify)

Protective Gloves Alkali resistant Eye Protection Goggles, face shield

Other Protective Equipment Eye wash fountain

SECTION 9 - SPECIAL PRECAUTIONS

Handling and Storage Precaution None

Other Precautions Do not take internally. Do not contact eyes or skin. Remove and launder contaminated clothing before reuse.

Prepared By [Signature] Title Toxicologist Date 12/13/82



The PQ Corporation

February 5, 1985

Mr. Steven Goring
PUCKORIUS ASSOCIATES
P. O. Box 2440
Evergreen, CO 80439

RECEIVED 2-11-85
PRP _____
CEH 2/11/85
FILE _____

2850559570
Research & Development Center
280 Cedar Grove Road
P.O. Box 258
Lafayette Hill, PA 19444
(215) 825-5000

Dear Mr. Goring:

In response to your inquiry to Mr. John Peters of PQ regarding the safety of the use of sodium silicate as a water treatment chemical, I can provide the following information:

Sodium silicate is considered as GRAS (Generally Recognized as Safe) by the U.S. FDA when it is used as a corrosion preventative in potable water. The safety of sodium silicate in this and other food-related applications was recently reviewed for the FDA by the Select Committee on GRAS Substances of the Federation of American Societies for Experimental Biology (FASEB). Their report, Evaluation of the Health Aspects of Certain Silicates as Food Ingredients - SCOGS-61 is available from NTIS as Pb 301-402/AS. On page 30 of this report, the Select Committee concludes:

"There is no evidence in the available information on ... sodium silicate, ... that demonstrates or suggests reasonable grounds to suspect a hazard to the public when [it is] used at levels that are now current or that might reasonably be expected in the future."

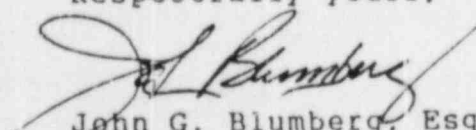
The PQ Corporation's product N[®] sodium silicate solution, has been authorized for USDA as a potable water treatment compound for use in federally inspected meat and poultry plants.

The EPA is currently reviewing the safety of water treatment additives, but their initial report is not expected until next year. A water chemicals codex has been recently published. Many of our products conform to the requirements listed for sodium silicate on page 63.

I have enclosed a copy of a review of the health effects and environmental safety of soluble silicates.

I hope this information proves helpful to you. If you have any further questions regarding PQ Corporation's products, please let us know.

Respectfully yours,


John G. Blumberg, Esq.
Product Safety Coordinator
(0275J)

Health, Safety, and Environmental Aspects of Soluble Silicates

W. L. SCHLEYER and J. G. BLUMBERG

The PQ Corporation, Research and Development Center, Lafayette Hill, PA 19444

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

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 120 years(6).

HEALTH AND SAFETY ASPECTS

Ingestion

Oral LD₅₀, 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 LD₅₀ 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 LD₅₀ 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 SiO₂/Na₂O 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 LD₅₀, the FDA conducted a series of

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

SiO ₂ /Na ₂ O 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	99	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.

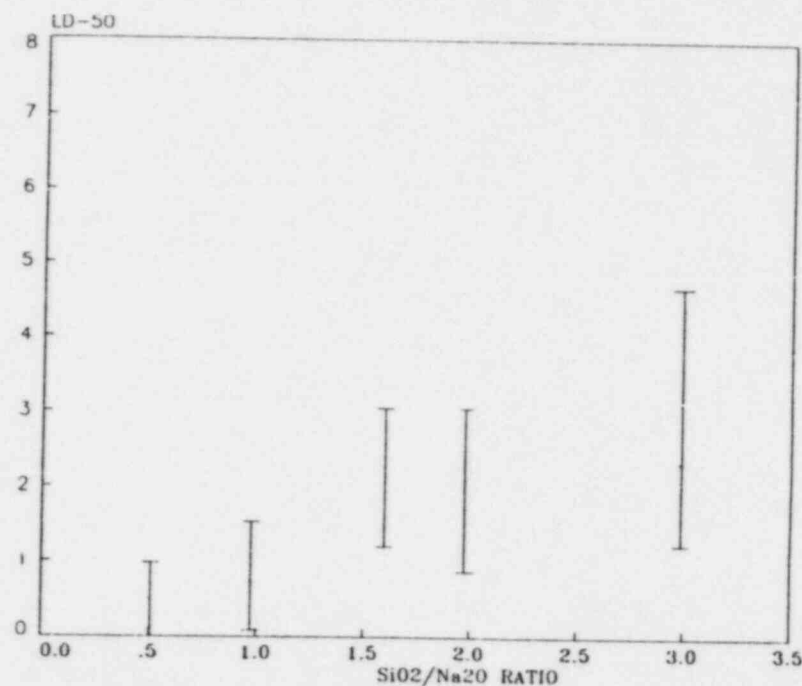


Figure 1. Ratio vs. LD₅₀ sodium silicate.

