CHAPTER - I

GENERAL INTRODUCTION
1.1 OVERVIEW OF THE PROPOSED WORK

It is our thesis that one of the keys to innovation and research is the creation and development of genuinely new materials. Thus, the step function advances in separation process engineering will best be achieved if new materials with suitable properties can be synthesised and developed. In the last few years scientists have developed and studied a new family of cation exchangers [1-12] which might be useful in separation processes. The understanding of the thermodynamics of cation exchange [13-17], kinetics and selective properties [12,18-20,113] of these new materials will not only lead to applications in separation processes but also in numerous other fields on global scale on account of their reported potential for immobilisation and solidification of hazardous radioactive isotopes in the waste products of nuclear power plants[21-43]. The primary objective in treating nuclear waste effluent is to eliminate activity to a desirable level suitable for local discharge. The methods of treatment used in nuclear industry are evaporation, chemical precipitation and ion exchange together with filtration. Recent investigations have been made on liquid treatment with more advanced processes including modification in precipitation techniques, use of inorganic ion exchangers, solvent extraction, membrane separation, electrical processes and high gradient magnetic separation [44-51]. The new technologies involve immobilisation of the rad waste through fixation of active species in aluminosilicate matrix such as zeolites, ceramics, cements, etc. under optimum conditions for obtaining stable and leach resistant waste forms [52-54].

We have long been of the view that the unmodified cement matrix using cement "straight from the bag " has a sharply limited potential for the immobilisation of waste constituents which are likely to remain soluble within the cement matrix. A suitably modified matrix might be a better host. At the same time, we are aware that the intensely alkaline nature of cement and the possibility of additional chemical reactions ensuing between sorber and solid-phase cement components sharply limit the range of materials which can successfully be used. It is known that hydrous titanium oxide is a good sorber, but it's Cs site selectivity is reduced significantly by the Ca$^{2+}$ content of cement. Calcined kaolin is also a good sorber but, in the long term, it is likely to participate in pozzolanic reaction. It is, however, significant to note that the title material was chosen for study because application of acid-base theory suggested that
it ought to sorb cations, thereby suggesting that the performance of aluminosilicate materials of similar structure can successfully be predicted.

1.2 RADIOACTIVE WASTE MANAGEMENT

Only a few areas have commanded as much attention for Scientists, Governments and General Public over the past thirty years as a subject of nuclear (radioactive) waste. The waste arises in various forms from peaceful uses of nuclear energy in research, industry, medicine and electricity production[55,67].

Concern about nuclear waste stems from "FEARS" about its associated radiation and the perception that these wastes cannot be controlled or safely managed over long periods of time. Though these fears are not scientifically justifiable, they have tremendously influenced the philosophy of radioactive waste management. The overriding concern today, therefore, is the protection of public from potential radiation exposure directly or indirectly. Emphasis is being placed on physically demonstrating that the most highly radioactive wastes can be safely managed and permanently isolated from the environment.

However, the above concerns must be seen in perspective in the context of overall environmental pollution hazard resulting from various energy production processes that help meet world's energy needs. It may also be noted that compared to most other types of industrial and toxic wastes, the radioactive wastes from nuclear power plants are significantly smaller in volume. Still, the importance has been laid on the better methods of its immobilisation and disposal. [56,57]

1.2.1 Objectives of Waste Management

Radioactive waste management has the following safety and environmental objectives:

(i) to comply with radiological protection principles for the present and future generations
(ii) to preserve the quality of the natural environment, i.e. to maintain the ecological balance of life forms including human beings

(iii) to minimise any constraints on future generations as far as practicable

It is relatively easy to achieve these objectives in the short term. On a long term basis the above objectives appear stringent but are consistent with ethical obligation to protect future generations to the same level as the present ones, and which is of utmost priority for our research that storage and disposal should be on long term basis.

1.2.2 Principles and Philosophy of Waste Management

(i) Dilute and disperse wastes to environment through effluents containing radionuclides in amounts far below the authorised radiological protection limits.

(ii) Delay and decay those wastes which contain only short-lived radionuclides.

(iii) Concentrate and confine those wastes which contain significant amounts of long-lived radionuclides.

Over the years, the above philosophy has been continuously under review, resulting in shifting of emphasis on the point (iii). This results in dispersal of only those streams to environment which have activity concentrations far below the accepted levels [58-63].

1.2.3 Origin of Wastes

Low Level Waste (LLW)

LLW contains negligible amounts of long-lived radionuclides. The levels of short-lived radionuclides are also generally low. They are produced by peaceful nuclear activities in industry, medicine, research and by some nuclear power operations. Such wastes may include items like gloves, rags, glasses, small tools, papers, filters, washings, etc. contaminated by radioactive materials.
Intermediate (Medium) Level Waste (ILW)

They contain lower levels of radioactivity and have lower heat content than high level wastes, but may require shielding during handling and transport. ILW may include resins from reactor operations, solidified chemical sludges and pieces of equipments of metals.

High Level Waste (HLW)

HLW arises from reprocessing of spent fuel from nuclear reactors. Spent fuel elements stored at reactor sites also fall in this category. They contain transuranic elements and fission products that are highly radioactive, heat generating and long-lived.

1.2.4 Categorisation of Waste

For technical and safety reasons various forms of nuclear wastes are usually categorised by their levels of radioactivity, heat content, potential hazard and their methods of treatment. For general purposes, however, the wastes are nominally labelled as low level, medium level and high level.

