Part I:  
CALCIUM SILICATE HYDRATES

(A) II\textsuperscript{0} TOBERMORITE:

The synthesis of II\textsuperscript{0} tobermorite is already described in chapter III. This synthetic product was then subjected to analysis for its characterization. Chemical analysis (Tab.1.i) of this compound shows the empirical formula Ca\textsubscript{4.98}Si\textsubscript{5.96}O\textsubscript{18}H\textsubscript{2.4} which closely resembles with the formula of normal II\textsuperscript{0} tobermorite\textsuperscript{(1-4)}. On examination under electron microscope, the synthetic product was found to be in the form of thin platy crystals having length 0.5 to 5.0 m\textmu (Fig. 1.A) characteristic for II\textsuperscript{0} tobermorite\textsuperscript{(5)}. This hydrothermally synthesized crystalline phase is also associated with little amorphous material. X-ray powder diffraction pattern of this synthetic product (Fig.-1.D) matches well with the standard pattern for II\textsuperscript{0} tobermorite as reported by Taylor et al.\textsuperscript{(6)} Reflections having d-spacings between 11.2 and 1.5 \AA\ match with the standard, both in position and intensity (Table I.ii). Indexing has been done for a pseudo orthorhombic cell, characteristic for II\textsuperscript{0} tobermorite\textsuperscript{(7,8)}. The lattice constants observed are:

\begin{align*}
a &= 11.3489 \text{ \AA} \\
b &= 07.3601 \text{ \AA} \\
c &= 22.4228 \text{ \AA}
\end{align*}
Infrared Absorptions:

Infrared absorption spectrum of synthesized 0 A tobermorite shows typical pattern for calcium silicate hydrates with characteristic absorptions of tobermorite. The IR spectrum (Fig. 1.B) consists of a sharp peak around 3590 cm⁻¹ which is due to the O-H stretching vibrations of water molecules. A weak band near 3450 cm⁻¹ is observed due to hydroxyl bonding, characteristic for tobermorite. The frequency of the O-H oscillations depends on the more or less covalent character of the bond Si-O. A strong band due to H-O-H deformation is appeared at 1630 cm⁻¹ (Table I.1) which is also a characteristic absorption. A clear band at 1210 cm⁻¹ again be due to the deformation oscillations of H-O-H, bonded with calcium. The prevailing ionic character of the bond Ca-O is probably responsible to reduce the deformation frequency. A broad band is observed ranging 1100-860 cm⁻¹ which arises from Si-O stretching vibrations. This is also identical with reported structural vibrations for tobermorite. A strong absorption at 670 cm⁻¹ along with weak band at around 630 cm⁻¹ might again be due to R-O-H bending. Al³⁺ which is often present in traces may be responsible along with interlayer calcium content for this absorption band.

Thermal Behaviour:

Two clear steps were observed in thermogram of synthetic tobermorite (Fig. 1.C). First break observed between 60-240°C
having 8.9 wt% loss (Table-1.i) corresponds to loss of water \(^{(7,17)}\). Second gradual weight loss between 240 and 750°C is about 5% of the sample's initial weight. This may be attributed to the elimination of hydroxyl groups \(^{(17,18)}\). After heating at about 300°C a unidimensional lattice shrinkage is observed in the synthetic II\(\alpha\) tobermorite and its 'c' axis spacing is found to be reduced. X-ray powder diffraction data of post heated (at \(\sim 300°C\)) II\(\alpha\) tobermorite (Table-1.iii and Fig.-1.E) confirm the lattice shrinkage and formation of a 9\(\alpha\) tobermorite, thereby suggesting the normal behaviour of synthetic II\(\alpha\) tobermorite. Some other properties of synthetic product which support its normal behaviour \(^{(3,4,7)}\) are as follows:

1. Comparatively higher calcium content (Table-1.i).
2. Absence of alkali (Table-1.i).
3. Well crystalline structure with frequent cleavage in c direction (Table-1.ii).
4. Resemblance in thermal decomposition pattern (Fig. 1.C) with normal II\(\alpha\) tobermorite. \(^{(7)}\)

This synthetic normal II\(\alpha\) tobermorite is subjected to the ion exchange experiments.

