

INDUSTRIAL
CHEMICALS
DIVISION



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PQ Australia Pty. Ltd.
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PQ Silicates Ltd.
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Bulletin 37-3

PQ[®] Soluble Silicates: For Protection of Water Systems From Corrosion

INTRODUCTION

Soluble silicates are economical, effective, and environmentally responsible chemicals which have been used for more than 70 years to protect metals from the corrosive effects of water.¹ They are classified as corrosion inhibitors because they can deposit protective films onto various metal surfaces, isolating the metal from any further corrosive attack, and because they raise water pH which can make it less corrosive to metals. Silicates do not contribute zinc or phosphorous to treated water.

Laboratory and field experience has shown that silicate corrosion inhibitors are effective in many different types of water. Protection is provided in both acidic and alkaline water. In harder water slightly more silicate is needed to achieve the same degree of corrosion inhibition, since some of the injected silica may react with hardness ions before it has a chance to bond onto metal surfaces

PQ[®] silicates have been successfully used for corrosion control in water supplies of municipalities, industrial plants, oil refineries, textile mills, private residences, apartment buildings, and office buildings. Their corrosion inhibition properties also make them key ingredients in such products as automobile antifreeze and laundry detergents.

WHAT ARE SOLUBLE SILICATES?

PQ Corporation manufactures sodium and potassium silicates. These soluble silicates are produced by fusing high purity silica sand and sodium carbonate (or potassium carbonate) at temperatures of 1000 - 1500°C. The resulting product is an amorphous glass that can be dissolved in water to produce silicate solutions, sometimes referred to as "waterglass." The silica in a silicate solution is present as both monomeric and polymeric anionic species (Figure 1), that exist in equilibrium with each other.²

Ratio and silicate concentration are two important factors that influence what species are present in solution. At concentrations typical for corrosion control, the silica monomer predominates.³

The proportion of silica to alkali in a sodium silicate is expressed as the weight ratio $\text{SiO}_2/\text{Na}_2\text{O}$. It is one of the main characteristics that influences product properties and distinguishes one product from another.

PQ manufactures liquid sodium silicates which range in ratio from 1.60 to 3.22. Typically, 2.00 or 3.22 ratio sodium silicate solutions, containing 25 to 30% SiO_2 , are used for municipal water treatment.

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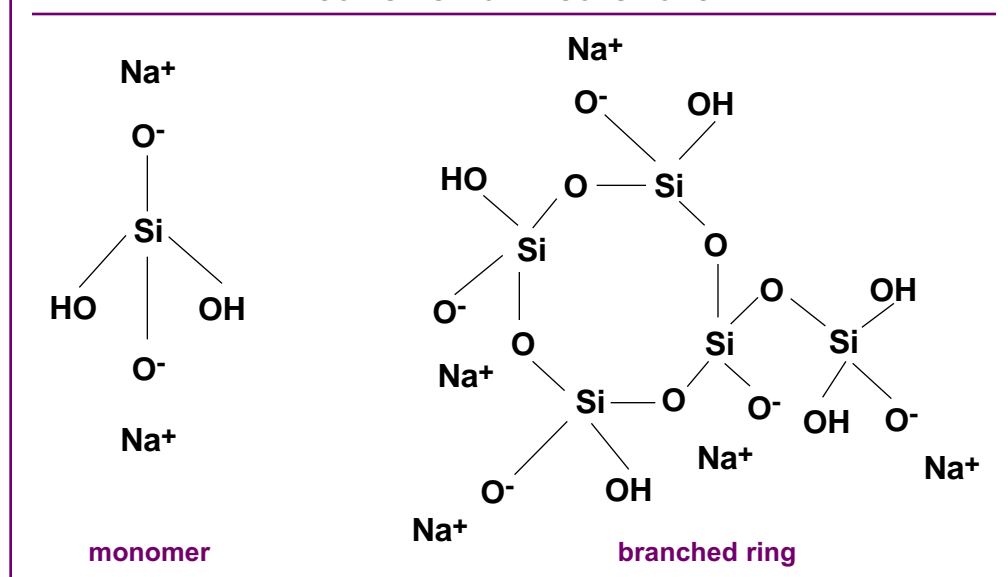
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FIGURE 1. TWO SILICA STRUCTURES FOUND IN SODIUM SILICATE SOLUTIONS



Terminology: Silica vs. Silicate

The term “silica” refers to the compound silicon dioxide (SiO_2 .) Water is typically analyzed for silica as part of normal water quality analysis procedures. Silica levels are usually reported as mg SiO_2/L .

