I. GENERAL INTRODUCTION

1.1. History

Enormous deposits of sandstone, clay, minerals, and sand of the sea shore contain silica and silicates. Mankind utilise these deposits in innumerable ways and forms for the advancement of science and culture. Cements, bricks, glasses, various types of synthetic silicates etc. are some of the important products prepared from silica and silicates. Most of the natural deposits are found in crystalline forms. Work on the structure of crystalline silicates, phase equilibria study of silica and other oxides of crystalline nature have been carried out by outstanding scientists. However, the science of finely subdivided form of silica and silicates that is, the Colloid Chemistry of silica and silicates has been developed only in the last two decades. Historically, the colloid chemistry of silica and silicates was initiated in 1864, when Thomas Graham published some work on properties of silicic acid, silica gel and other colloidal substances. Since then, the chemistry of siliceous matter came to near standstill for the rest of century and for the first decade of the present one. After this period, some scattered work on the observations of the preparation of hydrosol, hydrogel, hydrated compounds of alkali silicates, alkaline earth silicates and silicic acid was published. At this time silicates were looked upon as compounds of hypothetical silicic acids and attempts were made to demonstrate the
existence of these silicic acids by studying the hydrated silica obtained from different silicates on treating them with acids. This study could not reveal the facts about silicates. Theories then developed pertaining to the origin of clay minerals, considered as silicious matter, acceptable to geologists and minerologists. These theories, known as "residual clay" and "transportable clay" were developed on the assumption of the formation of clay or colloidal mineral as a result of surface weathering of rocks due to solutions containing water. Further work then developed on the phenomena of hydration, condensation and polymerisation. These simultaneous reactions were considered responsible for combination of tetrahedral silicon oxygen groups from colloidal point of view. From structural point of view, simple hydrous silicates are substances in which four oxygen atoms which surround a silicon atom are not bounded to another silicon atom. Therefore, each oxygen atom retains a net negative charge expressed structurally

\[
\bar{O} - Si - \bar{O} \quad (1)
\]

as in (1). The constitution of sodium silicate was not possible to explain from the consideration of such separate silicon-oxygen tetrahedral structure. It was thought that in sodium silicate, tetrahedra are linked in an endless disordered rows.
1.2 Sodium silicate

The behaviour of sodium silicates of composition $\text{Na}_2\text{O}:\text{SiO}_2$, ranging from mols 1:1 to 1:4 brings about all possible complications not only in the formation of various types of colloidal silica and silicates but also in the development of the theoretical aspects of the subject. R.W. Harman carried out systematic investigations on the aqueous system of sodium silicates by examining important physical properties like conductivity, transport number etc. and concluded that the proportion of colloidal silica increases as the ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ increases.¹

R.C. Ray, P.B. Ganguly and A.B. Lal concluded from the diffusion study of solutions of sodium silicate of varying compositions that sodium silicate solutions represent mixtures of sodium silicate ($\text{Na}_2\text{SiO}_3$) mixed with or loosely combined with non diffusible colloidal silica. It is stated that $\text{Na}_2\text{O}:\text{SiO}_2$ 1:1 mol is admixed with hydrated silica in molecular proportions in such a way as to form loose combinations, attaining $\text{Na}_2\text{O}:\text{SiO}_2$ ratios 1:2, 1:3 etc. Accordingly, different sodium silicate solutions of commerce are nothing but the silicate $\text{Na}_2\text{H}_2\text{SiO}_4$ ($\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$) mixed with 1, 2 or 3 molecules of hydrated colloidal silica, the unit structure of which is $\text{SiO}_2\cdot\text{H}_2\text{O}$. On this basis any intermediate fractional ratio becomes possible by simple variation of the amount of colloidal silica.²
C.W.Lentz, using organic silicon compound trimethylsilyl (hexa methyl disiloxane) prepared specific trimethyl silyl silicates having the same silicate structure as the mineral from which silicate derived. Products were examined with modern gas chromatographic techniques to elucidate the structure of mineral silicates. On the same principle, structure analysis of sodium silicate solutions of compositions ranging from 1:0.5 to 1:3.3 \( \text{Na}_2\text{O}:\text{SiO}_2 \) was made and it was concluded that these solutions contain \( \text{SiO}_4 \), \( \text{Si}_2\text{O}_7 \) and polysilicates and sodium silicates appeared to be equilibrium solutions of different types of silicates according to the different concentration of the solutions. P.C.Carman in his work on 'Constitution of colloidal silica' suggested that, structurally crystalline silicates and colloidal silicates can be explained on the similar principles except that the silica tetrahedra are linked to produce random three dimensional net work like silica gel. For silica sol, it is mentioned that silicic acid sol does not represent a system in equilibrium and there is constant tendency for an irreversible interaction of \( \text{OH} \) groups, splitting off water and forming siloxane linkages (equation 2).

\[
-\text{Si}-\text{OH} + \text{H}_2\text{O} -\text{Si} - \rightarrow -\text{Si}-\text{O}-\text{Si} - + \text{H}_2\text{O}
\] (2)
In this way $\text{Si(OH)}_4$ molecules condense to form particles of colloidal dimensions (equation 3).

$$n \text{Si(OH)}_4 = (\text{SiO}_2)_n + 2n \text{H}_2\text{O}$$

The equation (3) indicates that the polymerization involves the condensation of silanol ($\text{SiOH}$) groups to form siloxane ($\text{Si-O-Si}$) bonds. In order to explain the mechanism of formation of siloxane bonds, Tradwell and Wieland pointed out a fact while describing their hypothesis that tetravalent silicon remains unsaturated with respect to coordination number four\textsuperscript{11}. Clarifying this fact, W.A. Weyl revived this hypothesis and put forward the view that silicon has the coordination number six in fluosilicates even though it has coordination number four in other silicates\textsuperscript{12}. As hydroxyl ion ($\text{OH}^-$) has great similarity with fluoride ion ($\text{F}^-$), silicon ion ($\text{Si}^{+4}$) has also coordination number six with respect to oxygen in the form of hydroxyl group. This theory explains the polymerisation mechanism as shown in equation (4), which

