Chapter II

Theoretical Part

2.1 Properties of Natural and Synthetic Silica

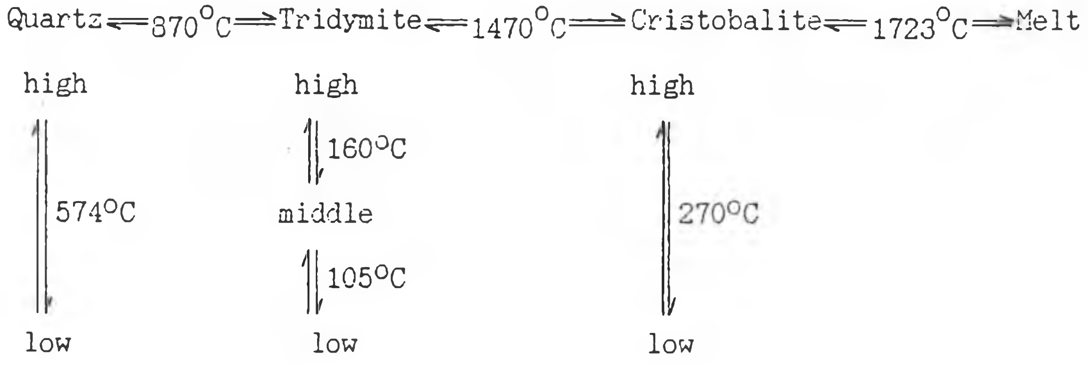
The term silica denotes the compound silicon dioxide. Silicon dioxide is the most common binary compound of silicon and oxygen, the two elements of greatest terrestrial abundance. It constitutes ca. 60 wt. % of the earth´s crust, occurring either alone or combined with other oxides in silicates. It is thus a ubiquitous chemical substance and, owing to its rich chemistry, is of great geological importance. Commercially, it is the source of elemental silicon and is used in large quantities as a constituent of building materials. In its various amorphous forms it is used as a desiccant, adsorbent, reinforcing agent, filler, and catalyst component. It has numerous specialized applications, e.g., piezoeletric crystals, vitreous-silica, optical elements, and glass ware. Silica is a basic material of the glass, ceramic, and refractory industries and an important raw material for the production of soluble silicates, silicon and its alloys, silicon carbide, silicon-based chemicals, and silicones.

Generally, silica can be seperated in 2 types, crystalline and amorphous, which both can be found in nature and synthesized for special uses. Both types have some common properties. At ordinary temperatures, silica is chemically resistant to many common reagents. Common aqueous acids do not attack silica, except for hydrofluoric acid which forms fluorosilicate anions, i.e., SiF_6^{2-} or volatile SiF_4. The rate at which the various forms (low-T modifications) of silica are dissolved by aqueous HF decreases with increasing density, ρ, in the sequence: vitreous silica (ρ = 2.2 g/cm^3) < tridymite (ρ = 2.22 g/cm^3) $\simeq$ cristobalite (ρ = 2.33 g/cm^3) < quartz (ρ = 2.65 g/cm^3). Coesite (ρ = 3.01 g/cm^3) is practically insoluble in aqueous HF. Stishovite (ρ = 4.35 g/cm^3) is even less soluble. Phosphoric acid attacks vitreous silica at elevated temperatures, forming a crystalline silicophosphate. The solubility of silica is greater in dilute than in more concentrated aqueous phosphoric acid. Quartz and vitreous silica are affected only slightly by aqueous alkali at room temperature. The attack is faster at higher temperatures. Precipitated amorphous silica is more reactive than vitreous silica which in turn is more reactive than quartz.

2.1.1 Forms of silica

Crystalline silica. Silica exists in a variety of polymorphic crystalline forms. According to the conventional view of the polymorphism of silica, there are 3 main forms at atmospheric pressure: quartz, stable below ca. 870°C; tridymite, stable from ca. 870-1470°C; and cristobalite, stable from ca. 1470°C to the melting point at ca. 1723°C. In all these forms, the structures are based on [SiO_4] tetrahedra linked in such a way that every oxygen atom is shared between two silicon atoms. The structures, however, are quite different in detail.