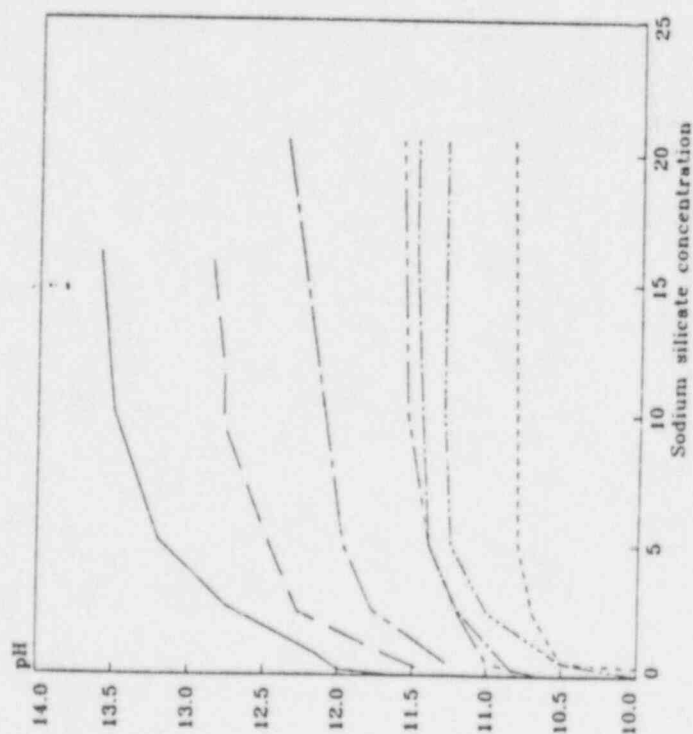


Figure 2. Concentration vs. pH. Key: ---, 3.7; - - - - -, 3.2; ---, 2.9; ---, 2.5; ---, 2.0; ---, 1.6; and —, 1.0 ratio.

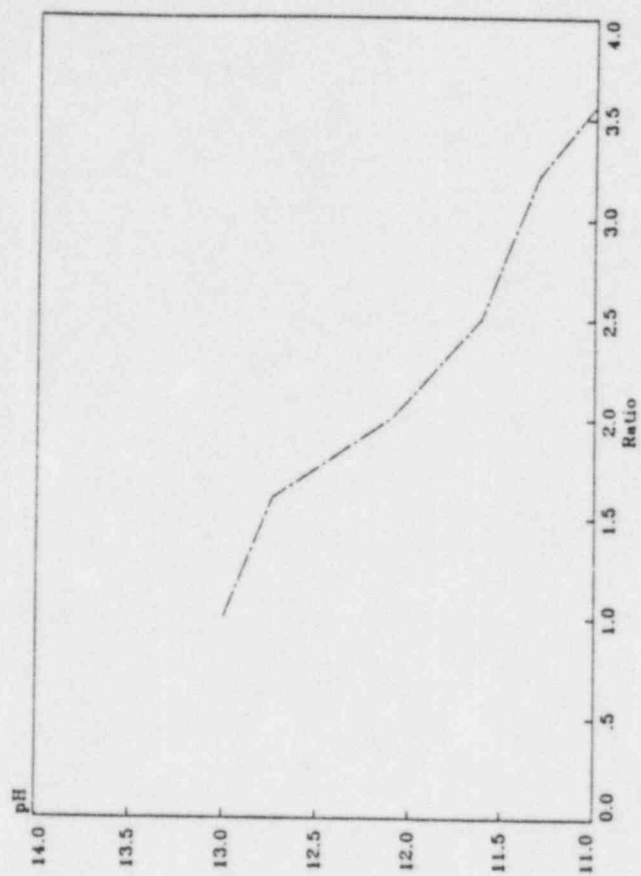


Figure 3. Ratio vs. pH.

