

Sodium and Potassium silicates

Versatile compounds
for your applications

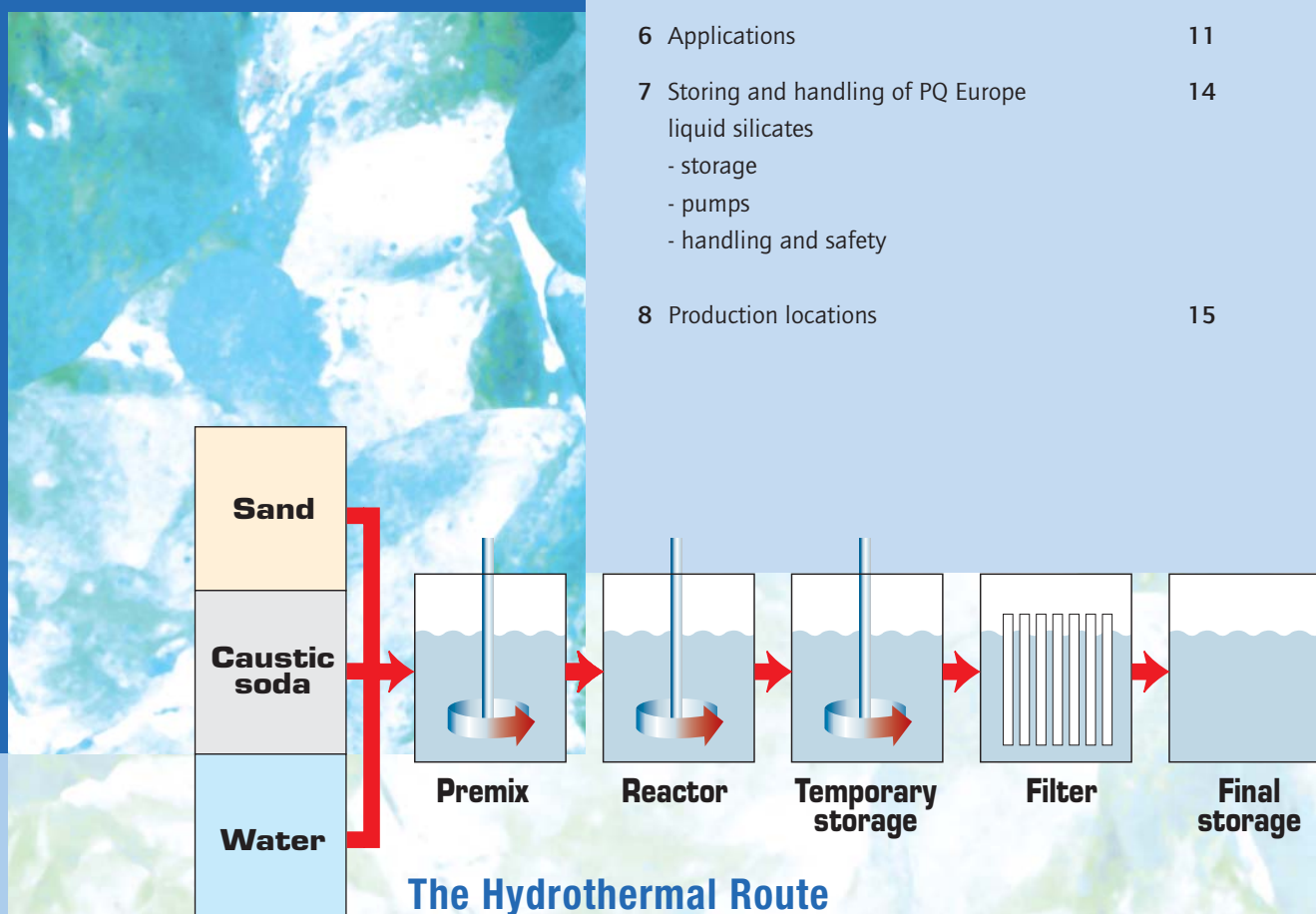
Introduction

PQ Europe represents the European subsidiary of PQ Corporation, USA. PQ Corporation was founded in 1831 and belongs today to the world's most successful developers and producers of inorganic chemicals, in particular on the field of soluble silicates, silica derived products and glass spheres. PQ operates worldwide over 60 manufacturing plants in 20 countries. PQ serves a large variety of industries, including detergents, high way safety, pulp and paper, petroleum processing and food and beverages with a broad range of environmental friendly performance products.

More than 150 years of experience in R&D and production of silicates in USA and Europe guarantee high performance and high quality silicates made according to ISO 9001 and ISO 14001 standards and marketed via our extensive network of sales offices, agents and distributors.