“Silicate” is a generic term for compounds that contain silicon, oxygen, and one or more metals. They can be naturally occurring or synthetic. As an example, PQ’s synthetic sodium silicate compounds can be represented by the generalized formula $\text{Na}_2\text{O} \cdot x\text{SiO}_2$, where “x” varies from 1.60 to 3.22 for commercial products.

Naturally occurring silicate minerals make up nearly 90% of the earth’s crust.⁴ Dissolved silica is a minor but ubiquitous constituent of the hydrosphere.⁵

Commercial soluble silicates have a higher degree of polymerized silica species than natural dissolved silica because of higher concentrations; however, when diluted they depolymerize to molecular species that are indistinguishable from natural dissolved silica.⁶

PHYSIOLOGICAL AND ENVIRONMENTAL EFFECTS OF SODIUM SILICATE

Sodium silicate adds silicate anions, together with sodium and hydroxyl ions, to water.

Silica is found to some extent in all natural waters and is believed to be ecologically harmless. The charged, polymeric nature of the silica found in synthetic silicate solutions is responsible for its reaction with metals and corrosion inhibition properties.

The sodium content of water will increase slightly with sodium silicate addition. This issue has been raised as a concern in some instances. At the highest dosages recommended for potable water treatment (24 mg SiO_2/L), PQ’s N[®] sodium silicate will contribute less than 5.6 mg Na/L to the water.

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Furthermore, when using N silicate at normal maintenance dosages of 4-12 mg SiO₂/L, the sodium contribution is 0.9-2.8 mg Na/L, respectively. When other sodium silicates are used, the sodium contribution will be different depending on the weight ratio of SiO₂/Na₂O. If no sodium addition is tolerable, potassium silicates offer an alternative.

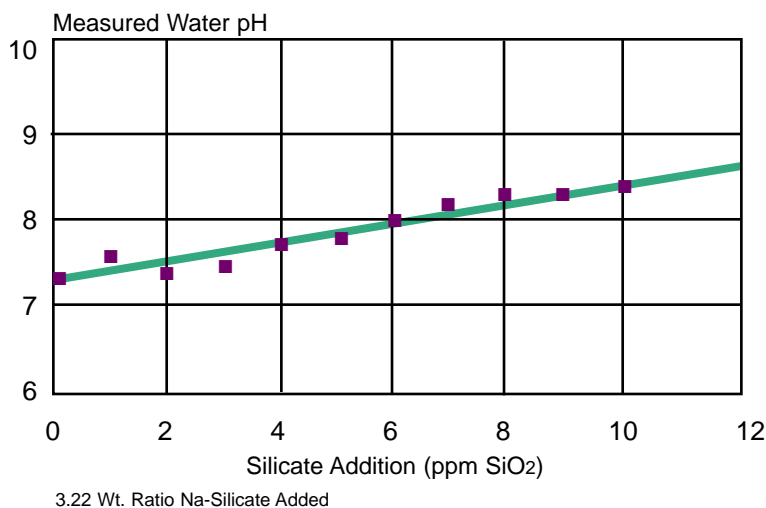
Neither sodium nor potassium silicate corrosion inhibitors contribute phosphorus or metals such as zinc to the ecosystem. These are concerns with other corrosion inhibitors, especially phosphorus-based types.

pH EFFECTS

Sodium silicates are alkaline chemicals. Treating water at typical levels of 4-24 mg SiO₂/L may raise the water pH anywhere from 0.1 to 2.0 pH units or more. The actual pH increase will depend on overall water quality and silicate dosage. See Figure 2 for example. Increases in pH will generally help minimize corrosion and will provide a synergistic effect along with deposition of monomolecular silica film.