At the temperature limits of their stability ranges, these forms interconvert. The transformations involve a change in the secondary (non-nearest-neighbor) coordination and require the breaking and reformation of Si-O bonds. The transformation processes, known as reconstructive polymorphic transformations, are slow, as shown by the fact that the high temperature polymorphs can persist outside their normal stability range. The transformations are aided by or may require the presence of impurities or added mineralizer such as alkali metal oxides. Indeed, it has been suggested that tridymite cannot be formed at all in the absence of impurities, and some modern texts assert that pure SiO_2 occurs in only two forms, i.e., quartz and cristobalite. In addition to the reconstructive transformations, each of the main forms of silica undergoes one or more transformations of a different sort, the so-called high-low, displacive, or martensitic transformations. These involve relatively small structural rearrangements such as minor rotations of the tetrahedra without bond-breaking. In general, they are quick and reversible. The transformation among the principal crystalline forms of silica may thus be represented in simplified form:



The vertical directions represent the quick, displacive polymorphic transitions, whereas the horizontal directions represent the sluggigh reconstructive transitions.

Noncrystalline silica. The noncrystalline forms of silica include bulk vitreous silica and a variety of other amorphous types.

Vitreous silica (silica glass) is essentially a supercooled frozen-in liquid traditionally formed by fusion and subsequent cooling of crystalline silica. It is hardly found in nature except for some exotic species, i.e., fused bodies resulting from lightning striking sand, or Libyan desert glass. Liquid silica is highly viscous, and freezing-in to the glassy form occurs readily at approx. 1100°C. In practice, vitreous silica is prepared by fusion of crystalline quartz or quartz sand. Vitreous silica is also made by flame or plasma hydrolysis of silicon tetrachloride, by thermal decomposition of silicate esters, or by sputtering of SiO_2. Glasses prepared by flame-fusion processes may contain significant amounts (> 1000 ppm) of hydroxyl impurity which affect optical transmission as well as thermal and mechanical properties.

The structure of vitreous silica is a continuous network of $[SiO_4]$ tetrahedra with a lower degree of order than the crystalline phases. The structure itself is subject to many speculations, involving microcrystal theories and a complete random approach. The following is generally accepted: silica glass differs form crystalline silica in having a broader distribution of Si-O-Si bond angles, and a less negative Gibb´s free energy of formation. As to the Gibb´s free energy of formation, ΔG of vitreous silica is -849.05 kJ/mol; ΔG of low-T cristobalite is -849.76 kJ/mol; ΔG of low-T tridymite is -852.18 kJ/mol; ΔG of low-T quartz is -857.08 kJ/mol. This means silica glass and cristobalite are closer to each other thermodynamicly than any other two silica species. From the width of the main broard diffraction peak in the glass diffraction pattern, the "crystallite size" in the case of silica glass was estimated at about 0.8 nm. Since the size of a unit cell of cristobalite is also about 0.8 nm, any crystallites would be only a single unit cell in extent; at such a scale, the terms amorphous and crystalline cease to make sense.

The properties of high quality vitreous silica which determine its uses include high chemical resistance, low coefficient of thermal expansion ($0.5\text{-}0.8 \cdot 10^{-6}\ K^{-1}$), high thermal shock resistance, high electrical resistivity, and high optical transmission, especially in the ultraviolet. Bulk vitreous silica is difficult to work because of the absence of network-modifying ions present in common glass. The traditional melting process requires temperatures of 2000°C and more.

Amorphous silica exists also in a variety of forms which are composed of small particles, possibly aggregated. Commonly encountered products include colloidal silica, silica gels, precipitated silica, and fumed or pyrogenic silica.

Amorphous silicas are characterized by small ultimate particle size and high specific surface area. Their surfaces may be substantially anhydrous or may contain silanol (SiOH) groups. They are frequently viewed as condensation polymers of silicic acid, $Si(OH)_4$.

Colloidal silicas (silica sols) are stable dispersions of amorphous silica particles in water. Commercial products contain silica particles with diameters of ca. 3-100 nm, specific surface area of 50-270 m^2/g, with silica contents of 15-50 wt.%. They contain small amounts ($<$ 1 wt.%) of stabilizers, most commonly sodium ions.

Silica gels contain 3-dimensional networks of aggregated silica particles of colloidal dimension. As formed, the pores are filled with the medium in which the gel is prepared. The medium gives the name to the product, e.g., hydrogel for water, alcogels for alcohols, etc. Simple removal of the liquid results in extensive shrinkage owing to surface-tension forces. Silica gels dried this way are termed xerogels. If the liquid in the pores is replaced by a substance which can be processed in the supercritical range (e.g., certain alcohols, or CO_2) and the gel is heated under pressure above the critical temperature of the liquid, resulting in the disappearance of the liquid-vapor interface, surface-tension effects are absent and a very voluminous dry silica gel (aerogel) is obtained.

Precipitated silicas are powders obtained by coagulation of silica particles from an aqueous medium under the influence of high salt concentrations or other coagulants.

Fumed silicas (aerosils, pyrogenic silica) are produced by vapor-phase processes, generally by the vapor-phase hydrolysis of silicon tetrahalides. Other methods include vaporization of SiO_2, vaporization and oxidation of Si, and high temperature oxidation and hydrolysis of silicon compounds such as silicate esters.