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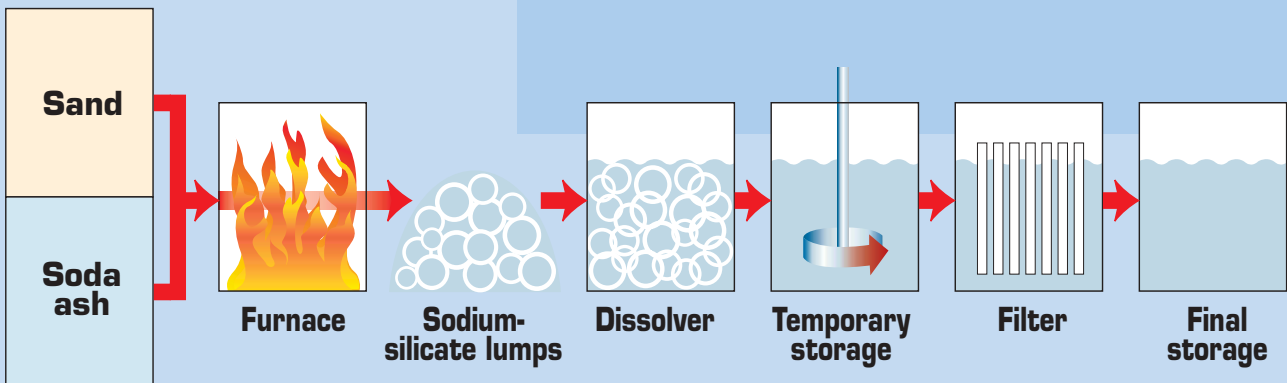
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The production process

Sodium and potassium silicate glasses (lumps) are produced by the direct fusion of precisely measured portions of pure silica sand (SiO_2) and soda ash (Na_2CO_3) or potash (K_2CO_3) in oil, gas or electrically fired furnaces at temperatures above $1000\text{ }^\circ\text{C}$ according to the following reaction:



The Furnace Route



Solutions of alkali silicates ("waterglass") may be produced either by dissolving the alkali silicate lumps in water at elevated temperatures (and partly at elevated pressure) or for certain qualities also by hydrothermally dissolving a reactive silica source (mainly silica sand) in the respective alkali hydroxide solution according to the equation:



In general, solutions are subsequently filtered to remove any residual turbidity and adjusted to yield products to a particular specification.

Amorphous silicate powders are made by drying aqueous solutions by means of spray or drum dryers. These products may then be further treated in order to modify powder properties, e.g. particle size, bulk density.

Crystalline alkali silicate powders of a specific composition but containing different amounts of water of crystallisation can be produced by various routes; e.g. sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) is normally produced by blending sodium silicate solutions and additional caustic soda (NaOH) to achieve a mother liquor with ratio $\text{SiO}_2 : \text{Na}_2\text{O} = 1.0$, from which the final product is crystallised.

The products are then separated, sieved and processed as required.

Raw materials

The main raw materials for the production of alkali silicates are quartz sand (or other silica sources), alkali carbonates (e.g. soda ash Na_2CO_3 , potash K_2CO_3), alkali hydroxides (e.g. NaOH , KOH), water and fuels / energy, e.g. oil, gas, electricity). Filter aids (mostly from natural sources) may also be used.



Ratio

The chemical composition of soluble silicates can be identified by the following formula: $(\text{SiO}_2)_x (\text{M}_2\text{O})$ where M is an alkali metal, usually Na or K. Generally silicates are identified by the SiO_2 : M_2O ratio. It has become practice in the silicates industry to characterize the chemical composition of the silicates in terms of both weight ratio and molar ratio. Since the molar weights of SiO_2 and Na_2O are almost the equivalent (60, resp. 62) only a small difference exists between the molar ratio and the weight ratio for a given sodium silicate. However, this is not applicable for potassium silicate, because of the large difference in molar weights of SiO_2 and K_2O (60 resp. 94).

The factors for converting from weight ratio to molar ratio for both sodium and potassium silicate are as follows:

- sodium silicate : 1.033 x wt ratio
- potassium silicate : 1.567 x wt ratio

PQ Europe normally expresses ratios on a weight basis.

Density

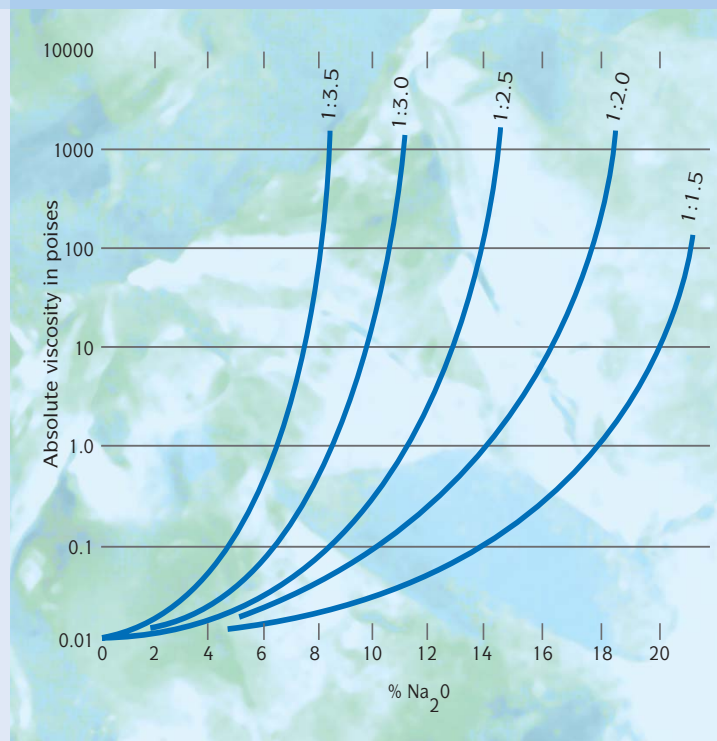
At a given ratio, the density of a solution is defined by the concentration or total solids content. The higher the ratio, the lower the density at a given concentration. In the silicates industry, density has long been expressed in degrees Baumé which can be converted to specific gravity using the following formula:

$$\text{S.G.} = 145 / (145 - \text{Be})$$

Our measurements of density are made at a standard temperature of 20 °C. The density of a silicate solution is inversely proportional to temperature: as temperature increases, density decreases.

