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SILICON COMPOUNDS TO
SUCCINIC ACID AND SUCCINIC ANHYDRIDE

CONTENT INDEX (vol 22)
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SILICON COMPOUNDS

Synthetic inorganic silicates,
Silicon halides,
Silanes,
Silicon esters,
Silicones,
Silylating agents,

SYNTHETIC INORGANIC SILICATES

Commercial soluble silicates have the general formula

$$M_2O \cdot mSiO_2 \cdot nH_2O$$

where M is 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. These materials 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 metal silicates have many uses, the largest and most rapidly growing of which arises from the ability to serve as a source 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). The common form was called wasserglass. Three principal uses in Europe during that time for waterglass 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 being produced in Germany by Wacker, in France by Kuhlmann, and in Britain by Gossage. In the United States, imported silicates were also being used as a corrosion-inhibiting coating for cannons and for treating wooden docks. Commercial production began in North America during the Civil War. Silicates were used in laundry soaps as a replacement for rosin, which was scarce because of the war. 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 (see Soap).

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 for detergents based mostly on their solution chemistry. 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 silicates might be regarded as value-added sand.

As of the mid-1990s, soluble silicates are used primarily as sources of reactive silica (57%), in detergency (qv) (23%), in pulp (qv) and paper (qv) production (7%), for adhesives and binders (5%), and in other applications (8%). The structure and chemistry of solutions containing polymeric silicate species have been characterized using modern analytical techniques. This improved understanding of silicate speciation contributes to the development of new markets. Thus, the sodium silicates constitute a versatile, stable, and growing commodity and are ranked among the top 50 commodity chemicals.

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 and dye adsorption studies, chemical derivatization and gas chromatography, and laser Raman, infrared (ftir), and ^{29}Si Fourier transform nuclear magnetic resonance (^{29}Si ft-nmr) spectroscopy. References 3–6 contain reviews of the general chemical and physical properties of silicate materials.

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 notation refers to the connectivity of silicon atoms (7). 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. These produce regions rich in SiO_2 polymers and other areas enriched in cations (8). 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.
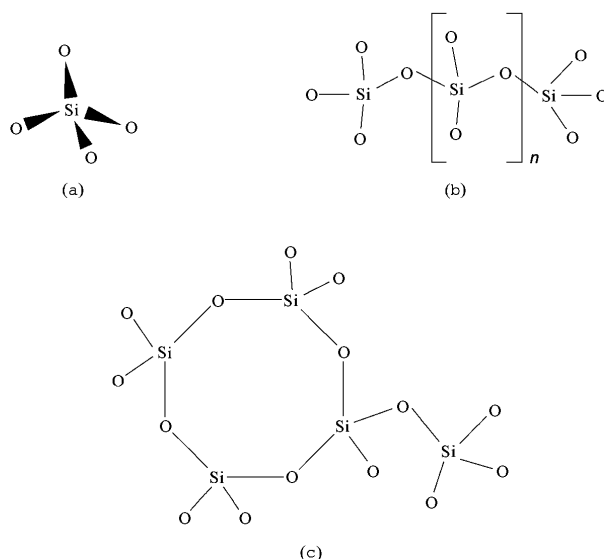
Fig. 1. Examples of Q^i structures for silicates: (**a**) monomer where Q^0 is present; (**b**) metasilicates where $Q^1[Q^2]_nQ^1$ is present; and (**c**) branched-ring structure where $\underbrace{Q^2Q^2Q^2Q^3Q^1}$ is present.

Table 1. Silicate Structural Categories

| Silicate type | Unit structure | Mineral examples | | | Q^i structures[a,b] |
		Name	CAS Registry Number	Formula	
oligosilicates, discreet					
orthosilicate	SiO_4^{4-}	zircon	[14940-68-2]	$Zr[SiO_4]$	Q^0
pyrosilicate	$Si_2O_7^{6-}$	thortveitite	[17442-06-7]	$Sc_2[Si_2O_7]$	Q^1Q^1
cyclosilicates, discrete cyclic					
trimer	$Si_3O_9^{6-}$	benitoite	[15491-35-7]	$BaTi[Si_3O_9]$	$(Q^2)_3$
tetramer	$Si_4O_{12}^{8-}$	papagoite	[12355-62-3]	$Ca_2Cu_2Al_2[Si_4O_{12}](OH)_6$	$(Q^2)_4$
hexamer	$Si_6O_{18}^{12-}$	dioptase	[15606-25-4]	$Cu_{12}[Si_6O_{18}]\cdot6H_2O$	$(Q^2)_6$
polysilicates, chains					
pyroxenes	$(SiO_3^{2-})_n$	wollastonite	[14567-51-2]	$Ca[SiO_3]$	$(Q^2)_n$
amphiboles	$(Si_8O_{22}^{12-})_n$	tremolite	[14567-73-8]	$Ca_2Mg_5[Si_8O_{22}](OH,F)_2$	$(Q^3Q^2)_n$
phyllosilicates, sheets	$(Si_4O_{10}^{2-})_n$	talc	[14807-96-6]	$Mg_3[Si_4O_{10}](OH)_2$	$(Q^3)_n$
tectosilicates, frameworks	$(SiO_2)_n$	silica, quartz	[7631-86-9]		$(Q^4)_n$