**Cation Exchange Studies with Zn\(^{2+}\)**

The mass balance data for cation exchange of II\(\alpha\) tobermorite with Zn\(^{2+}\) is summarised in Table-2.i. Analytical data reveal that significant amount of zinc (14 wt%) could be introduced
in to the framework of $\text{II}^\circ$ tobermorite. This indicates the good affinity of exchanger towards divalent zinc. The molar ratio of released calcium and incorporated zinc is observed in the range of 0.82 - 1.05 proving charge balance in an ion exchange phenomenon. In respect of analytical data, the ion exchange reaction can be represented as follows:

$$\text{Ca}^{2+}_{\text{Tobermorite}} + \text{Zn}^{2+}_{\text{Solution}} \rightleftharpoons \text{Zn}^{2+}_{\text{Tobermorite}} + \text{Ca}^{2+}_{\text{Solution}}$$ (i)

The relationship between fractional atomic replacement of calcium from exchanger & distribution coefficient ($K_d$) is shown in Fig.-2.B. For lower concentrations the ratio of calcium release and zinc uptake is very close to 1.0 (Table-2.i) which is expected for a true bi-bivalent exchange. After about 20% release of the original calcium content of exchanger, further release of calcium ions gradually decreases as also shown in Fig.-2.B. This indicates that a certain amount of total calcium content of $\text{II}^\circ$ tobermorite is favourably distributed in the structure, and is available for cation exchange.

To develop the thermodynamics of this ion exchange reaction, selectivity coefficients have been calculated for each concentrations, making assumption that the activity coefficient is unity for these dilute solutions. The ion exchange isotherm is shown in Fig.-2.A, indicating saturation of the exchanger with zinc after incorporating its 2.151 m-moles per gram. This could be corelated to the limited amount of releasable calcium of $\text{II}^\circ$
tobermorite which is responsible for its cation exchange activity. The free energy of the exchange reaction is computed following a modified version of the method of Gaines and Thomas (19) as described by Sherry and Walton (20). The details are already given in Chapter I. Thermodynamic equilibrium constant \( K \) has been graphically evaluated (20). Within the limits of experimental error, the value of free energy \( \Delta F_{305} \) is observed \( = -505 \pm 15 \text{ cal/equiv.} \). This negative value of free energy suggests the affinity of Zn\(^{2+}\) towards the exchanger’s anionic framework.

An ion exchanger should be nondegradable in nature so that it could be reused after some treatment. X-ray powder diffraction data of zinc exchanged tobermorite (Table-2.ii) when compared with that of 11Å tobermorite (Table-1.ii) indicate that the crystallinity and structure of the exchanger remains intact after cation exchange. Empirical formulae of zinc exchanged products have also been derived with the help of analytical data of the solid and solution phases, after equilibrated state (Table-2.ii).

To check the reversibility of the exchange reaction, back exchange of Zn-tobermorite (set-6, initially containing 1.87 mmols of zinc) was performed in similar experimental conditions, with a calcium solution of concentration 25 mmols dm\(^{-3}\). Only 0.42 mmols of zinc could be extracted from exchanger, showing poor back exchange and affinity of 11Å tobermorite towards divalent zinc. However, zinc can easily be removed from tobermorite by treatment with a dilute calcium-EDTA solution (containing 30.0 mmols of
calcium and 20.0 mmols of EDTA dm\(^{-3}\)). It seems useful and affective method to regenerate \(\text{IIA}^0\) tobermorite. Regenerated \(\text{IIA}^0\) tobermorite is checked with the help of X-ray powder diffraction (Table-2.iii & Fig. 2.E).