Viscosities of sodium silicate solutions as a function of concentration.

Fig. 1

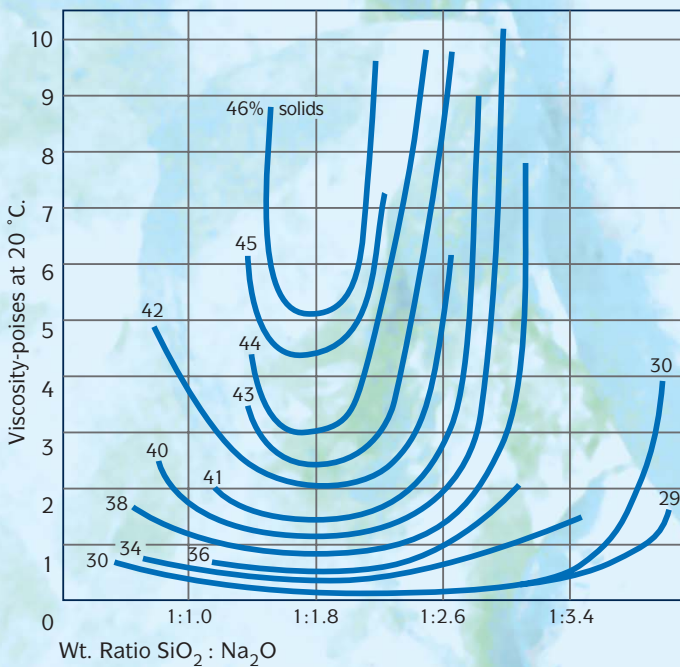


Viscosity

The viscosity of a sodium silicate solution is a function of concentration, density, ratio and temperature. Figure 1 shows that the viscosity strongly increases with increasing ratio. High ratio solutions will increase in viscosity until they become semisolid. Comparison of viscosity at constant solids content at different ratios shows that silicate solutions are at a minimum viscosity at 2.00 weight ratio. Viscosity increases as the weight ratio of the sodium silicate product becomes either more siliceous or more alkaline (Figure 2).

Viscosities of sodium silicate solutions as a function of ratio at constant solids.

Fig. 2



Viscosities of sodium silicate solutions as a function of temperature.

Fig. 3

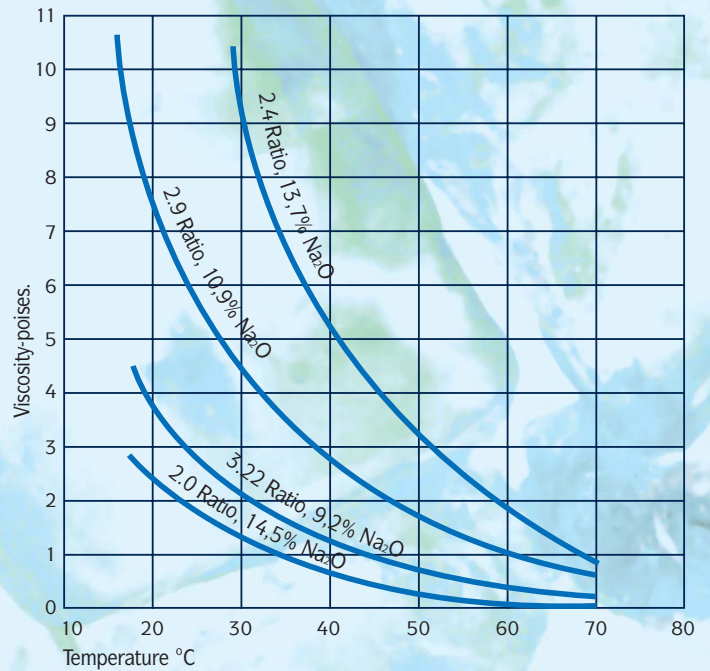


Figure 3 shows that viscosity of sodium silicate solutions at commercial concentrations can be decreased to less than 1 poise if heated sufficiently and if evaporation is prevented.

Potassium

Potassium silicate solutions are similar to solutions of sodium silicate. One significant difference, however, is that potassium silicate solutions are somewhat more viscous than corresponding sodium silicate solutions at equal concentrations.

But, like sodium silicate, the viscosity of solutions is affected by ratio, concentration, and temperature.

Potassium silicates

Versatile compounds for your applications

pH behavior and buffering capacity

The pH of silicate solutions is dependent on concentration and ratio. It is shown in figure 4 that pH decreases as ratio increases. Electrometric titrations with acids show that a high pH of silicate solutions is maintained until the alkali is almost completely neutralized. The buffering capacity (the ability of a solution to resist changes in pH) increases with increasing proportions of soluble silica. However, even dilute silicate solutions will maintain a relatively constant pH despite the addition of acid.

Stability of silicate solutions

All silicate solutions are alkaline, the pH of commercial silicate solutions ranges from approximately 10 to 13. The pH is a function of ratio and concentration and decreases with increasing silica content.