[a] Refers to the connectivity of silicon atoms. See Fig. 1.

[b] End groups or surface silicons for more condensed structures are ignored.
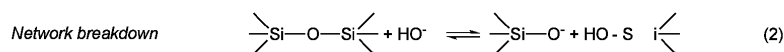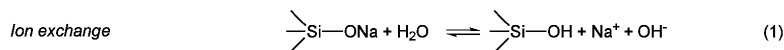
The physical and chemical properties of silicate glasses depend on the composition of the material, ion size, and cation coordination number (9). A melt or glass having a SiO_2/Na_2O ratio of 1, ie, sodium metasilicate [1344-09-8], is expected to possess a high proportion of $(SiO_3^{2-})_n$ chains. 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 elsewhere (10–12).

Crystalline Alkali Silicates. The most common crystalline soluble silicates belong to the metasilicate family, $Na_2OSiO_2\cdot nH_2O$, 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 (13). 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, ie, the so-called pentahydrate, are of commercial importance. However, solutions of silicates having values of $m < 1.6$ and solids $\geq20\%$ are unstable with respect to the octahydrate.

Other known mineral structures of sodium silicates include natrosilite [56941-93-6], $Na_2Si_2O_5$; magadiite [12285-88-0], $Na_2Si_{14}O_{29}\cdot11H_2O$; kenyaite [12285-95-9], $Na_2Si_{22}O_{45}\cdot10H_2O$; makatite [27788-50-7], $Na_2Si_4O_9\cdot5H_2O$; and kanemite [38785-33-0], $NaHSi_2O_5\cdot3H_2O$, in addition to the aforementioned synthetic metasilicates (14). Kenyaite and magadiite (15) are found associated with other siliceous mineral deposits formed in sodium carbonate-rich alkaline waters. Materials having similar chemical compositions have formed in sodium silicate solutions during glass dissolution, particularly when the ratio exceeds about 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 intercalation compounds were first described (16) in 1972. The synthesis of kenyaite was reported later (17). As of the mid-1990s these so-called tetrasilicates are receiving renewed attention in the detergent and catalysts markets owing to their layered structure.

Dissolution

The dissolution of soluble silicates is of considerable commercial importance. Its rate depends on the glass ratio, solids concentration, 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 (18).

Ion exchange $\equiv\!Si\!-\!ONa + H_2O \;\rightleftharpoons\; \equiv\!Si\!-\!OH + Na^+ + OH^-$ (1)

Network breakdown $\equiv\!Si\!-\!O\!-\!Si\!\equiv + HO^- \;\rightleftharpoons\; \equiv\!Si\!-\!O^- + HO\!-\!Si\!\equiv$ (2)

Thus, silica is removed from the glass following leaching of the alkali cations. The rate of SiO_2 extraction increases as the pH of the solution rises above 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 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 (19). Smaller cations having higher charge densities produce less soluble silicate glasses as $Li^+ < Na^+ < K^+$. 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 (20). 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 (21). 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 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 (22). 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 owing to incomplete fusion or on the surface owing to interaction of stored glass with air.

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 (23–25). Early work led to a dual-nature description of silicates as solutions composed of hydroxide ions, sodium ions, colloidal silicic acid, and so-called crystalloidal silica (26). 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 (27). Aggregation of particles was detected, however, in highly concentrated, high ratio silicate solutions. Well characterized sodium silicate solutions free of trace metal impurities and visible colloidal particles must be used when studying the properties of solutions. Conclusions from studies which do not control for ion impurities are suspect.

