

## The Importance of Silicon Nutrition in Soil Systems

*Silicon (Si) is central in numerous biochemical and geochemical subsurface reactions and processes that are instrumental in defining both the physical and chemical properties of soil systems.*

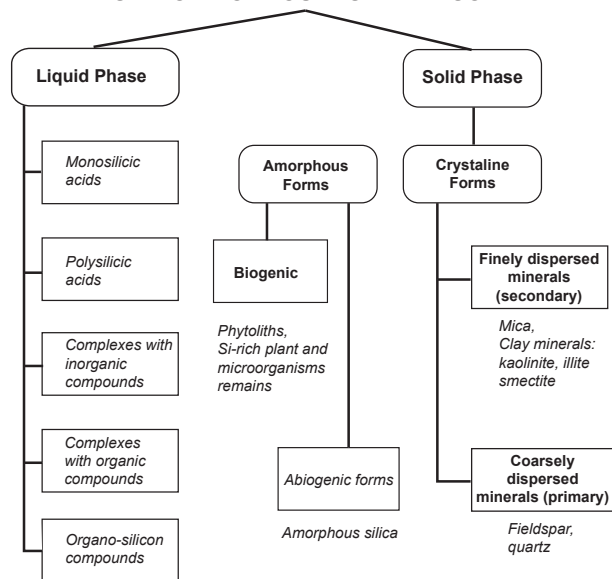
*Application of adequate amounts of silicates available for geochemical reactions have been reported to enhance cation exchange capacity, improved air-to-water ratios, formation of silicate-based compounds that result in improved structure/stability, improved phosphorus availability and the reduction and remediation of metal toxicity in soils.*

Silicon is the second most abundant element in the earth's crust. It can be found in many forms, but silicon compounds in the soil are usually classified with a Liquid Phase or a Solid Phase.

Silicon released into the soil solution from weathering of silicate-containing minerals is slow and is controlled and influenced by:

- Precipitation and the generation of Si mineral constituents
- Adsorption/desorption of silicate species on various solid phases
- Uptake of soluble silicon by vegetation
- **The retention of silicates in the soil profile**

### SILICON COMPOUNDS IN THE SOIL



V. V. Matichenkov and E. A. Bocharnikova 2001

The vast majority of silicon is found in the form of silicon dioxide ( $\text{SiO}_2$ ). This is the inert, solid form of silicon (quartz, Feldspar, mica) that is relatively inactive in soils.

It is the biogeochemically active liquid phase form of Si, such as monosilicic [orthosilicic acid ( $\text{H}_4\text{SiO}_4$ ) and its anion ( $\text{H}_3\text{SiO}_4^-$ )], polysilicic (containing multiple atoms of silicon) acids and organosilicon compounds that play distinctive and significant roles in soil formation processes, regulation of chemical properties in the soil solution and improved phosphorus nutrition.

### Silicon Depletion

It is generally recognized that the largest transfer of available-for-use, biogeochemically active silicon takes place between biomass (biogenic silica from plants and microorganisms) and the soil solution (dissolved Si in the form of monosilicic acid).

Crop residues represent a major source of biogenic silicon replenishment for soil profiles. The solubility of biogenic silica is 17 times higher than quartz ( $\text{SiO}_2$ ) and its contribution to the dynamics of soil and plant available Si is significantly higher than weathering of silicate-containing minerals.

It has become clear that it is this cyclical return of silicate species via plant residues to the soil as liquid and adsorbed phase fractions of Si that is a key source of soil solution Si concentrations. Yet it still takes many years for crop residues to dissolve and contribute as biogeochemical resources.

Centuries of removal of harvested agricultural products containing silicon (current removal rates exceed twice the natural replenishment rates) have resulted in the reduction of critical phyto-genic Si reserves. As a consequence, we now are faced with large areas of the country that has depleted sources of biogeochemically active silicon.

Scientists point out that Si deficits directly translate into a number of negative consequences for soils and plants. Lack of soluble silicon reserves in soil can lead to:

- Degraded soils as a result of the general decline in soil chemical and physical properties (texture, structure, stability)
- Disruption in soil formation processes
- Decreased soil exchange capacity
- Increased Phosphorous fixation
- Higher mobility of heavy metals
- Increased soil acidity
- Decrease in plants' resistance to biotic and abiotic stresses

### Supplemental Sources of Silicon

The use of silicate-containing supplements is now a recognized as essential to replenish Si reserves in Si depleted soils as well as to provide Si benefits to plants grown under artificial or "constructed" substrates such as sand-based golf greens and horticultural "soilless" mixes.