FIGURE 2. pH RESPONSE WITH SILICATE ADDITION

LAKE TAHOE WATER pH RESPONSE TO SODIUM SILICATE ADDITION



APPROVALS FOR USE

The use of sodium silicates for the control of corrosion in municipal water systems is approved by the American Water Works Association and the American National Standards Institute (refer to ANSI/AWWA Standard B404). Sodium silicate also has Food and Drug Administration (FDA) unpublished "generally recognized as safe" (GRAS) status as a corrosion preventative in water (at levels below 100 mg/L).⁷

The U.S. Environmental Protection Agency (EPA) recognizes that silicate inhibitors may be effective in controlling corrosion of lead and copper in potable water systems.⁸

THE NATURE OF SILICATE CORROSION INHIBITION

Studies have shown that soluble silicates are reactive with cationic metals and metal surfaces.⁹ This phenomenon is the basis by which silicates inhibit corrosion and is illustrated at the top of the following page.¹⁰

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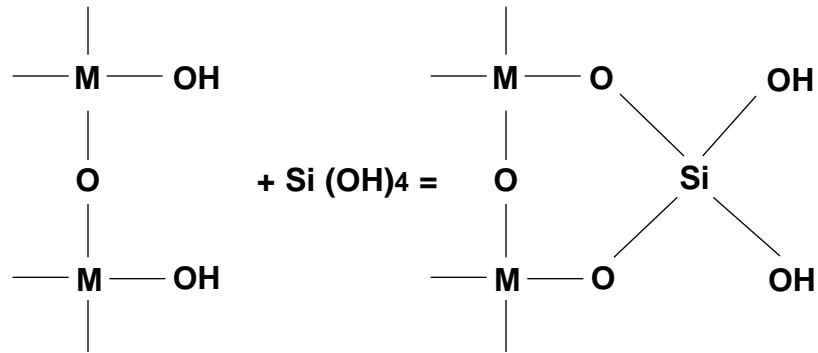
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FIGURE 3. DEPOSITION OF SILICA ON METAL SURFACE



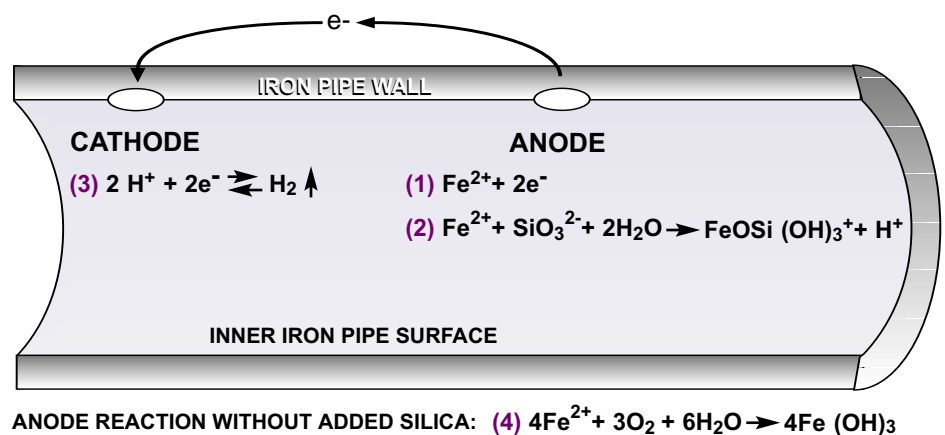
Monomeric and polymeric silica, introduced into a water distribution system as sodium silicate solution, is carried by flowing water to all parts of the distribution system. At the dilution levels used for water treatment, the majority of the silica depolymerizes to a reactive monomer form. The monomeric silica, which can be represented by $(\text{SiO}_3)^{2-}$, is adsorbed onto metal pipe surfaces at anodic areas, forming a thin monomolecular film on the interior of the pipe. This prevents any further corrosive reaction at the anode.

Corrosion will be inhibited when an anodic reaction of the type proposed between ferrous iron and silica (shown as equation (2) in Figure 4) occurs in place of the reaction which forms ferric hydroxide (shown as equation (4) in Figure 4). Protective films can be formed by such a reaction.