Vaporization: Silica vaporized principally by dissociation to gaseous SiO and O_2; these are the predominant vapor species, with some contribution from atomic oxygen and gaseous SiO_2. The total vapor pressure over the liquid at the melting point is in the range 1-10 Pa (10^{-5} - 10^{-4} bar). The boiling of silica is estimated as $2797 \pm 75^{o}C$. The heat of vaporization of SiO_2 at the melting point is given as 560 kJ/mol, whereas the heat of the reaction

$$SiO_2 \text{ (l)} \longrightarrow SiO + 1/2\ O_2$$

is 750 kJ/mol.

Biogenic silicas are natural amorphous silicas. They occur from small organisms in water (diatom) and in plants cells. Dissolved silica is absorbed by the diatom or plant to form a silica skeleton. Diatomite (silica from diatom structure) is usually used as filler or filter medium. Silica in plant has little industrial application yet.

Opal is a natural amorphous silica with a regular "lattice" arrangement of colloidal silica particles and a substantial amount of incorporated water. There is no utilization in industry. But it is used as jewel because of its beautiful rainbow reflection.

2.1.2 Uses

The diversity of silica forms and their properties lead to a broad range of applications. Silica is the basic raw material of the glass industry. The vitreous silica structure forms the basis of commercial glass compositions, whose properties are modified by the addition of other metal oxides. Silica is a main constituent of ceramics. In space technology, fused silica was used in windows for the Apollo spacecraft and in the thermal protection tiles on the Columbia space-shuttle orbiter.

Quartz: Because of its piezoelectric properties, synthetic quartz is used for frequency control in electrical oscillators and filters, and in electromechanical transducers.

Vitreous silica: Because of its chemical and thermal resistance, vitreous silica is used in laboratory glassware (up to

1000°C), in furnaces and radiant heaters, and as lamp envelops. Silica fibers are used in precision instruments, e.g., balances and thermal-expansion apparatus. Thin films of vitreous silica are applied to dielectric components. The low thermal expansion has made vitreous silica a material of choice for astronomical telescope-mirror blanks.

Amorphous silica: Colloidal silicas are used as binders and stiffeners, for modifying frictional properties of waxes and fibers, modifying adhesion between surfaces, reinforcing polymers, as polishing agents, and as viscosity agents. Silica gels are used to modify adhesives and the viscosity and the thixotropy of liquids, as adsorbents, drying agents, catalyst supports, and for other related purposed.

2.2 Silica in plants

Silica is found in the tissue of many plants. Monocotyledons contain 10-20 times as much SiO_2 as dicotyledons. Silica accumulates steadily through the season in above-ground tissues. Almost all biogenic silica is amorphous. In algae and diatom, silica is tightly endorsed in the organic material and is not exposed directly to the surrounding water. The skeleton is microporous silica that exhibits ion-selective properties. Some plants employ silica for building certain parts of the skeleton structure. In some plants, silica enhances resistance to fungus diseases and in young barley plants, silica appears to protect the plants from receiving injure by freezing. But many plants take up silica though the silica has no apparent useful function. In many plants dissolved silica appears to be taken into the plant merely as an inert component in the water and then is deposited wherever it is concentrated as water evaporates from the leaves.

Plants can take up silica in form of dissolved silica only. In some plants, the deposition of silica is restricted to certain characteristic regions and excluded from other regions. For example, as it is concentrated and converted to its colloidal form, it cannot pass the cell membranes and so remains where it is concentrated. Finally, in some plants the silica must enter into the plant metabolism since it is transported and deposited in very precise forms, as in the case of the hollow stinging needles or nettles.

In grass, silica is excluded from the cells and is deposited essentially as amorphous silica in spaces between cells. The silica is transported and then concentrated and gelled as water evaporates from the leaves. Edges of leaves of sorghum, wheat and corn are most highly silicified, because silica is found most highly concentrated where water is lost most rapidly.

As for rice, heavy deposition of silica is only found in the husk, leaf-blades, leaf-sheath and stems. In these parts, silica tends to localize in the epidermis, and such tendency is again related to transpiration streams. In rice husk, silica deposites in the form silica/cuticle/silica, i.e., forms a silica double layer. The structure of silica in several plants has been shown to consist of a dense gel with pores 1-10 nm diameter full of water. Table 5 shows the typical silica contents in some commercially used monocotyledons.

