CHAPTER II

THEORETICAL AND LITERATURE SURVEY

Natural and Synthesic Silica

Silica is by far the major component of the earth's crust. The term silica denotes the compound silicon dioxide (SiO_2), which is the most common binary compound of silicon and oxygen, the two elements of greatest terrestrial abundance. Commercially, it is the source of elemental silicon and is used in large quantities as a constituent of building materials in concrete, bricks and building stones. Its various amorphous forms are as a desiccant, adsorbent, reinforcing agent, filler and catalyst component. Silica is a basic raw material of commercial glass composition, 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 divided into two types, crystalline and noncrystalline or amorphous silica. Both can be found in nature and synthesized for special uses. Both types have some common properties. Silica melts at a high temperature (1723°C). Silica is chemically resistant to many common reagents. Common aqueous acids have virtually no effect on silica, except hydrofluoric acid, phosphoric acid and aqueous alkaline solutions at elevated temperature [3].

Crystalline silica   Silica exists in a variety of polymorphic crystalline forms. There are 3 main forms at atmospheric pressure. The different forms of quartz, tridymite, and cristobalite are transformed spontaneoustly with temperature so that from the standpoint of solubility there are only three phases to be considered. The quartz is stable below 870°C, tridymite stable from 870 to 1470°C and cristobalite stable from 1470°C to the melting point at 1723°C. In all these forms, the structures are based on $[SiO_4]$ tetrahedral linked in such as way that every oxygen atom is shared between two silicon atoms.

Quartz, the commonest phase found in nature, ranges from huge crystals, to amorphous-looking powders a few microns in size, to shapeless masses of chalecdony agate or flint consisting of densely packed, interlocked microscopic crystals.

Amorphous silica   Amorphous silica may be broadly divided into 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. 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. The structure of vitreous silica is a continuous network of $[SiO_4]$ tetrahedral with a lower degree of order than the crystalline phases. The properties of high quality vitreous silica which determine its uses include high chemical resistance, low coefficient of thermal expansion, high thermal shock resistance, high electrical resistivity, and high poetry transmission, especially in the ultraviolet.

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 silica is characterized by small ultimate particle size and high specific surface area. Their surfaces may be substantially anhydrous or may contain silanol (SiOH) groups.

Colloidal silicas (silica sols) are stable dispersions of amorphous silica particles in water. Commercial products contain silica particles with diameters of 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 rigid 3-dimensional networks of contiguous particles of colloidal silica. As formed, the pores are filled with the medium in which the gel is prepared. Silica gel is formed in a liquid medium, usually aqueous. The medium gives the name to the product, such as hydrogel for water, alcogels for alcohol, etc.

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. In vaporization, silica vaporized by dissociation to gaseous SiO and O_2 (vapor species), with some contribution from atomic oxygen and

gaseous SiO_2. The boiling point of silica is estimated as $2797\pm75^{\circ}C$, The heat of vaporization at melting point is given as 560 kJ/mol and the heat of the reaction is 750 kJ/mol.

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

Biogenic silicas are many types found in widely different kinds of living organisms as isolated particles, skeletal structures, and surface elements. Essentially all biogenic silica is amorphous. It often has a substructure of extremely small particles less than 50Å in diameter which have a surface of SiOH groups. Silica in plants is found in the tissue. Some plants employ silica for building certain parts of the skeletal structure, enhancing resistance to fungus or to protect the plants from injury by freezing etc [4].

The heavy deposition of silica in rice is in the husk, leaf-blades, leaf-sheath and stems. In rice husk, silica is deposited in the form of a silica/cuticle/silica forms a silica double layer. Table 2.1 shown the typical silica contents in some plants [5,6].

As rice husk has a high ash content and a high silica in ash content, greater than other plant, it is an interesting starting material. The composition of rice husk depends on geographical and meteorological factors and agricultural methods. The data may also be influenced by sample preparation and method of analysis. Table 2.2 shows the major components in rice husk.

Table 2.1 Ash and silica contents in diverse parts of different
commercial monocotyledons [5]

Plants	Part	Ash content g/Kg *	Silica in ash wt. %	Silica content g/Kg
rice	husk	200	96	192
	straw	150	82	123
wheat	halls	100	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

Table 2.2 Main organic and inorganic components in rice husk [5]

Components	Typical range (%)
ash content	13-29
cellulose	34-44
lignin	19-47
sugar*	17-26

* D-xylose, L-arabinose, methlyglucoronic acid and D-galactose

Rice husk is used as fuel, animal feed, fertilizer and for the production
of organic chemical products, of activated carbon production, etc.