Microscopic and x-ray examination of the film formed at the metal surface show two layers, with most of the silica in the surface layer adjacent to the water. When the hydrous metal oxide film has been covered with a silica film, silica deposition stops.¹¹ The film does not build on itself, and therefore will not form excessive scale. The film is an electrical insulator and blocks the electrochemical reactions of corrosion, yet it is thin enough that it does not obstruct water flow.¹²

Corrosion protection with PQ sodium silicates can be achieved by modifying the SiO_2 content of the water. Therefore the key water property is SiO_2 con-

FIGURE 4. POSTULATED ELECTROCHEMICAL REACTIONS OF IRON IN WATER, WITH AND WITHOUT ADDED SILICA



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tent, not pH or calcium level, as in other types of corrosion control practices. Alkalinity, pH, and water hardness may influence the effectiveness of silicate treatment.

In many cases, natural SiO₂ found in water probably has already “reacted” (i.e., adsorbed) with other metals in the water and may not be effective in reacting with metal pipes. Therefore, a fresh source of “reactive” SiO₂ is needed (as from soluble silicate solutions).

LENGTH OF CARRY

When silicate treatment is first started, the system near the point of application is coated immediately; then the film continues to form at greater distances. Eventually, with continued feeding and sufficient water flow rate, the treatment becomes effective throughout the entire system.

Once the film has been created, the protection is maintained as long as silicate treatment is continued; if stopped, the protection is gradually lost. If damaged, the film is self healing, as long as the silicate feed is continued.

METALS PROTECTED

Silicate treatment is effective in controlling corrosion of many different metals and in systems made up of a variety of metals.

**METALS THAT HAVE BEEN SUCCESSFULLY PROTECTED
BY TREATMENT OF SOLUBLE SILICATES:**

- | | |
|-----------------------------------|--------------------|
| ■ Lead | ■ Galvanized Steel |
| ■ Copper | ■ Bronze |
| ■ Cast Iron and
Ferrous Metals | ■ Red Brass |
| ■ Steel | ■ Yellow Brass |
| | ■ Nickel Alloys |

PROTECTION OF CEMENTICIOUS MATERIALS

Addition of silicate to water systems can protect cementitious materials from long term deterioration. The silicate reacts with available calcium to form insoluble calcium-silicate compounds. Studies have shown that silicate treatment may reduce the breakdown of asbestos-cement surfaces, thus prolonging the life of the material and minimizing the release of fibril asbestos.¹³

COST OF TREATMENT

The cost for silicate treatment will vary, depending on the amount of silicate being fed into the water system, and the quantities purchased.

**A GENERAL EQUATION FOR DETERMINING THE COST OF
SILICATE TREATMENT IS:**

$$\frac{[8.34] [a] [b]}{[c]} = \frac{\$}{\text{MG water}}$$

- a = desired SiO₂ dose (in mg/L or ppm)
b = \$/pound silicate solution
c = wt. % SiO₂ in silicate (decimal format)

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TESTING THE EFFECTIVENESS OF SILICATE TREATMENT

The effectiveness of silicate corrosion inhibitors can be evaluated in a number of ways. Options include:

1. Monitoring levels of dissolved metals (e.g., Fe, Cu, Pb) in water samples before and after treatment.
2. Conducting pipe-loop studies based on U.S. Army Construction Engineering Research Laboratory (USA-CERL) and/or American Water Works Association Research Foundation (AWWARF) procedures.
3. Conducting coupon testing based on ATSM Test Method D-2688, "Corrosivity of Water in the Absence of Heat Transfer."

