SILICON COMPOUNDS: ANTHROPOGENIC SILICAS AND SILICATES

1. Introduction

Commercial soluble silicates have the general formula:

$$M_2O \cdot mSiO_2 \cdot nH_2O$$

where M is generally an alkali metal and m, the modulus, and n are the number of moles of SiO_2 and H_2O, respectively, per mole of M_2O. The composition of commercial alkali silicates is typically described by the weight ratio of SiO_2 to M_2O; sodium silicates [1344-09-8] are the most common. Potassium silicate [1312-76-1] and lithium silicates [12627-14-4] are manufactured to a limited extent for special applications. Soluble silicates where M is the rubidium, cesium, tetramethylammonium (TMA), or tetraethylammonium(TEA) ion also exist, but are much less important commercially. The sodium and potassium silicates are usually manufactured as glasses that dissolve in water to form viscous, alkaline solutions. The modulus or ratio, m, in commercial sodium silicate products typically varies from 0.5 to 4.0. The most common form of soluble silicate has an m value of 3.3.

The soluble alkali silicates have many uses, the largest and most rapidly growing of which comes from their ability to serve as sources of reactive primary silica (qv) species. Knowledge of soluble glass has been traced to antiquity and Goethe is known to have experimented with it in 1768. Industrial development, however, began in Germany in the early nineteenth century (1). Sodium carbonate [497-19-8] (soda ash) and sand [14808-60-7] fused in an open-hearth furnace produced a glass, that was cooled, crushed, and dissolved in water. The common form was called “wasserglass”. Three principal uses in Europe during that time were in treating curtains to decrease flammability, as a dung replacement in textile manufacture and in making bar soaps. By the middle of the nineteenth century silicates were produced in Germany by Walcker, France by Kuhlmann and Britain by Gossage. In the United States, imported silicates were also used as a corrosion-inhibiting coating for cannons and for treating wooden docks. Commercial production began in North America during the Civil War to replace rosin in laundry soaps.

These glasses, amorphous polymeric salts of a strong base and a weak acid, give highly alkaline solutions that made them an economical builder for bar soaps and later detergents based mostly on their solution chemistry (see SOAP). Commercial availability of these solutions also led to other uses based primarily on their physical properties, ie, the glassy nature of highly concentrated sodium silicate solutions made them effective adhesives and binders. The third broad market for soluble silicates was provided later by the manufacture of synthetic pigments (qv), fillers, gels, clays (qv), and zeolites, where the silicate raw material might be regarded as value-added sand.

Currently, roughly 75% of the production of soluble silicates is used primarily as sources of reactive silica and in detergency. The structure and chemistry of solutions containing polymeric silicate species have been better characterized using modern analytical techniques. This improved understanding of silicate speciation contributes to the development of new markets. Thus, the sodium silicates remain a versatile material ranked among the top 50 commodity chemicals.

2. Structure

The crystalline mineral silicates have been well characterized and their diversity of structure thoroughly presented (2). The structures of silicate glasses and solutions can be investigated through potentiometric, light scattering and dye adsorption studies; chemical derivatization and gas chromatography; and laser Raman, Fourier transform infrared (ftir) and ^{29}Si Fourier transform nuclear magnetic resonance (^{29}Si ft–nmr) spectroscopy (3-5). References (6-9) contain reviews of the general chemical and physical properties of silicate materials.

2.1. Silicate Glasses. Synthetic silicates and silica are composed of oligomers of the orthosilicate ion, $[SiO_4]^{4-}$. Orthosilicate monomers have a tetrahedral structure. Silicate tetrahedra can be used to construct more complex structures according to Pauling's rules, ie, Si–O–Si bonds are permitted only at polygon corners. As shown in Table 1, structural categories are possible. The Q^s notation refers to the connectivity of silicon atoms (10). The value of the superscript, s, defines the number of nearest neighbor silicon atoms to a given Si (Fig. 1). Many framework structural modifications are available within these categories. Bonding the monomers at all vertices yields the completely condensed structure of quartz, $(SiO_2)_n$. Quartz does not exhibit a close-packed structure because of constraints imposed by Pauling's rules. Therefore, alternate vacancies are present in half of the tetrahedral positions. In the formation of soluble sodium silicate glasses, Na^+ and O^{2-} ions are introduced into the quartz network, breaking siloxane bonds, Si–O–Si, to form SiO^- sites, ie, nonbridging oxygen atoms. Sodium ions are thought to be distributed nonuniformly in the interstices of the disordered silica network. They produce regions rich in SiO_2 polymers and other areas enriched in cations (11). Mineral silicate structures are expected to exist in regions of short-range order as described by a random polymer order–disorder equilibrium model that is similar to the flickering cluster model of water structure. Thus, the glass state is envisioned as a complex mixture of silicate anions that contains alkali cations distributed in the interstitial voids bonded, on average, by a number of oxygen atoms equal to the cation coordination number. The physical and chemical properties of silicate glasses depend on the composition of the material, ion size, and cation coordination number (12). A melt or glass with a SiO_2/Na_2O ratio of 1, ie, sodium metasilicate, is expected to possess a high proportion of $(SiO_2{}^{3-})n$ chains. At a ratio of 2, sheets might predominate. However, little direct evidence has been shown for a clear predominance of any of these structures. The potential structures of silicate melts of different ratios are discussed in detail in Refs. (13–15).

2.2. Crystalline Alkali Silicates. The most common crystalline soluble silicates belong to the metasilicate family, $Na_2O{\cdot}SiO_2{\cdot}nH_2O$, in commercial notation. Anhydrous sodium monopolysilicate [6834-92-0], Na_2SiO_3, contains SiO_2 chains, whereas the hydrates $Na_2H_2SiO_4{\cdot}xH_2O$, where $x = n-1$, contain only the dihydrogen monosilicate ion (16). The structures of the series sodium dihydrogen monosilicate tetrahydrate [10213-79-3], sodium dihydrogen monosilicate pentahydrate [35064-64-3], sodium dihydrogen monosilicate heptahydrate [27121-04-6], and sodium dihydrogen monosilicate octahydrate [13517-24-3] vary primarily by the order and coordination of the hydrated sodium ion. However, some differences in the symmetry and interatomic bonding of the $[Si(OH)_2O_2]^{2-}$ groups are observed. Only the anhydrous and tetrahydrate forms (called pentahydrate in commerce), are of commercial importance. However, solutions of silicates with values of m <1.6 and solids ≥20% are unstable with respect to the octahydrate.

Other known mineral structures of sodium silicates include natrosilite, $Na_2Si_2O_5$ [56941-93-6]; magadiite, $Na_2Si_{14}O_{29}{\cdot}11H_2O$ [12285-88-0]; kenyaite, $Na_2Si_{22}O_{45}{\cdot}10H_2O$ [12285-95-9]; makatite, $Na_2Si_4O_9{\cdot}5H_2O$ [27788-50-7]; and kanemite, $NaHSi_2O_5{\cdot}3H_2O$ [38785-33-0], in addition to the aforementioned synthetic metasilicates (17). Kenyaite and magadiite (18) are found associated with other siliceous mineral deposits formed in sodium carbonate-rich alkaline waters. Materials with similar chemical compositions have formed in sodium silicate solutions during glass dissolution particularly when the ratio exceeds ~2.5. Silicate producers over the years have attempted to find markets for these nuisance by-products of sodium silicate manufacture. The preparation of magadiite and some of its intercolation compounds were first described in 1972 (19). The synthesis of kenyaite was later reported (20). Several crystalline silicates have received renewed attention in the detergent (21) and catalysts markets due to their layered structure.

3. Dissolution

The dissolution of soluble silicates is of considerable commercial importance. Its rate depends on the glass ratio, solids concentration, impurities content, temperature, pressure, and glass particle size. Commercially, glasses are dissolved in either batch atmospheric or pressure dissolvers or continuous atmospheric processes. Dissolution of sodium silicate glass proceeds through a two-step mechanism that involves ion exchange (qv) and network breakdown (22).