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 $3.2 \text{ SiO}_2/\text{Na}_2\text{O}$) 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 $\text{SiO}_2/\text{kg}/\text{day}$. 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

$\text{SiO}_2/\text{Na}_2\text{O}$ 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 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 SiO_2)		
	0	600	1200
Matings	77	77	77
Litters	54	51	49
No. Born	517	346	414
No. Weaned	182	83	44
% Weaned	35	24	11
Difference as % of Controls			
Born		67	80
Weaned		46	24

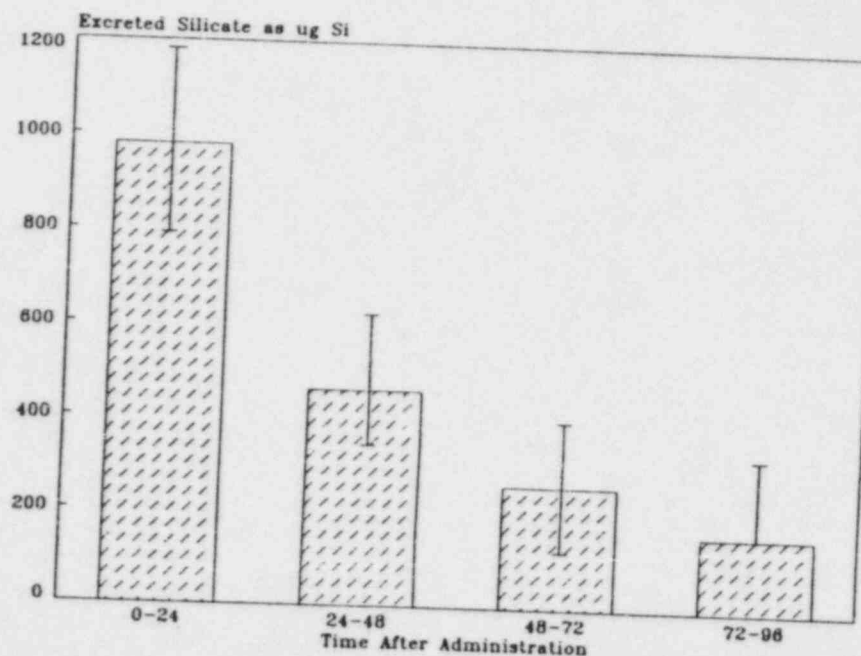


Figure 4. Urinary excretion of sodium silicate.

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

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

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

Skin Contact

Tests for the effects of skin contact of sodium silicates have been undertaken by both industry and governmental agencies. Since many soluble silicates are not stoichiometric compounds, but rather can be prepared with variable $\text{SiO}_2/\text{Na}_2\text{O}$ ratios, tests have been conducted at various points on the continuum of possible ratios, usually at points within the specifications 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 Transportation 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

SiO ₂ /Na ₂ O wt. ratio	CONC. wt. %	pH	CORROSIVITY + = corrosive	Ref.
3.2	99	4	-	28.
3.2	80	0	-	28.
3.2	36	3	-	28.
2.9	43	3	-	28.
2.5	37	3	-	28.
2.4	24	4	-	28.
2.0	99	8	+	28.
2.0	54	4	-	28.
2.0	8	>4*	-	29.
1.0	10	5.6*	+	29.
1.0	6	>8*	+	29.

* 2x average of intact and abraded score.

Table V. FHSA Skin Contact Data
Potassium Silicate

SiO ₂ /K ₂ O mol. ratio	CONC. wt. %	pH	CORROSIVITY + = corrosive	Ref.
3.45	29	0	-	28.
3.33	39	2	-	28.
2.5	85	8	-	30.

Table VI. DOT Skin Contact Data
Sodium Silicate

SiO ₂ /Na ₂ O wt. ratio	CONC. wt. %	pH	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

SiO ₂ /Na ₂ O 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/m³ 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/m² of type A zeolite for 24 months, and 50 mg/m³ type A zeolite for 12 months. No evidence of fibrosis was observed in the animals in either study.