The wastes are also categorised as short-lived or long-lived in accordance with their half-lives. Those with half-lives greater than 30 years are generally considered long-lived. There is yet another categorisation of wastes as solid, liquid and gaseous. This classification is mainly useful from the point of view of treatment of wastes.

1.2.5 Treatment and Storage of Radioactive Liquid Waste

Liquid wastes by their mobile nature need to be stored carefully and managed efficiently. The line of their treatment depends very much on their category.

a) Low Level Waste

The treatments are specific with respect to sites and the operations and consist mainly of chemical precipitation and ion exchange treatment. The treated effluent is
then discharged into a water body after ensuring adequate dilution. The sludge (solid) or the resin containing radioactivity is fixed in cement matrix and disposed off as solid waste.

b) Intermediate Level Waste

The ILW or MLW, mostly from fuel reprocessing plant, is chemically treated in a way similar to LLW. The sludge which is highly active is conditioned and stored in solid matrix. More recently calcium silicate hydrates have been suggested for immobilisation of spent and higher active waste concentrates[64-66].

c) High Level Waste

It arises from the processing of spent fuel for the recovery of plutonium. It is highly acidic and presently stored in borosilicate glass shields.

Storage as liquid cannot be relied upon in the long run. The waste will, therefore, need conditioning in the immediate future. The conditioning consists of immobilisation of waste in cement/calcium silicate matrix. It should be leach resistant. Conditioning, therefore, acts as a primary barrier against the escape of waste and will be transferred to ultimate storage in deep geological formations to ensure their isolation from living environment (biosphere) for a few million years.

Liquid radioactive wastes containing significant amounts of long-lived radioactivity should not be advised to be buried locally or disposed off into the sewage system. The future development of nuclear energy is partly dependent on our ability to handle, store and dispose radioactive waste in a safe and acceptable manner.

1.2.6 Composition of Intermediate Level Waste (g/l) [68]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>114.170</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.025</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>9.980</td>
</tr>
<tr>
<td>OH⁻</td>
<td>21.220</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>4.800</td>
</tr>
</tbody>
</table>
\[
\begin{array}{ll}
\text{NO}_3^- & 160.200 \\
\text{CO}_3^{2-} & 6.240 \\
\text{Cs}^+ & 0.010 \\
\text{Sr}^{2+} & 0.010 \\
\end{array}
\]

(Specific gravity - 1.19)

1.3 ROLE OF INORGANIC ION EXCHANGERS

Inorganic ion exchangers display a very promising behaviour in immobilisation and solidification of waste. Acid zirconium phosphate [23,69-74] shows some promise as a sorber; nevertheless, it reacts in a complex manner with cement and further studies of its action have been given a low priority. In the last couple of years some work has been done [23,75] to use the family of synthetic hydrothermal cement exchangers like tobermorites and xonotlite in separation and solidification of $^{137}\text{Cs}$ and $^{90}\text{Sr}$ isotopes, which constitute hazardous active components of nuclear waste effluent. These are good to excellent sorbers for $\text{Cs}^+$ within the cement matrix and as they appear to be stable, future studies are likely to concentrate on their use in eradication of cations from waste forms. Preliminary indications from leach test data[23] are that tobermorite-cement mixtures give significantly lower long-term $\text{Cs}^+$ leach rates relative to Ordinary Portland Cement (OPC) controls.

Zeolites and clay minerals form two large families of cation exchangers which have been known to mineralogists and chemists for more than 200 years. Of these two groups, zeolites have been used extensively as additives to cements in industry. Among the applications of zeolites one may mention hydrocarbon separation, intensive drying of liquids, industrial gases, air and natural gas, removal of sulphur compounds from petroleum, air separation, catalysis and cation separations by exchange processes [76].

Recently, hydrous calcium silicates of tobermorite \([\text{Ca}_5\text{Si}_6\text{O}_{18}\text{H}_2\cdot 4\text{H}_2\text{O}]\) and xonotlite \([\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2]\) groups have been recognised by several workers [23-25,77] as another family of natural cation exchangers which exhibit selective properties, in some cases better than zeolites and clay minerals.
Most countries intend to dispose off their radioactive wastes by converting them into a solidified waste form which is to be buried within the earth. In view of the foregoing information and the literature available on calcium silicate hydrates, it seems that their general structure and composition have been studied in mineralogy with special references to their similarity with the layered silicate minerals [78,79].

The present thesis focuses on an extensive work on synthesis, characterisation, cation exchange properties and leach behaviour of the newly discovered silicate mineral waste forms and their potential candidature in nuclear waste management. It's significant importance and application in the nuclear industry have been extensively studied. This relatively rare mineral, later claimed to play an essential role in the hydration reaction of cements and lime-silica products was produced during cement binding process[75]. The hydration products range from low temperature poorly crystalline calcium silicate hydrates (C-S-H) to well crystallised stoichiometric mineral phases [80]. The formation of various calcium silicate hydrates during the hydration process of cements has been thoroughly investigated by Taylor and co-workers[12]. They have reported their composition, structure, properties and importance in cement hydration with rich information. After their investigations calcium silicate hydrates were extensively studied for their various properties. Substantial progress has been made in synthesising a large variety of calcium silicate hydrates [1,2]. It was observed that they could be easily synthesised from reactive silica, calcia and alumina sources which are quite inexpensive and readily available. Since calcium silicate hydrates are rare in nature, studies have now been carried out mostly on synthetic samples. Tobermorite can also be very easily synthesised hydrothermally with good purity and crystallinity. In the present work tobermorite has been investigated for its ion exchange properties towards Cs$^+$ and Sr$^{2+}$ ions present in the intermediate level nuclear waste effluent.