Tab. 5. Ash and silica contents in diverse parts of different commercial monocotyledons (Sacher and Wien, 1988; Matthes, 1990)

plant	part	ash content in g/kg *)	silica in ash in wt.%	silica content in g/kg *)
rice	husk	200	96	192
	straw	150	82	123
wheat	hulls	ß100	69	69
	leaf sheet	110	91	100
corn	leaf blade	120	64	77
barley	straw	6	54	3
oats	straw	70	47	33
bamboo	nodes **)	20	57	11

*) referred to dry biomass

**) inner part

2.3 Aqueous Chemistry of Silica

An important aspect of silica chemistry concerns the silica-water system. The interaction between silica and water produces many phenomena, which relate to the ways by which silica is precipitated in rice husk, and by which it must be treated during processing. These phenomena are:

- solubility and precipitation
- agglomeration
- polymerization

Solubility and precipitation, follow the general equation:

$$SiO_2 + a \cdot H_2O \overset{K}{\rightleftharpoons} [Si_{aq}] + b \cdot H^+ \quad ;$$

$[Si\ aq]$ is an aqueous species of silicon, e.g., H_3SiO_3. The sign of b depends on the acidity or basicity of solution. K is the solubility constant. For any phases of silica, the solubility constant is given by

$$-RT \ln K = G_{diss} = G[Si_{aq}] - G(SiO_2) - a \cdot G(H_2O) \quad ;$$

$$G(H^+) = 0 \quad \text{as reference state, if} \quad b < 0$$

$$= G(H_2O) - G(OH^-) \quad , \text{if} \quad b > 0.$$

Gibb's free energy of amorphous form is lower (less negative) than for a crystalline form because $G(SiO_2)$ now involves the surface energy term $M \cdot \sigma \cdot \Gamma$ which is always positive; M = molar mass, σ = interface tension solid/water, Γ = specific surface. Thus, G_{diss} becomes more negative, and K becomes larger. So, the tendency of amorphous material to dissolve is higher. Total silica solubility follows the three-step equilibrium:

$$SiO_2 + H_2O \overset{K_1}{\rightleftharpoons} H_2SiO_3 \quad , b = 0$$

$$SiO_2 + H_2O \overset{K_2}{\rightleftharpoons} H^+ + HSiO_3^- \quad , b = 1$$

$$SiO_2 + H_2O \overset{K_3}{\rightleftharpoons} 2H^+ + SiO_3^{2-} \quad , b = 2$$

From thermodynamic calculations, the solubilities of an amorphous silica with $\Gamma = 250\ m^2/g$ and low-T quartz are shown on the next page:

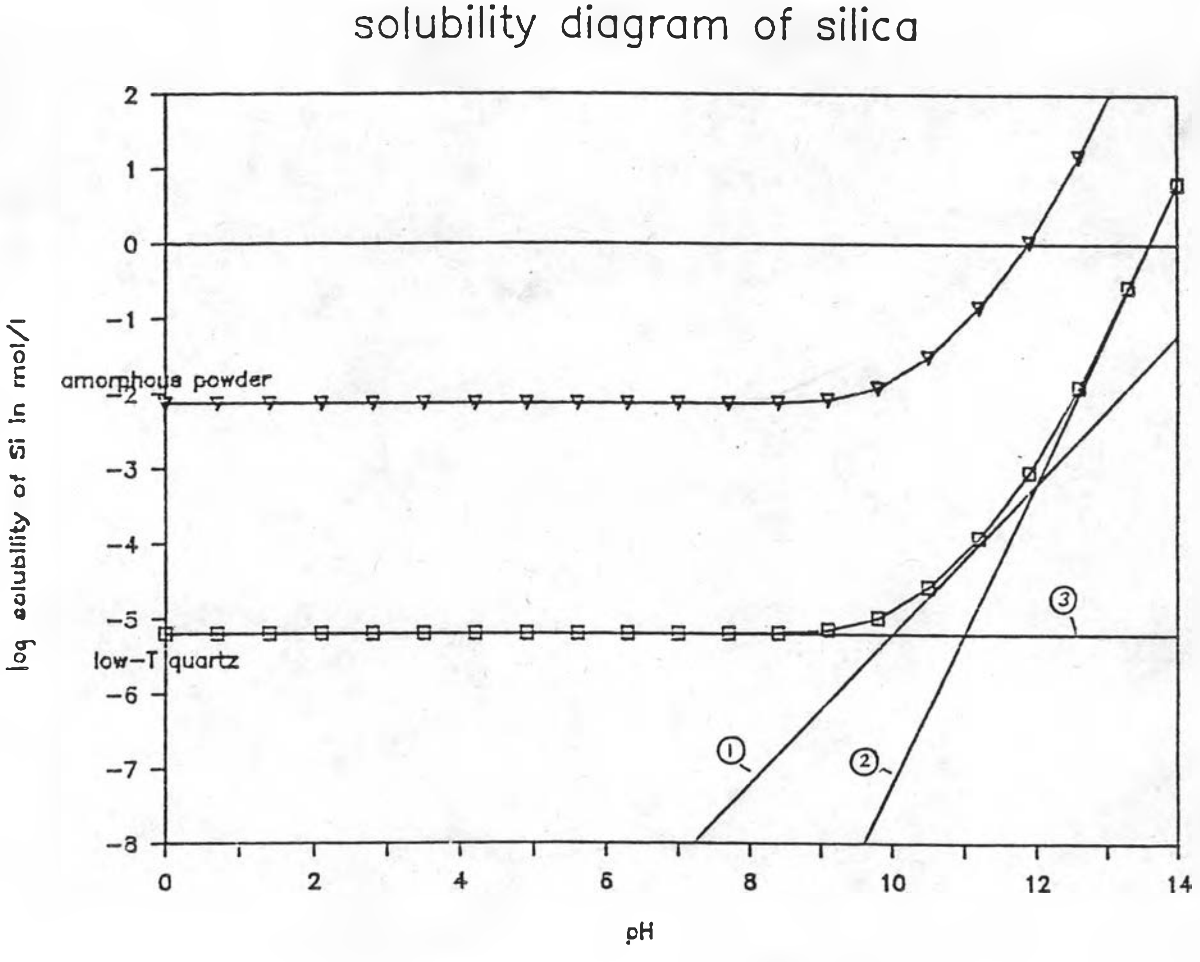


Fig. 3. Solubility diagram of silica for low-T quartz and an amorphous powder with 250 m^2/g specific surface in aqueous solution as a function of pH; species: 1 = $HSiO_3^-$, 2 = SiO_3^{2-}, 3 = H_2SiO_3

This is the answer why the rice husk contains a lot of silica. As low-T quartz (natural silica source) has a very low solubility, water transport in the rice plant takes the soluble form of silica away from the root-soil contact. Higher concentration of silica will be accumulated at the epidermis. By the evaporation of water from the epidermis, amorphous silica slowly deposits from quite high concentrations of dissolved silica.

With the slow evaporation of water, after seeds of colloidal silica particle appear and start to grow, agglomeration of silica particles occurs by means of surface charge forces.

The amount of H^+ effects surface charging and hence agglomeration of the colloidal silica particles as shown below.

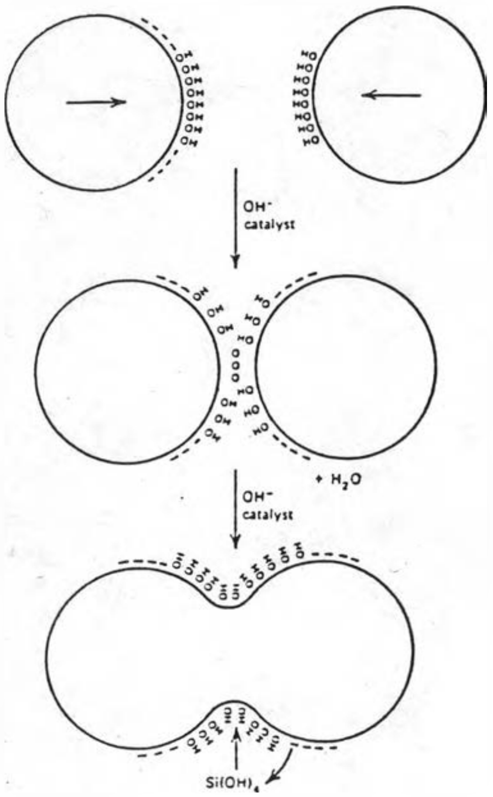


Fig. 4. Agglomeration mechanism of colloidal silica particles, after Iler, 1979

The surface charging at pH $\neq$ 2.2 renders two reactions of agglomeration:

$$\equiv \mathrm{Si\text{-}OH} \rightleftharpoons \equiv \mathrm{Si\text{-}O^-} + \mathrm{H^+} \quad \text{at pH} > 2.2$$

$$\equiv \mathrm{Si\text{-}OH} \rightleftharpoons \equiv \mathrm{Si^+} + \mathrm{H_2O} \quad \text{at pH} < 2.2$$

The pH dependence is shown in figure 5.