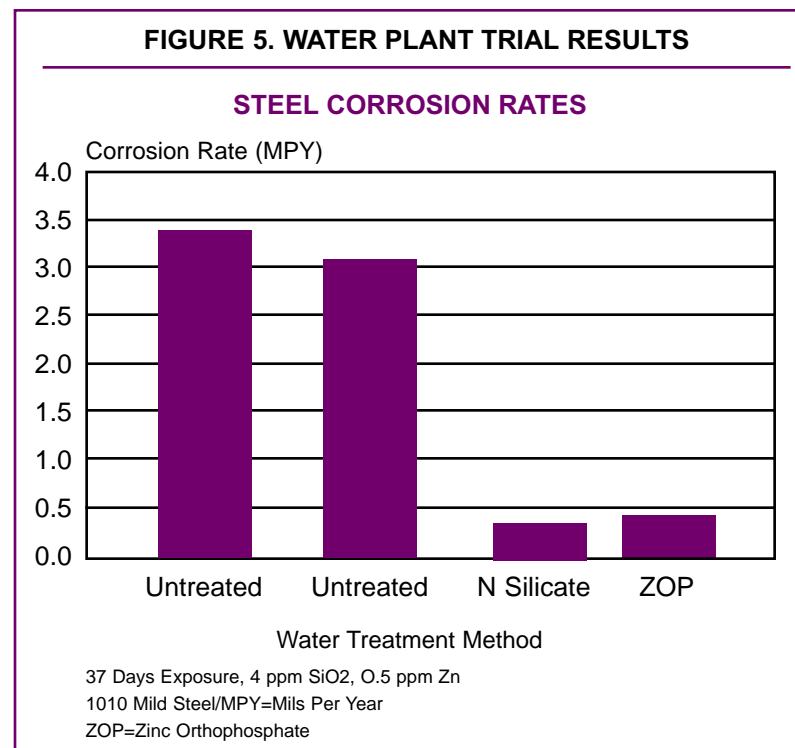
Results from a coupon test are presented in Figure 5. The water source was a surface water in southern California. The treatment levels of silicate and zinc orthophosphate used were cost equivalent.

These results are valid for the specific water tested and actual test conditions. The effectiveness of silicates on other waters may vary.

Current theory postulates that the presence of some corrosion product on the metal surface will enhance the effectiveness of the silicates since the reaction is believed to be between silica species and cationic metals (Figure 4). It is therefore recommended that coupon specimens and pipe loops be exposed to untreated water for a "conditioning" period prior to passivation. This practice will also be more representative of conditions that exist in actual water systems where corrosion has already occurred.

During lab or pilot testing, as in actual field use, a relatively high passivation dose of SiO₂ is required initially for at least 30 days in order to establish the protective film on metal surfaces.

PQ technical service personnel are available to assist in evaluations of silicate corrosion inhibitors.



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SUGGESTED PQ SILICATES FOR MUNICIPAL WATER TREATMENT

Either PQ's N[®] or D[®] sodium silicate solutions can be used for corrosion control. The choice will depend on water quality and operator preference. Since D silicate is slightly more alkaline than N, it may be preferred in lower pH waters (e.g., water with pH below 6.0).

TYPICAL PROPERTIES OF PQ SODIUM SILICATES

PQ Product Name	N [®]	D [®]
Wt. Ratio (SiO ₂ /Na ₂ O)	3.22	2.00
%Na ₂ O	8.9	14.7
%SiO ₂	28.7	29.4
Density @20°C (°Be')	41.0	50.5
(lb./gal.)	11.6	12.8
(g/cm ³)	1.38	1.53
pH	11.3	12.7
Viscosity @20°C (cps)	180	400

OTHER SILICATES

In addition to solutions, PQ offers silicates in powder and glass form. The products (e.g., SS[®] or METSO[®]) can be mixed with other inhibitors to produce blended products.

SILICATE DOSAGES

Although there is natural silica (SiO₂) in many waters, it may or may not have any inhibiting effect and is generally not considered in determining the dosage of the silicate treatment.

PASSIVATION DOSAGE

Normally, relatively high dosages of silicate are required during the first 30 to 60 days of treatment in order to form the initial protective coating. This initial silicate dosage is referred to as a passivation dosage and should be 24 mg/L above the background silica level.

The actual amount of time required to establish the initial coating will depend on the amount of silicate injected, water quality, water flow rates, and system length.

MAINTENANCE DOSAGE

After the first 30 to 60 days of treatment, or once film formation has been verified (i.e., by SiO₂ balance), the dosage can be reduced to a maintenance dose. It is advisable to reduce the silica dose incrementally, for example by lowering it to 12 mg SiO₂/L for a period of time (e.g., 30 days), then 8 mg SiO₂/L, and possibly even down to 4 mg/L. Silica balances should be done over the system as the dosage is decreased in order to verify that the protective film remains intact.

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CALCULATING SILICATE DOSAGES

It is important to remember that commercial sodium silicate solutions consist of various proportions of silica (expressed as weight percent SiO₂), alkali (expressed as Na₂O), and water. The required silicate injection is based on the %SiO₂ in the silicate, the water flow rate through the system, and the desired incremental SiO₂ level.