Researchers have confirmed that the application of Si soil amendments has a positive effect on the chemical and physical properties of cultivated substrates.

As reported by Matichenkov & Bocharnikova 1994, the practical implication of Si fertilizers provides the following benefits to soils:

- Promotes restoration of degraded soils and increases soil fertility
- Increases soil resistance to wind and water erosion
- Neutralizes aluminum toxicity in acid soils
- Increases P availability and plant P nutrition
- Reduces P, N and K leaching from cultivated areas
- Restores heavy metal and hydrocarbon-polluted areas
- Increases productivity in soilless mixes

All these effects are caused by the change in soil mineral composition that results from silicate addition (Si fertilizers) and/or formation of new clay minerals, which are characterized by high biogeochemical activity.

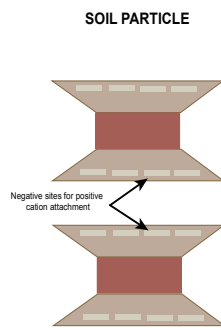
Calcium silicate products are the most commonly applied Si amendments for field application. Stainless steel mill slag by-products are recognized for their rich source of calcium silicate.

To be beneficial as soil amendments/conditioners and sources of silicon for plants, silicon fertilizers must provide a high percentage of silicon in a soluble form. Many states are now requiring that silicon fertilizers provide a statement of percent of soluble silicon on their packaging or label.

Adequate amounts of silicates available for geochemical reactions have been reported to enhance cation exchange capacity, improved air-to-water ratios, formation of silicate-based compounds that result in reduction of metal toxicity, improved soil structure/stability and improved phosphorus availability.

### Silicon and Soil Mineral Characteristics

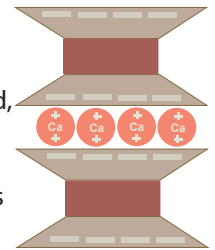
Soil structure refers to the arrangement of soil separates into units called soil aggregates. These aggregates can occur in different patterns, resulting in different soil structures.



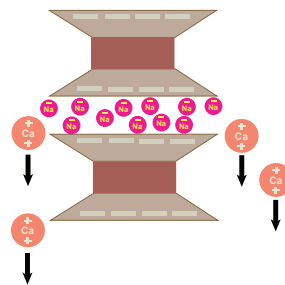
Clay and organic matter particles in the soil carry negative charges of varying strength on their surfaces that act as exchange sites positively charged cations try to attach.

The availability of these cations is related to soil CEC and they are in competition with other cations such as sodium ( $\text{Na}^+$ ) and hydrogen ( $\text{H}^+$ ) for space on soil particle surfaces.

Polyvalent cations like calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ) and aluminum ( $\text{Al}^{3+}$ ) create ionic bond attachment sites that hold together small particles of soil separates (sand, silt and clay) together and also form larger aggregates. Calcium is particularly important inasmuch as it is associated with giving soil its friable, loamy, permeable structure.

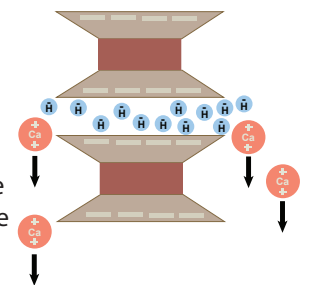


High quantities of monovalent cations like sodium ( $\text{Na}^+$ ) will displace polyvalent cations such as Ca and lead to Ca leaching that can weaken and reverse the process of soil structure formation.

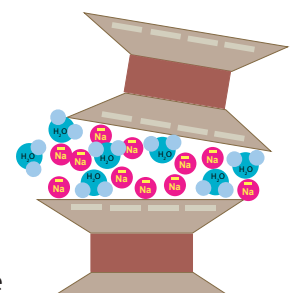


This displacement phenomenon is explained within the definition of cation exchange capacity as the *Law of Mass Action* and *Le Chatelier's principle (The Equilibrium Law)* are applied. Both laws address changes in conditions on a chemical equilibrium as you change concentration. Simply put, large quantities of one cation can displace different cations from soil particle sites.

A similar decrease in Ca cations on soil particle surfaces occurs in acid soils (low pH) where high levels of hydrogen ( $\text{H}^+$ ) can displace Ca. The main problem with high levels of either  $\text{Na}^+$  or  $\text{H}^+$  is not so much one of toxicity, but rather a rapid decline in soil structure and loss of favorable structural properties that result in impaired drainage, increased compaction and loss of stability.