Synthetic unsubstituted and substituted 11Å tobermorites have been recommended for cation exchange properties owing to their

- remarkable cation exchange capacity towards different alkali- and alkaline earth-
  cations

- non-degradable nature and their possible applications in various exchange processes
in alkaline medium

- probable catalytic activity
- their importance in cement hydration process
- high degree of compatibility with ordinary portland cements; it might be useful in immobilisation and solidification of actual alkaline rad waste
- easy and low cost synthesis

In view of the foregoing statements, it is intended to study extensively the chemistry of ion exchange and intercalation properties of tobermorites for their significant scope of application in various fields of interest.

1.4 ION EXCHANGE

The phenomenon of ion exchange was first reported by British Agriculture chemists in 1850 and reviewed by Kelley [81]. However, later on it was discussed by several workers in different ways [82,83]. Gradual developments emerged and now this is a well established separation process. Ion exchange process is based upon exchange equilibria between ions in solution and ions of like signs on the surface of an essentially insoluble, high molecular weight solid. The exchange reaction is stoichiometric and thereby differs from simple sorption. The distinction, however, is sometimes difficult to apply, since nearly every ion exchange reaction is accompanied by sorption and desorption.

Ion exchange is now taking over many of the applications in different fields of science. Natural ion exchangers, such as clay and zeolites, have been recognised and used for several decades. Synthetic ion exchange resins are being widely used for water softening, water deionisation, solution purification and analytical separation of ions.

Therefore, the ion exchange studies are generally carried out keeping in view the applied aspects of ion exchange. The important properties of an effective ion
exchanger are:

(1). it should be insoluble in water and organic solvents.

(2). it should be rigid in nature and non-degradable and capable of being used for different types of exchange processes.

(3). the exchanger should possess active or counter sites (ions), that may be able to exchange reversibly with other ions in a surrounding solution without any substantial change in material.

(4). It should have the capacity to get regenerated.

An ion exchanger should either be cation exchanger or anion exchanger depending on the active sites. The cause of ion exchange in silicates is mostly the substitution of Si by Al, which leads to a net negative charge, which is compensated by cations and, therefore, most of the silicate exchangers are effective cation exchangers. However, formation of polar groups in certain silicate minerals makes a few exceptions in so far as they behave as anion exchangers. The calcium silicate hydrates are cation exchangers. The cation exchange behaviour of tobermorites generally depends on

(1). nature of the cation species, cation charge and size for both anhydrous and hydrated phases

(2). temperature

(3). concentration of the cation species in solution

(4). anion species associated with the cations in the solution

(5). structural characteristics of a particular exchanger

1.4.1 Theory of ion exchange

Ion exchange systems are fairly complicated. The simplest possible system
consists of three phases, viz. exchanger, external solution and vapour, and each phase (barring vapour) normally consists of at least three components. In addition, neither the exchanger nor the external solution behaves ideally (as understood in the thermodynamic sense) under normal operating conditions. Despite it’s importance, the theory of ion exchange yet seems to remain incomplete [83].

When an ion exchanger is immersed in a solution containing ions, various changes may take place in addition to an ion exchange reaction, such as: swelling, adsorption of non- or weak-electrolyte and salt imbibition. In the case of calcium silicate hydrates, swelling is not significant and the extent of salt imbibition is also small under the usual operating conditions. The rigid framework in calcium silicate hydrates does not permit any significant degree of swelling. In this way, the ion exchange phenomenon of tobermorite may be considered unaffected with these changes.

1.4.2 Thermodynamics of Cation Exchange

A few established theoretical concepts are described here mainly to quantify the ion exchange data.

Consider the exchange reaction:

\[ A^+ + BT = B^+ + AT \quad \ldots \quad (1) \]

where A and B are the exchangeable cations and T is the non-exchangeable portion, the bulk in the present case is silicate crystalline phase. For this exchange reaction three equilibrium quotients are [83,84]

\[ K_a = \frac{a_A}{a_A s} = K_c \frac{f_A f_B}{f_A c f_B c} = K_c (f_A c f_B c / f_A s f_B s) \ldots (2) \]

\[ K_c = \frac{a_A}{a_A c} = K_c \frac{B_A}{B_A c} = \frac{A_B s / A_A s B c}{A_B s / B c m_s / B_A c m_s} \]

where \( a^A \) and \( a^B \) are thermodynamic activities,
$m_A^s$ and $m_B^s$ are molarities in the solution phase,

$f^A$ and $f^B$ are activity coefficients,

$A$ and $B$ are equivalent cation fractions of ions $A$ and $B$ and

the subscripts 'c' and 's' denote 'crystal phase' and 'solution phase', respectively.

The equivalent fraction may be defined as

$$
\frac{A_c}{m_c} = \frac{m_A^{\text{c}}}{m_A^{\text{c}} + m_B^{\text{c}}} \quad \text{......... (3)}
$$

where $A_c$ stands for equivalent cation fraction of ion $A^+$ in crystal phases and $m_A^A$ and $m_B^B$ are the concentrations (mole Kg$^{-1}$) of the ions $A^+$ and $B^+$, respectively, in crystal phases. A similar expression can be made to define equivalent fractions of ions $A^+$ or $B^+$ in solution phases. $K_a$ in Eq. (2) is the thermodynamic equilibrium constant, $K$ the mass action quotient (and for univalent ions the selectivity quotient) and $K_c$ is the modified selectivity quotient, also often called Kielland quotient [83].