Rice husk ash

The major inorganic component of rice husk is ash, It varies from 13-29 % of the weight of rice husk. The silica content of the ash is very high, around 94-96 %. The other components of the ash are K_2O, CaO, Fe_2O_5, P_2O_5, SO_3, Na_2O, MgO and Cl (Table 2.3)

The physical characteristics and the chemical reactivity of silica in rice husk ash depends on temperature and soaking time. In an X-ray diffraction pattern of husk ash showed a broad "amorphous" peak around $22.2°$ [7].

The rather wide range of values shown for the elements determined, indicates varying impurities in the samples and the accuracy of the analytical produces used. The data in table 2.4 compares ash composition of different wood ashes and rice husk ash.

Table 2.3 Analysis of rice husk ash (% dry basis) [8]

Constituent	% Weight
SiO_2	86.9-97.3
K_2O	0.58-2.5
Na_2O	0.00-1.75
CaO	0.20-1.50
MgO	0.12-1.96
Fe_2O_3	trace-0.54
P_2O_5	0.20-2.85
SO_3	0.10-1.13
Cl	trace-0.42

Table 2.4 Ash composition of different wood ashes in comparison
to rice husk ash [5]

Plant	SiO$_2$	P$_2$O$_5$	MgO	CaO	Na$_2$O	K$_2$O	Cl$_2$
beach wood	5	6	10	50	6	20	-
birch wood	12	8	14	30	9	23	-
oak bark	3	3	8	37	2	26	-
pine wood	10	9	6	25	9	27	-
spruce wood	2	4	6	30	6	7	43
rice husk	96	-	1.5	1.5	1.5	1.5	-

Some specific impurities may depend of the origin of the rice as well as
the applied fertilizer. The following values are found according to different
sources (Table 2.5)

Table 2.5 Impurities levels (ppm) in rice husks of different origin [5]

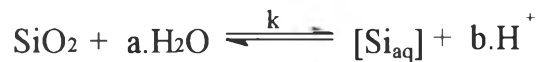| Cation	USA1	USA2	USA3	Japan	Malaysia
Al	200	-	200	-	-
Mn	1500	500	500	200	200
Fe	900	-	-	-	-
Na	400	-	-	-	-
K	-	4000	200	8000	1200
Mg	3000	900	600	200	300
Ca	4000	1000	1000	100	1000

For new materials were prepared from rice husk or rice husk ash, such as
the preparation of silicon carbide, silicon nitride, silicon with solar cell grade
purity or high purity amorphous silica, etc.

Solubility of Silica

Solubility is a basic factor in the behavior of silica. The consideration of interaction between silica and water produces many phenomena. Total silica solubility follow the three-step equilibrium [3]:

$$SiO_2 + H_2O \underset{}{\overset{k_1}{\rightleftharpoons}} H_2SiO_3$$

$$SiO_2 + H_2O \underset{}{\overset{k_2}{\rightleftharpoons}} H^+ + HSiO_3^-$$

$$SiO_2 + H_2O \underset{}{\overset{k_3}{\rightleftharpoons}} 2H^+ + SiO_3^{2-}$$
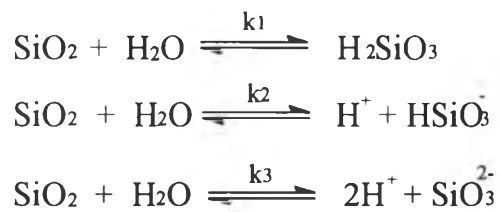
The general equation is

$$SiO_2 + a.H_2O \underset{}{\overset{k}{\rightleftharpoons}} [Si_{aq}] + b.H^+$$