$$2\text{H}_2\text{O} - \text{Si} - \text{OH} = \text{Si} - \text{O} - \text{Si} + 2\text{H}_2\text{O}$$

shows that when silicon cation ($\text{Si}^{+4}$) is screened by six hydroxyl anions ($\text{OH}^-$) reaction is completed. In other words, to complete the reaction to acquire stability, hydroxyl anions
adjust their electron distribution by six co-ordination number with respect to one silicon cation. Visualising this conception, W.A. Weyl and Hauser approached to the problem entirely in new way by bringing into consideration the role of forces on the surface, surface composition and surface configuration of silicates and described the atomic arrangement on silicate glasses, and colloidal silicates in terms of forces. They further pointed out that in the field of such substances attention must be paid to surface of colloidal substance. This theory holds for every substance characterised by its colloidal properties, because colloidal science deals with the science of surfaces. Therefore, in colloidal chemical approach, attempts are made to explain properties and phenomena which may not clearly be understood only from the consideration of structure of the products as in such cases surfaces of the products are equally important from properties and phenomena points of view.

1.3 Colloidal silica and silicates

Taking into consideration this important aspect of the surface property of compounds, R.K. Iler defined colloidal silica and silicate of finely sub-divided form as 'any water insoluble inorganic silica or silicate, either amorphous or crystalline, having a specific surface area greater than about 25 m²/g.' However it has been pointed out that this
definition also includes higher porous silica or silicates having mechanically strong, non-dispersible structures like zeolites. Porevolume, porediameter, poresize distribution, absorption, active centers closely associated with the phenomenon of adsorption, ion exchange capacity etc. are also equally important in evaluation and in co-relation of various products, particularly of the same chemical composition. Clays and minerals of similar chemical compositions have been studied and colloid chemistry of these natural colloidal silicates has been comprehensively reviewed by Marshall & Grim. Research work on synthetic colloidal silicates has been carried out in connection with the study of artificial zeolities, fertility of soils, the production of ceramics, the drilling of oil wells, the manufacture of catalysts for the petroleum industry, and the manufacture of many industrial products such as rubber, paper, building materials and cements. As in this present thesis, investigations are on the noncement hydrated calcium silicates (HCS), so consideration is limited primarily to the system CaO + SiO₂ + H₂O. (5)

1.4 Lime-silica-water system

Structurally important compound of the system CaO + SiO₂ + H₂O is called tobermorite from the name of place -TOBERMORY- in Scotland where it was discovered by Heddle in 1893. In cement chemistry, tobermorite is referred to
in the crystalline as well as in ill-crystalline or amorphous forms. Structures of natural crystalline HCS as wollastonite, xonotlite etc. have been investigated by X-ray diffraction study, but the products of the system \((\text{CaO} + \text{SiO}_2 + \text{H}_2\text{O})\) prepared at temperature below 100°C have shown disconcerting results. This led to uncertain interpretations mainly because the hydrous lime-silica products are gelatinous colloids and with change in the concentration of calcium oxide in solution, the ratio \(\text{CaO} : \text{SiO}_2\) for the solid phase continually alters. Detailed study of this behaviour of the system \(\text{CaO} + \text{SiO}_2 + \text{H}_2\text{O}\) confused the investigators and variety of results and opinions appeared in the literature till 1930\(^\text{17}\). However, two assumptions mainly discussed were: i) pronounced adsorption of lime on silica in presence of water in HCS formation and ii) formation of some solid solution of HCS below 100°C.

In the past, these assumptions were supported on the belief that at temperature below 100°C or particularly at room temperature any actual chemical combination of lime with silica does not take place\(^\text{18}\). Evidences for the chemical combinations of silica with at least part of the lime were fully established in detail and from some of the following listed experimental results, it now seems practically concluded that the chemical combination of silica with lime takes place at room temperature and below 100°C.
Lime acts on silica gel or silica sol with destruction of original structure of gel or sol and this reaction is much more rapid at 100 °C than at 30 °C. Kolthoff and Stenger, from the study of comparative action of lime and alkali on sol, showed that insoluble calcium silicate is formed indicated by comparatively very high adsorption of lime than alkali.

Maffei analysed data obtained from adsorption study and showed that the constants of the Freundlich and Langmuir adsorption isotherms vary in such manner which suggests that calcium oxide is first adsorbed by silica gel and then reacts chemically.

Study of the reactions of calcium oxide and silica, obtained from various compounds have been carried out in detail and results have been presented by typical graphical method where it has been indicated that the compound CaO·SiO₂·H₂O is formed at temperature below 100 °C due to chemical reaction.

Preparation of HCS by double decomposition reaction of calcium chloride or nitrate solution and sodium metasilicate also suggests chemical reaction. Measurement of heat of solution by Cirilli for the reaction of freshly precipitated silica and lime water interaction gave large enough value to suggest chemical reaction. Also, the silica in solution decreases markedly with increase in lime concentration consistent qualitatively with maintenance of a solubility product for calcium silicate. Under electron
radiation, an electron diffraction spectrum soon appears and examination by X-ray gives a diffraction spectrum that is apparently the same as one produced by microscopically crystalline hydrated calcium silicate \textsuperscript{24,25}.

To summarise, apparently one or more HCS are formed at low lime concentrations and at temperature below 100°C. One of these compounds is probably CaO·SiO\textsubscript{2}·H\textsubscript{2}O whether there are others, and what their composition may be, are matters that seemed to be less well established till 1947.