A simplified form of the selectivity coefficient, $K_d$ (distribution coefficient) is frequently used for cation exchange in zeolites and is defined as 'the ratio of the amount of sorbed ion per gram of the solid phase to that of the amount of unsorbed ion per ml of solution'. When ions of different charges $V_A^+$ and $V_B^+$ are involved, the quotients described in expression [2] are readily rewritten for the exchange reaction as

$$
V_A^+ V_B^+ V_A^+ V_A^+ \quad \text{......... (4)}
$$

and the selectivity coefficient becomes

$$
\alpha = \frac{V_A A_C B_S}{V_S A_S B_C} \quad \text{......... (5)}
$$
The ionic strength is fixed by the unit cell dimensions and contents in the solid phase. However, the ionic strength can be varied continuously by dilution in the aqueous phase. Therefore, the overall normality as well as the equivalent cation fractions are required for complete specification of the equilibria.

Consideration of the mass action quotient indicates, that the exchange isotherm is fully described if $A_S$ is plotted against $A_C$ because $A_S = 1 - B_S$ and $A_C = 1 - B_C$. Thus, the ion exchange isotherm is a plot of $A_C$ as a function of $A_S$ at a given concentration of the equilibrium solution and at a constant temperature [83]. The type of exchange isotherm contour determines the selectivity for the ions. The thermodynamics of the ion exchange reactions, particularly in respect of zeolites, has been thoroughly studied and developed by several workers [83-87]. The selectivity coefficient, equilibrium quotient, free energy, enthalpy and entropy changes of ion exchange reactions are the most useful thermodynamic parameters. These are also extremely important to understand the behaviour as well as mechanism of ion exchange in respect of any ion exchanger. The method of Gaines and Thomas [87] is generally applied to calculate changes in standard free energies, enthalpies and entropies of exchange reactions from the corrected selectivity data. Sherry and Walton have employed a modified form of their equation, which neglects imbibement of electrolyte by the crystals and assumes the water activity to be unity [59].

The working equation is

\[
\ln K = (b-a) + \int_0^1 K_C \ dZ_A
\]

where,

\[
K = \text{equilibrium constant}
\]

\[
a = \text{charge of the incoming ion in exchanger}
\]

\[
b = \text{charge of the releasing ion in exchanger}
\]

\[
K_C = \text{modified selectivity coefficient and}
\]

\[
Z = \text{equivalent fraction of incoming ion in solid phases}
\]

The second term on the right hand side of Eq(6) can be evaluated graphically by
calculating the area under the curve in a plot of corrected selectivity coefficients as a function of equivalent fraction of the incoming ions in solid phase. The standard free energies, enthalpies and entropies of exchange reaction may then be computed using the relations

$$\Delta F^0_T = -RT \ln K \quad \text{(7)}$$

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \quad \text{(8)}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta F^0_T}{T} \quad \text{(9)}$$

where, \( R \) = universal gas constant, and \( T \) = Kelvin temperature.

The free energy change of an exchange reaction has usually a negative value [88-91].

Besides being useful in radioactive and nuclear waste treatment, the principles of ion exchange find wide applications in several other areas like water softening and demineralisation, separation and extraction of ions, removal of ammonia from water, fillers in detergents, catayasis and also in agriculture, horticulture, etc.

1.5 PROFILE OF SILICATE PHASES

Extensive studies on synthesis and cation exchange properties of these silicate materials have been carried out in our laboratories. In nature, hydrous calcium silicates are identified as late stage hydrothermal alteration products of contact metamorphic calcium silicate rock. Though these are rare minerals, but they play an extremely important role in hydration process of portland cements [75], where the products range from poorly crystalline calcium silicate hydrates \([C-S-H]\) to well-crystallised
stoichiometric mineral silicate hydrates in CaO-SiO₂-H₂O system [80]. These minerals can be easily synthesised from lime, reactive silica and alumina which are quite inexpensive and easily available materials. Isomorphous substitution of Al for Si in 'dreierketten' of tobermorite has been observed which not only stabilises the tobermorite structure to a higher temperature but also significantly controls its selective properties [92-94]. Recent studies on ²⁷Al and ²⁹Si solid state high resolution magic angle spinning nuclear magnetic resonance (MASNMR) on aluminium substituted tobermorites have shown tetrahedral coordination of Al [95,96]. Such structural information is useful to resolve the question of true thermodynamic exchange vis-a-vis chemical reaction in calcium silicate minerals, i.e. the structure-property relationship of the exchange process. The Cs⁺ selective property of Al-substituted tobermorite has been attributed to its layered structure with numerous ≡Si-O-Si≡ bridges between layers [22,97] analogous to exchange exhibited by ganophyllite [98].

The background data on the subject reveal that such synthetic phases are being investigated for their applications as suitable materials for fixing up ¹³⁷Cs and ⁹⁰Sr radioactive isotopes through cation exchange and subsequently converting them into cesium aluminosilicates of pollucite [(CsNa)AlSi₂O₆] type insoluble phases [21]. In the light of recent literature and investigations in many developed countries like U.S.A., Japan and Russia this new family of cation exchangers deserves attention for their applications in rad-waste treatment.