Ion exchange:

$$\equiv Si - ONa + H_2O \rightarrow \equiv Si - OH + Na^+ + OH^- \tag{1}$$

Network breakdown:

$$\equiv Si - O - Si \equiv + HO^- \rightarrow \equiv Si - O^- + HO - Si \equiv \tag{2}$$

Thus, silica is removed incongruently from the glass following leaching of alkali cations. The rate of SiO_2 extraction increases as the pH of the solution rises > 9. Extraction of alkali occurs more readily at pH values below the pK_a of the glass surface silanol functionalities. If sufficient hydroxide activity is not generated in the ion exchange step, the silica network does not decompose extensively and glass leaching results. The transition state in the decomposition process may involve pentacoordinate silicon atoms. The presence of Na^+ in the glass network retards the overall dissolution rate by hindering nucleophilic attack by hydroxide. The rate of SiO_2 removal from a potassium silicate glass depends on the rate of alkali leaching and not on the quantity of alkali removed (23). Smaller cations with higher charge densities produce less soluble silicate glasses as follows: $Li^+ < Na^+ < K^+$. The presence of multivalent metal ion impurities, eg, Al^{3+}, Ca^{2+}, or Fe^{3+}, also significantly reduces glass solubility. A correlation exists between the ratio of free and total silanol groups and glass solubility (24). This ratio varies linearly as different metal ions are added to Na-, K-, or Li-based silicate glasses (4.0 mol ratio). The addition of water depresses this ratio significantly.

A tower operated at atmospheric pressure for dissolving glass has been described (25). The dissolution rate is independent of liquor concentration and circulation rate. The principal factors are temperature, glass composition, and particle surface area. The glass must be sized to avoid a phenomenon referred to as a sticker, which occurs when a dissolving glass mass solidifies. Studies of the dissolution rate of a 2.0 ratio sodium silicate glass into concentrated solutions indicate that the rate of dissolution, expressed as kg dissolved per hour per kg of glass, is independent of the initial particle size (26). In addition, only linear increases in the solution concentration as a function of time were observed under conditions in which Na^+ ion exchange was suppressed by an increase of Na^+ activity of the dissolving liquor. The rate of increase in solution concentration appears to be related inversely to the sodium ion activity. It is also expected that the dissolution process would be sensitive to the amount of ${CO_3}^{2-}$ ion either in the glass due to incomplete fusion or on the surface due to interaction of stored glass with air.

3.1. Silicates in Solutions. The distribution of silicate species in aqueous sodium silicate solutions has long been of interest because of the wide variations in properties that these solutions exhibit with different moduli (27–29). However, they have been called the “Cinderella anions” because their chemistry was so intractable that they had little appeal to classical inorganic chemists (30). Early work described soluble silica containing solutions as dual-natured, ie, composed of colloidal silicic acid, and so-called crystalloidal silica (31) in addition to hydroxide and sodium ions. Crystalloidal silica was assumed to be analogous to the simple species then thought to be the components of crystalline silicate compounds. These include charged aggregates of unit silicate structures and silica (ionic micelles) and well-defined silicate anions.

Subsequent research using light-scattering techniques showed that stable silicate solutions did not contain large particles. Aggregation of particles was detected, however, in highly concentrated, high ratio silicate solutions (32). This work also showed that well-characterized sodium silicate solutions free of trace metal impurities and visible colloidal particles must be used when studying the properties of solutions. Even today one must regard conclusions from studies that do not use well-characterized solutions as suspect. Oligomers in solutions of a variety of alkali silicates were studied by preparing, separating, and identifying trimethylsilyl derivatives using gas chromatography (33-36). This work gave strong evidence for the presence of a variety of $Si_1{-}Si_8$ silicate structures, even in highly alkaline, dilute silicate solutions. Highly polymerized Q^1, Q^2, and Q^3

species were detected, especially in solutions with compositions close to the solubility limit of amorphous silica. Conclusions concerning the quantitative speciation of silicate solutions are weakened because derivatization methods induce polymerization and rearrangement reactions (37). Gel chromatography (38) indicated that solutions contained a complex mixture of silicate anions in dynamic equilibrium.

Laser Raman spectroscopy and ^{29}Si ft−nmr spectroscopy directly examine the structure of silicate species in solution. Early laser Raman spectroscopic studies concluded that dilute, 0.3 *M* sodium silicate solutions of varying ratios ($m = 0.33–3.3$) contained an equilibrium mixture of monomeric silicate, $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$, and polymeric anions, regardless of their histories and methods of preparation. Subsequent research showed that monomeric and dimeric silicate species polymerize to form cyclic polysilicate anions, especially under alkaline conditions (pH 11) and that the distribution of ionic species changes upon aging of the solution (39–41). Increasing the size of the cation, M, in the series Li^+ to Cs^+ at constant silica concentration and ratio increases the molecular weight of the silicate anions possibly due to more favorable ion-pair formation between larger anions and larger cations (42). The ^{29}Si ft−nmr spectra of alkali silicate solutions of varying ratios have been measured and the types of Si environments and their relative concentrations have been estimated (43,44) (Fig. 2). Other researchers have employed more specialized techniques, such as two-dimensional (2D) nmr, to identify tentatively 18 individual ionic species in potassium silicate solutions (45–48). Linear species seem limited to dimers and trimers. Cage-like structures based on three-, four-, and five-membered rings were detected, especially in weakly alkaline solutions. The double four-membered ring cage structure or cubic octameric silicate anion, $Q^3{}_8$, is the dominant anion in TMA or TEA silicates (49,50).

Model-building studies showed that structures based on cyclic Si_4 and Si_5 species were compatible with the observed properties of larger solution-phase silicate ions. The proportion of four- and five-membered rings increased as the silicate particles grew (51). It is postulated that structures with fivefold symmetry account for the production of spherical particles and for the tendency of silicates to avoid crystallizing (28).

Among the techniques for species determination in soluble silicates, ^{29}Si nmr gives the most information about steady-state silicate solutions, but trimethylsilylation and ir spectroscopy provide the best means for studying the dynamics of nonsteady-state systems (34,47). Steady state is attained rapidly in relatively pure systems under alkaline conditions, ie, $pH > 10$. These steady states and the times to achieve them appear to be influenced by impurities (52), their concentration and state of distribution, eg, in colloidal silicate particles (28). These impurities, eg, CO_3^{2-}, Cl^-, SO_4^{2-}, Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, and others, roughly in order of prevalence, come from the sodium carbonate, sand, water, refractories and other sources and can range from > 2000 to $<$ 1 ppm. For example, chloride has been analzyed from 130 to 1900 ppm and Mn^{2+} from 100 to 1.8 ppm. They can vary with processing conditions and locations of manufacturing facilities.

In acidic solutions, steady state is achieved more slowly. Polymerization of smaller species appears to occur sequentially; a given polymer species first increases in size and then disappears, presumably because of its inclusion in higher order polymers. In very alkaline solutions, depolymerization of silicate species appears to be rapid, since crystalline Na_2SiO_3 and $Na_2H_2SiO_4{\cdot}8H_2O$ yield equivalent distributions of silicate species in water upon dissolution.

Electrochemical and nmr data were combined (53,54) to develop a descriptive model for the polymerization and protonation of silicate species in sodium silicate solutions. Thirteen polynuclear species are employed. This model yields useful insights into the changes in polymerization of sodium silicate solutions as $[H^+]$, $[Na^+]$, and $[SiO_2]$ change. Higher order polynuclear species predominate as $[SiO_2]$ increases or pH drops under alkaline conditions. The results suggest that polymers near the solubility limits of amorphous silica contain up to 50 Si atoms and the average charge to Si ratio is roughly 0.5. It is expected that these large particles possess a significant portion of their silanol sites trapped internally or on the surface of the particle and that the average connectivity value, s, approaches a limiting value of 3.5 (34).

4. Polymerization in Solution

Polymerization and depolymerization of silicate anions and their interactions with other ions and complexing agents are of great interest in precipitated silica, silica sol, silica gel, and catalyst manufacture, detergency, oil and gas production, waste management, and limnology (55–63). The complex silanol condensation process may be represented empirically by

$$\equiv \mathrm{Si-OH} \overset{K_a}{\leftrightarrow} \equiv \mathrm{Si-O^-} + \mathrm{H^+} \tag{3}$$

$$\equiv \mathrm{Si-O^-} + \mathrm{HO-Si}\equiv \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} \equiv \mathrm{Si-O-Si}\equiv + \mathrm{HO^-} \tag{4}$$

Condensation occurs most readily at a pH value equal to the pK_a of the participating silanol group. This representation becomes less valid at pH values above 10, where the rate constant of the depolymerization reaction (k_{-2}) becomes significant and at very low pH values where acids exert a catalytic influence on polymerization. The pK_a of monosilicic acid is 9.91 ± 0.04 (64). The pK_a value of $\equiv$Si–OH decreases to 6.5 in higher order silicate polymers (65), which is consistent with pK_a values of 6.8 ± 0.2 reported for the surface silanol groups of silica gel (66). Thus, the acidity of silanol functionalities increases as the degree of polymerization of the anion increases. However, the exact relationship between the connectivity of the silanol silicon and SiOH acidity is not known.