No significant change was observed in the thermogravimetric curve (Fig. 2.C) of zinc exchanged tobermorite, (set 6 containing 12.82 wt% of zinc) except slight increase in the water content. This is probably due to the introduction of few water molecules in Zn-tobermorite , since zinc possesses better affinity with water as compared to that of calcium.

Attempts have been made to prepare intercalated compounds with exchanged metal ions which are present inside the tobermorite structure. However, on treatment with a dilute solution of dithizone, most of the zinc from zinc-exchanged tobermorite comes out from tobermorite framework in the form of Zn-dithizone complex, instead of retaining inside the structure.

Following reaction is possible:

\[
\text{Zn(H}_2\text{O)}_n^{2+} + \text{dithizone} \rightarrow \text{Zn-dithizone + nH}_2\text{O} \quad (\text{ii})
\]

In this way, it is not possible to introduce bigger organic molecules in the rigid structure of tobermorite having small interlayer gaps which seem to be suitable for cations only.

**Cation Exchange Studies with Fe\(^{3+}\)**

Cation exchange experiments on \(\text{IIA}^0\) tobermorite with Fe\(^{3+}\)
were performed in similar experimental conditions at room temperature (298°C) taking thirteen solutions with different Fe³⁺ concentrations, ranging from 100 to 5000 ppm initially. Both solid and solution phases were analysed for the quantity of iron and calcium, after reaching at steady state on shaking 7 days. It was observed that synthetic II₄ tobermorite shows great affinity towards Fe³⁺ ions. As much as ~16 wt% of iron could be introduced in to the exchanger. The calcium release from tobermorite is appropriate (Table-3.i), particularly for lower iron concentrations. Ion exchange reaction can be represented as follows:

\[
3\text{Ca}^{2+}\text{Tobermorite} + 2\text{Fe}^{3+}\text{Solution} \rightleftharpoons 2\text{Fe}^{3+}\text{Tobermorite} + 3\text{Ca}^{2+}\text{Solution} \quad \text{(iii)}
\]

Analytical data (Table-3.i) reveal that the molar ratio of calcium released and iron incorporated is in the range of 1.46 - 1.30. Slightly lower values are observed with higher iron concentrations. The reason might be the availability of limited exchangeable calcium in II₄ tobermorite. The slight inconsistency in equivalence of Ca²⁺/Fe³⁺ at higher iron concentrations may be attributed to significant adsorption of iron in concentrated solutions as well as greater affinity of Fe³⁺ towards dreierketten of II₄ tobermorite. The fractional atomic replacement of calcium from tobermorite is represented in Fig. 3.B as a function of distribution coefficient. This figure and analytical data (Table-3.i) show the decrease in the calcium release with increasing initial iron concentration. However, in this particular case almost 50% of the original calcium content of II₄ tobermorite has been released during cation
exchange. This is extremely high in comparison to those reported for various other cation exchange equilibria of 11A tobermorite (21, 22).

Thermodynamics of this exchange reaction has also developed in the same manner as described for zinc exchange. The distribution coefficients \( K_d \) have been calculated for each concentration as 'the ratio of the amount of iron sorbed per gram of tobermorite to the amount of unsorbed iron per ml of solution.' The range of the values of \( K_d \) observed is 1860 - 48. The ion exchange isotherm of this exchange reaction is shown in Fig.-3.A, indicating the saturation of solid phase with iron. Free energy of the reaction has worked out at \( 298^\circ K \). The value of free energy \( \Delta F_{298} \) observed is \(-498 \pm 15 \text{ cal./equiv.} \). Such negative value of free energy at \( 298^\circ K \) is a valuable support to show affinity of exchanger towards \( Fe^{3+} \) ions. A proportional relationship is observed between \( \log_{10} K_d \) and fractional atomic replacement of calcium from tobermorite (Fig. 3.B) which also indicates comparatively greater release of calcium from tobermorite for iron exchange.