Fluorophlogopite gel - Recently mica group of minerals have also been reported to show ion selectivity for cesium. Sodium / potassium fluorophlogopite gel is an inorganic sorbent which exhibits a remarkable potential as cesium and strontium sorber.

1.6 (A) CALCIUM SILICATE HYDRATES

1.6.1 Tobermorite and Xonotlite (Natural and Synthetic)

Both, tobermorite and xonotlite have been found in nature in several localities of Crestmore, California and Scotland. The mineralogy of these compounds, their structure, chemistry and other properties have been studied mainly with a view to
compare these rare minerals with other layered silicates, particularly with those of montmorillonite group [1,2,6,12,99-106]. Gradual refinements have been made in the structure of tobermorite. The work of Megaw and Kelsey [106] and Mamedov and Belov [79] is specially important. Recently the structure of natural 11 Å tobermorite mineral was completely studied in details by Hamid with the help of X-ray diffraction studies [103].

These relative rare minerals later could be synthesised from reactive silica, calcia and alumina sources. The details are reported by Kalousek [1] and by Taylor et al. [26].

The synthesis of tobermorite from solutions and from zeolites is described by Mitsuda [107]. The thermal properties of tobermorites are found to be very interesting. Formation of three distinct phases of tobermorite is observed on heating by Mitsuda and Taylor [108]. They differentiate the tobermorites as normal and anomalous. The normal and anomalous behaviour of tobermorites was determined by heating the samples at 300°C for 20 hours followed by their identification by X-ray diffraction. The tobermorites are described as "normal" if their basal spacing decreases to ~0.9 nm on heating at 300°C and "anomalous" if the spacing remains 1.1 nm after dehydration. The term 'mixed tobermorite' applies to tobermorites which show intermediate behaviour, i.e. they contain both normal and anomalous tobermorites in comparable amounts. The term mixed tobermorite is also applied to the tobermorites which gives a broad peak at about 1.05 nm upon heating at 300°C [2].

Barrer has suggested that several layered silicates should exhibit cation exchange due to their special anionic framework [109]. The Al-substituted tobermorite has also been reported to exhibit base exchange behaviour. The Al-substituted 1.1 nm type tobermorites have been reported to have cation exchange and selective properties. Cation exchange in respect of Cs⁺ has been investigated in some detail; the Cs⁺ uptake of tobermorite is said to be caused by substitution of Si⁴⁺ by Al³⁺ and H₃O⁺ subsequently participating in exchange with Cs⁺ [75]. Ion exchange and selective properties of substituted tobermorites have also been reported in respect of Rb⁺ and Na⁺ [110].

McCulloch et al. have also confirmed the Cs⁺ uptake in Al-substituted 11Å tobermorite [111]. But there has been some disagreement about the amount and
mechanism of uptake of different alkali and transition metal cations. However, a comparatively lower uptake capacity for monovalent cations has been confirmed. The isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral sites of the tobermorite structure has been studied. The resultant charge deficiency is said to be compensated by the addition of alkali metal ions which are supposed to be present in the interlayer spaces [112]. Alkali metal ion exchange and selective properties of Al-substituted tobermorite have been reported by Tsuji and Komarneni. The Kielland plots and separation factors for Na$^+$, Rb$^+$ and K$^+$ have also been discussed by them [113].

Komarneni and Roy have compared the cation exchange capacities of Al-substituted tobermorites with that of unsubstituted tobermorites[92].

**Different Routes of Synthesis**

Synthesis of tobermorite using different sources of lime, silica and alumina has been reported by Komarneni and Roy. Table 1.1 summarises different conditions of the synthesis[80].

Such studies have been done on both cesium and rubidium. Other applications of tobermorites such as inexpensive solidification of hazardous industrial waste have also been suggested [92]. A method of storing radioactive wastes using modified tobermorite matrix is described [114]. Heavy metal removal from aqueous solutions by tobermorite and zeolite is also reported elsewhere [115]. The solid state high resolution $^{29}$Si-NMR spectroscopy of synthetic 14Å-, 11Å- and 9Å-tobermorites has been done by Wieker et al. [116]. They have contributed significantly to the understanding of the structure and crystallochemical behaviour of tobermorites. Extensive $\text{Si-O-Si}^-$ bridges between the SiO$^4$ tetrahedral chain of anomalous tobermorite are suggested to check the collapse of basal spacing on heating. Wieker et al. and Guggenheim et al. have also attributed the cesium selective property of Al-substituted tobermorite to its layered framework and have compared it with ganophyllite [116,117]. Ion exchange properties of 11Å tobermorite have been subsequently investigated by Shrivastava and Glasser. The kinetics of exchange reactions has been studied. Remarkable cation exchange capacity of this cation exchanger has been reported in respect of several transition
metal ions [118, 119].