1.5 Hydrated calcium silicate

Later on, with the rapid development of the portland cement industry the chemistry of hydrated calcium silicates (HCS) was examined extensively, primarily in an attempt to understand the setting of hydraulic cements. Hydration reactions play important role in setting of portland cements as a result of which HCS of crystalline or illcrystalline nature are formed at room temperature. Fundamental difficulties in understanding the behaviour of such reactions and reasons for greater complexity of HCS system lies in the fact that calcium ion (Ca\textsuperscript{++}) has greater ionic radius and more electropositive character which permit number of different types of co-ordination with various oxygen atoms attached to silicon atoms in the system.
To elucidate complex behaviour of HCS of portland cement containing lime rich tricalcium silicates and β-dicalcium silicates of compositions 3CaO\(\cdot\)2SiO\(_2\)aq and 2CaO\(\cdot\)SiO\(_2\)aq respectively, H.F.W. Taylor systematically examined different products with the help of X-ray photographs. HCS were prepared at room temperature by (i) action of water on tricalcium silicate, (ii) double decomposition of calcium nitrate by sodium silicate and (iii) reaction of calcium hydroxide with silica gel. By X-ray study it was found out that a considerable degree of crystalline character is obtained in these apparently amorphous compounds. Compositions of these phases varied between approx. CaO\(\cdot\)SiO\(_2\)\(\cdot\)nH\(_2\)O and 3CaO\(\cdot\)2SiO\(_2\)\(\cdot\)nH\(_2\)O without significant change in X-ray patterns. A second phase HCS with a composition in neighbourhood of 2CaO\(\cdot\)SiO\(_2\)\(\cdot\)nH\(_2\)O, having X-ray pattern differing slightly from tricalcium silicate was also examined. These results of X-ray data of HCS suggested a layer structure, possibly showing similarity to the clay minerals.

HCS of the compositions varying from CaO\(\cdot\)SiO\(_2\)\(\cdot\)nH\(_2\)O to 3CaO\(\cdot\)2SiO\(_2\)\(\cdot\)nH\(_2\)O were prepared hydrothermally to get crystalline HCS. The X-ray patterns of hydrothermally prepared HCS showed many lines which are not disclosed by samples prepared below 100°C. The structure of hydrothermally prepared HCS compared well with natural HCS - Xonotlite, however, it gave certain additional lines indicating a new
modification of xonotlite. Detail study of X-ray data of various products prepared with the mixture of lime and silica gel by hydrothermal treatment in molar ratio of CaO:SiO₂:3:2, yielded HCS of CaO:SiO₂:H₂O composition, indicated by the X-ray pattern of similarly prepared material of CaO:SiO₂ 1:1. Systematic stepwise identification of the products prepared by hydrothermal reactions from 100°C to 200°C with mixtures of calcium oxide and silica gel, in the molar ratio of CaO:SiO₂ 2:1 were carried out. Formation of compounds Ca₂SiO₄ and Ca₃SiO₅ was similarly examined. The starting material CaO:SiO₂ in molar ratio of 2:1, yielded HCS( CaO.SiO₂.nH₂O) as the initial product at lower temperature. More prolonged hydrothermal treatment gave tricalcium silicate-afwillite which yielded HCS of CaO.SiO₂.nH₂O composition as the initial product up to at least 120°C and finally gave dicalcium silicate. These results indicated initial formation of the compound of CaO.SiO₂.H₂O composition at least below 100°C, and even in the vicinity of 120°C in the case of hydrothermal reactions.

H.F.W. Taylor and Co-Workers then studied water content of HCS of composition of 1 - 1.5 CaO.SiO₂.xH₂O, prepared by i) hydration of tricalcium silicate ii) hydration of dicalcium silicate iii) double decomposition of calcium nitrate sodium silicate reaction and iv) reaction of lime and gel below 100°C. Dehydration isobars and X-ray photographs of
samples partly or fully dehydrated under various conditions, together with a natural HCS - riversideite, were studied. Three distinct states of hydrations having $x = 2.5$ (approx.), 1.0 and 0.5 were observed. Interlayer spacing values of X-ray study suggested that during dehydration to the monohydrate 'a' and 'b' axes are unaffected but, further dehydration causes them to shrink slightly, this result probably indicated that one molecule of water is essential to the structure of the layer. The expelled water can be replaced completely if the water content has not been reduced below 1.0 molecule of water. It was examined that the water to silica ratio, after any given condition of hydration, is independent of lime to silica ratio of the samples. According to the H.F.W. Taylor and coworkers this seems to rule out the theory that the variable lime content is due to the adsorption of calcium hydroxide. The products formed on complete dehydration at 800°C show formation of Wollastonite. The high degree of order maintained throughout the dehydration process indicated the existence of structural resemblance between $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ and $\beta$-Wollastonite.

S.A. Greenberg has reported a study of some of the conditions under which HCS is synthesized and has examined the products. HCS were prepared at 93°C at atmospheric pressure and with hydrothermal conditions in saturated steam.
at 148°, 170° and 180° C. \( \text{CaO:SiO}_2 \) molar ratios of 1:4, 1:2, 1:1, 2:1 and 4:1 were used in the reaction mixtures. The products were examined and identified by Debye Scherrer patterns. Thermal dehydration curves, differential thermal analysis and surface area measurements were used to study the properties of HCS formed under different conditions. The products formed from 2:1 and 4:1 molar \( \text{CaO:SiO}_2 \) ratios, contained unreacted calcium hydroxide. In maximum ratio of 3:2 (\( \text{CaO:SiO}_2 \)), S.A. Greenberg assumed that all the silica had reacted. When an excess of silica is present in the reaction mixture in \( \text{CaO:SiO}_2 \) ratio of 1:2 and 1:4, products formed contained strong lines for 'c' spacing of 14.5 Å and weak 11.3 Å lines which are present in natural HCS known as crestomereite. From the results of this investigation it was shown that products formed from 1:1, 1:2 and 1:4 \( \text{CaO:SiO}_2 \) mixtures contained very little unreacted calcium hydroxide.

Important observations have also been made in the examination of HCS by thermal dehydration study. Thermal dehydration curves of HCS, hydrated silica, calcite and calcium hydroxide have been reported. The thermal dehydration curve of HCS is continuous which is characteristic of zeolites. A similar continuity is noted in the dehydration curve of hydrated silica. The completeness of the calcium
hydroxide reaction in HCS is apparent, since no calcium hydroxide break is observed in 450° to 650° C range. The calcium hydroxide curve shows breakdown in 450° to 650°C region. However a break in the curve between 750° and 825°C is also presented in the calcite and in the calcium hydroxide curve which is obviously due to carbonate decomposition. The total per cent water contents were 15 in HCS and 16.8 in the hydrated silica. The resemblance is marked between the dehydration curves of the HCS and hydrated silica. Both loose majority of their water below 300°C.