The following general equation can be used to determine silicate solution feed rates in gallons per day:

$$\frac{[8.34] [a] [b]}{[c] [d]} = \frac{\text{gallons silicate solution}}{\text{day}}$$

a = water flow rate (MGD)
b = desired SiO₂ dose (mg/L or ppm)
c = wt. %SiO₂ in silicate (decimal format)
d = density of silicate (lb./gal.)

Example:

a = 2MGD
b = 24 mg SiO₂/L
c = 0.287 (wt. %SiO₂)
d = 11.6 lb./gal.

$$\frac{[8.34] [2] [24]}{[0.287] [11.6]} = \frac{120.2 \text{ gal. silicate solution}}{\text{day}}$$

Alternatively, the following more specific relationships can be used:

Using N[®] Silicate

To obtain: 1 mg SiO₂/L
Inject: 2.50 gal. N[®] per MG Water

For example, to get an incremental dosage of 8 mg SiO₂/L into a water stream flowing at 10 million gallons per day, 200 gallons per day N silicate must be injected (2.5 x 8 x 10 = 200).

Using D[®] Silicate

To obtain: 1 mg SiO₂/L
Inject: 2.25 gal. D[®] per MG Water

For example, to get an incremental dosage of 8 mg SiO₂/L into a water stream flowing at 0.5 million gallons per day, 9 gallons per day D silicate must be injected (2.25 x 8 x 0.5 = 9).

In situations with low water flow rates it may be necessary to dilute the sodium silicate solution in order to get feed rates within the operating range of typical metering pumps.

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DETERMINING WHEN A PROTECTIVE FILM HAS BEEN FORMED IN A DISTRIBUTION SYSTEM BY SILICA BALANCE

One way to monitor formation of the protective silica film is to do a silica (SiO_2) balance around the distribution system. This involves first determining the normal background level of SiO_2 in the water to be treated, and monitoring it periodically to make sure any changes are recognized.

The silicate treatment will involve introducing a known incremental amount of SiO_2 (e.g., 24 mg/L). Once treatment begins, water samples at strategic end points of the distribution system are periodically checked for SiO_2 . Once the incremental level of SiO_2 at the ends of the distribution system matches the amount being introduced, no more SiO_2 is being consumed (i.e., becoming part of the protective film). This means the initial protective coating has been formed, and the treatment dosage can gradually be reduced to a maintenance dosage which will maintain the protective film.

It is important to continuously feed the silicate maintenance dose in order to preserve the film. If silicate treatment is stopped, the film will gradually dissolve.

DETERMINATION OF SILICA

Test kits for determination of silica, as well as continuous monitoring equipment, are available from firms such as:

Hach Chemical Company

**P.O. Box 389
Loveland, Colorado 80539**

Classical laboratory procedures for the determination of silica by colorimetric and photometric techniques may be found in standard texts on inorganic analysis.

Such procedures are published in "Standard Methods for the Examination of Water and Waste Water," American Public Health Association, Washington, D.C., or in current ASTM Book of Standards (ASTM Designation D-859, "Standard Test Method for Silica in Water").

Test methods for silica determination should be reviewed concerning possible interference effects that may influence the accuracy of results.

METHODS OF FEEDING

Sodium silicate solutions can be easily added to water by means of positive displacement metering pumps. Piston, plunger, diaphragm and gear pumps are suitable. Chemical feed rates can be adjusted by changing the length and speed of the piston or diaphragm stroke, or by adjusting the gear speed.

Silicate solution should be injected at a point near the discharge of the water treatment plant, after final filtration, (i.e., at the clear well). With groundwater, the silicate can be injected at the well site. The silicate feed pump can be wired to activate based on water flow rates, or in conjunction with water transport pumps, in order to maintain the proper proportion of silicate to water.



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Aside from a suitable storage tank and feed pump, no special equipment is required to use silicate. The silicate solution can be stored in drums, day-tanks, or if delivered in tanker trucks, in bulk storage tanks. It can be fed at delivered concentration or diluted with water. If diluted, this must be considered when calculating dosages.

The internals of the silicate feed pumps should be flushed with water when they are taken out of service (e.g., during routine maintenance.) For additional information refer to PQ bulletin 17-70, "Storage and Handling of PQ Liquid Sodium and Potassium Silicates."