Table 1.1 Tobermorite synthesised from different sources of raw materials[92]

<table>
<thead>
<tr>
<th>S.No</th>
<th>Initial sample mixture</th>
<th>Component ratio C/S/A/Ma</th>
<th>Temp (°C), Pressure duration (days)</th>
<th>Mineralogy (XRD) after treatment</th>
<th>Cation exchange capacity (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na₂SiO₃·9H₂O + AlCl₃·6H₂O + CaO</td>
<td>0.93:1:0.1</td>
<td>180°C, Saturated steam, 4 days</td>
<td>Al-substituted tobermorite (AC) calcite</td>
<td>185*</td>
</tr>
<tr>
<td>2</td>
<td>Na₂SiO₃·9H₂O + AlCl₃·6H₂O + CaO</td>
<td>0.93:1:0.1</td>
<td>180°C, Saturated steam, 5 days</td>
<td>Al-substituted tobermorite (AC) calcite</td>
<td>158</td>
</tr>
<tr>
<td>3</td>
<td>Na₂SiO₃·9H₂O + AlCl₃·6H₂O + CaO</td>
<td>0.93:1:0.1</td>
<td>180°C, 30MPa, 14 days</td>
<td>Al-substituted tobermorite (M, C) calcite</td>
<td>153</td>
</tr>
<tr>
<td>4</td>
<td>Na₂SiO₃·9H₂O + AlCl₃·6H₂O + CaO</td>
<td>0.9:1:0.1</td>
<td>180°C, 30MPa, 14 days</td>
<td>Al-substituted tobermorite (M, VC) calcite</td>
<td>136</td>
</tr>
<tr>
<td>5</td>
<td>Na₂SiO₃·9H₂O + AlCl₃·6H₂O + CaO</td>
<td>0.9:1:0.1</td>
<td>180°C, 30MPa, 14 days</td>
<td>Pectolite Plagioclase</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Phillipsite NV+ amorphous SiO₂ + CaO + NaOH</td>
<td>0.7:0:5:0:2:0:2</td>
<td>180°C, saturated steam, 4.5 days</td>
<td>Al-substituted tobermorite (A, VC) calcite</td>
<td>197</td>
</tr>
<tr>
<td>7</td>
<td>Phillipsite NV+ amorphous SiO₂ + CaO</td>
<td>0.5:0:5:0:2:0:2</td>
<td>200°C, 80 M Pa, 28 days</td>
<td>Al-substituted tobermorite (A, C)</td>
<td>162</td>
</tr>
<tr>
<td>8</td>
<td>Clinoptilolite ID + SiO₂ + CaO</td>
<td>0.8:0:3:0:3:0:3</td>
<td>200°C, 30 M Pa, 28 days</td>
<td>Al-substituted tobermorite (A, VC) calcite</td>
<td>139</td>
</tr>
<tr>
<td>9</td>
<td>Phillipsite NV+ amorphous SiO₂ + CaO</td>
<td>0.8:0:5:0:2:0:2</td>
<td>80°C, saturated steam, 22 days</td>
<td>Al-substituted tobermorite (PC) calcite</td>
<td>128*</td>
</tr>
<tr>
<td>10</td>
<td>amorphous SiO₂ + Al₂O₃+CaO</td>
<td>0.9:0:9:0:09</td>
<td>200°C, 30Mpa, 28 days</td>
<td>Al-substituted tobermorite (AC) xenotlite</td>
<td>16</td>
</tr>
<tr>
<td>11</td>
<td>9SiO₂(Quartz)+CaO</td>
<td>0.45:0.5</td>
<td>175°C, saturated steam, 19 days</td>
<td>Tobermorite (AC)</td>
<td>12*</td>
</tr>
</tbody>
</table>

* Average of duplicate determinations
A = anomalous, M = mixed, C = crystalline, PC = poorly crystalline, VC = very crystalline
Synthesis of xonotlite from lime-silica mixtures has also been investigated [1, 2]. Substantial developments have been made in the refinements of the structure of xonotlite, particularly by Mamedov and Belov and by other workers [120, 121]. Cation exchange capacity of synthetic xonotlite has been determined and pseudomorphism in xonotlite has been discussed in relation to its ion exchange properties [92]. Recently, solid state $^{27}$Al and $^{29}$Si magic angle spinning NMR spectroscopy (MASNMR) has been combined with electron energy loss spectroscopy (EELS) to determine the location of Al-substitution in semicrystalline C-S-H gel present in hydrated synthetic slag glass. The gel has been found to contain mainly pentameric silicate chains in which central silicon is substituted by aluminium [122].