Differential thermal analysis (DTA) curves were presented for (i) HCS, (ii) unreacted equimolar mixture of calcium hydroxide and hydrated silica, (iii) hydrated silica and (iv) wollastonite. The dehydration curves of the samples having CaO:SiO₂ 1:2 and 1:4 mol, prepared hydrothermally at 148° and 170° C respectively are typical as for these compounds, relatively small amounts of calcium carbonate impurities are indicated. The water contents of the samples prepared at 148° C decreased from 17.1 to 13.8 per cent with a rise in SiO₂:CaO ratio from 2:1 to 4:1. Similarly in corresponding samples prepared at 170° C, the reduction was from 14.8 to 10.9 per cent.

Considering results of this study and particularly indicating the similarity of dehydration curves of HCS and
that of hydrated silica, S. A. Greenberg reported that theory that HCS is built up of $\text{Ca}^{+2}$ and $(\text{H}_2\text{SiO}_4)^{-2}$ group, as reported previously by Roller and Ervin, and also by Thilo, is substantiated by this study. It is observed in this study that the comparison of surface area of samples with a large excess of calcium oxide or of silica, the compounds have lower surface area than those of the $\text{CaO}:\text{SiO}_2$ or $2\text{CaO}:\text{SiO}_2$ ratio compounds. This would be expected in the samples with an excess of calcium hydroxide or hydrated silica in the reaction mixture. The unreacted material would of course, have a much lower surface area than that of HCS.

1.6 Interaction of lime-silica-water

To understand precisely the initial interaction between calcium ions and silica and the nature of silica, S. A. Greenberg considered following theoretical aspects.

(i) Surface of silica gels and quartz are covered with acidic $\text{SiOH}$ group which dissociate as in (6)

$$-\text{Si}-\text{OH} \leftrightarrow -\text{Si}-\overset{\cdot}{\text{O}} + \text{H}^+$$

and in addition, small amount of monomeric silicic acid and its ions and colloidal silica are found in the solution.

(ii) According to theory, the reaction of calcium hydroxide and the $\text{SiOH}$ surface is weak acid and a strong base (equation 7)

$$-\text{Si}-\text{OH} + \text{Ca(OH)}_2 \leftrightarrow (-\text{Si}-\overset{\cdot}{\text{O}})_2\text{Ca} + 2\text{H}_2\text{O}$$
Although calcium silicates are relatively insoluble a certain amount of hydrolysis takes place in two steps (8 & 9).

\[ \text{(a) } (\text{-Si-O})_2 \text{Ca} \rightleftharpoons 2\text{-Si-O} + \text{Ca}^{++} \]  

\[ \text{(b) } 2\text{-Si-O} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{-Si-OH} + 2\text{OH}^{-} \]  

(iv) The hydrolysis of surface SiO\text{--} proceeds because of low ionization constant of silicic acid.

(v) When silica is allowed to react with neutral salt, a decrease in pH results, explained by reaction (10)

\[ \text{--Si-OH + M X} \rightleftharpoons \text{--Si-OM + H X} \]  

Experiments were carried out with calcium hydroxide and Calcium nitrate solutions to measure conductivity or pH of solution on addition of silica. Adsorption isotherms at 30\(^\circ\) and 82\(^\circ\) were obtained on silicas with surface areas varying from less than one to 750 m\(^2\)/g. and water contents ranging from almost zero (quartz) to 19.2 per cent. From theoretical considerations of the results, important conclusions were drawn.

1) Hypothesis of chemisorption of calcium ions by acidic SiOH groups in initial step in the reaction of lime and silica was confirmed.
ii) Evidence of the presence of SiOH groups on the surface and in the pores of amorphous silica showed that silica is condensation polymer of silicic acid.

iii) The effect of the pH on the hydrolysis of the SiO-Ca bond was indicated.

iv) The similarity between the surface areas determined by nitrogen adsorption and those found by sorption measurement assuming a cristobalite structure indicated that local order of amorphous silica is that of cristobalite.

According to R.K. Iler, the arrangement of hydroxyls would be as shown in (11) instead of arrangement as shown in (12)

$$\begin{align*}
\text{SiOH} + \text{Ca(OH)}_2 & \rightleftharpoons \text{SiO}^\circ \text{Ca} + 2\text{H}_2\text{O} & (11) \\
\text{Si-OH} + \text{Ca(OH)}_2 & \rightleftharpoons \text{Si-O} \text{Ca} + 2\text{H}_2\text{O} & (12)
\end{align*}$$

1.7 Reaction of calcium hydroxide and colloidal silica

Greenberg also carried out investigations to understand the chemical reaction of calcium hydroxide with colloidal silica in the presence of excess water by examining periodically the liquid and solid phases during the course of reaction by measuring electrical conductivity, pH and
taking DTA of solid. At this stage, Greenberg found difficult to propose a complete mechanism of the chemical reaction but stated that because of insolubility of calcium silicate in the presence of excess calcium hydroxide, it was reasonable to assume that reaction of colloidal silica with calcium hydroxide solution must occur in situ and not in solution. According to this hypothesis calcium hydroxide is first chemisorbed by silica, then in the presence of Ca\(^{++}\) and OH\(^{-}\) ions water diffuses into silica structure, hydrolysis of Si-O-Si bonds results (pH 12.3 ± 0.2) and simultaneously the SiO\(_4\) tetrahedra orient into the tobermorite structure.