Polymers in solutions of a variety of alkali silicates have been studied by preparing, separating, and identifying trimethylsilyl derivatives using gas chromatography (28–31). This work gives strong evidence for the presence of a variety of $Si_1\text{–}Si_8$ silicate structures, even in highly alkaline, dilute silicate solutions. Highly polymerized Q^1, Q^2, Q^3, and Q^4 species were detected, especially in solutions having compositions close to the solubility limit of amorphous silica. Conclusions concerning the quantitative speciation of silicate solutions are weakened, however, because the derivatization method induces polymerization and rearrangement reactions (32). Gel chromatography (33) indicates that the solutions contain a complex mixture of silicate anions in dynamic equilibrium.

Laser Raman spectroscopy and ^{29}Si ft-nmr spectroscopy have been used to examine directly the structure of silicate species in solution (34–41). Early laser Raman spectroscopic studies concluded that dilute, 0.3 M sodium silicate solutions of varying ratios ($m = 0.33\text{–}3.3$) contain 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 (34–36). The ^{29}Si nmr spectra of alkali silicate solutions of varying ratios have been measured and the types of Si- containing species and their relative concentrations have been estimated (Fig. 2) (37). Other researchers have employed more specialized techniques, such as two-dimensional nmr, to identify tentatively 18 individual ionic species in potassium silicate solutions (38–41). Cage-like structures based on three-, four-, and five-membered rings were detected, especially in weakly alkaline solutions. 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 (5,42). Structures having fivefold symmetry are postulated to account for the production of spherical particles and for the tendency of silicate particles to avoid crystallizing (5).
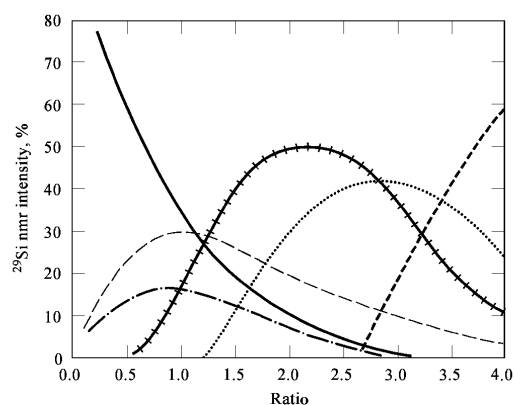

Fig. 2. Distribution of silicon centers in soluble silicate solutions from ^{29}Si Fourier-transform nmr spectroscopy (7,37), where (—) represents Q^0; (— — —), Q^1; (—·—); Q^2 (ring); (—+—+—), Q^2 (chain); (· · ·), Q^3; and (– – –), Q^4. See Table 1. Values are estimated.

Among the techniques for species determination in soluble silicates, ^{29}Si nmr spectroscopy gives the most information about equilibrium silicate solutions, but trimethylsilylation provides the best means for studying the dynamics of nonequilibrium systems (29,42). An equilibrium state is attained rapidly in relatively pure systems under alkaline conditions, ie, pH > 10. These equilibrium states and the time needed to achieve them appear to be
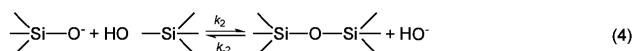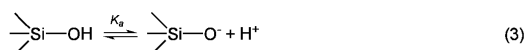
influenced by impurities, their concentration, and state of distribution, eg, in colloidal silicate particles (23). These impurities, eg, CO_3^{2-}, Cl^-, SO_4^{2-}, Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, and others, roughly in order of prevalence, come from the sodium carbonate, sand, water, refractories, and other sources and can range from >2000 to <1 ppm. For example, chloride has been analyzed from 130 to 1900 ppm and Mn^{2+} from 100 ppb to 1.8 ppm. They can vary with processing conditions and locations of manufacturing facilities.

In acidic solutions, equilibrium 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. Depolymerization of silicate species appears to be rapid, because crystalline Na_2SiO_3 and $Na_2H_2SiO_4 \cdot 8H_2O$ yield equivalent distributions of silicate species in water upon dissolution.

Sjrberg and co-workers combined emf and nmr data to develop a model to describe polymerization and protonation of silicate species in sodium silicate solutions (43,44). Thirteen polynuclear species are described. 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 (29).