1.6 (B) Na/K FLUOROPHLOGOPITE GEL

1.6.1 Sol-gel Method

A precursor for potassium fluorophlogopite (KFP) gel has been prepared by combination of a fluoridated magnesium silicate sol, FMS and a potassium alkoxy aluminate complex that was modified by acetylacetone, K (acac) A. Three variations of the overall process are illustrated in Scheme I [124].

```
SCHEME I
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- 3Mg, dry MeOH
- 3Si(0H)$_4$
- 3Mg(OR)$_2$ + 3 Si(OR)$_4$, R = Me, Et
- H$_2$O + H$_2$O, MeOH
- Translucent 'Mg, Si' Sol
- 2H(0aq.) MeOH
- FMS Sol
- K(OCH$_3$(CH$_2$OMe)$_2$ + Al(OBu)$_3$
- KA(OR), K(OR)$_3$
- K(acac) A solution
- FMS Sol and K (acac) A
- Dry H$_2$O$_2$
- Calcine & Fire
- Spin or dip coat
- Thin films
The hydrolysis and condensation of a mixture of tetra-ethylorthosilicate (TEOS) and magnesium methoxide, facilitated by hydrogen peroxide in methanol, have been described for the preparation of sol-gel precursors for synthetic forsterite, Mg$_2$SiO$_4$ and enstatite, MgSiO$_3$ (125-127). The principal role of H$_2$O$_2$ in these syntheses was to prevent precipitation of Mg(OH)$_2$. A magnesium containing catalyst, generated in-situ, also enhanced the hydrolysis and condensation of TMOS (also generated in situ) during hydrolysis with methanolic H$_2$O$_2$ (128).

A partially hydrolysed magnesium silicate sol (124) was treated with aqueous HF to facilitate the formation of Mg-F bonds since, in the KFP structure, each fluoride ion is bonded to magnesium (129). The strategy was to minimise the formation of compounds that contained highly stable Al-F bonds, over Mg-F bonds of lower bond energy (130,131). To further safeguard against reaction of HF with Al, acetylacetone (acacH) was used to form a complex with aluminium. This modification also prevented precipitation of aluminium methoxides when the (K(acac)A) complex was combined with the FMS sol in methanol (124). This protocol, referred to as method A, is outlined in Scheme 1. When concentrated and dried, the mixture of sol and metal complex formed a clear glass.

For preparation of a powder, the crushed glass was moistened with 30% H$_2$O$_2$ to assist in removal of carbonaceous byproducts. Then it was dried, calcined at 600 °C, and fired for 4 hours at each of the three temperatures, 800, 950 and 1100°C.

A multistep addition of HF was devised for the synthesis of the FMS sol to increase the effectiveness of the fluoridation step and to test the validity of HF with the Mg-containing component. Method B involved the addition in 10 portions of the following solutions in the order given.

(i) 3:3 Mg : Si solution of alkoxides
(ii) 30% aqueous H$_2$O$_2$ solution in methanol, and
(iii) 49% aqueous HF solution in methanol (124).
1.7 Structure of Tobermorites and Xonotlite

1.7.1 Structure of Tobermorites

The 11Å tobermorite is one of the members of the group called tobermorite minerals. It is a calcium silicate hydroxyhydrate. The actual chemical composition of tobermorite depends on the experimental conditions, preparative method and Ca/Si ratio of the reaction mixture. These various tobermorites differ in Ca/Si ratio which ranges from 0.7 to 1.0 [2].

Synthetic 1.1 nm tobermorite is similar to that of natural 1.1 nm tobermorite mineral in all respects. The work of Megaw and Kelsey [106] is specially important in which they have described tobermorite possessing a pseudo-orthorhombic unit cell containing two identical layers parallel to (001) plane and displaced relative to each other; the SiO$_4^{2-}$ tetrahedral portions in "puckered chains" with hydrogen attached to O$_2^{-}$ anions of the tetrahedra parallel to 'b'. The Ca-O octahedra show four O$_2^{-}$ neighbours in complex sheets 4Ca$_2$Si$_3$O$_9$ and two O$_2^{-}$ in the sheet of the next level as schematically shown in Fig.1.1. These sheets are like double sided corrugated paper having a strong central sheet reinforced on each surface by longitudinal toothed ridges and grooves between these ridges. They have also reported that tobermorite shows similar disorder phenomenon like that of wollastonite [106]. Tobermorite also possesses Dreierketten as present in wollastonite. The term Dreierketten was used by Thilo et al. meaning a metasilicate chain linked so as to repeat at intervals of three tetrahedra [102]. Mamedov and Belov suggested the possibility of the existence of double chain in tobermorite similar to that in xonotlite [79]. The structure of natural 1.1 nm tobermorite mineral was described by Hamid [103] following Megaw and Kelsey's model [106]. He also observed the disordered structure of tobermorite with the existence of Dreierketten. According to this structure, tobermorite has infinite Si$_3$(O/OH)$_9$ chains running parallel to b-axis which are linked together by calcium atoms (Figs. 1.2 and 1.3). The mean Si-O distances in the Si$_3$(O/OH)$_9$ chain is 2.64 Å, 11 Å-tobermorite normally has five calcium atoms in its empirical formula. The environments of Ca(1) and Ca(2) are fairly similar. Both these are coordinated with seven oxygens. In the case of Ca(1) two oxygens are in the range of 2.42-2.46Å O(3) and O(6). The seventh oxygen OH(9) has a distance of 2.60Å. Ca(3) and Ca(4) are
Fig. 1.1 Structural principle of tobermorite (Megaw & Kelsey)

(a) two central sheets of layers projected on (001)
(b) the upper half of layer projected on (001)

Fig. 1.2 Some different types of silicon-oxygen chains

(a) single dreierkette
(b) double dreierkette (Si$_6$O$_{17}$) ribbons
Fig. 1.3 A three dimensional view of the tobermorite structure

Fig. 1.4 Structural model of a three dimensional view of anomalous tobermorite
also coordinated by seven oxygens but with a slightly different arrangement as compared to Ca(1) and Ca(2). In general, Ca(1), Ca(2), Ca(3) and Ca(4) are coordinated with four coplanar oxygen atoms; two oxygens above or below the coplanar oxygen group forming a tetragonal pyramid (Fig. 1.2). The octahedral coordination of Ca(5) is found to be very distorted (weak Ca-O interaction). Like other calcium silicate hydrates tobermorite also contains many stacking modifications with multiple values of `a' and `c' described by a few workers [104].

b) Structure of Xonotlite

Xonotlite occurs as a natural mineral and can also be readily synthesised hydrothermally [1]. Xonotlite is formed reproducibly, when sufficient reactive starting materials are treated hydrothermally at 150-400 °C in 1:1 Ca/Si ratio. Its formation from lime-silica mixtures proceeds through the intermediate stages of C-S-H (II), C-S-H (I) and tobermorite.