Elucidation of the reaction proceeding in fresh concrete mixtures between solid tricalcium silicate and water required knowledge of the solubility product of HCS. Experiments were carried out with products of CaO:SiO\(_2\) :: 0.8:1, 1:1, 1.2:1 and 1.5:1 to get precise solubility product. From the data obtained in this study, considerations were made for equations 13 to 18.

\[
2(Ca^{++}) + (H^+) = (OH^-) + (H_2SiO_4^-) + 2(H_2SiO_4^{--}) \tag{13}
\]

which shows electroneutrality

\[
(SiO_2) = (H_4SiO_4) + (H_3SiO_4^-) + (H_2SiO_4^{--}) \tag{14}
\]

which states that the soluble silicic acid (SiO\(_2\)) is monomeric and is composed of three species, the undissociated form $H_4SiO_4$ and the two ions $H_3SiO_4^-$ and $H_2SiO_4^{--}$.
Each of this equation shows equilibrium with solids and aqueous solution. From (15) and (16) solubility products $K_{sp_1}$ and $K_{sp_2}$ are written as in (17) and (18).

$$K_{sp_1} = \text{Ca}^{++} + aH_2SiO_4^{--}$$

$$= (\text{Ca}^{++})(H_2SiO_4^{--})^{f^+2}$$

$$K_{sp_2} = a\text{Ca}^{++} a^2 H_3SiO_4^{--} \text{ or } (\text{Ca}^{++})(H_3SiO_4^{--})^2 f^{+3}$$

where 'a' refers activity and 'f' is the mean activity coefficient in each equation.

Detail considerations on this line showed it reasonable to conclude from the results that except for the hydrate of CaO$_2$SiO$_2$ 0.8:1, all other hydrates obey equation (17). Even then how the calcium hydroxide in excess of 1:1 CaO$_2$SiO$_2$ ratio is involved in Ca$_2$SiO$_4$ solid was not clear. Brunauer, Kantro and Weise from the relation between surface areas and CaO$_2$SiO$_2$ mole ratios concluded that calcium hydroxide is not adsorbed. Also extraction of calcium hydroxide with organic solvents demonstrated that the excess calcium hydroxide is not adsorbed on the silicate surface. Therefore, S.A. Greenberg,
T. N. Chang and Elaine Anderson concluded that the excess calcium hydroxide is in solid solution in the CaH$_2$SiO$_4$ crystals. Further, it was proposed that in the equilibrium between aqueous solutions and hydrates with CaO:SiO$_2$ mole ratios 1:1 and 1.5:1 two equations describe the system (19 & 20).

\[ \text{CaH}_2\text{SiO}_4 (S) = \text{Ca}^{++} \text{aq} + \text{H}_2\text{SiO}_4^{-} \text{aq} \quad (19) \]

\[ \text{Ca(OH)}_2(S) \text{(absorbed)} = \text{Ca}^{++} \text{aq} + 2\text{OH} \text{aq} \quad (20) \]

In addition to these reactions H$_2$SiO$_4^{-}$ aq may hydrolyse to H$_3$SiO$_4^{-}$ aq and then to H$_4$SiO$_4$ aq species according to the dissociation constants of silicic acid. However, the equilibria that exist for hydrates with CaO:SiO$_2$ mole ratios less than 1:1 are not well understood yet. In the system CaO:SiO$_2$:H$_2$O at low CaO contents apparently it is silica dissolved in calcium hydroxide. The increase in solubility of silica with pH has been explained by the relationship and the equation (21).

\[ \text{SiO}_2 (S) + n\text{H}_2\text{O} = \text{H}_4\text{SiO}_4 \text{aq} \text{ for the dissociation of } \text{H}_4\text{SiO}_4^{-} \text{ and H}_3\text{SiO}_4^{-}. \quad (21) \]

Equation (21) describes the equilibrium between silica and a saturated solution of monosilicic acid. This solubility is fixed at pH 7. However, as the pH of the solution is increased by addition of Ca(OH)$_2$, H$_3$SiO$_4^{-}$ and H$_2$SiO$_4^{-}$ form to increase the solubility of the silica.
The surface area of these samples was measured by water and nitrogen (BET) adsorption methods. Results for surface area by these two methods differ markedly and two reasons were given: (1) water penetrated the layer of the HCS crystal but nitrogen could not penetrate giving smaller value for surface area, (2) the difference was ascribed to the fact that HCS sheets may be aggregated or rolled into fibers which may cause formation of regions on the surface which are not available to nitrogen. This study has provided the evidence, to support the view that HCS with CaO:SiO₂ mole ratios above unity contain calcium hydroxide in solid solution in CaH₂SiO₄.

On describing the study of the heterogeneous reaction between silica and calcium hydroxide solutions in the temperature range 30 °C to 85 °C, it is considered necessary by S.A. Greenberg that the silica dissolves, so that the reaction in solution may proceed. Theoretically following six processes were expected.

(i) Chemisorption of calcium hydroxide by surface silanol groups

(ii) The solution of silica in the aqueous phase silica reacts with water to form a saturated solution of monosilicic acid. The solubility of the SiO₂(S) + H₂O = H₄SiO₄(aq) silica increases with pH because of the formation
of $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ ions.

(iii) The reaction of monosilicic acid and its ions in solution with calcium hydroxide in solution (22)

$$H_4SiO_4 \text{aq} + Ca^{++} \text{aq} + 2OH^- \text{aq} = n_1CaO\cdot SiO_2 \cdot n_2H_2O(S) \quad (22)$$

(iv) Formation of nuclei of calcium silicate hydrate.
(vi) Growth of nuclei
(vi) Flocculation and precipitation of crystals.

Study of rates of reactions of several silicas with calcium hydroxide solution by measuring conductances of the solution as a function of time and observing the influence of amount of silica, the concentration of calcium hydroxide, temperature and type of silica it was concluded with molar ratios of $CaO:SiO_2$ 1:0.25, 1:0.5, 1:1, 1:2 and 1:3 that of the above six assumed processes proceeding in the overall reaction, the rate determining step was the solution of silica. This study demonstrated that the solution of silica controlled the kinetics of the overall reaction (equation 23).

$$SiO_2(S) + Ca^{++} \text{aq} + 2OH^- \text{aq} = n_1CaO\cdot SiO_2 \cdot n_2H_2O \quad (23)$$