Silicate polymerization–depolymerization in dilute solutions at pH values up to ~10 is sensitive to pH and other factors that generally influence colloidal systems, eg, ionic strength, the nature of ions present, dielectric constant, and temperature. Larger particles grow at the expense of smaller particles (Ostwald ripening), especially in strongly alkaline solutions where the latter dissolve more readily. This results from the tendency of the smaller particles to condense at the surfaces of the larger particles. For example, polymerization occurs primarily on particle surfaces when colloidal silica particles are dispersed in a soluble silicate solution. Lower pH values and higher ionic strength conditions promote the growth of smaller particles.

A quantitative description of the polymerization–depolymerization kinetics requires a more complete representation of the specific anions formed in solution, an understanding of the influence of trace impurities for commercial systems and greater knowledge of the activity variations of the potential condensation sites present on the silica in solution.

Silicate solutions of equivalent composition may exhibit different physical properties and chemical reactivities because of differences in the distributions of polymer silicate species. This effect is keenly observed in commercial alkali silicate solutions with compositions that lie in the metastable region near the solubility limit of amorphous silica. Experimental studies have shown that the precipitation boundaries of sodium silicate solutions expand as a function of time, depending on the concentration of metal salts (67,34). Apparently, the high viscosity of concentrated alkali silicate solutions contributes to slow approach to steady state.

5. Chemical Activity

5.1. Silica Polymer–Metal Ion Interactions in Solution.

The reaction of metal ions with polymeric silicate species in solution may be viewed as an ion-exchange process. Consequently, it might be expected that silicate species acting as ligands would exhibit a range of reactivities toward cations in solution (68). Silica gel forms complexes with multivalent metal ions in a manner that indicates a correlation between the ligand properties of the surface Si–OH groups and metal ion hydrolysis (69,70). For Cu^{2+}, Fe^{3+}, Cd^{2+}, and Pb^{2+}

$$\mathrm{p}K^{\mathrm{S}}1 = 0.09 + 0.62\mathrm{p}^{*}K_1 \tag{5}$$

where $K^{s}{}_1$ and $^{*}K_1$ are the stability constants of the surface complex and metal ion hydrolysis complex, respectively. Metal ion adsorption on silica gel may be initiated at a pH value corresponding to surface nucleation. This seems to relate to a reduction of cation–solvent interactions leading to conditions favorable for adsorption of hydrated metal ions from solution. Metal ion hydrolysis may be required before adsorption (71); direct participation by unhydrated ions has also been proposed. Other studies suggest that cations adsorb to silica gel surfaces as a result of hydroxyl ion adsorption, which carries an equivalent amount of cations to the surface (72). This is consistent with the observation that silica suspended in solutions of polyvalent metal salts begins to adsorb metal ions when the pH value is raised to within 1–2 pH units of the OH^- concentration at which the corresponding metal hydroxides precipitate (73).

At a given pH value, the solution activities of Ca^{2+}, Mg^{2+}, and Cu^{2+} decrease to a greater extent in the presence of SiO_2 derived from 2.0- and 3.8-ratio silicates than they do in solutions prepared from sodium orthosilicate (74). Highly polymerized silicate anions appear to interact with metal ions in solution in a manner analogous to silica gel, and the interaction decreases as the degree of silicate polymerization decreases. The increased acidity of the larger polymers most likely leads to this reduction in metal ion activity through easier development of active bonding sites in silicate polymers. Thus, it could be expected that interaction constants between metal ions and polymer silanol sites varies as a function of time and the silicate polymer size. The interaction of cations with a silicate anion leads to a reduction in pH. This produces larger silicate anions which, in turn, increases the complexation of metal ions. Therefore, the metal ion distribution in an amorphous metal silicate particle is expected to be nonhomogeneous. It is not known whether this occurs, but it is clear that metal ions and silicate react in a complex process that is comparable to metal ion hydrolysis. The products of the reactions of soluble silicates with metal salts in concentrated solutions at ambient temperature are considered to be complex mixtures of metal ions and/or metal hydroxides, coagulated colloidal size silica species, and silica gels.

5.2. Effect on Oxide–Water Interfaces. The adsorption (qv) of ions at clay mineral and rock surfaces is an important step in natural and industrial processes. Silicates are adsorbed on oxides to a far greater extent than would be predicted from their concentrations (75). This adsorption maximum at a given pH value is independent of ionic strength, and maximum adsorption occurs at a pH value near the pK_a of orthosilicate. The pH values of maximum adsorption of weak acid anions and the pK_a values of their conjugate acids are correlated. This indicates that the presence of both the acid and its conjugate base is required for adsorption. The adsorption of silicate species is far greater at lower pH than simple acid–base equilibria would predict. This may be due to ion–oxide surface interactions or to ions already present on the surface. Alternatively, this deviation may reflect varying silicate polymer acidity. Similar behavior has been observed for the adsorption of aqueous silica to the surface of γ-$A1_2O_3$ (76). Divalent metal ions tend to reduce silicate adsorption.

The addition of polymeric silicate anions to oxide mineral suspensions increases the magnitude of the negative surface charge of the mineral particles (77). When silicate solutions are used instead of NaOH to adjust the pH of suspensions of ground quartz in 0.1 mM $PbCl_2$, the pH of maximum positive particle surface charge shifts to lower values and the pH range of positive charge narrows. These effects are more pronounced for polymeric silicates. A similar reduction of the influence of multivalent cations on quartz surface properties occurs in 0.1 mM $FeCl_3$ and mixtures of $PbCl_2$ and $FeCl_3$ regardless of Ca or Mg hardness. The influence of silicate polymers on iron oxide sol surfaces has also been studied (78). The effectiveness of soluble silica in discharging and recharging the surfaces generally depends on the modulus of the original sodium silicate solution (79). Thus, soluble silicates adsorb specifically to oxide surfaces and play a significant role in maintaining a negative surface charge on oxide particles in the presence of cations that could otherwise reverse the surface charge.

6. Characteristics

The characteristics of soluble silicates relevant to various uses include the pH behavior of solutions, the rate of water loss from films, and dried film strength. The pH values of silicate solutions are a function of composition and concentration. These solutions are alkaline, being composed of a salt of a strong base and a weak acid. The solutions exhibit up to twice the buffering action of other alkaline chemicals, eg, phosphate. An approximately linear empirical relationship exists between the modulus of sodium silicate and the maximum solution pH for ratios of 2.0–4.0.

$$\mathrm{pH} = 13.4 - 0.69m \tag{6}$$

This relationship permits the ratio of a pure, concentrated sodium silicate solution to be estimated. The rate of water loss from silicate solutions and films increases at higher ratios. If films or solutions are dried at a given temperature and humidity, a change in condition initiates further drying or rehydration, depending on whether or not drying is sufficient to insolubilize the silicate. Hydrated glass films made from silicates with higher ratios or from those containing metal ions that reduce solubility rehydrate less rapidly. Finally, the dried-film characteristics depend on the glass ratio. Silicates with higher ratios produce more brittle films.

7. Manufacture and Processing

Soluble silicate glasses are usually manufactured in oil- or gas-fired, open hearth regenerative furnaces (80). Continuous-flow glass melters are equipped with high intensity gas burners or plasmas (81,82). These technologies offer significant advantages over conventional batch-melting processes. Glass composition and shutdown and start-up procedures can be changed rapidly because no large molten glass reservoir is maintained (83). In conventional processes, the glass is made by the reaction of sand and sodium carbonate (soda ash) at 1100–1400°C, a temperature sufficiently high to provide a reasonable rate of quartz dissolution in the molten batch and manageable melt viscosity. Furnace life is dependent on the quality of the refractories, corrosivity of the melt and manufacturing technique. Generally, 3 years would be regarded as normal between rebuilds. The liquidus diagrams for sodium silicate glasses and lines of constant melt viscosity are shown in Fig. 3. The rate of reaction of quartz with Na_2CO_3 is controlled by silica diffusion and varies inversely with the square of the radius of the quartz particles (72). As the Na_2CO_3 melt envelops the sand grains, the silica network breaks down and diffuses slowly into the melt. Thermogravimetric analysis indicates that the kinetics of the reaction of sodium carbonate and SiO_2 may be adapted to a modified Ginstling and Brounsthein model (84,85). The glass melts are highly corrosive toward refractory materials compared with the common bottle glasses and the furnace must be carefully designed. Electric melting furnaces can be used satisfactorily where low cost electric power is available (86) and offer the advantage of eliminating contact with products of fuel combustion, eg, SO_x, which could affect the glass.