Xonotlite forms prismatic needle-like crystals or fibrous aggregates with elongation parallel to `b' axis. Synthetic crystals have a characteristic lath-like appearance in the optical or electron microscope. Beyond the Bragg classification of the silicate structures, N.V. Belov [121] described condensed ring chain complexes of the type [Si₆O₁₇]α in xonotlite. He also mentioned the similarities of quartz with xonotlite mineral.

The crystal structure of xonotlite was determined by Mamedov and Belov in 1958 [79]. They found that the double Dreierketten of empirical formula (Si₆O₁₇)₁₂⁻ was present along with Ca and OH ions. Fig. 1.4 shows one of these chains and represents the projection of the structure along the chain direction. In another investigation Mamedov and Belov identified xonotlite in close structural relation to cuspidine and tilleyite on one hand and to wollastonite on the other, especially in the occurrence of [CaO₆]α columns [119]. In xonotlite, however, one third of these columns are octahedral, two thirds of them are in the same coordination [CaO₆] in the shape of trigonal prisms as observed in the apatite. The good cleavage parallel to (100) plane in xonotlite is explained on the basis of sheetwise orientation of the [Si₆O₁₇] groups; a weaker cleavage parallel to (001) is caused by the walls of the [CaO₆]α columns. A pseudo period of the b = 3.66 Å is very distinct and typical for the
xonotlite derived structures, whereas the true period is $b = 7.32\text{Å}$ with an angle $\beta = 90^\circ$. The characteristic [Si$_6$O$_{17}$] ribbons are seen in Fig. 1.5 with an Si-O-Si angle of $158^\circ$ [120] and a very typical ambiguity of orthorhombic and triclinic arrangements of these chains as discussed by Mamedov and Belov [79]. These can be compared having identical cell parameters $b_0$ and $c_0$ but different $a_0$ to explain the polytipism of xonotlite [79].

![Diagram of xonotlite structure]

**Fig. 1.5** Structural model of xonotlite
1.8 SCOPE OF THE PRESENT STUDY

Barrer has suggested that the structure of several layered silicates should favour cation exchange due to their typical anionic framework (109). Until recently his suggestions donot seem to have been investigated in respect of calcium silicates of the tobermorite hydrates. Recently, hydrous calcium silicates of the tobermorite and xonotlite groups have been discovered as cation exchangers which exhibit exchange and selective properties, in some respects much better than those of zeolites and clay minerals. Most of this work has been done on aluminium substituted synthetic tobermorites (77,92,112-115,119,123).

It has now been established that a calcium silicate hydrate close to Ca$_5$Si$_6$O$_{18}$H$_2$.4H$_2$O, which plays an essential role in the hydration process of cements and is identical with natural 11Å-tobermorite mineral, exhibits remarkable cation exchange properties. Cation exchange studies on 11Å tobermorite have been made in respect of a few cations. Some workers have also studied the ion exchange in xonotlite but cation exchange properties, thermodynamics and mechanism of such cation exchange reactions are yet to be fully understood.

The calcium silicate hydrates are attractive for investigations because of the following reasons:

1. Their remarkable cation exchange capacity towards different kinds of cations including alkaline earths, alkali and transition metals.

2. Non-degradable nature, which enables their use in different types of exchange processes.

3. Purity and their easy synthesis from reactive silica and calcia which are quite inexpensive and readily available.

4. Probable catalytic activity as normally found in many exchanged zeolites, clays and other silicates.

5. Their importance in cement hydration processes.
6. Their myriad applications in various silicate-related fields like ceramics and clay mineralogy.

With this scope and background the cation exchange properties of synthetic 11Å tobermorite and xonotlite in respect of hazardous cations like Cs⁺ and Sr²⁺ were proposed to be systematically investigated on the basis of ion exchange, X-ray diffraction, thermal and related studies. Attempts have also been made to formulate the thermodynamics and mechanism of such ion exchange reactions.

The high leach resistance of calcium silicate hydrate at elevated temperatures increases the range of geological environments in which the waste may be finally buried; in particular tobermorites are well adapted for disposal in deep drill-holes, both in continental as well as marine environments. Its long-term geological stability is significant in establishing public confidence in the ability of the nuclear industry to immobilise intermediate level wastes for the very long periods required.

Intermediate level wastes arising from the operation of nuclear reactors are intensely radioactive and must be isolated from the biosphere for extremely long periods up to one million years. Most countries intend to dispose of their wastes by converting them into a solidified form and burying this within the earth. Subsequent leaching of the waste form by circulating ground waters is the most likely mechanism by which radionuclides could be returned to the biosphere. It is, therefore, desirable that the waste form should be constructed from a highly stable material possessing an extremely low solubility in ground water. Thus, the waste-form itself should function as an 'immobilisation barrier' fully capable of preventing any significant release of radionuclide to the biosphere for 10⁵⁻¹⁰⁶ years. The waste-form would be disposed off in a repository sited in a geological environment carefully selected for its capacity to minimise access of underground water to the waste and possessing low permeability so as to inhibit circulation of these ground waters. This constitutes the so-called 'geological barrier' which is essentially independent of the immobilisation barrier. Ideally, each of these barriers should be independently and fully capable of preventing any significant entry of rad-waste species into the biosphere.
Immobilisation of ILW in OPC

The most popular immobilisation barrier that has been advocated by the nuclear power industry over the last two decades has been to incorporate ILW in OPC. This immobilisation and solidification of ILW can more readily and effectively be achieved by using certain additives to OPC. It has been investigated in the present study.
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