Although a great deal of information about the structures and solubilities of these substances has been
reported, their physicochemical natures are not completely understood. For further elucidation of physicochemical nature of colloidal hydrated calcium silicates, the study of solubility relationship in calcium oxide - silica - water system was carried out at 25°C. This work was conducted to evaluate solubility constant Ksp₂ (equation 18) and to examine the factors that control solubility in HCS system for CaO:SiO₂ molar ratios less than 1 and above about 1.75. HCS were prepared by 1) mixtures of silica gel and water where increasing amounts of calcium oxide were allowed to react, 2) samples of hydrated tricalcium silicates were added in decreasing quantities to water to produce solids with decreasing CaO:SiO₂ ratios in equilibrium with the aqueous phases. These reactions were equilibrated for 90 and 150 days respectively. From the results of pH, CaO and SiO₂ concentrations in liquid at equilibrium, molar CaO:SiO₂ in liquid and solid phases in this study, four regions were proposed for various equilibria. In each of these regions one or more solid species exist (1) silica at low calcium contents with CaO:SiO₂ mole ratios of 0.14 and less; (ii) partially reacted silica plus some hydrated calcium silicate in the CaO:SiO₂ mole ratio range between 0.23 and 1.0; (iii) hydrated calcium silicate, Ca₆₂SiO₁₄, with a varying amount of calcium hydroxide dissolved in it in the overall mole ratio range above 1 and less than about 1.75 and (iv) mixtures of the solid hydrated calcium silicate and
solid calcium hydroxide for the overall CaO:SiO₂ ratios above about 1.75.

In an effort to study the involvement of calcium hydroxide in mixtures with CaO:SiO₂ ratios less than 1 the reaction (24) was considered.

\[
\text{SiO}_2(S) + n\text{Ca}^{++}(aq) + 2n\text{OH}^- (aq) = \text{SiO}_2 \cdot n\text{Ca(OH)}_2(S)
\]  

(24)

By considering this reaction and taking the results of values of logarithm Ms/aL where Ms is the moles of calcium hydroxide per mole of SiO₂ in the solid and aL is the activity of calcium hydroxide in the aqueous phase it is shown that the ease of entrance of calcium hydroxide into silica structure decreases with an increase in the amount of calcium hydroxide in the solid phase.

The nature of the various solid phases, will be more clear by quoting S.A. Greenberg and T.N. Chang.  

"For CaO:SiO₂ mole ratios less than 0.14 the system behaves like silica since the solubility increases with pH. However, above CaO:SiO₂ ratio of 0.23 the concentration of silicic acid decreases with pH and calcium ion concentration. At a ratio of 0.23 "free" silica is no longer present because the solubility decreases with pH. Nevertheless, it has been shown that the amount of silica
that dissolves in hydrochloric acid solution increases with calcium oxide content to 100 per cent at a CaO:SiO₂ mole ratio of 1. It is possible to assume, therefore, that in addition to the hydrated calcium silicate found by the X-ray measurements, there must be some partially reacted, stabilised silica species present in the mixtures with CaO:SiO₂ mole ratios less than 1. Even with a sample which has a CaO:SiO₂ mole ratio of 0.32, broad bands in X-ray diffraction pattern demonstrate the presence of amorphous silica. Evidence for a substance with composition Ca(H₃SiO₄)₂ is not strong. The evidence for a substance with a formula CaH₂SiO₄ in solids containing CaO:SiO₂ mole ratios > 1 is fairly substantial.

"It has also been demonstrated that products of the reaction of calcium oxide, silica and water mixtures begin to dissolve completely in hydrochloric acid at a CaO:SiO₂ mole ratio of 1. Therefore, in the CaO:SiO₂·H₂O system silica is completely depolymerized at this mole ratio".

"In a study of the reaction of aqueous solutions of calcium ions and monosilicic acid, the evidence indicates that the insoluble product forms by the reaction of Ca²⁺ and H₂SiO₄⁻ ions".

It is obvious from the discussion on system lime-silica-water that much work is based mainly on the
consideration of mechanism of formation of crystalline or ill-crystalline hydrated calcium silicate formulated as Ca\(0.\text{Si}_2\text{O}_6\cdot\text{H}_2\text{O}\) in connection with the reaction of tricalcium silicates and dicalcium silicates in aqueous medium. Discussion also included HCS prepared hydrothermally as well as that prepared at temperature below 100 °C. Literature on silica rich calcium silicates, for example Ca\(0.2\text{Si}_2\text{O}_6\cdot\text{H}_2\text{O}\) and Ca\(0.3\text{Si}_2\text{O}_6\cdot\text{H}_2\text{O}\) that is calcium disilicate and calcium trisilicate commonly known as colloidal calcium silicates for filler and allied industries is scanty and details of patented processes are not readily available.

1.8 Precipitated silica

Three distinct types of colloidal silica reported in literature are 13:

i) Polysilicic acids of low molecular weight.

ii) Polymerized silicic acids of high molecular weight consisting of network polymer units of colloidal dimensions (present in solution approaching gel point).

iii) Discrete particles of amorphous silica of colloidal size.

Since it is the purpose here to discuss type (iii) attention will be given to the finely divided form of silica. The common features of this type of precipitated silica are
that they are openpacked, fluffy and light in weight. They differ from dried silica gels which also consist of amorphous silica but particles of dried silica gel are linked together in varying degrees to form dense, hard closed-packed masses. Precipitated silica is synthesized by depolymerizing silica in one way or another and repolymerizing to the desired colloidaly subdivided form. Reported methods of preparation of precipitated silica under strong flocculating conditions are: (i) dissolution of silica in hot sodium carbonate solution and then cooling to precipitate silica, (ii) reaction of sodium silicate with ammonium chloride and ammonium fluoride, and (iii) extraction of clay with sulphuric acid.

All these processes are patented and large number of patents relating to the precipitation of silica from solutions of alkali metal silicates with acid using variables of concentration, pH and temperature to prevent gel and to form precipitated silica which can be readily filtered and washed are reported in literature. R.K. Iler has remarked that the precipitated silica having surface area less than about 200 m$^2$/g. is generally readily filterable. Different methods of preparation bring about the diversity of physical characteristics. As precipitated silica are used for a wide variety of applications, their evaluation and characterisation are essential.
1.9 SURFACE CHEMISTRY OF SILICA AND SILICATES

General aspects of surface area determination:
The two principal physical features of synthetic silica and silicates, upon which their properties of commercial value depend, are surface and pore structure. The role that 'Surface' and 'Pore' play can only be understood in relation to the phenomenon of adsorption. Whether there is physical adsorption or chemisorption, the formation of monomolecular layer on the surface of the substance provides an insight into the physical and chemical nature of the surface. Development of theories of physical adsorption, particularly by Langmuir, Harkins, Freundlich and Polanyi by extensive studies on monomolecular films on aqueous substrates supplied convincing evidence of monolayer adsorption. Later work concentrated on efforts to describe and analyse adsorption in terms of different types of isotherms by interpreting the relation between the pressure of the adsorbate gas and the amount adsorbed at a specified temperature.