k is the solubility constant which is given by

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

$$G(H^+) = 0 \qquad\qquad , if\ b<0$$

$$= G(H_2O) - G(OH^-) \qquad , if\ b>0$$

The sign of b depends on the acidity or basicity of solution. The Gibb's free energy of the amorphous form is lower than a crystalline form. G_{diss} is more negative and k is larger. Thus amorphous material to dissolve is higher. The solubility of amorphous silica with low-Tquartz are shown on the Figure 2.1.
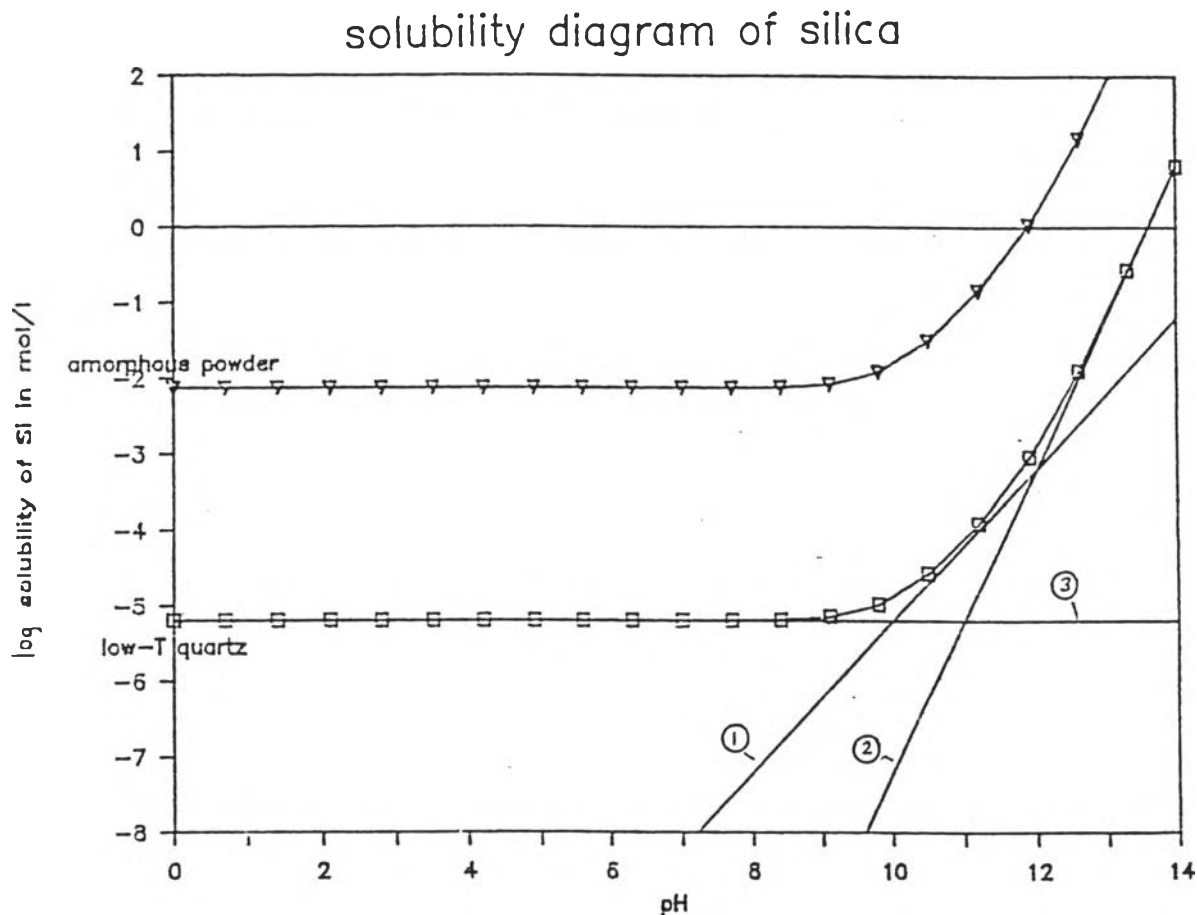
Figure 2.1 Solubility diagram of silica for low-T quartz and an amorphous powder with 250 m^2/g specific surface in aqueous solution as a function of pH; species: 1 = HSiO$_3^-$, 2 = SiO$_3^{2-}$, 3 = H$_2$SiO$_3$

Solubility of Amorphous Silica

Effect of pH   From pH 9 to 10.7, there is an apparent increase in the solubility of amorphous silica, owing to the formation of silicate ion in addition to the monomer.