The stability of a sodium silicate solution depends to a large extent on pH. All sodium silicate solutions will polymerize to form a silica gel when the pH value is reduced below 10.

Reaction with acids (sol and gel formation)

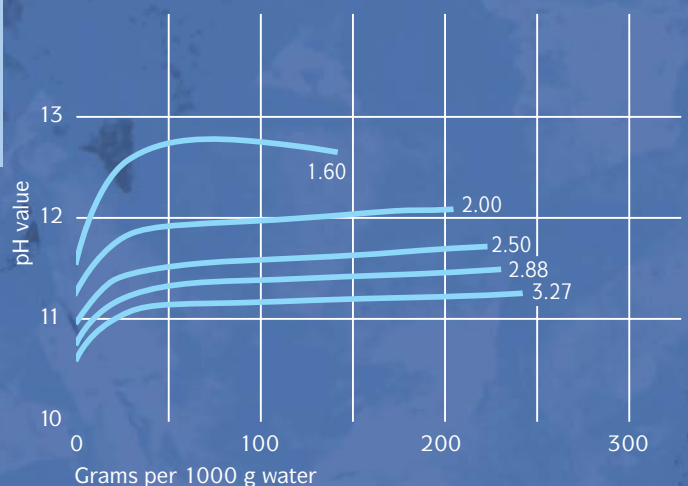
Sodium silicates react with acidic compounds. When solutions of relatively high concentrations are acidified, the soluble silicate anions polymerize to form a gel. When relatively dilute concentrations of dissolved silica are acidified, activated colloidal silicate solutions (sols) can be formed. The degree of polymerization of the silicate anions of sodium silicate solutions depends

on solution concentrations, temperature, pH and other factors. As figure 5 shows, gelation occurs most rapidly at neutral pH.

Time-delayed gelation (unstable sols) can occur in pH ranges of 8-10 and 2-5. Gel formation is generally very rapid in the intermediate range (5-8). Colloidal silica sols can be prepared from sodium silicates through ion exchange, dialysis and other means.

pH Values for solutions of silicates of various ratios.

Fig. 4



Reactions with acid forming products (in-situ gel formation)

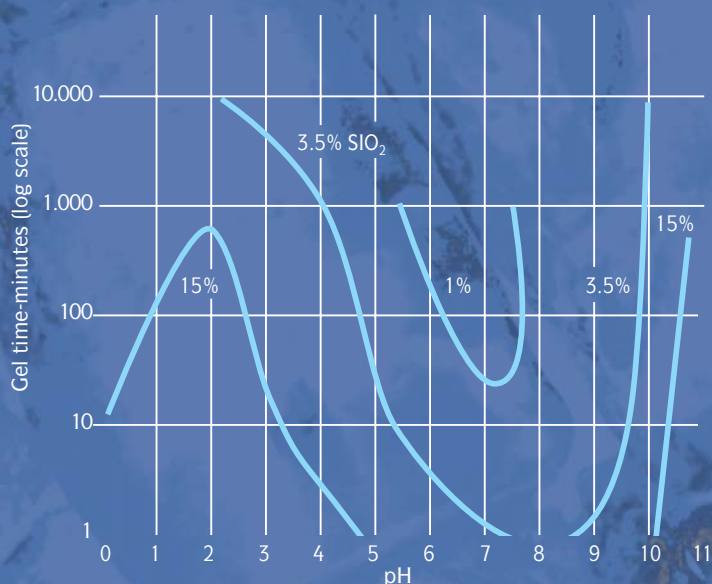
A large number of applications of silicates are based on the ability of in-situ formation of a silica hydrogel. When silicates react with acid forming products such as organic esters, the alkalinity of the silicate solution is consumed by the hydrolysis of these esters over an extended period of time. The gel forms an adhesive bonding with the surrounding substrate (e.g. sand, fly ash, cement and wood).

Precipitation reactions, reactions with metal ions

Solutions of sodium silicates react with dissolved polyvalent cations such as Ca^{2+} , Al^{3+} , and Mg^{2+} to form insoluble forms of silicate. This type of reaction can be used to form pigments or compounds which can be used as extenders or fillers, ion exchange media, catalysts, adsorbents, and other products.

Gel times of 3.2 ratio sodium silicate- H_2SO_4 mixtures at 25 °C.

Fig. 5



Calcium chloride reacts instantaneously with silicate solutions. The reaction is also an effective mechanism for insolubilizing a silicate bond or coating.

Sodium aluminum silicates are formed by reactions between aluminum compounds and sodium silicate. The resulting products can serve as ion exchange media for water softening, as synthetic zeolites or molecular sieves. The extent and rate of reaction of silicates with various metallic salts depends on the nature of the salt and its physical and molecular structure. For example, mineral calcium carbonates, such as calcite, exhibit limited interaction with soluble silicate, whereas precipitated calcium carbonate shows high reactivity.

Interaction with organic compounds

Relatively few organic compounds are compatible with concentrated soluble silicate solutions.

Simple polar solvents can cause phase separation or dehydration. In mixtures with water immiscible lipophilic substances, the silicate separates into the aqueous phase, although in the case of liquid detergent formulations this phenomenon can often be overcome by the addition of a suitable emulsion stabilizer. A few compounds such as glycerine, sugar sorbitol and ethylene glycol are miscible and are sometimes used as humectants.

