Fundamentals of Silicate Chemistry

National Silicates
an affiliate of PQ Corporation

Sodium and potassium silicates are composed of a mix of silicate anions whose composition and handling can have an impact on the performance of the products in which they are used. Knowledge of these anionic species distributions, the properties one can expect from different types of distributions, and the factors affecting distributions can be valuable in developing product and process designs. As the leaders in silicate technology, PQ/National Silicates' characterization methods development contributes to their customers' ability to understand and manipulate silicate product properties, and to improve their own products and processes in which silicates are used in order to be more competitive in their marketplace.

WHAT IS SILICATE SPECIATION?

The fundamental building block of silicate solutions is the tetrahedral silicate anion with a silicon atom at the center of an oxygen cornered four sided pyramid illustrated as the monomer in Figure 1A. Associated with each oxygen atom is typically a hydrogen, sodium or potassium atom, or it may be linked to other silicon atoms through tetrahedral coordination.

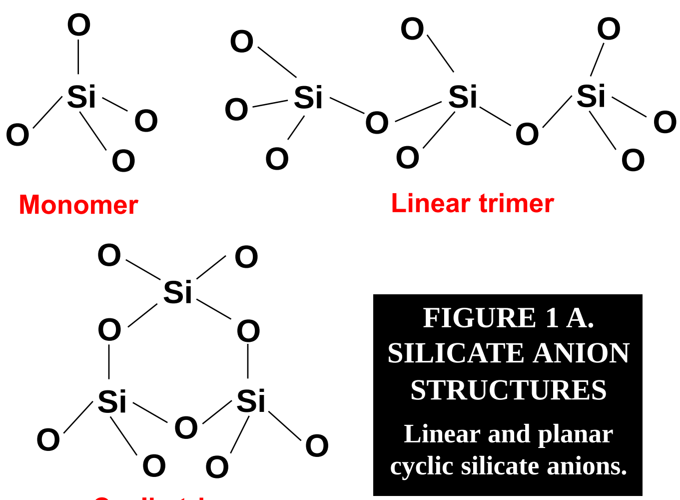


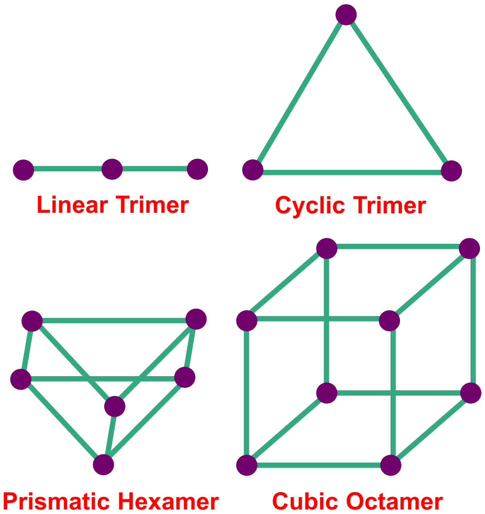
FIGURE 1 A. SILICATE ANION STRUCTURES

Linear and planar cyclic silicate anions.

A shorthand method of representing these silicate products uses the ratio of SiO_2 to Na_2O as follows: $xSiO_2$:M_2O. M is an alkali metal, either sodium (Na) or potassium (K), with x representing the weight ratio of silica to metal oxide. For example, N® brand liquid sodium silicate has a ratio of 3.22 SiO_2 to Na_2O. PQ manufactures liquid sodium silicates with SiO_2:Na_2O ratio as low as 1.6, and anhydrous sodium metasilicate with a ratio of 1.0. Potassium silicates are produced with weight ratios ranging from 1.6 to 2.5 SiO_2:K_2O.

The mix of silicate anions in a soluble silicate solution is much more complex than the simple ratio representation would indicate. The tetrahedral monomers can be linked together through a shared oxygen (hence the SiO_2 representation instead of SiO_4) in two and three dimensional structures. The electrical charges of the anions are balanced by the sodium or potassium cations. Figure 1B shows some examples of the types of anions that can make-up silicate solutions.

FIGURE 1 B. SILICATE ANION STRUCTURES



Linear, planar cyclic and three dimensional silicate anion structures with dots representing silicon atoms. The oxygens linking the silicon atoms lie between the dots but are not shown.

$Silicon^{29}$ nuclear magnetic resonance (NMR) spectroscopy provides a basic shorthand method for characterizing silicate anion mixtures and to help understand how they change under different conditions. It uses the relationship between each silicon atom and its neighbors, counting how many other silicon atoms each is connected to through an oxygen atom.

- Q_0 - the silicon atom is not bonded to any other silicons. This characterizes the silicon in the monomeric silicate anion, SiO_4^{-4}.
- Q_1 - the silicon atom is bonded to one other silicon atom. Examples are the silicons in a two silicon atom chain or at the ends of longer chains.
- Q_2 - the silicon atom is bonded to two other silicon atoms. Examples are the silicon atoms in the middle of a linear anion or forming a planar cyclic structure.
- Q_3 - the silicon atom is bonded to three other silicon atoms. Examples are silicon atoms at the corner of a three dimensional structure.
- Q_4 - the silicon atom is bonded to four other silicon atoms. Examples are silicons in the interior of polymeric colloidal silica or silicon atoms in the interior of silica gel particles.