Alexander, Heston and Iler measured the solubility of a very pure amorphous silica in water at different pH values (adjusted with HCl or NaOH) showed the following variations:

pH	Solubility of Amorphous Silica (25°C) (ppm)
6.8	120
9	138
9.5	180
10	310
10.6	876

Effect of temperature   The solubility of silica at temperatures from 0 to 200°C is shown in Figure 2.2. At 22-100°C the solubility was about 30 % higher than for most powder and gel.
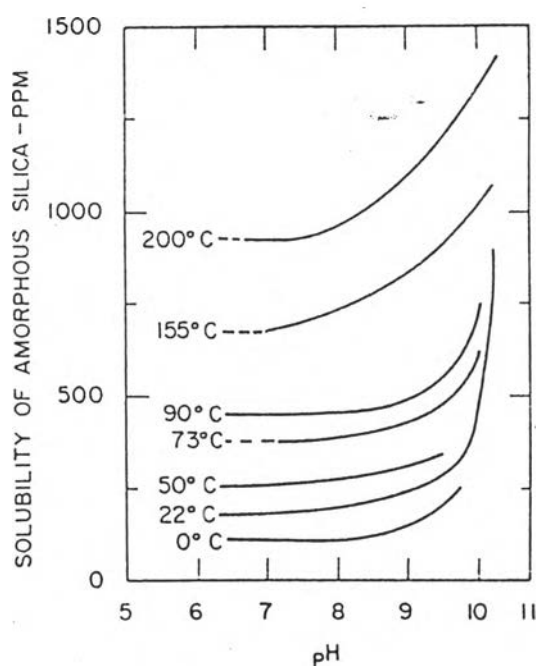

Figure 2.2 Solubility of amorphous silica versus pH
at different temperature

Effect of particle size on solubility   The solubility of silica is higher when the silica surface is convex, and lower when it is concave. It is a matter of the radius of curvature of the surface, the smaller the radius the

greater the effect on solubility. As shown in Figure 2.3 smaller particles with a smaller positives radius of curvature have a higher equilibrium solubility. On the other hand, in a crevice, such as where two particles are in contact, the radius of curvature is negative and the equilibrium solubility is low. Alexander was obtained data that solubility increased with decreasing size that shown as Figure 2.4 [3].
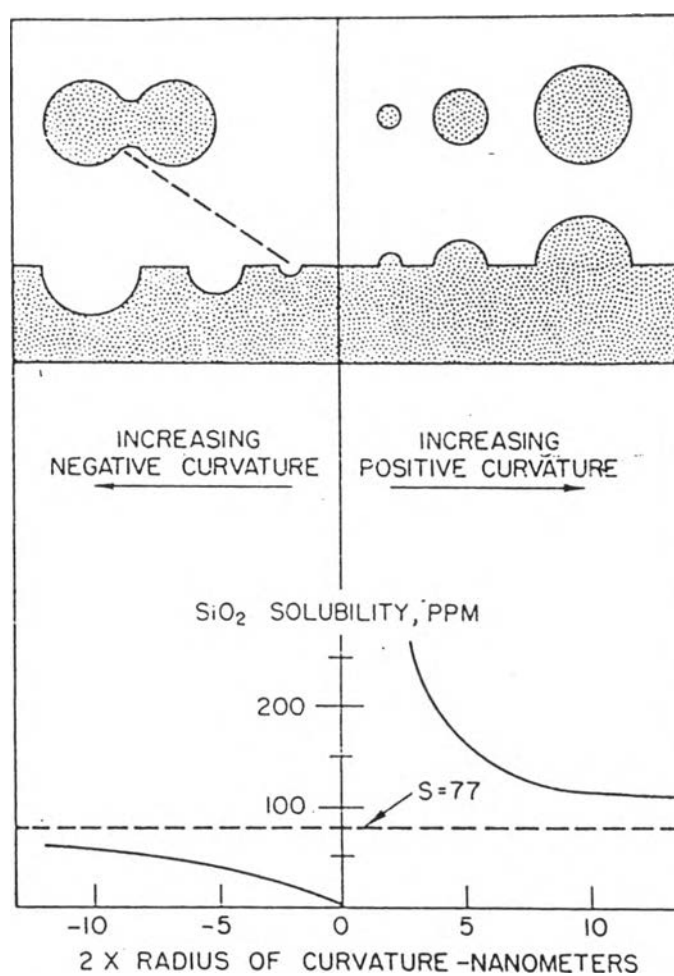