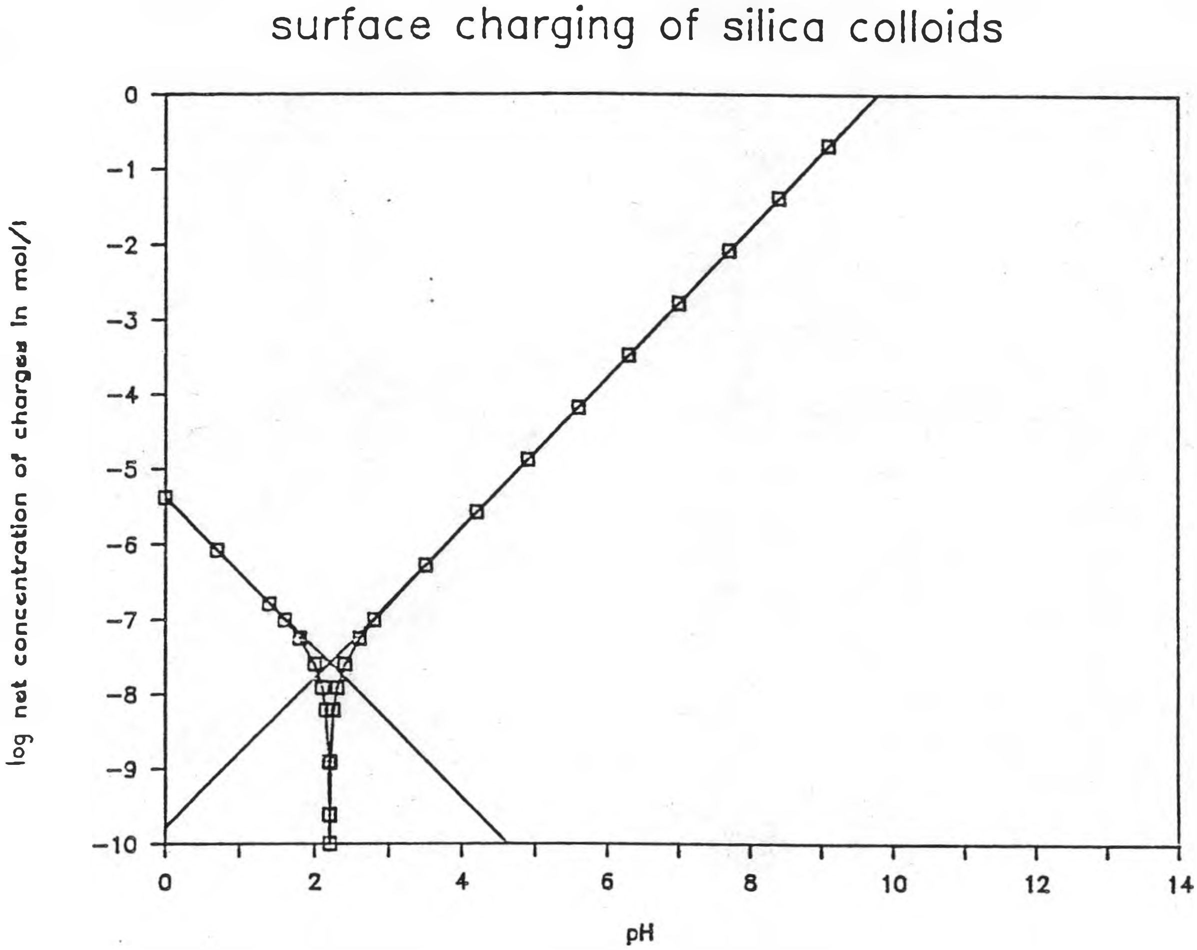


Fig. 5. Effective surface charging of colloidal silica particles in aqueous solutions as a function of pH

Finally, polymerization occurs as the pH-independent forward reaction

$$2\equiv Si-OH \longrightarrow \equiv Si-O-Si\equiv + H_2O$$

competing with either a OH^- or H^+ catalysed (i.e., pH dependent) cleavage reaction for the ≡Si-O-Si≡ bridges.

The pH dependence of polymerization with solubility of amorphous silica and agglomeration are illustrated on figure 6.