Adsorption

The functional versatility of dissolved silica, as provided by sodium and potassium silicates, is markedly demonstrated by its ability to alter the surface characteristics of various materials in different ways. Silicates adsorb onto charged mineral and oxide

surfaces. The resulting effects can be, coagulation/flocculation, dispersion/deflocculation, emulsification/demulsification and corrosion inhibition depending on the following choices:

- silicate type ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio)
- solution concentration
- choice of sodium or potassium alkali source
- solution conditions - principally pH

Complex formation

Silicates react with multivalent metal ions in solution to form complexes, thus inactivating these ions. The result is an enhancement of the action of surfactants in detergents (builder action).

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Properties of potassium silicates vs. sodium silicates

Generally, potassium silicates resemble sodium silicates in their properties, but the differences are finding increased recognition and expanding industrial applications. One easily recognized difference is flame color: the violet color of potassium versus the intense yellow of sodium.

This is the basis of one of the early uses of potassium silicate as a binder for carbon electrodes. Benefits of potassium over sodium silicates include:

A convenient source of potassium

Where potassium is a necessary ingredient, it is often convenient to introduce it as silicate. This is important in certain catalyst gels, welding rod coatings and concentrated liquid detergents.

No efflorescence

Potassium silicate coatings are less likely to develop a conspicuous white carbonate film, or efflorescence, on exposure to the atmosphere.

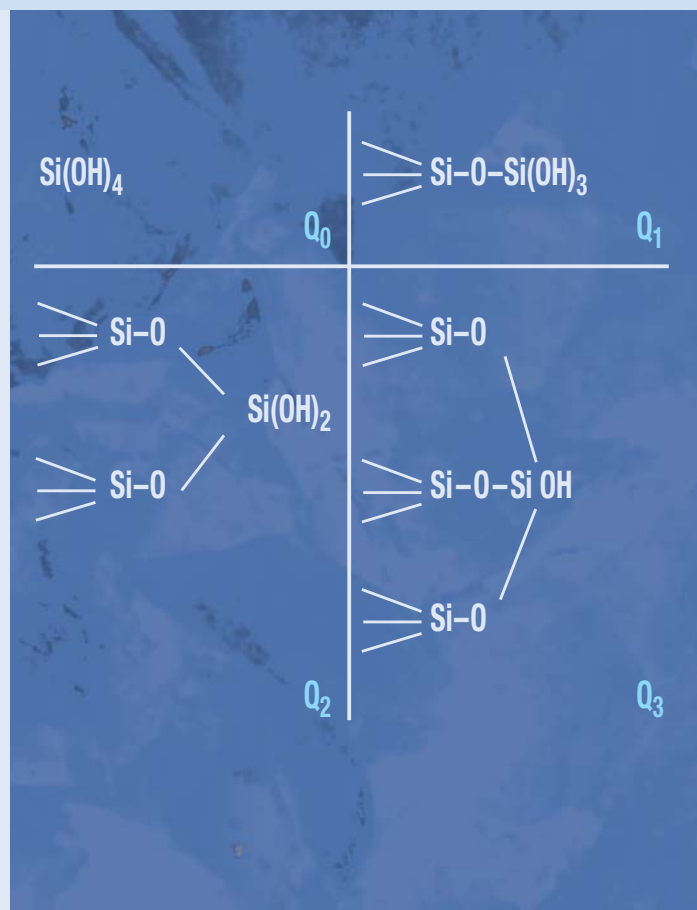
Consequently, potassium silicate is preferred for decorative coatings, paints and ceramic binders.

Higher solubility

Potassium silicates are often used in the formulation of liquid, heavy duty detergents and in built liquid and paste potassium soaps because of their greater solubility and compatibility with other ingredients.

Greater refractoriness

Even at the same silica to alkali molar ratio, potassium silicates soften and flow at a higher temperature than corresponding sodium silicates. For this reason, they are used in various high-temperature binders.



- Q₀ = not linked to a second silicate group
- Q₁ = linked to only one other silicate group
- Q₂ = linked to two silicate groups
- Q_n = linked to silicate groups

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Chemistry of silicate solutions

Commercial alkali silicate solutions can be divided into two fractions:

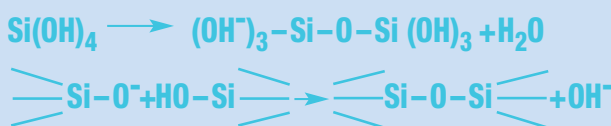
1. dissolved molecules:
 - sodium/potassium ions, hydroxide ions and silicate ions (SiO_4^{4-})
2. colloidal fraction

The very large colloidal fraction is a complex mixture of polysilicate anions; larger species up to colloidal size. The colloidal particles are reactive due to their negative charge at pH values above approximately 3.5 and their hydroxylated surface is capable of adsorbing cations and polar substances.

In concentrated commercial solutions of sodium silicate (25% SiO_2), up to 75% of the silica is present in the polymerized or colloidal form.

The surface of the particles is probably saturated with adsorbed sodium ions. Since the colloidal fraction plays a very important role in understanding properties and applications of silicates we will briefly deal with the size and structure of these silicate particles.