Five types of isotherms were considered for satisfactory mathematical interpretation of the results of physical adsorption of gas on solid by Brunauer S., Deming, L.S., Deming, W.E. and Teller but important theoretical aspect of the multilayer adsorption theory was further developed by Brunauer, Emmett and Teller which is best known
and widely used as BET theory. This theory is an extension of the Langmuir interpretation of monomolecular adsorption and its derivation is based on the same kind of picture and assumption that condensation forces are the principal forces in physical adsorption. The important equation developed from the theory is BET equation,

\[
\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{P}{P_0},
\]

Where \( V \) is the volume of the gas adsorbed at an equilibrium pressure \( P \) and absolute temperature \( T \) and expressed in ml (STP) per gram of solid. \( P_0 \) is the saturation pressure of the adsorbate and \( V_m \) is the volume adsorbed per unit mass of the adsorbent when the surface is covered with a complete unimolecular layer. The constant \( C \) is related to the heat of adsorption of the first layer. In practice, BET equation is successfully used for determining surface area of solids. Estimation of surface area involves measurement of the volume of nitrogen gas adsorbed by the solid at liquid air temperature measured at various pressures, construction of an isotherm from the results, application of BET equation to evaluate \( C \) as well as \( V_m \) and calculation of surface area taking 16.2 \( \AA^2 \) area of one molecule of nitrogen which it occupies on monomolecular layer. Nitrogen gas at liquid air temperature is found most suitable in these experiments as sharp knee band in the plot of \( \frac{P}{V(P_0 - P)} \) vs \( \frac{P}{P_0} \) is
obtained which gives higher C value for lower P/Po to get reproducible results. Many investigators have attempted to modify BET equation and surface area is determined accordingly but each has got its own limitation and hence they have been proved applicable only within very narrow range.

Electronmicroscopy and X-ray scattering techniques have been developed to measure millimicron range particle size of amorphous silica and silicates and surface area is conveniently calculated from the results. Other methods of surface area measurement include fatty acid adsorption, dye sorption, iodine adsorption, exchange sorption of radioactive isotopes, heat of adsorption etc., but the gravimetric method is most frequently used for adsorbates which condense at room temperature e.g. water. One of the earliest use of this technique and the first application of the BET theory to hydrated paste was made by Power. The most accurate results can be obtained by means of the McBain-Bakr sorption balance which employs helical vitreous silica spring. A vacuum dessicator apparatus can give just about as accurate results as the sorption balance, with a less labour. The partial pressure, here too, is controlled by saturated solutions. The dessicator method has the advantage that relatively large number of samples can be exposed to the same atmosphere simultaneously. Results of surface area of silica and silicates determined by dessicator method using water as adsorbate at room temperature and BET.
method using nitrogen at liquid nitrogen temperature have been compared and discussed by E.J. Chessick and J.E. Sturm.

1.10 General aspects on pore volume and pore size distribution: Measurement of total surface area by gas adsorption method indicates the porosity within submicroscopic size particles which have cracks, cavities, holes or pores within their structure, but when the capacity of an adsorbent is to be accounted for, the volume of the pore spaces is of paramount concern. Evaluation of pore spaces in submicroscopic structure is carried out by the measurement of pore volume and pore size distribution to study the detail surface chemistry of synthetic silica and silicates.

It may be mentioned that number of research techniques have been developed for the measurement of pore volume and pore size distribution in the study of active carbon and accordingly active carbon has been divided in two system: (1) micro-pore, (2) macropore. Micropore system is arbitrarily defined as pores having diameter range 10 to 1000 Å and macropore system having diameter above 1000 Å. As the micropores contribute nearly all the available surface for activation process, methods have been developed in respect of them for the determination of pore volume and pore size distribution based on the theory of capillary condensation. Zsigmondy was the first to apply Kelvin's equation to the
relationship between adsorption and pore structure based on the capillary condensation theory and additional understanding of pore size distribution was also obtained by considering the complete adsorption desorption isotherm or hysteresis relationships. In practice therefore the data of volume of gas adsorbed per gram of powder at specified temperature plotted against pore radius calculated from P/Po values using Kelvin's equation, and differentiation of this plot gives important quantitative information of pore size distribution. Further attempts to explain hysteresis results from theoretical point of view have been made by McBain "bottleneck" theory and by Foster and Cohan 'open-pore' structure.

Important practical methods of pore volume or pore size distribution determination can briefly be mentioned as follows:

1. Direct measurement by electron microscope;
2. X-ray evaluation by examination of low angle scattering pattern representative of pores;
3. Gas flow analysis as applied to the evaluation of bulk density and particle density;
4. Calculation from an analysis of gas adsorption-desorption isotherms obtained in the surface area measurement by BET theory.
5. Liquid phase sorption by applying knowledge of molecular size of several organic liquids which are used over a considerable range of pore size distribution. 

Judgement of comparative openness of packing in different powders is obtained by following two methods:
1. Examination of flow property of the powder by adding water till powder sticks to the wall of its container and does not flow freely;
2. Examination of linseed oil absorption capacity till the total mass of the powder molded into single mass.

1.11 Surface structure of silica and silicates:

Inspite of development of evaluation techniques in the study of surface chemistry, the effect of surface microporosity on the adsorptive properties of silica and silicates appear to have received but little attention eventhough it would have important ramifications in catalyst industries. However study of manufacture of microporous silicates by Sing and Co-workers, particularly by fast precipitation and decreasing pH when silicas are precipitated from sodium silicate, has initiated examination of effect of microporosity on the products.
Besides the knowledge of surface area, pore volume, pore size distribution, surface chemistry of synthetic silica and silicates involves important aspect of number and arrangement of their surface silanol groups, the study of which is required in order to understand physicochemical principles in application to different industries as fillers, catalysts, catalysts supports, adsorbates, chromatographic agents and so on.