The glass product can be drawn and formed into solid lumps or drawn directly into a rotary dissolver. The glass lumps can also be dissolved in a pressure apparatus at pressures up to 100 psig. The concentrations and ratios of the solutions are monitored during manufacture with alkali–gravity–viscosity (AGV) charts (Fig. 4). These charts and a knowledge of the density and Na_2O content of the solution may be used to determine the approximate ratio and solids concentration of a product. Lump glass is sold as such to processors having dissolving capability or ground to powders of various particle sizes and size distributions. Silicate solutions up to a ratio of $\sim$ 2.6 can be manufactured in an autoclave at $\sim$ 160°C by dissolving finely ground sand in a NaOH solution. Higher ratio silicates can be prepared from amorphous silica. Caustic soda can be added to reduce the ratio. The choice of the process to obtain a certain ratio is usually based on economics. The solids concentration of the commercial solutions depends on the maximum viscosity that can be tolerated. Figure 5 illustrates the variation of the viscosity of the solution with concentration. The more siliceous products show abrupt increases in viscosity with solids content. This property is valuable in certain adhesive applications. As a high ratio solution is evaporated, the viscosity will increase to a point where solid solutions or highly hydrated glasses form. These materials have commercial significance since the rate of dissolution of soluble silicate solids is a function of particle size, ratio, and water content. These dried silicate solutions, or hydrous silicates, which contain 20% water are stable enough to be handled commercially. They dissolve with a rapidity compared to the ground glasses, making them attractive in certain applications. Thus, powdered soluble silicate products having a wide range of ratios and dissolution properties can be manufactured to meet the demands of diverse applications (Table 2). Hydrous silicates are manufactured in drum dryers or spray towers.

Crystalline sodium metasilicates are manufactured by processing highly concentrated solutions of sodium silicate (1.0 ratio) or by direct fusion of sand and soda ash, followed by grinding and sizing. Solutions at a metasilicate ratio are dried in a dryer (rotary moving bed or fluid bed). The metasilicate solution is sprayed onto the bed and the beads formed are screened as they leave the dryer. The fines are recycled to provide seed material for further growth. This process yields a uniformly sized, readily soluble, anhydrous sodium metasilicate (ASM) product. The only commercially available hydrated sodium metasilicate, $Na_2H_2SiO_4 \cdot 4H_2O$, often called a penthydrate, is manufactured by preparing a 72.2 °C solution at the composition of that hydrate and allowing the mass to cool.

Sodium orthosilicates are produced by blending ASM and NaOH beads or by fusion and grinding as in the direct manufacture of ASM. The relationships of the processes are shown in Fig. 6. Potassium silicates are manufactured in a manner similar to sodium silicates by the reaction of K_2CO_3 and sand. However, crystalline products are not manufactured and the glass is supplied as a flake. A 3.90 mole ratio potassium silicate flake glass dissolves readily in water at $\sim$ 88°C without pressure by incremental addition of glass to water. The exothermic heat of dissolution causes the temperature of the solution to rise to the boiling point.

Lithium silicate solutions are usually prepared by dissolving silica gel in a LiOH solution or mixing colloidal silica with LiOH.

8. Commercial Products

The average composition and pertinent properties of commercial soluble silicates are given in Table 3. The largest volume of these materials is sold as liquids, which are differentiated by the SiO_2/Na_2O ratio and specific gravity. The powdered forms are useful as ingredients in dry-blended products; to control silicate reactivity; for convenience in handling and storage; or to increase silicate solution concentrations above the ranges available in liquid form. Sodium orthosilicate and metasilicates afford high alkalinity. The federal specifications covering commercial silicates are shown below:

Commodity	Specification No.
sodium metasilicate	O-S-604 D
type I, pentahydrate	
type II, anhydrous	
sodium orthosilicate	P-S-651 E
sodium silicate solution	O-S-605 D

8.1. Handling and Storage.

Liquid silicates are available in drums or bulk quantities. Bulk shipments are transported by truck, rail, or tanker; large volumes are transferred by gravity or pumping. Closed, vented, carbon-steel tanks with capacities of 45–57 m^3 (45,000–57,000 L) are recommended for rail and < 23 m^3 (23,000 L) for tank trucks. Silicate powders are available in bulk, 50 (23 kg) and 100 lb (45 kg) Bags, 300–400 lb (136–182 kg) Fiber Drums, or 2000 lb (908 kg) Semi-Bulk Bags; a pressure-differential bulk unloading system is recommended for transfer. A minimum storage capacity of 28 metric tons is advisable for bulk. The storage bins should be controlled for humidity because of the hygroscopic nature of powdered silicates and to minimize uptake of CO_2 (87). Although the packaging of most bagged products is designed to provide humidity protection for reasonable periods of time, additional protection may be required if unusually high humidity or prolonged storage is anticipated.

9. Health and Safety Factors (Toxicology)

9.1. Toxicology.

In general, the toxicological properties of alkali silicates are related to the alkalinity of the test solutions and not the silicate species (88). Contact-exposure effects can range from irritation to corrosion, depending on the concentration of the silicate solution, the silica-to-alkali ratio, the sensitivity of the tissue exposed, and the duration of exposure. Sodium silicate solutions of commercial concentrations with $m < 1.8$ and silicate powders with $m < 2.4$ attack the skin when tested according to Federal Hazardous Substances Act (FHSA) protocols (89). Trace quantities of silicon in the form of one or more of its aqueous silicate polymorphs might serve as an essential sequestrant or masking agent protecting organisms against aluminum poisoning (90,91). Soluble silicates are rapidly absorbed and eliminated if ingested or inhaled (92,93).

Compounds of silicon and oxygen are the primary constituents of the earth's land mass. Dissolved silica is a minor yet ubiquitous constituent of the hydrosphere. Commercial soluble silicates have a higher degree of polymerization than natural dissolved silica because they contain higher SiO_2 concentrations; however, they are thought to depolymerize rapidly to molecular species that are indistinguishable from natural material upon dilution (94).

9.2. Occupational Safety and Health Association (OSHA). This group has set no specific limits for sodium and potassium silicates (95). A prudent industrial exposure standard could range from the permissible exposure limit (PEL) for inert or nuisance particulates to the PEL for sodium hydroxide, depending on the rate of dissolution and the concentration of airborne material. Material safety data sheets issued by silicate producers should be consulted for specific handling precautions, recommended personal protective equipment, and other important safety information.

9.3. Transportation and Disposal (96). Only highly alkaline forms of soluble silicates are regulated by the Department of Transportation (DOT) as hazardous materials for transportation. When discarded, they are classified as hazardous waste under the Resource Conservation and Recovery Act (RCRA) due to corrosive characteristics (97). Typical members of this class are sodium silicate solutions and powders yielding solutions with pH values of 12.5 or greater. In the recommended treatment and disposal method, the soluble silicates are neutralized with aqueous acid ($6\,M$ H^+ or equivalent), and the resulting silica gel is disposed of according to local, state, and federal regulations. The neutral liquid (a salt solution) can be flushed into sewer systems according to local, state, and federal regulations and permits.

9.4. Additives to Food and Potable Water. Sodium silicate is generally recognized as safe (GRAS) by the Food and Drug Administration (FDA) in fabrics and when exposed to food (98). It is also recognized as a secondary direct food additive when used in boiler water for food-contact steam (99). The safety of sodium silicate in these and other food-related applications has been extensively reviewed (100). Sodium metasilicate has been affirmed GRAS for washing and lye peeling of fruits, vegetables, and nuts; in tripe denuding and hog scaling; and as a corrosion inhibitor in canned and bottled drinking water (101). Sodium silicate and sodium metasilicate are authorized by EPA and many state agencies as drinking water additives for clarification of potable water or as a corrosion inhibitor in piped water systems (102). A specification for sodium silicate appears in the American Waterworks Association Standards (103).