Polymerization in Solution

Polymerization and depolymerization of silicate anions and their interactions with other ions and complexing agents are of great interest in sol–gel and catalyst manufacture, detergency, oil and gas production, waste management, and limnology (45–50). The complex silanol condensation process may be represented empirically by

$$\text{Si—OH} \overset{K_a}{\rightleftharpoons} \text{Si—O}^- + H^+ \qquad\qquad (3)$$

$$\text{Si—O}^- + \text{HO—Si} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Si—O—Si} + \text{HO}^- \qquad\qquad (4)$$

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 (51). The pK_a value of Si—OH decreases to 6.5 in higher order silicate polymers (52), which is consistent with pK_a values of 6.8 ± 0.2 reported for the surface silanol groups of silica gel (53). 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.

The state of ionization of the silica particle surface controls the rate of polymerization following homogeneous nucleation. The rate of reaction of dissolved silicate at the surface of amorphous SiO_2 is proportional to the density of ionized silanol groups. The degree of surface ionization also influences the value of the surface tension and hence the rate of homogeneous nucleation. Addition of salts to increase ionic strength accelerates homogeneous nucleation and deposition of silicate by increasing the extent of SiOH ionization and decreasing SiO_2 solubility. Incorporation of these concepts into a quantitative theoretical model of homogeneous nucleation accurately predicts the rate of silica particle growth under well-defined laboratory conditions (50).

Silicate polymerization in dilute solutions at pH values up to ca 10 is sensitive to pH and other factors that generally influence colloidal systems, eg, ionic strength, 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.

Extensive research on sol–gel processing of silicic acid esters, eg, tetraethoxysilane (TEOS), $Si(OC_2H_5)_4$, in alcohol–water mixtures has elucidated silica polymerization in nonaqueous solvents (54,55). The relative rates of hydrolysis and condensation depend on the substrate, water, and catalyst (acid or base) concentrations; these rates determine the polymer structure. For example, acid-catalyzed hydrolysis of TEOS at low water concentrations produces linear polymers. These solutions yield fibers upon spinning. Conversely, high H_2O/TEOS ratios favor the formation of highly cross-linked polymers under acidic conditions. Microspherical silica particles form in the presence of ammonia (56). Catalyst and substrate concentrations have similar effects on alkali silicate polymerization in aqueous solution. Silica polymers produced by acid hydrolysis of TEOS and acidification of sodium silicate exhibit a ladder framework structure of three SiO units in width through the linear condensation of oligomers. This solution forms fibers upon unidirectional freezing (48). Numerous investigators have attempted to produce polysiloxane (silicone) fluids by the esterification of alkali and mineral silicates. However, the process yields polymers of insufficient molecular weight for practical utility. If the concentration of SiO_2 is sufficiently high, ca 1 wt %, interparticle aggregation and ultimately network formation (gelation) occur, yielding a continuous structure throughout the medium. The gel structure initially encompasses the entire system and appears to be uniform, but subsequent condensation within the gel causes shrinkage and release of water, ie, syneresis. In more concentrated solutions, network formation occurs to a sufficient extent to produce a gel point at a lower total conversion of low to high molecular weight polymers (57). Therefore, the pH values of the maximum gelation rate of dilute silicates are lower than those for more concentrated solutions, given a constant initial degree of polymerization. Furthermore, a second-order reaction mechanism predicts the pH changes that are observed during polymerization; this prediction is based on the initial pH value of the solution and the acid-dissociation constants of the silanol groups. 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 (29,58). Apparently, the high viscosity of concentrated alkali silicate solutions contributes to the slow approach to equilibrium.

Chemical Activity

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 (59). 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 (60,61). For Cu^{2+}, Fe^{3+}, Cd^{2+}, and Pb^{2+},

$$pK_1^s = 0.09 + 0.62p^*K_1$$

(5)

where K_1^c 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 (62); direct participation by unhydrated ions has also been proposed (61). 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 (63).

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 (64). Thus, 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. 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 (65).

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 vary 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 silicates 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.

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 (66). 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-Al_2O_3 (67). 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 (68). 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 (69). The effectiveness of soluble silica in discharging and recharging the sol surface increases with the modulus of the original sodium silicate solution. 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.

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 to 4.0.

$$pH = 13.4 - 0.69m$$

(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 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 having higher ratios produce more brittle films.