The basic building block in the polymerization is the monomer mono silicic acid (this tetrahedral unit carries four negative charges and is written as SiO_4^{4-}). Mono-silicic acid ($\text{Si}(\text{OH})_4$) is an unstable compound and has the property of polymerization involving sharing of OH- groups between Si atoms. This results in the formation of siloxane (Si-O-Si) bonds and the elimination of water.

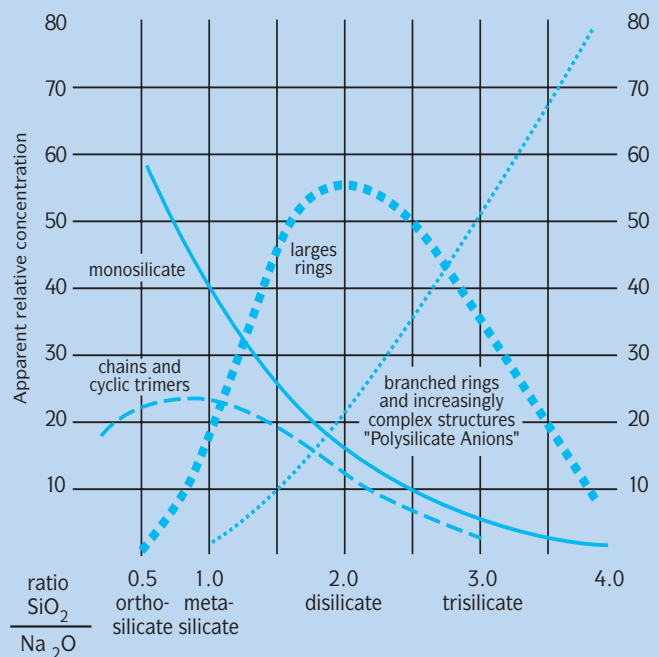


The polymer species are not of uniform size, they may be linear or cyclic. They can be characterized by the number of oxygen bridges to other silicon atoms. A method of describing silicate polymeric species is presented alongside. The capital Q represents the silicate group and the suffix represents the number of other groups to which it is attached.

Polysilicate ions have been identified with up to 12 Si atoms. These polymeric species are in thermodynamic equilibrium. The type and relative distribution of these

Qualitative interpretation of Silicate Anion Structure Equilibria Source: G. Engelhardt, et al., "Z.Anorg, Allg. Chem.," 4188, 17-28 (1975)

Fig. 6



silicate groups depend upon the ratio and the concentration of the particular silicate solution. As the ratio increases, the presence of the higher polymeric species increases; the complexity of the solution increases and so does the viscosity. Solutions having a ratio of 2 or less will tend to be nearer to true solutions containing monomeric SiO_4^{4-} and $\text{Si}_2\text{O}_5^{2-}$ ions usually in a hydrated form. With increasing concentration, the larger polysilicate anions prevail; when solutions are diluted there is an instant partial depolymerization and re-arrangement.

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Applications

Bleaching of pulp

Hydrogen peroxide bleaching is an established technology for pulp bleaching, offering an alternative to chlorine-based bleaching processes. PQ Europe silicates are an important component in hydrogen peroxide bleach liquors.

In this function, the silicates act to stabilize the peroxide, resulting in brighter pulp at a lower cost. The sodium silicates deactivate metals such as iron, copper, and manganese, which catalyze the decomposition of hydrogen peroxide. In addition, silicates buffer the bleach liquor at the pH at which the peroxide is most effective.

For more information we refer to our brochure 'Waterglass in Bleaching of Mechanical Pulps'.

Deinking of wastepaper

PQ Europe sodium silicates are key ingredients in deinking formulations. They help remove inks from the paper surface and enhance dispersion which prevents the ink particles from redepositing on the fibers.

Silicates also contribute alkalinity to the deinking operation, and they allow the process to be carried out at a lower pH than possible when using caustic soda alone.

Deinking at a lower pH minimizes alkali darkening, which tends to be a problem with mechanical pulps.

Silicates also stabilize hydrogen peroxide which may be added to deinking formulations. Silicates work efficiently in both washing and flotation deinking processes, and with a variety of inks and papers, including newsprint, colored or varnished magazine stock, and rotogravure stocks.

For more information we refer to our deinking brochures.

Detergency

As detergent builders in spray-dried, agglomerated, or dry-blended formulations, PQ Europe sodium silicates offer several properties to enhance detergents:

■ Alkalinity and buffering

The alkalinity of sodium silicates enables them to neutralize acidic soils, emulsify fats and oils, and disperse or dissolve proteins. Their buffering capacity, stronger than most alkaline salts, maintains the desired pH in the presence of acidic compounds or in dilution.

■ Calcium and magnesium sequestration

Sodium silicates act as a water softener by sequestering calcium and magnesium ions. Sodium silicates are especially effective in removing magnesium. This ensures optimal performance of the surfactant system even in hard water.

■ Corrosion inhibition

The polysilicate ion forms a physical barrier to alkali attack and protects sensitive glazed dishware, glass, and metallic surfaces, including metal pipes.

In the formulation of spray-dried detergent powders, silicate solutions are easily added to the detergent slurry, where they help control the viscosity at the proper level for producing a powder of the desired density. Sodium silicate acts as a binder in heavy-duty laundry detergent and autodish washing tablets.