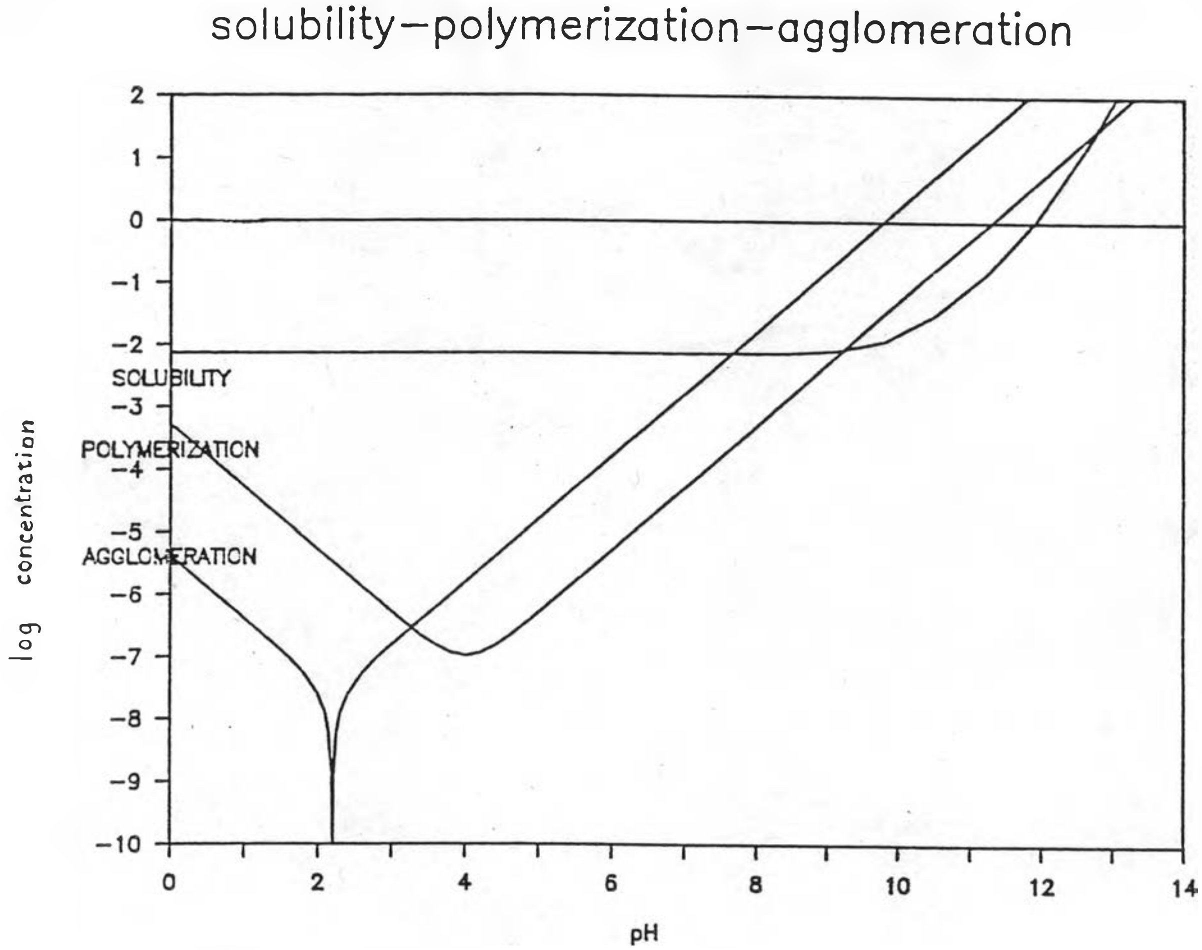


Fig. 6. Synoptic presentation of solubility, surface charging, and polymerization of colloidal silica in aqueous solution as a function of pH

The difference between agglomeration and polymerization can be distinguished: Agglomeration happens by Van der Waals forces in the surface layer of ≡Si-OH and chemisorbed water, while polymerization occurs as a formation of new ≡Si-O-Si≡ bridges. At low pH, solubility is low, Ostwald ripening is significant for particle size < 1 μm only, and polymerization is the predominant step. As a consequence, dissolved silica tends to form extended fractal agglomerates of very small particle size. At moderately high pH, pH < 10, solubility is fairly high already, Ostwald ripening yields increasingly larger colloids, and surface charging enforces agglomeration, however less fractal than at low pH. At very high pH, pH > 10, Ostwald ripening over-rules all other mechanisms yielding large spherical colloids. The presence of univalent ions are able to promote clevage of ≡Si-O-Si≡ bonds, thus promoting polymerization like H^+. The mechanism is not understood in detail yet. The sketch on next page (Iler, 1979) illustrates the above sequence and subsequent mechanisms. Two concurring paths can be seen: Path B occurs at higher pH and in the absence of cations. This results in agglomerates of larger particles or, at high pH, coarse silica sols. The main mechanism is particle size increase by Ostwald ripening as already understood by the solubility diagram. Path A occurs at low pH and/or in the presence of cations. Here, particle agglomeration overrules particle growth, resulting in fine colloidal silica networks not coarsened by Ostwald ripening.