Figure 2.3 Variation in solubility of silica with radius of curvature of surface. The positive radii of curvature are shown is cross-section as particles and projections from a silica surface. Negative radii are shown as depressions or holes in the silica surface, and in the crevice between two particles.
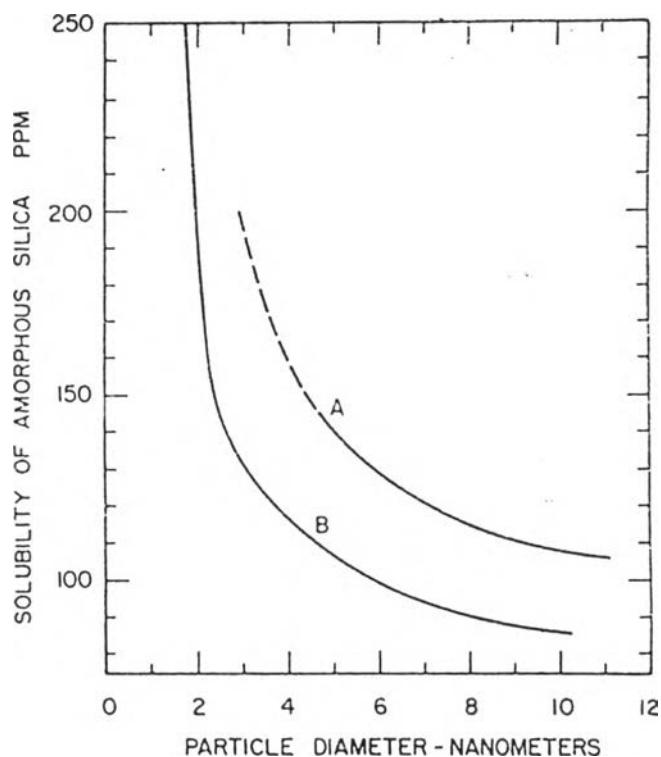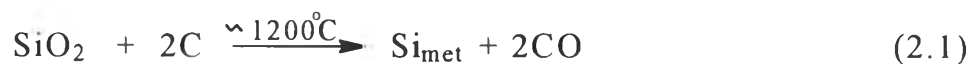
Figure 2.4 Relation between solubility of amorphous silica in eater at 25°C
and particle diameter: A-particles made at 80-100°C at pH 8;
B-particles made at 25-50°C at pH 2.2.

Literature survey

Silicon-based chemicals [9, 10] may be derived from the carbothermal reduction of silica to metallurgical grade silicon (Si_{met})

$$SiO_2 \ + \ 2C \ \xrightarrow{\sim 1200°C} \ Si_{met} + 2CO \qquad (2.1)$$

The silicon metal used to make other products, such as organometallic silicon compounds in the development of new chemical reagents, polymers and ceramics. The first reaction of the Si_{met} is reacted with Cl_2 or HCl to make $SiCl_4$ which is reactant for silicone polymer formation.

$$Si_{met} + 2Cl_2 \longrightarrow SiCl_4 \qquad (2.2)$$

$$Si_{met} + HCl \longrightarrow HSiCl_3 + SiCl_4 \qquad (2.3)$$
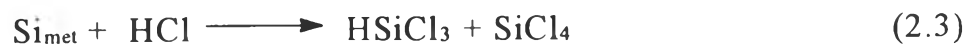
Carbothermal reduction requires high heat and specialized equipment. The result is an energy and equipment intensive process. The reaction of silicon with chlorine or HCl requires specialized, expensive equipment to deal with toxic and corrosive materials.
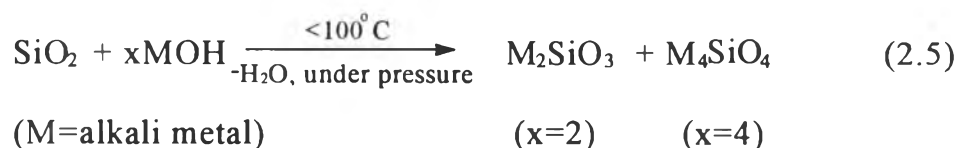
Most silicone polymers derive from the "Direct Process" such as

$$MeCl + Si \xrightarrow{\text{Cu/Zn/250-500}^{\circ}\text{C}} MeSiCl_3 + Me_2SiCl_2 + Me_3SiCl + ..$$
$$(2.4)$$

Me_2SiCl_2 is hydrolyzed and polymerized to give polydimethylsiloxane, the basic silicone polymer.

New synthetic routes to materials are highly desirable, especially if they rely on low-cost SiO_2 and on processing methods that avoid the energy-intensive and equipment-intensive carbothermal reduction step [11,12].