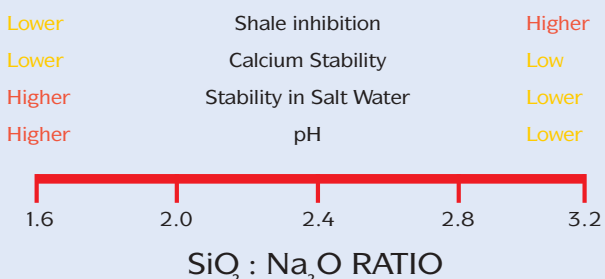
Drilling fluids

Drilling operators are able to replace oil based muds with water based muds that contain soluble silicates to stabilize shale and clay sections in a cost effective way. This allows them to comply with increasingly stringent environmental regulations while maintaining borehole stability.

The stabilization mechanism is the result of the in-situ gelation and precipitation of silicates when exposed to neutral shale pore fluid and/or polyvalent ions.

The relationship between silicate ratio and a number of drilling mud properties is listed in the figure below. Higher ratio, more polymeric materials typically form gels more readily and inhibit shale better than lower ratio products, but are less stable in brines and salt water. A compromise between shale inhibition and salt water stability is usually found in a 2.0 ratio product.

Oilfield Product Characteristics



Adhesives

For materials such as paper and foil, PQ Europe sodium silicate adhesives offer several advantages:

- Good spreading and penetration.
- Good bond formation.
- Set-rates controllable over wide limits.
- Strong, rigid bond that resists heat and moderately resists water.

2.8 to 3.2 ratio silicates are very useful as adhesives or binders due to their higher content of polymeric silica. These materials are converted from a liquid to a solid by the removal of very small amounts of water. Silicates are a cost effective alternative to PVA adhesives and dextrin in many applications. While sodium silicates for adhesives are shipped ready for use, they can be modified with clay, casein, and organic additives for special applications.

Water treatment

Activated silica is an excellent, cost effective polymer acting as a co-flocculant in cleaning industrial water, removal of humus in drinking water and cleaning of water in disposal plants.

For all of these applications, activated silica can replace polyacrylamide products.

Used in conjunction with alum, ferric salts, and other primary coagulants, activated silica increases the speed of floc formation, as well as floc size, density, and stability. Activated silica offers more efficient coagulation at low temperatures and can also act as a filter aid. Many industries achieve a clear effluent by using activated silica to capture finely divided impurities into fast-forming floc. The floc is separated from the water by sedimentation and/or filtration.



Making drinking water safer

Sodium silicates are one of the solutions recognized by environmental authorities to reduce lead, copper, and other heavy metals in drinking water. They function as a corrosion inhibitor to form a microscopic film on the inside of water supply pipes, preventing the leaching of lead solders and other metals throughout the system.

Unlike other corrosion inhibitors, sodium silicate adds no phosphate or zinc to the water supply.

Also when compared to phosphate-based corrosion inhibitors, sodium silicates have a beneficial effect on pH.

Added in the proper amount, sodium silicate can raise system pH into the alkaline range to lower lead levels in a municipal water system. Acidic ($\text{pH} < 7$) and very soft water tends to dissolve more lead than water with a pH in the 8 to 10 range, which sodium silicate can help to maintain.

Small amounts of silicate can be added to water supplies containing high levels of iron or manganese to eliminate "red water" staining.

Foundry binders

PQ Europe sodium silicates are well known as environmentally sound foundry sand binders.

The use of inorganic sodium silicate binder systems promotes cleaner foundry environments because these binder systems are nontoxic, produce essentially no fumes, are odor-free, and are easy to use.

Sodium silicate binders are set by reaction with CO_2 gas or reaction with other acid producing compounds such as aliphatic organic esters. The only source of fumes in these processes are the ester catalysts, which are used in very small amounts, and additives, which are used to improve shakeout and humidity resistance. Reclamation of silicate-bound sands is widely practiced. Spent sands from sodium silicate castings are low in residual organics, which permits easier and less expensive disposal.

Grouting

Grouting, or soil solidification, combines PQ Europe sodium silicates with one or more chemicals that will react with the silicate to form a grout-gel bond. Sodium silicate and a gelling agent (sodium aluminate or esters) are mixed and injected into the ground to react and form an instant grout.

Grouting can be used in several situations:

- To strengthen soil formations that are not strong enough to carry the required load, such as underwalls and footings of structures.
- To make porous soils impermeable, which stops water penetration.
- To prevent water loss from cracks in dams and other containment structures.

PQ Europe research has extended the knowledge of product properties and usefulness to include a wide range of applications. Moreover, new uses are being studied continually. If you have a problem that silicate might help to solve, we invite you to consult us.