**Mössbauer studies on iron exchanged tobermorite:**

To study the valency and spin states of iron cations as well as steric peculiarities of their nearest surroundings, the mössbauer spectroscopic studies have been performed on iron exchanged tobermorite derived from set 5 (Table-3.1) and containing \( \sim 7 \) wt% of iron. The plot of mössbauer spectrum (Fig.-3.E) consists of one doublet with isomeric shift \( \delta = 0.35 \pm 0.01 \text{ mm/sec}^{-1} \).
and quadrupole splitting $\Delta = 0.72 \pm 0.01$ mm sec$^{-1}$. Such value of $\delta$ is typical for Fe$^{3+}$ in high spin state in octahedral surrounding of oxygen but large value of $\Delta$ and line width $\Gamma = 0.468 \pm 0.01$ mm sec$^{-1}$ shows that, oxygen octahedra are neither ideal nor similar over the bulk. To estimate the content of non-distorted octahedra of oxygen surrounding of the Fe$^{3+}$ cations, the Mössbauer spectrum has been treated by computer as superposition of two doublets. After resolving the spectrum, it has been observed that the doublet with relative intensity of $29 \pm 5\%$ and $\delta = 0.36 \pm 0.01$ mm sec$^{-1}$ may be attributed to Fe$^{3+}$ cations, placed in non-distorted octahedra because line width is small ($\Gamma = 0.31 \pm 0.01$ mm sec$^{-1}$). Quadrupole splitting $\Delta = 0.50 \pm 0.01$ mm sec$^{-1}$ is also not high. The second doublet with relative intensity of $71 \pm 5\%$ has practically the same isomeric shift $\delta = 0.35 \pm 0.01$ mm sec$^{-1}$ but the quadrupole splitting $\Delta = 0.85 \pm 0.01$ mm sec$^{-1}$ and line width $\Gamma = 0.47 \pm 0.01$ mm sec$^{-1}$ are considerably more than that of the first one. This doublet can be attributed to Fe$^{3+}$ surrounded by distorted oxygen octahedra. In this way, Mössbauer study provided rich information particularly about surroundings of Fe$^{3+}$ cations.

With the help of these data, we suppose that the incorporated Fe$^{3+}$ ions take positions of released Ca$^{2+}$ ions. The iron present in place of fifth calcium atoms$^{(8)}$ is expected to be present in distorted octahedral surroundings of oxygen atoms while rest of the iron might be present in place of Ca(4) or other calcium atoms$^{(8)}$ showing regular octahedral surroundings. The regular
tetragonal pyramidal surroundings of these Ca atoms\(^8\) are expected to be changed in regular octahedra in case of Fe\(^{3+}\), due to comparatively greater attraction of iron with oxygen. Thermogravimetric curve of iron exchanged tobermorite (Fig.-3.C) shows a break between 660-740\(^0\)C although the total water loss is almost same for both the compounds (II\(^0\)A tobermorite and iron exchanged tobermorite). Farmer et al.\(^{17}\) suggested that water loss above 400\(^0\)C is due to the elimination of hydroxyl groups. In case of iron exchanged tobermorite, the observed break at higher temperature could be due to firm attachment of OH groups to Fe\(^{3+}\) cations. Thus, there are reasons to suggest that the Fe\(^{3+}\) cations enter in to the structure of II\(^0\)A tobermorite and take positions in spaces vacated by Ca\(^{2+}\) ions without damage to its crystallinity.

The X-ray powder diffraction data of iron exchanged tobermorite (Table-3.ii) do not show any appreciable change in comparison of original II\(^0\)A tobermorite (Table-1.ii), thereby indicating the unaffected crystallinity of ion exchanger after cation exchange, when placed in dilute solutions of Fe\(^{3+}\). This X-ray diffraction study has been carried out on sample obtained from set No. - 6 (Table-3.i) having empirical formula \(\text{Ca}_{3.31}\text{Fe}_{1.18}\text{Si}_{0.6}\text{H}_{18.2}\cdot\text{H}_2\text{O}\). Empirical formulae of other exchanged samples have also been derived with the help of analytical data.