Synthetic silica or silicates obtained by hydrolysis of polymerisation in the liquid phase have comparable surface properties steam from their complete surface hydroxylation. Therefore, in recent times of studies of physical and chemical properties of silanol surface in respect to effect of temperature chemical reactions, reaction with alcohol, halogen and alkali have developed to explain surface chemistry and surface structure of synthetic silica and silicates.

Boer and co-workers have studied the influence of temperature on silanol groups of pure silica prepared by the liquid phase hydrolysis of silicon tetrachloride and have found that physisorbed water was removed from the surface by heating in air at 120°C or by evacuation at room temperature. Variation of chemisorbed water was also studied at different temperatures. However, this study does not distinguish between strongly bound physisorbed water and surface arrangement involving geminal hydroxyls
i.e. a pair of hydroxyls bounded to the same surface silicon atom. G.J. Young and J.A. Hockey report that the dehydration of silica in vacuum at temperature above 450-500°C indicate virtually complete removal of the surface hydroxyl groups and A.V. Kiselev states that temperature higher than 400-500°C is required for complete removal of this type of hydroxyl groups. At present, it is accepted that surface action that occurs on dehydration is elimination of water from pairs of hydroxyls attached to adjacent surface silicon atoms forming strained siloxane bridge system

\[ (-\text{Si} - \text{O} - \text{Si} -). \]

Silanol groups being acidic in nature as confirmed with spectroscopic evidence by Basila, bring about chemical reactions with alcohols, halogens, and alkalies. Reactions of silanol groups with alcohol form 'estersils' and detail investigations of subject have been reported by R.K. Iler. Physical properties have been studied of compounds formed by the reaction of aluminium trichloride and borontrichloride with silanol. H.P. Boehm and S.A. Greenberg have studied the reaction of calcium hydroxide solution with hydrated silicas particularly mentioning that "neutralisation of the silanol groups is said to occur within the pH range 5-13, the hydrogens of the surface silanols being replaced stoichiometrically by
calcium ions and a different phenomenon appears to occur in sodium hydroxide solutions.

Recently techniques of Infrared spectroscopy have been applied to the study of surface chemistry of silica particularly to understand the distribution of physisorbed and chemisorbed water\textsuperscript{88,89}. In spite of various interpretations offered to the patterns obtained in infrared spectroscopic studies, it is generally agreed that absorption bands in the 2.74 region are due to single surface hydroxyls and that those appearing at 2.95 and 6.1 when molecular water is present, are due to physisorbed water held on the surface by hydrogen bonding of the type in scheme presented as under.

\begin{center}
\begin{tikzpicture}
\node (H1) at (0,0) {H};
\node (H2) at (1,0) {H};
\node (O) at (0.5,-1) {0};
\node (H3) at (-0.5,-2) {H};
\node (H4) at (0.5,-2) {H};
\node (O2) at (0.5,-3) {0};
\node (O3) at (0.5,-4) {0};
\node (Si) at (-1,-5) {Si};
\node (Si2) at (1,-5) {Si};
\draw (H1) -- (O);
\draw (H2) -- (O);
\draw (H3) -- (O2);
\draw (H4) -- (O2);
\draw (O2) -- (O3);
\draw (O3) -- (Si);
\draw (O3) -- (Si2);
\end{tikzpicture}
\end{center}

Hydrogen bonding of surface silanol group.
Recent theoretical explanation of the surface structure and surface silanol on freshly prepared silica explaining experimental observations and results contribute to the understanding of surface chemistry of silanol groups. According to DeBoer, density measurements, specific surface area determinations and the limiting value of $n_{OH}$ 4.6 ($n_{OH} =$ number of hydroxyl groups per 100 Å²) have led to the proposition that the solid structure of pure annealed silica closely resembles that of cristobalite or tridymite. Assuming that such a structure represents an annealed silica, J.A. Hockey explained surface properties of the solid at various stages of the annealing process. Explaining the reaction,

$$\text{Si}-\text{OH} + \text{HO} \rightarrow 0-\text{Si}-\text{OH} \rightarrow O\text{SiO} \rightarrow \text{Si}-\text{OH} + \text{H}_2\text{O}$$

It is stated that silicas originate from lattice imperfections caused by the incomplete polycondensation and faster the polycondensation proceeds, the greater will be the possibility of lattice faults. On heating to about 200°C the reaction proceeds but on cooling and rehydration the strained siloxane regenerates the geminal arrangement as revealed by infrared spectroscopic observations. Heating to higher temperatures (>450°C) completely removes.
surface arrangements of silanol groups and also promotes lattice relaxations which anneal the solid, alleviate the strain in siloxane bridge and thereby render siloxane bridge resistant to hydrolysis. On further prolonged heating to 500°C or more, the oxygen atoms of the siloxane bridges are able to fit into vacant spaces between the lattice surface oxygen atoms and so produce a surface whose characteristics are dominated by the relatively large oxygen atoms which cause the resistance to dehydration of fully dehydrated pure silica.

1.12 Objective and abstract of thesis

The object of selecting the work on "study of silicates" has been to investigate the use of marine gypsum for the preparation of hydrated calcium silicate of definite characteristics for its application in rubber industry. This has lead to the detail investigation of mechanism of the reaction and evaluation of the properties of the hydrated calcium silicates obtained. Further the reaction of calcium hydroxide and active silica has been investigated in detail to prepare the hydrated calcium silicates of similar chemical compositions having distinctly different surface properties required for different industrial application and to elucidate the mechanism of the reaction, composition and properties of the products. Comprehensive study of surface
chemistry of HCS and precipitated silica has been carried out. This included dehydration-hydration study, differential thermal analysis, surface area by BET method, pore diameter, pore volume, oil absorption pore size distribution etc. The study on the mechanism has been undertaken with a view to establish that hydrated calcium silicates are admixtures of calcium monosilicates and silica and to show that adsorbent properties of the HCS are due to silanol groups on the surface.