10. Economic Aspects

Worldwide silicate production is estimated to be $\sim 4 \times 10^6$ metric tons per year; the 2005 prices for typical products are given in Table 4. The price for a liquid product, normalized to a 100% solids basis, is usually close to the price of the corresponding bulk glass. International trade of silicates, especially liquid products, is limited by the cost of transportation rather than production costs. As much as one-third of the delivered cost to a buyer in the United States can be due to freight costs. Bureau of Census statistics for the production of silicates (104) are shown in Table 5. Production grew rapidly during the 1990s, but has been relatively stable for the past few years as usage in detergency has declined. Rationalization and consolidation has led to the recent mothballing or closing of five plants in the United States. Capacity utilization has remained high and could be strained if markets expand again (105).

Manufacturers of sodium silicates had been historically regional in focus, but in the last 25 years the role of global suppliers has emerged. The main merchant producers of soluble silicates in the United States are The PQ Corporation, OxyChem and Ineos Silicas. Several companies including PPG Industries, W. R. Grace, J. M. Huber, Engelhard Corp. and Albemarle produce silicates primarily for captive use. There are roughly 25 soluble silicate plants in the United States. Production capabilities are more than adequate for current demands. Key producers worldwide are The PQ Corporation with plants in both North and South America, Europe, Asia and Australia. In Japan, Toso Sangyo, Fuji Chemical, and Nippon Chemical are large producers and the MS Jain Group supplies India, the Middle East and Africa. Clariant, Cognis, Rhodia, FMC Foret and Ineos Silicas are also major players in Europe.

11. Analysis and Test Methods

Classical wet chemical methods and instrumental techniques are used for the analysis of soluble silicates (106). Silica is determined by gravimetric techniques or by the fluorosilicate volumetric procedure.

$$\mathrm{Si(OH)_4 + 6\,NaF \rightarrow Na_2SiF_6 + 4NaOH} \qquad (7)$$

The sodium hydroxide is titrated with HCl. In a thermometric titration (107), the silicate solution is treated first with hydrochloric acid to measure Na_2O and then with hydrofluoric acid to determine precipitated SiO_2. Lower silica concentrations are measured with the silicomolybdate colorimetric method or instrumental techniques.

X-ray fluorescence, atomic absorption and plasma emission spectroscopies, ion-selective electrodes, and ion chromatography are utilized to detect principal components as well as trace cationic and anionic impurities. ftir, ft–nmr, laser Raman, and X-ray photoelectron spectroscopic techniques allow identification of the molecular structure of silicates in solid materials and solutions.

12. Uses

Alkali silicates are used as components, rather than reactants, in many applications. In many cases they only contribute partially to the overall performance. Utility factors are generally not as easy to identify. Their benefit usually depends on the surface and solution chemical properties of the wide range of highly hydrophilic polymeric silicate ions deliverable from soluble silicate products or their proprietary modifications. In most cases, however, one or two of the many possible influences of these complex anions clearly express themselves in final product performance at a level sufficient to justify their use (108). Estimates of the 2005 U.S. consumption of sodium silicates are shown in Table 6.

12.1. Detergency. If the volume of sodium silicate used to make zeolites is included in this market classification, then the largest single use for soluble silicates is in soaps and detergents (~36%). (see DETERGENCY) The soluble silicates help provide constant pH values in an effective range and aid in the saponification of oils and fats by means of their alkalinity and buffering capacity. They confer crispness to spray-dried detergent granules because of their glassy nature upon dehydration. In addition, silicates enhance the effectiveness of surfactants (qv) by lowering the activity of certain metal ions, help disperse soil particles, and prevent corrosion of soft metal, eg, tin, aluminum, copper, and brass, owing to complex formation. In dishwashing detergents, silicates protect chinaware and metal utensils from the problem of chelate blush. In addition, they reduce the activity of Mg^{2+} hardness and work well with soda ash and zeolites that selectively reduce Ca^{2+} hardness (109).

12.2. Water Treatment. Silicates are used in water treatment to prepare activated silica sol, a stable, acid-polymerized silicate suspension that functions as an aid in the alum coagulation of matter suspended in raw and wastewater streams; to inhibit corrosion of metal surfaces in contact with water; to stabilize reduced iron and manganese in water supplies; and in boiler water (110–112). Similar applications are found in other areas where large quantities of water are consumed, such as detergency, papermaking, bleaching, and oil recovery. These applications are based on the alkalinity of silicates and the ability of the polymeric silicate anion to form complexes with metal ions in solution and adsorb at charged interfaces. Silicates are effective in high hardness systems where ions other than Mg^{2+} and Ca^{2+} are present; compared with other inorganic sequestration agents they are insensitive to Ca^{2+}.

12.3. Corrosion Control. Silica in water exposed to various metals lead to the formation of a surface less susceptible to corrosion. A likely explanation is the formation of metallosilicate complexes at the metal water interface after an initial disruption of the metal oxide layer and formation of an active site. This modified surface is expected to be more resistant to subsequent corrosive action via lowered surface activity or reduced diffusion.

12.4. Waste Treatment. Soluble silicates when effectively used in the formation of a cement solidified waste form cause a reduction in leaching rate (113,114). This effect could be described by assuming that the rate of leaching was attenuated by changes in reactant or product diffusion through the solid. The concept of a permeability reduction, in addition to any specific solubility reduction due to the formation of a new silicate species, explains why these waste forms often show higher levels of leachability when mechanically degraded. It also has been used to explain why substances which would not be expected to react with soluble silica can show reduced leachability (115).

12.5. Mineral Beneficiation. Sodium silicates are used in froth flotation as strong and selective settling agents, where they increase the hydrophilicity of the mineral particles. Small amounts of silicates may activate the flotation of some calcium-containing minerals. Soluble silicates are excellent dispersants of slimes formed by finely ground minerals (116). Silicates are adsorbed selectively at mineral surfaces in low concentrations and promote separation of particles of different sizes by causing different rates of settling. However, excess silicate settles all minerals. Soluble silicates deactivate certain mineral surfaces to flotation by preventing absorption by a collector, such as oleic acid. Higher ratio silicates are more active and appear to derive their values from their ability to attenuate particle separation at low cost by the development of appropriate hydrophobic and hydrophilic surface properties. The latter effect results from simple anion adsorption, whereas the former is inherent to the mineral or a result of collector adsorption. Silicates are inexpensive additives to the wet ore grinding process, where they reduce wear on steel grinding balls and rods (117); 85% of those steel losses are due to corrosion (118).

12.6. Adhesives and Binders. Silicates are often used to bind sand, in foundries, or other minerals by means of an acid added directly, as in the CO_2 process, or indirectly with an organic ester that hydrolyzes to a carboxylic acid and gels the silicate sand or mineral mass (119–121). Silicates are used extensively as adhesives in spiral tube winding, fiber drums, end sealing, laminating metal foil to paper, and in corrugated boxes. They are also employed in the manufacture of refractory and acid-resistant mortars and cements. Potassium silicates are preferred when high refractory qualities and a nonblooming surface are required. In gunning applications, sodium silicates might be preferred because of their tackiness. Soluble potassium silicates are employed as binders of phosphors to black-and-white television screens. Silicates are used in pelletizing, granulating, and briquetting of fine particles and as a vehicle for water-based coatings. If a water- or humidity-resistant system is not required in any of the preceding applications, simple air drying or heating is sufficient (122,123). However, a setting agent, ie, a reactive pigment or heavy metal salt; post-treatment, ie, baking or curing with an acid wash; or glyoxal curing is necessary where water resistance is required (124). Lithium enhances the water resistance of silicate-sand foundry binders (125). The degree of water resistance depends on the setting agents and the method and temperature of curing. Water resistance is essential for welding-rod coatings, roofing granules, and zinc-rich paints for iron and steel.

12.7. Enhanced Oil Recovery. Silicates are employed in enhanced oil recovery for reasons that are related to their function in detergency and ore beneficiation. The presence of silicate can enhance surfactant effectiveness, especially in hard water reservoir brines (126). The addition of silicates, both before and during direct surfactant floods, eg, micellar–polymer preflushes and low tension waterflooding with silicate, indicates that they retard surfactant adsorption by the substrate and improve sweep efficiency. The latter phenomenon may involve selective permeability reduction (127–129). In this manner silicates improve water wetting in the reservoir. The dissolved silica in silicates enables the flooding solutions to function as a buffering fluid by preventing undesirable mineral–fluid reactions that slow chemical propagation. Silicate polymerization and gelation has been used in subterranean formations to plug large cavities and reduce unwanted fluid flows. The controlled placement and *in situ* gelation of silicates can solve many problems encountered in the drilling and completion of wells and the production of oil and gas through water flooding and enhanced treatment technologies (130,131).