The dissolution of SiO_2 in strong base, gives a wide variety of inorganic silicates.

$$SiO_2 + xMOH \xrightarrow[\text{-H}_2\text{O, under pressure}]{<100^{\circ}\text{C}} M_2SiO_3 + M_4SiO_4 \qquad (2.5)$$

(M=alkali metal)   (x=2)   (x=4)

Kitahara and Asano found that SiO_2 dissolves to a higher amount in anhydrous methanol than in water, as shown in equation (2.6)

$$SiO_2 + 4CH_3OH \xrightarrow[\text{under pressure}]{200^\circ C} Si(OCH_3)_4 + 2H_2O \qquad (2.6)$$
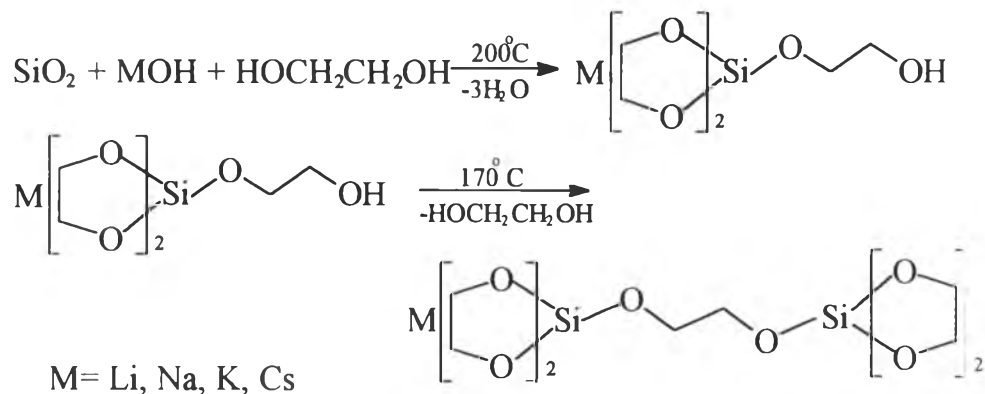
Rosenheim explored the chemical reactivity of the hexacoordinate silicon compound tris(catecholo)silicate, I, readily made by reaction of silica, sand or even quartz with catechol (1,2-dihydroxobenzene) in basic media (in equation (2.7)). Unfortunately, I is quite stable and can only be modified usefully by reaction with strong nucleophiles: [2,13]
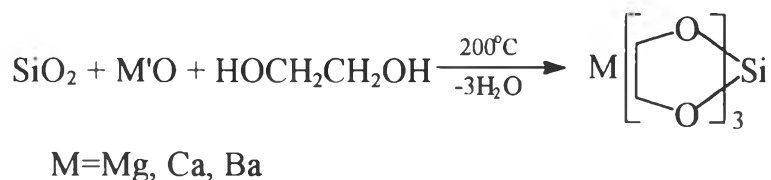

$$(2.7)$$
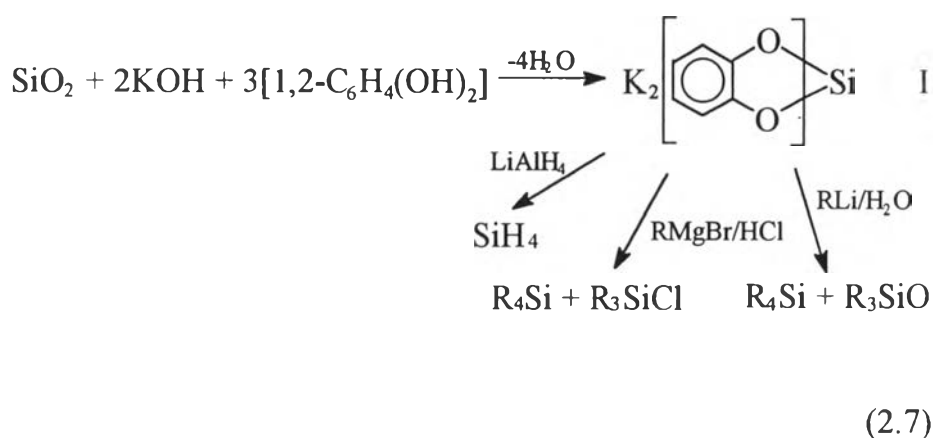
Barnum reported that reaction of catechol with silicic acid or colloidal silica in ammonium hydroxide solution gives large colorless crystals of a silicon-catechol complex that contains ammonia of crystallization $(NH_4)_2[Si(C_6H_4O_2)_3].H_2O$ [14,15].