Manufacture and Processing

Soluble silicate glasses are usually manufactured in oil- or gas-fired open-hearth regenerative furnaces. Newer continuous-flow glass melters are equipped with high intensity gas burners or plasmas (70,71). These latter technologies offer significant advantages over the conventional batch-melting processes. Glass composition and shutdown and start-up procedures can be changed rapidly because no large molten glass reservoir is maintained (70). 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, three years is regarded as normal between rebuilds. The liquidus diagrams for sodium silicate glasses and lines of constant melt viscosity are shown in Figure 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 (73,74). 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 (75) and offer the advantage of eliminating contact with products of fuel combustion, eg SO_x, which could affect the glass.
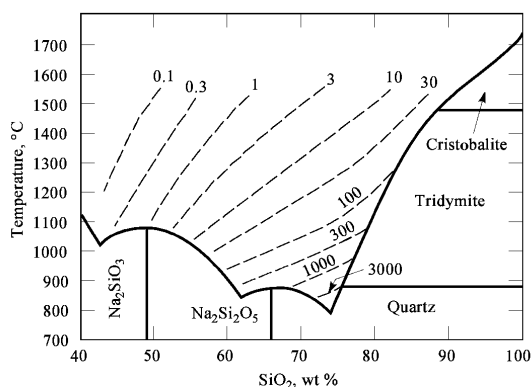
Fig. 3. The viscosity and liquidus curves for molten sodium silicates, where the numbers on the dashed lines are viscosity in Pa·s (1).

Courtesy of The PQ Corp. To convert Pa·s to poise, divide by 10.

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 690 MPa (100 psi). The concentrations and ratios of the solutions are monitored during manufacture using 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 ca 2.65 can be manufactured in an autoclave at ca 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 increases to a point where solid solutions or highly hydrated glasses form. These materials have commercial significance because 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 ca 20% water, are stable enough to be handled commercially. They dissolve with 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.
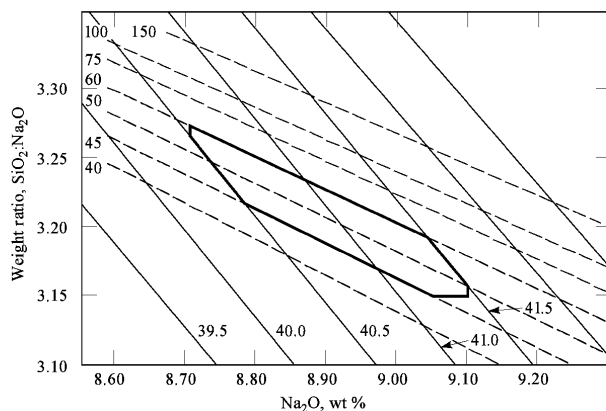

Fig. 4. An alkali–gravity–viscosity (AGV) control chart for a 3.22-weight ratio sodium silicate solution, where (—) and (———) represent lines of constant density and viscosity, respectively. The area enclosed within the emboldened box represents the range of properties for a typical product. Courtesy of The PQ Corp.
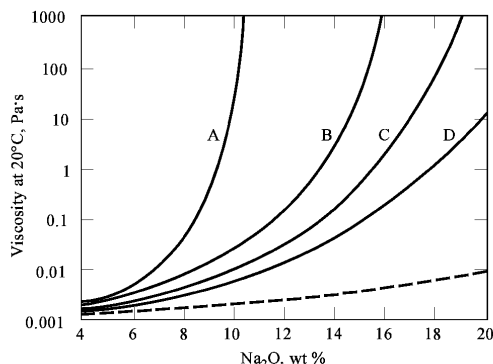
Fig. 5. Viscosities of sodium silicate solutions vs percent solids: A, ratio of 3.22: B, 2.4; C, 2.0; D, 1.6; and (– – –), NaOH. To convert Pa·s to poise, divide by 10.

Courtesy of The PQ Corp.

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

| Silicate, wt % ratio | Particle size, μm (mesh)[b] | Time needed to dissolve, min | | | | | |
| | | at 25°C | | | at 50°C | | |
		50%	75%	100%	50%[c]	75%	100%
3.22 ratio sodium							
anhydrous glass	230 (65)	3600			30[d]		
hydrated[e]	149 (100)	19	45		0.9	1.3	1.7
2.00 ratio sodium							
anhydrous glass	230 (65)	600	4200		17		60
hydrated[e]	149 (100)	0.45	0.90		0.25	0.37	0.48
2.50 ratio potassium, anhydrous glass	230 (65)	60	450	2900	12	45	

[a] Three parts water to one part silicate powder by wt.

[b] Tyler screen.

[c] Unless otherwise noted.

[d] Value corresponds to 15% dissolved.