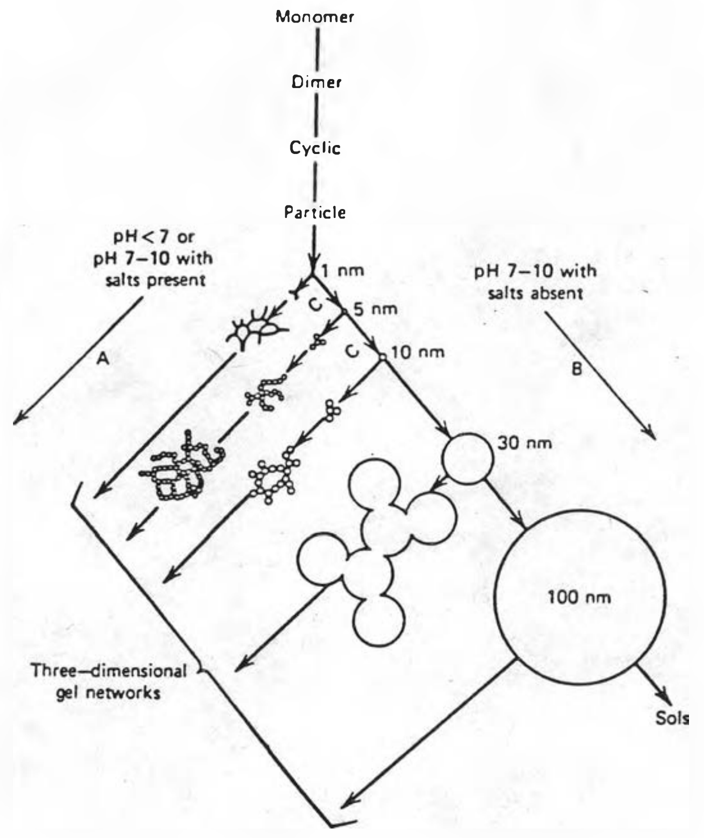


Fig. 7. Structure of amorphous silica; influence of the pH and the presence of salts; after Iler, 1979

2.4 Biochemical Degradation of Organic Matter

Many novel routes of powder preparation in materials science refer to organometallic compounds via chemical processes for the sake of homogenity and sub-micron particle size distribution control. Such technology is very expensive and may not be suitable to promote a basic development of materials science. Rice husk is a ready-prepared precursor of silica by nature. The key question is how to remove the organic matrix without spoiling the properties of the silica. As a support or even alternatively to acid and heat treatment, degradation of organic matter was studied to find the suited method for extracting silica from the organic matrix. Biochemical degradation is very interesting as a "soft" technology and an inexpensive route with low risk of environmental pollution.

Generally, plant cell walls are composed of polysaccharides, proteins, glycoproteins, and phenolic compounds. The most general form of polysaccharides in the plant cell wall is cellulose. Polysaccharide chains were generated from monosaccharide by the action of enzymes in the plant cell. By the enzymatic treatment, organic matter can be re-converted to its primary structure on a molecular scale. The dominant composition in husk are polysaccharides which do not only protect the seed, but also serve as an energy reserve (Brett and Waldron, 1990). Polysaccharides of the cell wall will act upon their degradation as soluble carbohydrates as energy reserves for young seedling during germination. There are many kinds of enzyme in plants. The most interesting group for cell-wall degradation are the endolyases. Their action to break down cell-wall polymers is cleaving polysaccharides.

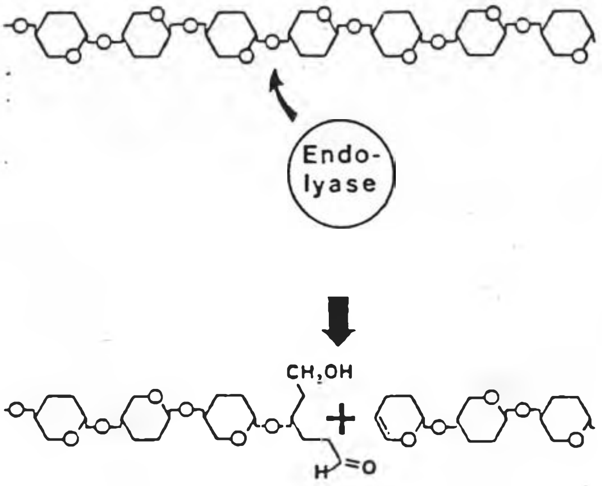


Fig. 8. Sketch of cellulose chain cleavage by the action of an endolyase type enzyme

There are many examples, how these enzymes influence the plants, e.g., shedding of plant parts (leaves, flowers, fruits), wood rot, and the ability of ruminants to digest cellulose. One kind of endolyase is commonly used in industry, which is celluclase (trade name: Celluclast). This material is, however, not extracted from plants, but produced by certain specialized fungus cultures.