Survey of applications of PQ Europe silicates

Sodium silicates

Application	Silicate function	Principal benefit
Detergents Household laundry, powders and autodish Liquid detergents and cleaners	Corrosion inhibitor, buffer Dispersion, buffer	Corrosion protection, detergency Detergency, corrosion protection
Pulp and paper Peroxide bleaching of pulp Deinking Raw water treatment	Chemical reaction Detergency Flocculation	Conserves peroxide Ink removal Clearer effluent
Paper board Spiral-wound tubes	Adhesion	Adds rigidity, economical
Water treatment Lead and copper control Raw and wastewater treatment Corrosion prevention Iron and manganese stabilization	Chemical reaction Flocculant Film formation Chemical reaction	Reduces levels of toxic metals Improves formation of flocs Inhibits corrosive attack Removes red color
Construction Hardening concrete Soil solidification/grouting Sprayed concrete	Chemical reaction, sealant Gel reaction Chemical reaction	Reduces permeability Economical binder Accelerates setting
Textiles Peroxide bleaching Pad-batch dyeing	Chemical reaction Buffering	Conserves peroxide Dye fixation
Ceramics Refractory cements Slurry thinners	Binder Dispersion	Improves strength Reduces water
Petroleum processing Drilling muds Corrosion prevention Emulsion breaking	Colloidal control Chemical reaction Chemical reaction	Inhibits clay dispersion Reduces wear Breaks emulsion
Metals Ore beneficiation Foundry molds and core binders Pelletizing/briquetting	Dispersion Binder Binder	Separation aid Fast set Increases green strength

Potassium silicates

Application	Silicate function	Principal benefit
Welding electrodes	Binder	Improves melting properties
Industrial cleaners	Sequestration, corrosion inhibition	Detergency
Decorative coatings and paints Refractories	Binder Gel formation	Non blooming
Horticultural industry	Nutrient	Specialty fertilizers

Liquid sodium and potassium silicates constitute two families of products which range from moderately to strongly alkaline. Due to these properties storage and handling of these products require special attention.

Storage

■ Bulk storage of liquid silicates

Liquid silicates can be stored in either horizontal or vertical tanks constructed of carbon steel, stainless steel, fiberglass reinforced plastic, or other suitable materials.

NOTE: Aluminum, galvanized steel, zinc and glass are generally not used as construction material since they can be corroded by the alkaline silicate.

The tanks and their supporting structures should be designed to contain liquid silicates with densities ranging from 1.31 to 1.68 g/cm³.

They should meet all local code requirements and regulations.

■ Tank location

Whenever possible it is desirable to locate liquid silicate storage tanks in a heated building area, to minimize the possibility of the silicate freezing and to avoid pumping problems in cold weather due to the products' increased viscosity. Storage temperature of liquid silicates should not exceed 60 °C.

NOTE: The freezing point of sodium and potassium silicate solutions is near that of water. If they freeze, a separation of the silicate constituent can occur.

Remixing by normal procedures may not be sufficient to reconstitute the solution to its original properties. Therefore, it is necessary to make adequate provisions with storage and handling equipment to prevent freezing.

■ Tank maintenance

It is advised to clean tanks once a year if they are used to store liquid silicates with ratios > 2.6.

Pumps

Pumps for handling liquid silicates should be selected on the basis of the viscosity of the product(s) to be handled, temperature conditions, required flow rates and piping system characteristics.

Pumps should be equipped with casing drains to permit draining and washing when the need arises. Ordinary iron pump bushings are satisfactory. Mechanical seals can also be applied. Carbon graphite bushings should not be used.

NOTE: It is suggested that you consult your pump supplier for additional information and assistance needed to select the proper type and size of the pump for the silicate products you process.

Packaging

Sodium and potassium silicates are supplied in drums, containers and in bulk.

Handling and safety

Because of their alkalinity, care should be exercised in working with sodium and potassium silicates. All persons involved in handling the products should be thoroughly instructed in their proper handling, safety precautions and first aid procedures in case of skin or eye contact or ingestion. More information about handling, safety and labeling is provided in Product Safety Data Sheets supplied by PQ Europe.



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Production locations



Finland	- Naantali
France	- Lamotte
Germany	- Worms
Germany	- Wurzen
Italy	- Livorno
The Netherlands	- Maastricht
The Netherlands	- Winschoten
Norway	- Glomfjord
Sweden	- Karlstad

Head Office

PQ Europe

De Brand 24
P.O. Box 664
3800 AR Amersfoort
The Netherlands
tel. +31 33 450 9030
fax. +31 33 450 9031

Customer Service Desk

PQ Europe

Ankerkade 111
6222 NL Maastricht
The Netherlands

tel. +31 43 352 5982
fax. +31 43 352 5919

Production locations

Finland

PQ Finland Oy

Satamatie 2
21100 Naantali
Finland

France

PQ France S.A.S.

Usine de Lamotte
B.P. 30
60350 Trosly Breuil
France

Germany

PQ Potters Europe GmbH

Werk Worms
Mainzer Straße 184
67547 Worms
Germany

PQ Potters Europe GmbH

Am Wachtelberg 8a
04808 Wurzen
Postfach 167
04801 Wurzen
Germany

Italy

PQ Italy S.r.l.

Via Leonardo da Vinci, 3/7
57123 Livorno
Italy

The Netherlands

PQ Nederland B.V.

Ankerkade 111
6222 NL Maastricht
The Netherlands

PQ Nederland B.V.

P. van Dijkstraat 9
9672 AJ Winschoten
P.O. Box 166
9670 AD Winschoten
The Netherlands

Norway

PQ Norge Silicates AS

Nedre Industriområde
8161 Glomfjord
P.O. Box 107
8160 Glomfjord
Norway

Sweden

PQ Sweden AB

Tegelbruksgatan 4
65672 Skattkärr
P.O. Box 414
65109 Karlstad
Sweden

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