**Sodic Soils.** A soil high in sodium is also known as a "sodic soil," one in which sodium occupies an excess amount of space on soil exchange sites. When sodium levels accumulate beyond the critical level of about 5% of a soil's Base Saturation, a corresponding decline in soluble calcium initiates a collapse



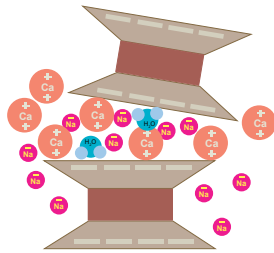
in soil structure, dispersion of soil particles and a decline in permeability. Scientists report that when sodium's base saturation exceed 7-8%, soils experience major problems with drainage and compaction.

**Silicon and Sodic Soils.** When calcium silicate fertilizers are applied to a sodic soil, two important phases occur -- modification and stabilization.

When calcium silicate is applied to soils, it rapidly breaks down to free calcium ions ( $\text{Ca}^{2+}$ ) and monosilicic acid ( $\text{H}_4\text{SiO}_4$ ).

**The soil Modification Process** corresponds to a cation exchange process where the calcium ions ( $\text{Ca}^{2+}$ ) released from calcium silicates in the soil solution migrate to the surface of the soil particles and displace sodium ions (hydrogen ions in acid soils).

This increased the base saturation of calcium and reduces the base saturation of sodium ions (hydrogen ions in acid soils). Improved soil flocculation and agglomeration result from the exchange of these ions. The soil usually become more friable and granular after this phase.



**The soil Stabilization Process** refers to a chemical reaction where in alkaline soils, monosilicic acid combines with calcium hydroxide to form calcium silicate hydrate (CSH). CSH is a gel-like polysilicic polymer compound with unique cementitious characteristics.

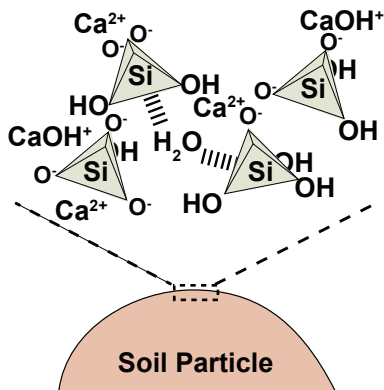


Illustration of CSH gel-like polysilicic polymer formation and attachment to soil particle surface.

In acid soils, monosilicic acid reacts with aluminum hydroxide to form hydroxy-aluminosilicates (HAS) that have similar cementitious characteristics.

The microstructure of untreated compacted expansive clay soils are totally different from the same soil types following treatment with calcium silicate fertilizers. Significant changes in soil microstructure by silicon-treatments has been confirmed using scanning electron microscopy. **Silicon-treated soils exhibit a more granular, open fabric structure with increased inter-aggregate pore size. These new silicate matrix-enhanced soil profiles result in:**

- Improved hydraulic conductivity
- Increased strength
- Enhanced chemical reactivity
- A more stable soil platform

**There is general agreement that silicon is a constructive soil element and that applications of calcium silicate can play a significant role in modifying and improving the surface, mineralogical properties and cation exchange capacity of soils.**

## PHOSPHORUS-SILICON INTERACTIONS IN SOILS

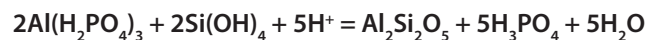
Supplemental applications of fertilizer containing phosphorus (P) beyond levels that may be available naturally are usually required to achieve optimum growth and productivity in agricultural, turfgrass and horticultural enterprises.

Both organic and inorganic forms of P are important sources for plant growth, but their availabilities are controlled by soil characteristics and environmental conditions. Soluble forms of P are absorbed from the soil solution in the form of orthophosphate ( $\text{HPO}_4^{2-}$  or  $\text{H}_2\text{PO}_4^-$ ). The  $\text{H}_2\text{PO}_4^-$  form is dominant in acidic soils ( $\text{pH} < 7.2$ ) and the  $\text{HPO}_4^{2-}$  form is prevalent in alkaline soils ( $\text{pH} > 7.2$ ).

### Phosphorus Fixation

Plant available phosphorus in the soil solution is often limited by phosphorus fixation, a process by which soluble phosphorus is rapidly adsorbed onto inorganic soil constituents and becomes less soluble and less available to plants. Phosphorus fixation can greatly limit plant-available P but it can also contribute to runoff and erosion delivery mechanisms, resulting in elevated nutrient additions to water bodies. This can lead to abnormally high production of algae and aquatic vegetation, depletion of dissolved oxygen content and in some cases, the production of toxins and odors.

Iron (Fe) and aluminum (Al) oxides, commonly found in weathered soils are noted for their P fixing capacities. Fixation occurs as phosphate ions phosphate ions in the soil solution exchange with the hydroxyl groups of the Fe and Al oxides on clay minerals.