Iron exchanged tobermorites show very poor back exchange. After treatment with concentrated calcium solution (0.22M) in similar experimental conditions, no significant amount of iron was released
from exchanger. Iron exchanged samples were also treated with thiocyanide solution, which has great tendency of complexation with Fe\(^{3+}\). It is surprising to note that iron still remains in tobermorite framework showing very stable composition of Iron(III) exchanged tobermorite. It was also not possible to introduce thiocyanide in to the tobermorite framework, as it does not possess enough interlayer spaces between two silicate chains.\(^{8}\)

**Cation Exchange Studies with Pb\(^{2+}\)**

In earlier studies on exchange properties of 11\(^{0}\)A tobermorite\(^{(21-24)}\), all the cations tried, are having lower ionic radius than Ca\(^{2+}\), which is a releasing ion. The remarkable cation exchange capacity of tobermorite towards these ions (except Mg\(^{2+}\))\(^{(22)}\) is also attributed to the smaller size of exchanged cations. We studied cation exchange properties of synthetic normal 11\(^{0}\)A tobermorite with bigger cation like Pb\(^{2+}\) (atomic weight 207 and ionic radius 1.2\(^{0}\)A) as compared to that of Ca\(^{2+}\) (atomic weight 40.08 and ionic radius 0.98\(^{0}\)A). Though the nature of this exchange is almost similar to that of exchange reactions with other bivalent cations, yet there are some interesting features of Pb\(^{2+}\) exchange.

The ion exchange experiments were typically carried out at 294\(^{0}\)K with thirteen different concentrations of Pb\(^{2+}\) solutions initially ranging between 100 to 5000 ppm. Analytical data of solid and solution phases are reported in Table-4.1. Mass balance data suggest that the uptake of lead is less as compared to other cations. As much as only 0.74 mmols of lead could be introduced
per gram of tobermorite after shaking with a 24.13 mmols dm$^{-3}$ Pb$^{2+}$ solution. The molar ratio of calcium released and lead incorporated is very appropriate, i.e. ranging from minimum of 0.97 to maximum 1.15, regardless of initial lead concentration. This suggests a true ion exchange phenomenon which can be represented as:

$$\text{Ca}^{2+}_{\text{Tobermorite}} + \text{Pb}^{2+}_{\text{Solution}} \leftrightarrow \text{Pb}^{2+}_{\text{Tobermorite}} + \text{Ca}^{2+}_{\text{Solution}} \quad (\text{iv})$$

Analytical data reveal that, as much as $\sim 18.5\%$ of original calcium content of tobermorite was released during cation exchange with Pb$^{2+}$. This is probably because one out of five calcium atoms (20% of original calcium content) is favourably situated for cation exchange in II$^0\text{A}$ tobermorite$^{(8, 21, 22)}$. The exchanger becomes saturated with respect to Pb$^{2+}$ ions when 15.43 wt% of lead are exchanged with calcium ions, even when whole of the supposed releasable calcium of II$^0\text{A}$ tobermorite is not released. This is probably because of massive geometry and weight of Pb$^{2+}$ which obviously occupy greater space than Ca ions, in compact framework of tobermorite. After inclusion of certain amount of lead, these ions may prevent further introduction of lead in tobermorite structure. The linear relationship between $\log_{10} K_d$ and fractional atomic replacement of calcium (Fig.-4.B) breaks at saturation point.

In the thermodynamic studies of this exchange reaction, the value of free energy calculated at 294°K is $\Delta F_{294} = -210 \pm 15$. 
cal./equiv. This is comparatively higher value of free energy but is sufficient to suggest that II\text{A} tobermorite has fairly good affinity and exchange capacity towards Pb\textsuperscript{2+} ions, even though it has a greater mass number and larger ionic radius.

There is always a possibility of damage in crystallinity of the exchanger, when treated with some heavier ions. It should be noted that Ca\textsuperscript{2+} \textrightleftarrows Pb\textsuperscript{2+} exchange does not damage the crystallinity and structure of II\textsuperscript{A} tobermorite. This is evident from X-ray powder diffraction data of the lead exchanged tobermorite.