ENVIRONMENTAL ASPECTSOccurrence

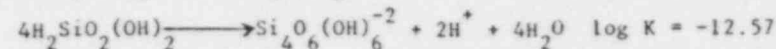
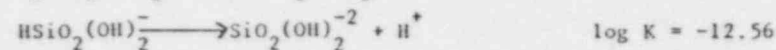
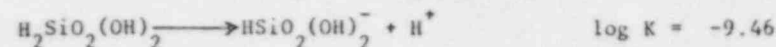
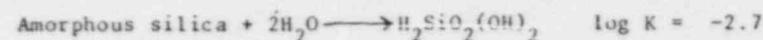
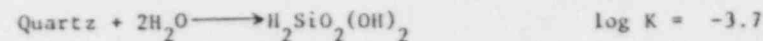
Compounds of silicon and oxygen are the primary constituents of earth's land masses. Dissolved silica is a minor but ubiquitous constituent of earth's hydrosphere. Ground waters contain the highest concentrations of dissolved silica: the median value in the U.S. is 17 ppm(42). Of earth's surface waters, 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 H₂SiO₂(OH)₂, rather than Si(OH)₄ or H₄SiO₄ in order to emphasize its diabasic character, and the tendency of silicon, like other metalloids, to coordinate with hydroxo and oxo ligands.



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

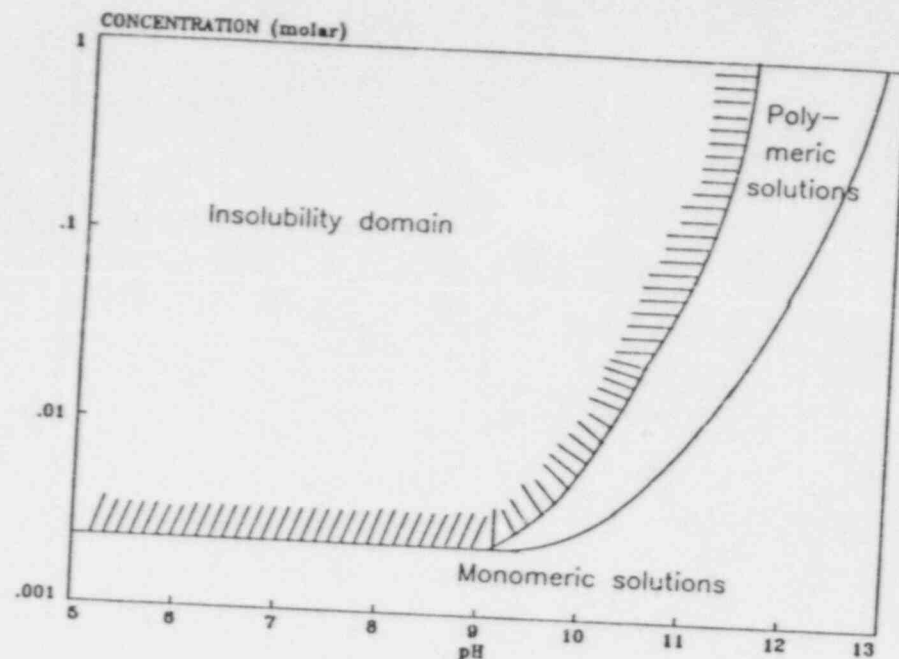


Figure 5. Soluble silicate speciation.

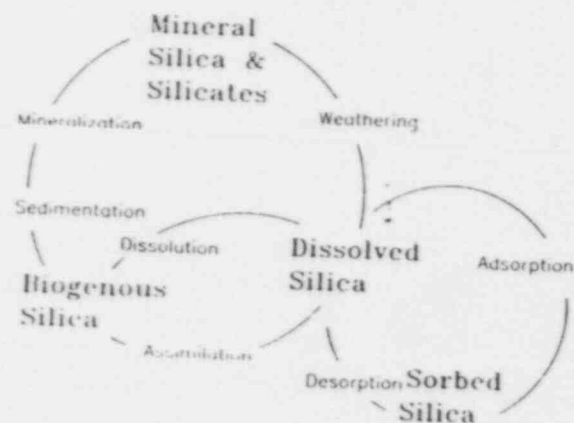


Figure 6. The natural silica cycle.

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 is 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 affinis	24hr.	3200ppm	69.
" "	48hr.	2400ppm	69.
" "	96hr.	2320ppm	69.
Water flea			
Daphnia magna	96hr.	247ppm	70.
Snail eggs			
Lymnea	96hr.	632ppm	70.
Amphipoda	96hr.	160ppm	70.

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

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