In 1991, Laine [2,10] described the synthesis of pentacoordinate anionic and hexacoordinate dianionic silicate complexes by direct reaction of SiO_2 with equivalent amounts of either group I metal hydroxides or group II metal oxides in excess ethylene glycol as shown in equation (2.8) and (2.9).
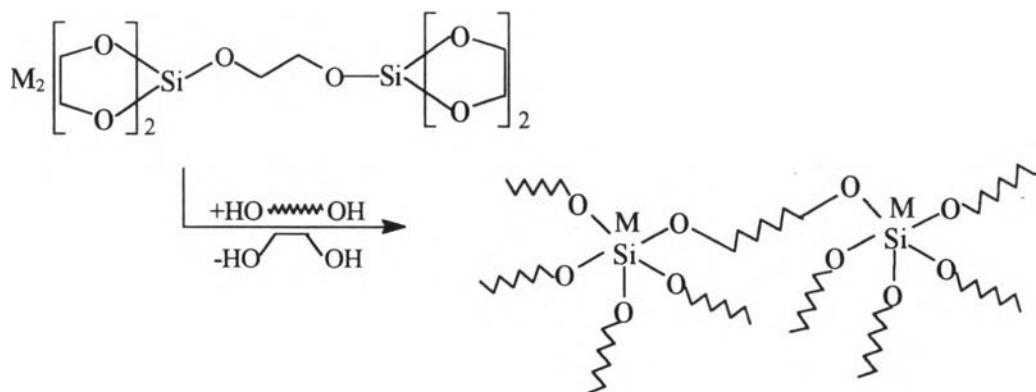
$$SiO_2 + MOH + HOCH_2CH_2OH \xrightarrow[-3H_2O]{200^\circ C} M\left[\underset{O}{\overset{O}{\Big\langle}}Si\right]_2 O \frown OH$$

M= Li, Na, K, Cs

(2.8)

$$SiO_2 + M'O + HOCH_2CH_2OH \xrightarrow[-3H_2O]{200^\circ C} M\left[\underset{O}{\overset{O}{\Big\langle}}Si\right]_3$$

M=Mg, Ca, Ba

(2.9)

These compounds provide facile access to novel materials ranging from ion conducting and liquid crystalline polymers, to compounds exhibiting novel charge transfer behavior to ceramic precursors. (equation (2.10))


(2.10)

The basic concept extends from Frye's observations [16,17] that spirosilicate reacted in MeOH with amine bases (e.g. Et₃N) at ambient temperature to form pentacoordinate, anionic silicates with ammonium counterions. These species were not stable above ≈ 100°C, reverting to the tetracoordinate spirosilicate as shown in equation 2.11.
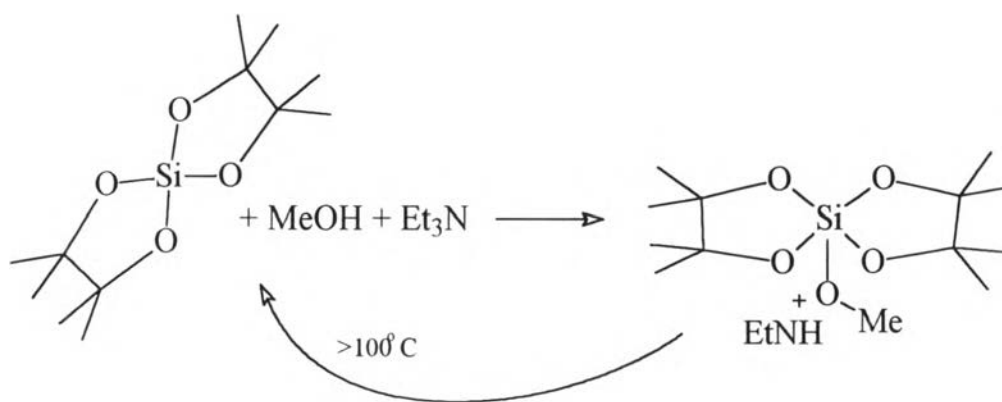

$$(2.11)$$

In related work, even silicic acid was observed to dissolve in excess triethanolamine (TEA) at temperatures of 200-250°C.

$$SiO_2 + TEA \xrightarrow{\Delta} (HOCH_2CH_2)_nN[CH_2CH_2OSi(OCH_2CH_2)_3N]_{3-n} + 2H_2O$$
(excess)

$$(2.12)$$
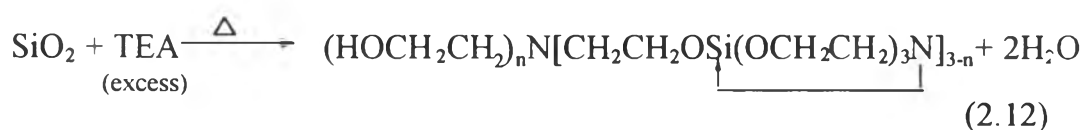
This structure is a silatrane complex which is a pentacoordinate silicon derivative formed from the reaction of trialkanolamines, such as TEA with trifunctional silicon substrates (RSi(OMe)₃) to yield highly crystalline, monomeric silanes.