Acid soils containing soluble or exchangeable Al also fix P through precipitation reactions in the soil solution.

### Silicate Interactions

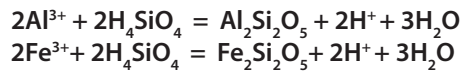
It is highly reported that soluble silicates not only decrease P sorption (one substance holding on to another) capacities of soils but also help to maintain P concentration of soil solutions during P depletion.

**As early as 1936, Tiulin suggested that increased P availability is due to replacement of phosphate anions by silicate ions in the soil colloidal system. Tiulin's work has been repeatedly confirmed by researchers worldwide.**

The overall effect of silicate interaction on P sorption may be explained by:

- **Immobilization and saturation of active Fe and Al hydroxide sorption sites by polysilicic polymers -- effectively precluding P from attaching to these areas of the soil surface.** The silicon-based polymers essentially form a "polymer barrier" that reduces/prevents permanent adsorption of phosphorus onto the soil surface.

- **Inactivation of ionic Fe and Al by the formation of insoluble compounds with silicates.** This is accomplished by simple complexation reactions between monosilicic acid and Fe and Al ions in the soil solution forming insoluble precipitates that can be leached from the rootzone.



- **Phosphorous desorption in the presence of silicon sorption due to P loosely sorbed onto silicate compounds.** A certain amount of P will be adsorbed onto silicon polymers that exist on soil surfaces. However, the bond strength is weak so P remains in plant available form.
- **Inactivation of ionic Fe and Al in the soil solution through the formation of insoluble compounds by monosilicic acid.**

It should be noted that P fixation may not be limited to clay soils. It is suggested coating of Fe and Al oxides/hydroxides can occur on sand grains and may also fix P.

## HEAVY METALS IN SOILS

Heavy metals occur naturally in the soil environment as a result of weathering of parent materials. Soils are also a major sink for heavy metals released into the environment from industrial areas, mine tailing, disposal of wastes, spillage and a number of other sources. **A major problem associated with most metals is that they do not undergo microbial or chemical degradation so their concentration in soils persists for a long time following their introduction.**

The fate and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. The most common heavy metals found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu) and mercury (Hg).

These metals are important in agriculture related industries since they are all capable of decreasing production and introducing toxicity due to their risk of bioaccumulation and biomagnification in the food chain. Moreover, there is also measurable risk of groundwater contamination associated with these metals.

**Heavy metals may exist in soils for years with varying bioavailability, mobility and toxicity.**

### Remediation

Remediation of heavy metals is necessary to reduce associated risk, retain or renew the availability of soils for use and enhance food security. **The overall objective of any soil remediation approach is to create a final solution that is protective of human health and the environment.**

Remediation of heavy metals vary widely and range from isolation to physical separation and extraction. Immobilization technologies that use amendments to accelerate the debilitation of metal mobility and toxicity in soils is a practical approach to metal toxicity in agriculture-related industries.

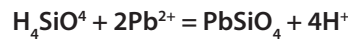
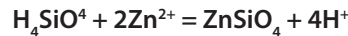
The object of immobilization is to alter the original soil metals to more geochemically stable states. Sorption, precipitation and complexation are common processes for immobilization of heavy metals.

### Silicon Interactions with Metals

The dominant mechanism by which metals are immobilized is by precipitation of hydroxides within a stable and solid soil matrix.

The use of calcium silicate amendments is considered a very viable remediation approach inasmuch as its use satisfies:

1. **Precipitation reactions** needed to inactivate the heavy metal hydroxides.



A second feature of the precipitation reactions is that monosilicic acids form insoluble silicates. During the precipitation reactions, pH increases and the mobility of heavy metals decreases.

2. **Geochemical solidification/stabilization processes** required for long term retention of the metals in the solid soil matrix. Reactions involving incorporation of heavy metals within the polysilicate matrix has some similarities with the formation of CSH and HAS described above.

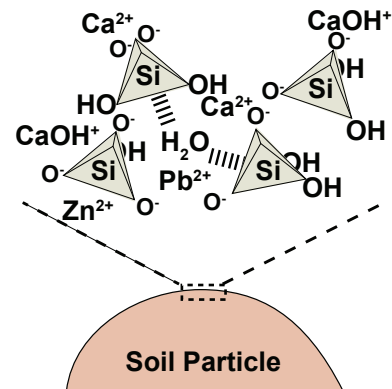


Illustration of heavy metals (Pb and Zn) becoming "entombed" within CSH gel-like polysilicic polymer formation and attachment to soil particle surface.

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