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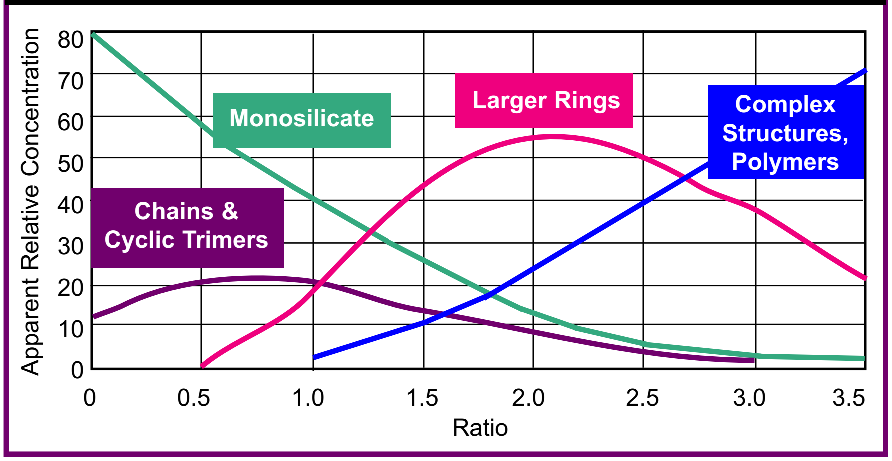
HOW DOES IT VARY?

There are two major factors which influence the distribution of anions — the ratio of silica to alkali, and the concentration of solids.

FIGURE 2. QUALITATIVE INTERPRETATION OF SILICATE ANION STRUCTURE EQUILIBRIA - 1 MOLAR SOLUTION



Moving from high alkali, low ratio products to low alkali, more siliceous high ratio products (left to right in Figure 2) moves through a change in species distribution from high monomer (Q_0) content and low numbers of complex structures (Q_4) to reduced monomer and more complex structures. This change ranges through a rise and fall in content of intermediate chains and cyclic trimers, and larger rings (Q_1, Q_2, & Q_3). Above 2.0, colloidal structures start to form as solids in the solution; at very high ratios these structures produce gelling of the solution.

SILICATE CHEMISTRY IN APPLICATIONS

Just as different ratio silicate products have different anionic species distributions, chemical alterations of an individual silicate product can result in a chemical environment that changes in anionic species distribution. The following changes in chemical environment will shift anionic species distribution. These changes occur at varying rates, depending on various conditions.

● ***Alkali Change*** - Adding alkali to a high ratio silicate to reduce the ratio of SiO_2 to Na_2O or adding colloidal silicate or other silica source to a high ratio silicate to increase ratio will result in a shift in anionic species distribution (respeciate) to the distribution of the new ratio based on the new SiO_2 or Na_2O content. The equilibrium time for this shift depends on the magnitude of the change, the initial concentration of the silicate, the temperature and agitation. A full strength silicate at room temperature with slow stirring will take more than 48 hours to respeciate. Dilute solutions (<1%) could respeciate in minutes.

● ***Dilution*** - Similar to alkali addition to silicate, water addition causes respeciation that is governed by the same concentration, temperature and agitation parameters. It will be less pronounced than the change due to alkali addition.

● ***Other ingredients/contaminants*** - Transition metals such as iron or trivalent elements such as aluminum or boron can incorporate into the structure of silicate anions. There is a threshold level beyond which types of anions do not incorporate; the level varies with the element. An example where aluminum incorporates into the silicate anion is the aluminosilicate gel formed as a precursor in zeolite synthesis. These ions have limited impact on species distribution.

Silicate anions provide cation exchange sites. Within the anion distribution determined by ratio and solids concentration, alkali ions tend to be distributed to a greater degree on the smaller anions. Precipitates or flocculates may form when hardness ions such as calcium or magnesium exchange with alkali cations associated with three dimensional anions found in higher ratio silicates.

MEASUREMENT

As the leaders in silicate technology, PQ Corporation and National Silicates utilize modern chemical characterization methods such as Si^{29} NMR and vibrational spectroscopy, to obtain detailed insight into the complexities of silicate solution chemistry. Armed with this knowledge, PQ/National Silicates are able to:

1. Produce developmental products at silica to alkali ratios above the limits imposed by conventional furnace processes.
2. Improve the performance of their existing product line to enhance customer value.
3. Support customers when they require assistance in the optimal use of liquid silicates in their processes.

PQ/National Silicates would be happy to discuss how any of the characterization methods they have developed can be of use to their customers to improve their products or processes.

CONCLUSION

Commercial silicate solutions are complex distributions of a range of silicate anions that are important for high value users to control for product quality and consistency. Unique among silicate manufacturers, we are advancing silicate technology using fundamental knowledge of silicate solution chemistry to assist customers in using silicates successfully for enhanced product value. We encourage our customers as partners to explore silicate solution chemistry and control for future advances of their own technology.

As part of the PQ Corporation/National Silicates commitment to Continuous Quality Improvement, we apply our discoveries in silicate solution chemistry to our existing product lines. This assures our customers that our products will maintain continuing quality, consistency and value.