12.8. Bleaching.

Silicates are utilized in combination with hydrogen peroxide to improve pulp and textile bleaching efficiency (132,133). Approximately 40% of the improvement in bleaching efficiency, as measured by brightness, can be attributed in equal measure to increased alkalinity and ionic strength of the bleaching bath. Silicate polymers also inactivate iron and manganese species that catalyze peroxide decomposition (134). However, it is a concern in the industry that the benefits of silicate might be partially offset by the formation of siliceous deposits on bleaching and papermaking equipment and on pulp fibers (135).

12.9. Deflocculation and Slurry Thinning.

Silicates are used as deflocculants, ie, agents that maintain high solids slurry viscosities at increased solids concentrations. Soluble silicates suppress the formation of ordered structures within clay slurries that creates resistance to viscous flow within the various systems. Laboratory trials are necessary, since the complexity of the systems precludes the use of a universal deflocculant. Silicates are employed in thinning of limestone or clay slurries used in the wet-process manufacture of cements and bricks, clay refining, and petroleum drilling muds (see also FLOCCULATING AGENTS).

12.10. Soil Stabilization/Grouting.

Sodium silicates have been used in soil stabilization for ~100 years. They can be used for water control and soil stabilization in tunneling and excavation projects. These grouts are strong, reliable and environmentally safe. There are many setting (gelation) agents for these systems; however, inorganic agents are generally used when seeking high strength and organic agents, eg, esters, when seeking greater control over the gel time. The latter advantage is negated somewhat by increased cost and reduced strength. This controlled placement and gelation technology is also used in oil field applications and being adapted for *in situ* stabilization of soils contaminated with hazardous wastes.

13. Derivatives

In the chemical processing industry (CPI), alkali silicates are valued as a reactive source of $(SiO_2)_n$ structural units. They may be viewed (136) as silica dissolved and/or dispersed in an hydroxide ion-rich aqueous system. Soluble silica as an intermediate reacts with acids and bases to form a wide range of final products from seemingly simple condensed forms of relatively pure noncrystalline silica, precipitates, gels and sols to highly complex crystalline metallosilicates like those found in the broad class of aluminosilicates, zeolites. The key properties of an intermediate is likely to be silica concentration, ratio, supporting cation, type and level of impurities and consistency in these factors. These factors are particularly important when manufacturing catalysts, highly selective sorbents and other high performance materials where trace metals could effect final product performance.

13.1. Silica Sols, Precipitated Silicas and Silica Gels. Solutions of soluble silicates may be modified by ion exchange, acid addition, and post-treatment. These products, generally the result of polymerizing silica, are distinguished primarily by their SiO_2 and H_2O content, pore volume and surface area, particle size and morphology, and content of residual salts. Using small angle X-ray scattring (SAXS) and nmr at pH values of 3.9 and 7–8 the growth of amorphous silica particles and gels as they formed was found to be fractal (137,138). Initially, silicate monomers and oligomers polymerized or aggregated to form essentially spherical primary particles with radii < 1 nm. Within $\sim$10 min, at a rate that was a function of $[OH^-]$ and, if present, $[F^-]$ these primary particles, did not grow, but aggregated to form spherical clusters with sizes near 2 nm. Within 40 min these aggregates clustered to form 8 nm spherical particles which in time simply clustered to form larger aggregates with a finite cutoff size of $\sim$ 100 nm. The geometry of these larger aggregates can vary greatly from roughly spherical dense grape-like structures to more open octopus-like aggregations. The gel structures in this study continued to change over a year, the Q^3/Q^4 content increased and the particles lost their fractal nature. Hydrogen-bonded structures are likely to be the basis for these polymers because the energy of activation is low and entropy considerations are lessened (139).

Silica sols (140) are manufactured by polymerization of diluted 3.3 ratio sodium silicate solutions by H^+/Na^+ ion exchange and concentration. This process yields a dispersion of colloidal silica particles used in antislip agents, castings, binders, and polishing solutions for silicon wafers.

Precipitated silicas (141,142) are made by counteracting the interparticle forces that hold large polymeric silicate anions in solution by the addition of an organic compound or a sodium salt and mineral acid. The anions grow and aggregate into clusters that are filtered, washed, dried, classified, and sometimes surface treated.

Silica gels (143) are prepared by acidifying concentrated 3.3 ratio sodium silicate solutions. Acidification rapidly produces a gel network, called a *hydrogel*, after it passes through the sol stage. *Xerogels* and *aerogels* (qv) are manufactured by gelation, followed by milling, washing, and drying. These powdered products have a wide range of properties (144) and are used as reinforcing agents or fillers in rubber (white carbon black), plastic films and paints, carriers, anticaking and flow-control agents, defoamers, desiccants, toothpaste thickeners and abrasives, beer clarifiers, and as catalyst and chromatography supports.

13.2. Synthetic Insoluble Silicates. Insoluble crystalline silicates, ie, mineral type compounds, are synthesized from soluble silicates by precipitation, gelation, ion exchange, and hydrothermal techniques. Hydrothermal treatment of partially neutralized, high mole ratio ($m = 12–50$), sodium silicate solutions yields neutral alkali polysilicates that exhibit a layered structure and high ion-exchange capacity (145,146). These and other lamellar silicates can be utilized either alone or modified via pillaring (147) as adsorbents and catalysts (148).

The zeolites, $M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot zH_2O$, where M is usually an alkali or alkaline earth metal ion, are of great commercial importance today. These materials, which serve as a model system for the advanced inorganic materials revolution currently underway (149), are made by hydrothermal methods and their architectural variations seem limitless. Synthetic zeolites are generally purer and less expensive than their natural analogues and almost all commercial applications utilize the former (150). These crystalline materials contain SiO_4 tetrahedra in which some of the Si atoms are replaced by A1 (or other metals) in the basic structural network. Zeolites have an open framework structure, which varies as the Si/A1 ratio and mobile charge-neutralizing cation, M, vary (151). These microporous materials, referred to as molecular sieves (qv), are used as ion exchangers, selective adsorbents, and catalysts (152). Other applications include radioactive waste treatment, plastics additives, and controlled release of chemicals.

The nature and concentration of the modifier of the SiO_4 framework, eg, Al, influence the structure and ion-exchange properties of the zeolite. Gallo-, ferro-, and titano-silicate zeolites have been synthesized (153–155). Solvent properties may control zeolite structure formation. For example, silica-sodalite prepared in ethylene glycol is composed of four- and six-membered ring structures, whereas the structure of highly siliceous zeolites obtained from aqueous reaction systems and organic bases contain five-membered rings (156,157). Framework structure and acidity influence the function of zeolites as catalysts. Solid state ^{29}Si nmr has become a powerful tool in the investigation of the synthetic insoluble silicates (158).

Another insoluble silicate of commercial interest is the magnesium silicate smectite clay, hectorite, which may be prepared from 3.2-ratio sodium silicate, LiF, $MgSO_4$, and Na_2CO_3 (159). This inorganic thickening agent produces translucent, thixotropic gels that are not tacky, gummy, or stringy. They are used in antiperspirants, gel toothpastes, shampoos, cosmetics (qv), paints (qv), and cleaning products. Although numerous other crystalline silicates can be prepared at high temperatures and pressures, eg, asbestiform minerals and calcium silicate, the commercial applications and volumes are not significant in comparison with those of hectorite and zeolites. In many cases, these materials are of interest in understanding the chemistry of cement formation and mineral development. However, there are several significant products and markets for amorphous silicates made by reaction of soluble salts of magnesium, aluminum, calcium, and other metals with soluble alkali silicates. The precipitation of this class of materials has been reviewed (160). These materials are useful as sorbents, ion exchangers, rubber reinforcers, paint hardeners, fillers, thixotropes, and pigments.