[e] Has 18.5 wt % H_2O.

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 pentahydrate, is manufactured by preparing a solution of pentahydrate composition at 72.2°C 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 these processes are shown in Figure 6.
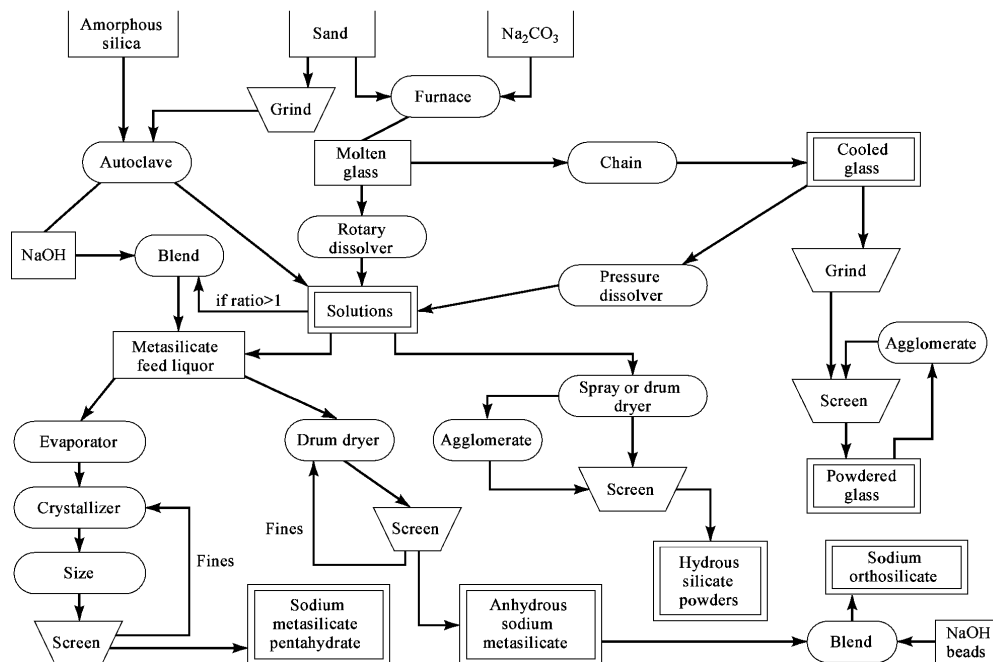

Fig. 6. Manufacturing routes for commercial sodium silicates.

Courtesy of The PQ Corp.

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 ca 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.

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, 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 number
sodium metasilicate	O-S-604D
type I, pentahydrate	
type II, anhydrous	
sodium orthosilicate	P-S-651E
sodium silicate solution	O-S-605D

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[e]	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·s (4×10^7 P).

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

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

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

[f] Value is wt % of M_2O.

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, or carbon-steel tanks with capacities of 45–57 m^3 are recommended for rail cars and not less than 23 m^3 for tank trucks. Powdered silicates are available in 50- or 100-lb (23 or 45-kg) bags, 300 or 350-lb (136 or 159-kg) fiber drums, or 2000-lb (907-kg) semibulk 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 (76). 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.

Regulatory Status

Additives to Food and Potable Water. Sodium silicate is generally recognized as safe (GRAS) by the FDA in fabrics and when exposed to food (77). It is also recognized as a secondary direct food additive when used in boiler water for food-contact steam (78). In addition, it has unpublished GRAS status as a corrosion inhibitor in potable water. The safety of sodium silicate in these and other food-related applications has been extensively reviewed (79). Sodium metasilicate has been affirmed GRAS for washing and lye peeling of fruits, vegetables, and nuts (80); in tripe denuding and hog scaling; and as a corrosion inhibitor in canned and bottled drinking water (81). The use of sodium silicate in canned emergency drinking water at concentrations up to 100 ppm is described in a U.S. federal military specification (82). 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 (83). A specification for sodium silicate appears in the Water Chemicals Codex (84) and the American Waterworks Association Standards (85).

Transportation and Disposal. Only highly alkaline forms of soluble silicates are regulated by the U.S. Department of Transportation (DOT) as hazardous materials for transportation. When discarded, these are classified as hazardous waste under the Resource Conservation and Recovery Act (RCRA). Typical members of this class are sodium silicate solutions having silica-to-alkali ratios of less than 1.6 and sodium silicate powders with ratios of less than 1.0. 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 (86).