SAFETY

Sodium silicate solutions are inorganic compounds. They are not explosive or flammable and are not classified as hazards in U. S. Department of Transportation shipping regulations.

Due to their moderate alkalinity, care should be taken to prevent contact of silicate solutions with eyes and skin. Personnel involved in unloading and/or handling silicate solutions should use protective clothing and equipment to prevent accidental contact. This equipment generally consists of hard hat, chemical goggles or face shield, alkali-resistant gloves, safety footwear and coveralls.

If silicate is splashed into the eyes, flush immediately with warm water and seek medical attention. If splashed on the skin, sodium silicate solution should be washed off with water, preferably warm water. If allowed to remain in contact with the skin, irritation may result.

Wet silicate spills are slippery and will dehydrate to form glass-like films; therefore, it is recommended that minor spills be rinsed with water immediately.

Some dried deposits of liquid silicate may form sharp edges (e.g., if spilled around openings of sample jars), and care should be taken in such cases since skin cuts may result. Such cuts should be washed with water and given appropriate medical attention to prevent infection.

Additional safety information is contained in Material Safety Data Sheets supplied by PQ Corporation.

SUMMARY TABLE

1. Soluble silicates are economical, effective, and environmentally responsible chemicals that have been used for more than 70 years to protect metals from the corrosive effects of water. They do not contribute zinc or phosphorus to the environment.
2. Silicates are approved as direct additives to potable water. They are nonhazardous, nontoxic, and nonflammable. They do not impart any taste or odor to water.
3. American Water Works Association Standard for Liquid Sodium Silicate (ANSI/AWWA B404) recognizes the use of sodium silicate in water treatment.
4. The U.S. Environmental Protection Agency recognizes that silicates may be effective in controlling lead and copper corrosion in potable water systems.
5. At the dilutions typical in water treatment, most of the added silica is in the monomeric form.

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6. The silica in sodium silicate solutions carries a negative charge and will migrate to anodic areas where it can react with metallic ions and form a protective film that inhibits corrosion.
7. The alkali present in silicate will typically raise pH. Increases in pH generally lead to decreased corrosion rates.
8. The film does not build on itself and will not obstruct water flow.
9. In areas of low water flow the supply of silica may eventually be exhausted within the effective range of the electrical forces around the anode. A sufficient water flow is required to supply additional silica.
10. In areas of low flow, the pH contribution of the silicate may also be reduced.
11. If only part of the area is protected, the remainder takes all the attack of the corrosive medium. Therefore it is important to use enough inhibitor.
12. The efficacy of the silicate treatment may vary with the type of metal.
13. The treatment has inhibited corrosion in systems where two dissimilar metals are in contact.
14. A passivation dose of 24 mg SiO₂/L is recommended during the first 30-60 days of treatment in order to quickly establish the protective film.
15. After the protective film has been formed, it can be maintained by feeding less silicate. In most waters a maintenance dosage of 8 mg SiO₂/L is effective.
16. The minimum recommended maintenance dosage is 4 mg SiO₂/L
17. Higher dosages of silicate have been shown to give better protection from corrosion.
18. Higher dosages of silicate speed the formation of the protective film.
19. Optimum silicate dosage will depend on specific water chemistry and system characteristics.
20. The preferred sodium silicate solution for treating water with pH greater than 6.0 is 3.22 ratio SiO₂/Na₂O. For waters with pH of 6.0 or lower, 2.00 ratio SiO₂/Na₂O is preferred.
21. Silicate solutions from PQ are supplied ready to use, or may be diluted.
22. Contact PQ Corporation for product samples or additional information.

ABBREVIATIONS

MGD: Million Gallons per Day

mg/L: Milligram per Liter

cps: Centipoise

ppm: Parts per Million

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FACTORS FOR UNIT CONVERSIONS

Quantity	Equivalent Values
Mass	1 kg=1000g= 0.001 metric ton = 2.20462 lb
Volume	1 m ³ = 1000 liters = 106 cm ³ = 106 ml = 22.83 imperial gallons = 27.41 gallons
Concentration	1 mg/L = 1 ppm = 0.0001%
Viscosity	1 centipoise = 1 millipascal-second = 0.01 poise

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