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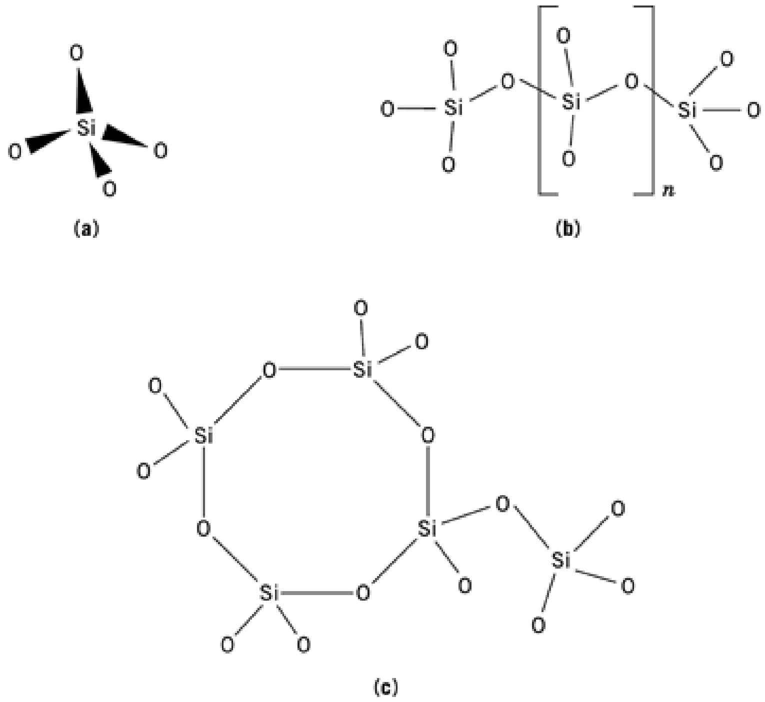

Fig. 1. Examples of Q_s structures for silicates: (**a**) monomer where Q^0 is present; (**b**) metasilicates where $Q^1[Q^2]_nQ^1$ is present; and (**c**) branched-ring structure where $\underbrace{Q^2Q^2Q^2Q^3}Q^1$ is present.

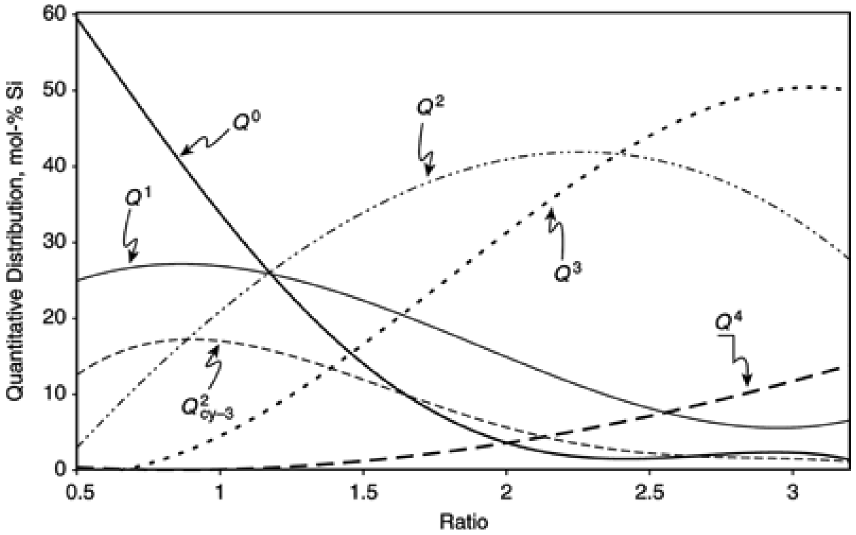

Fig. 2. Distribution of silicon species in soluble silicate solution: estimated from data in Ref. 43 p. 86.

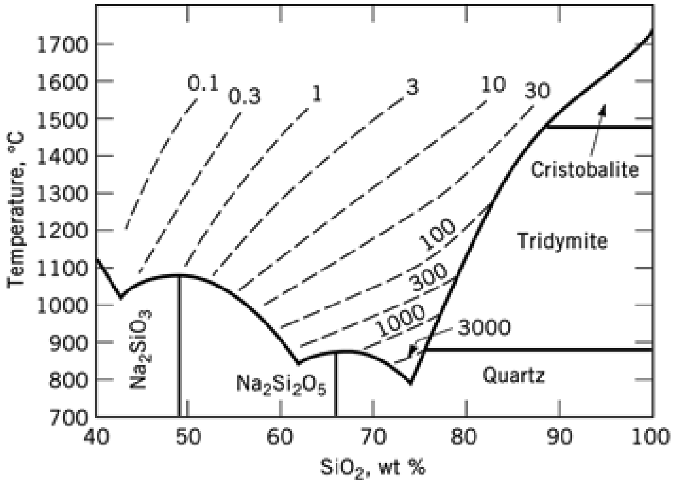

Fig. 3. The viscosity and liquidus curves for molten sodium silicates, where the numbers on the dashed lines are viscosity in Pa (1). (Courtesy of the The PQ Corp. To converts Pa·s to poise, divide by 10.)

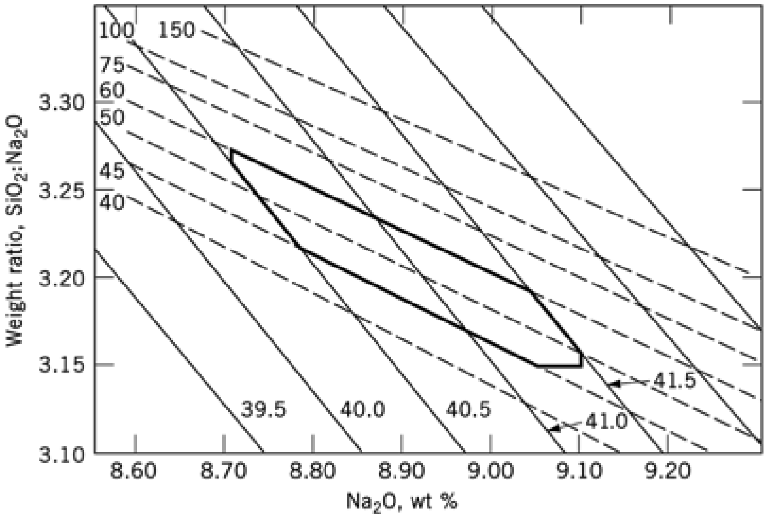

Fig. 4. An−AGV control chart for a 3.22-weight ratio sodium silicate solution, where (—) and (– – –) represent lines of constant density and viscosity, respectively. The area enclosed within the emboldened box represents the range of properties for a typical product. (Courtesy of The PQ Corp.)

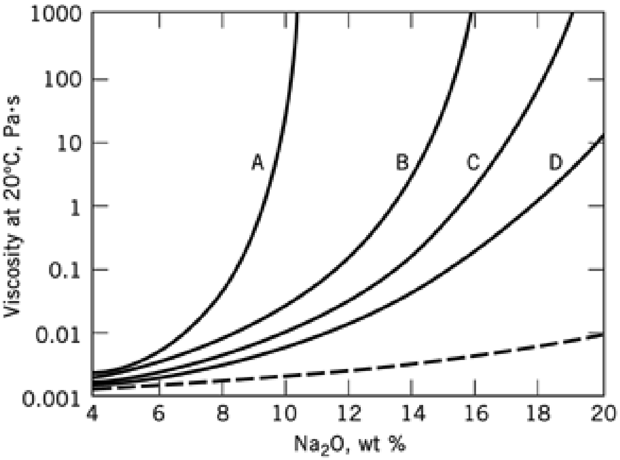

Fig. 5. Viscosities of sodium silicate solutions vs percent solids: A, ratio of 3.22: B, 2.4; C, 2.0; D, 1.6; and (– – –), NaOH. To convert Pa to poise, divide by 10. (Courtesy of The PQ Corp.)

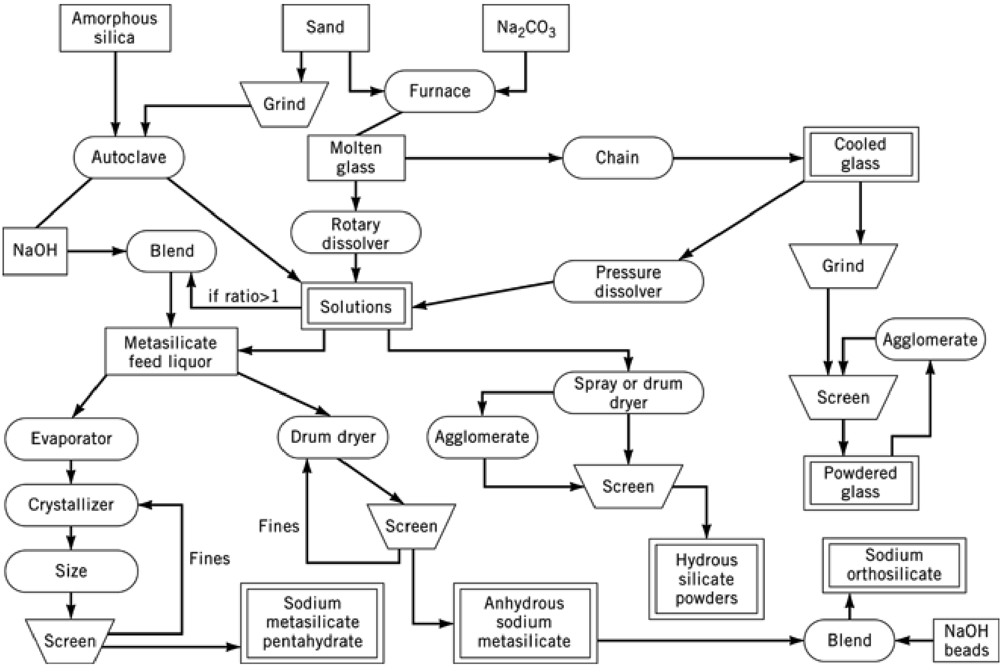

Fig. 6. Manufacturing routes for commercial sodium silicates. (Courtesy of the PQ Corp.)