Silatrane [8, 18-20] complexes have been known for more than 30 years. In 1960, Finestone prepared $C_6H_5Si(OCH_2CH_2)N$ (melting points 208-209°C)

and $CH_3CH_2OSi(OCH_2CH_2)_3N$ (melting points 100-102°C) which were the first silatrane complexes. He suggested the existence of transannular dative bonding between the nitrogen and silicon atoms. In 1961, Frye, Vogel and Hall found 1-substituted silatranes (Z= H, CH_3, C_2H_5, $C_{10}H_{19}O$, etc.). Voronkov called these compound silatranes [18].
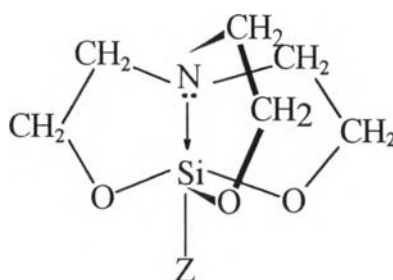
Silatrane Complex

In 1995, Laine [21] used higher boiling amine (bp.> 200°C) bases as a catalyst and reactants, in place of group I or II hydroxides or oxides. This invention provided neutral and mixed neutral/anionic polymetallooxanes of varying molecular weights so as to be classifiable as monomers, oligomers and polymer.

This invention relates to polymetallooxane comprising the moiety:
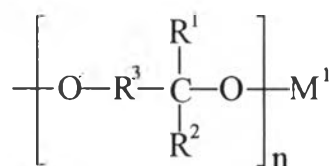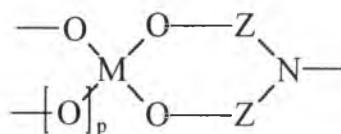

wherein

n is 1.5, 2, 3, 4, 5, or 6;

M^1 is selected from the group consisting of Si, Ge, Sn, Al, Ga Ti, Zr, or Hf;

R^1 and R^2 are selected from the group consisting of H, OH, C_{1-8} alkyl C_{1-8} hydroxyalkyl, C_{1-8} thioalykyl or combinations thereof;

O' is bond to M^1 another M^1 atom, M^2 or H, wherein M^2 is a group I or II metal of the Periodic Table;

R^3 is independently selected from the group consisting $(CR_2)_y$, $(CR_2CR_2)_yN(CR_2)_y$ and combination thereof, wherein R selected from the group consisting of H, OH, C_{1-8} alkyl, C_{1-6} alkoxy and combination thereof and where y is number from 1 to 10.

The polymetallooxane composition of structure above, further comprising the heterocyclic moiety:
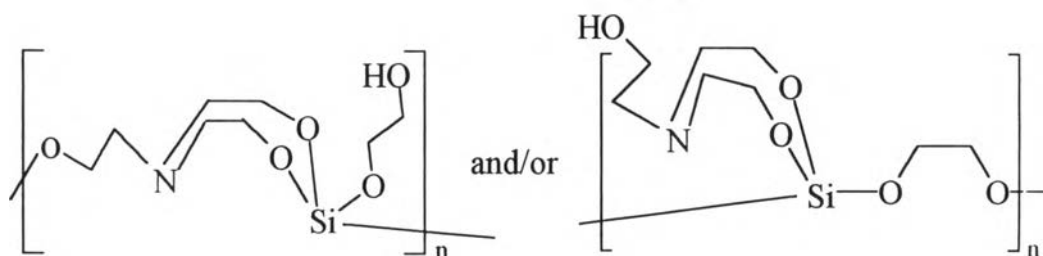

wherein

M is Al or Ga, p is 0 and M is Si, Ge or Sn, p is 1

Z is the residue of an amine reactant.

Example:

$$SiO_2 + N(CH_2CH_2OH)_3 + HOCH_2CH_2OH \xrightarrow[-HOCH_2CH_2OH]{heat}$$

(2.13)

Thus this present study was intended to provide synthetic polysiloxane from rice husk or pure silica with amine in ethylene glycol by a one step reaction and characterize the structure of the products. A still further object of the present mode is to provide a method of making ceramic material, preceramic materials, ceramic fibers or coatings.