Table 1. **Silicate Structural Categories**

		Mineral examples		
Silicate type	Unit structure	Name	Formula	Q^s structures[a]
Oligosilicates, discreet				
orthosilicate	SiO_4^{4-}	zircon	$Zr[SiO_4]$	Q^0
pyrosilicate	$Si_2O_7^{6-}$	thortveitite	$Sc_2[Si_2O_7]$	Q^1Q^1
Cyclosilicates, discrete cyclic				
trimer	$Si_3O_9^{6-}$	benitoite	$BaTi[Si_3O_9]$	$(Q^2)_3$
tetramer	$Si_4O_{12}^{8-}$	papagoite	$Ca_2Cu_2Al_2[Si_4O_{12}](OH)_6$	$(Q^2)_4$
hexamer	$Si_6O_{18}^{12-}$	dioptase	$Cu_{12}[Si_6O_{18}]\cdot 6H_2O$	$(Q^2)_6$
Polysilicates, chains				
pyroxenes	$(SiO_3^{2-})_n$	wollastonite	$Ca[SiO_3]$	$(Q^2)_n$
amphiboles	$(Si_8O_{22}^{12-})_n$	tremolite		
$Ca_2Mg_5[Si_8O_{22}](OH,F)_2$	$(Q^3Q^2)_n$			
Phyllosilicates, sheets	$(Si_4O_{10}^{2-})_n$	talc		
$Mg_3[Si_4O_{10}](OH)_2$	$(Q^3)_n$			
Tectosilicates, frameworks	$(SiO_2)_n$	silica, quartz		$(Q^4)_n$

[a] Refers to the connectivity of silicon atoms; end groups or surface silicons for more condensed structures are ignored.

Table 2. **Solution Rates of Amorphous Silicate Powders**[a]

		Time needed to dissolve					
		at 25°C			at 50°C		
Silicate, wt % ratio	Particle size,[b] µm (mesh)	50%	75%	100%	50%[c]	75%	100%
3.22 ratio sodium							
anhydrous glass	230 (65)	60 h			15% in 30 min		
hydrated, 18.5 wt % H_2O	149 (100)	19 min	45 min		54 s	76 s	100 s
2.00 ratio sodium							
anhydrous glass	230 (65)	10 h	70 h		17 min	1 h	
hydrated, 18.5 wt % H_2O	149 (100)	27 s	54 s		15 s	22 s	29 s
2.50 ratio potassium							
anhydrous glass	230 (65)	60 min	7.5 h	48 h	12 min	45 min	

[a] 3 pt water, 1 pt silicate powder.

[b] Tyler screen.

[c] Unless noted.

Table 3. **Commercial Sodium and Potassium Silicates**

Commercial silicates	SiO_2, wt %	Wt ratio[a] $SiO_2:M_2O$	Modulus[a], $SiO_2:M_2O$	Softening point,[b] °C	Flow point,[c] °C	H_2O, wt %	°Baumé[d], at 20°C	d_{20}^{20}, g/cm^3	Viscosity, at 20°C, Pa·s	pH
anhydrous glasses										
sodium silicates	75.7	3.22	3.33	655	840					
	66.0	2.00	2.06	590	760					
potassium silicates	70.7	2.50	3.92	700	905					
hydrated amorphous powders										
sodium silicates	61.8	3.22	3.33			18.5				
	64.0	2.00	2.06			18.5				
solutions										
sodium silicates	31.5	1.60	1.65				58.5	1.68	7.00	12.8
	36.0	2.00	2.06				59.3	1.69	70.00	12.2
	26.5	2.50	2.58				42.0	1.41	0.06	11.7
	31.7	2.88	2.97				47.0	1.49	0.96	11.5
	28.7	3.22	3.32				41.0	1.39	0.18	11.3
	25.3	3.75	3.86				35.0	1.32	0.22	10.8
potassium silicates	20.8	2.50	3.93				29.8	1.259	0.04	11.30
	19.9	2.20	3.45				30.0	1.261	0.01	11.55
	26.3	2.10	3.30				40.0	1.381	1.05	11.70
	29.5	1.80	2.83				47.7	1.490	1.30	12.15
crystalline solids										
sodium orthosilicate	28.8	60.8[f]	0.50			9.5				
anhydrous sodium metasilicate	47.1	51.0[f]	1.00			2.0				
sodium metasilicate pentahydrate	26.4	29.3[f]	1.00			42.0				
sodium sesquisilicate [1344-09-8]	24.1	36.7[f]	0.67			38.1				

[a] M represents Na or K.

[b] Viscosity reaches 4 MPa (4×10^7 P).

[c] Viscosity reaches 10 kPa (10^5 P).

[d] To convert Be° to sp gr, divide 145 by (145−Be°).

[e] To convert Pa to P, divide by 10.

[f] Value is wt % of M_2O.

Table 4. **2005 Prices of Silicate Products**

	Truckload prices FOB plant, $/2000 lb		
Product	Bulk	Bags (50 lb)	Drums
sodium silicate lump glass			
3.22 ratio	726		
2.00 ratio	882		
anhydrous sodium metasilicate	824	852	918
sodium metasilicate pentahydrate	543	571	623
potassium silicate flake glass, 2.50 ratio		1492	
hydrous sodium silicate			
2.00 ratio, 18% water		1117	
3.22 ratio, 18.5% water		999	
hydrous potassium silicate, 1.63 ratio, 15% water		2160	

Table 5. **Production and Shipment of Sodium Silicates, 1955–2004[a], 10^3 t (2200 lb)**

Year	Sodium silicate solution[b] Production	Sodium silicate solution[b] Shipment	Sodium metasilicate[c] Production	Sodium metasilicate[c] Shipment	Sodium Orthosilicate Production[d]
1955	570	422	142	117	34
1965	533	414	228	186	38
1970	570	423	204	162	31
1975	656	501	190	165	
1980	730	493	152	132	11
1985	627	422	97	92	
1990	740	494	98	93	
1995	1020		82		
1996	1004		79		
1997	1101		76		
1998	1097		70		
1999	992		63		
2000	1031		66		
2001	1070		66		
2002	1053		58		
2003	1074		61		
2004	1122[e]		64[e]		

[a] Ref. 104.

[b] Soluble sodium silicate glass solid and liquid (anhydrous). Excludes quantities consumed in the manufacture of meta-, ortho-, and sesquisilicates. Includes quantities consumed in the manufacture of glass powder, hydrated glasses, and precipitated products. Shipment figures include unspecified amounts shipped to other plants for the manufacture of meta-, ortho-, or sesquisilicates.

[c] All sodium metasilicate products (SIC No. 2819743) on a 100 wt % sodium metasilicate pentahydrate basis.

[d] Estimated production data for 100 wt % sodium orthosilicate (SIC No. 2819745).

[e] Data through first three quarters times 1.33.

Table 6. **Estimated Distribution of Sodium Silicate Consumption**

	Percentage of U.S. Market			
Market	1975	1985	1995	2005
Detergent, non-zeolite	30	26	23	20
Silica Source	37	45	57	55
zeolites - detergent	1	5	18	16
silicate-based pigments	20	21	16	16
cracking catalysts	10	12	15	13
silica gels	3	2	4	4
silica sols	1	2	3	3
titania pigments/other	2	3	1	2
Other Applications	33	29	20	25
adhesives	4	5	2	2
roofing granules	3	4	4	3
mining applications	2	1	1	2
water treatment	2	2	2	2
pulp/paper and textile	6	6	7	11
miscellaneous[a]	16	11	4	5

[a] Including welding rods, cements, ceramics, foundry binders and agricultural and food uses.