X-ray diffraction studies have been performed on sample No. 6 (Table-4.ii) containing 8.5 wt\% of lead and sample No. 12 containing 15.4 wt\% of lead (Table-4.iii). The basal spacings and intensities remain almost unchanged. On examination under electron microscope, no significant change has been observed in morphology of lead exchanged tobermorite (Fig. 4.G).

No marked change has been observed in thermogram of lead exchanged tobermorite (Fig. 4.C) derived from set No. 12. A slight decrease in the water content of lead exchanged tobermorite is noted by thermogravimetric analysis, which could be due to the weight enhancement in tobermorite after uptake of heavy lead ions. In any case, this decrease is not sufficient to conclude participation of H\textsubscript{3}O\textsuperscript{+} ions in exchange reaction of tobermorite, as suggested earlier\textsuperscript{(23)}. Back exchange is quite significant in this case. About 90\% of the lead from lead-exchanged tobermorite could be extracted (data obtained on set No. 7 containing 10 wt\% of lead).
by treating it with a solution having initially $0.125 \text{ mol dm}^{-3}$ Ca ions. Lead exchanged tobermorite can be converted back into original II$\text{A}$ tobermorite (Table-4.iv) by treatment with slightly concentrated solution ($0.250 \text{ m dm}^{-3}$) of calcium under similar experimental conditions. Comparatively smaller ionic radius of calcium than lead, may be responsible for effective back exchange in this case. This is an important property for applications of II$\text{A}$ tobermorite as an ion exchanger for lead and other heavy ions.

The ion exchange studies on $\text{Ca}^{2+} \leftrightarrow \text{Pb}^{2+}$ exchange of synthetic normal II$\text{A}$ tobermorite strongly support its potential for applications as efficient cation exchanger for removal of lead and other heavy metal ions which are normally present in nuclear and industrial waste, causing severe radiation hazards and pollution for human beings, animals and plant kingdom.

**Cation Exchange Studies with Mn$^{2+}$**

Cation exchange studies on II$\text{A}$ tobermorite with a series of transition metal ions confirm its affinity towards most of these bivalent cations. In this sequence, we studied cation exchange behaviour of synthetic normal II$\text{A}$ tobermorite with Mn$^{2+}$, which possess good catalytic activity towards several reactions of applied importance.

It has been possible to prepare Mn-exchanged tobermorites containing 0.8 to 11.5 wt% manganese, by treatment of synthetic II$\text{A}$
tobermorite with aqueous manganese solutions, initially 100 to 5000 ppm. In this way, a significant amount of manganese could be introduced in to the tobermorite structure. Analytical data (Table-5.i) show the release of calcium in equivalent amount, suggesting cation substitution by Mn$^{2+}$. The relationship between fractional atomic replacement of calcium from tobermorite and distribution coefficient (Fig. 5.B) is found almost similar as in the case of Zn$^{2+}$ exchange. The ion exchange isotherm for this exchange is shown in Fig. 5.A indicating saturation of solid phase with manganese. The free energy of the exchange reaction is determined at room temperature, having value $\Delta F_{303} = -492 \pm 15 \text{ cal./equiv.}$ This is again very close to that found in the case of Zn$^{2+}$ exchange ($\Delta F_{305} = -505 \pm 15 \text{ cal/equiv}$). Such a negative value of free energy is a good support to suggest affinity of exchanger towards Mn$^{2+}$ cations.

After such a high uptake of cations, the crystallinity of the exchanger may be affected. The X-ray powder diffraction study of Mn exchanged tobermorite (Table-5.ii and Fig. 5.D) ruled out the possibility of damage in crystal structure, showing most of the peaks, characteristic of crystalline II$^0$ tobermorite. X-ray diffraction study has been performed on Mn-exchanged tobermorite containing 11.5 wt% of manganese with an empirical formula:

$$\text{Ca}_3\text{Mn}_{1.5}\text{Si}_6\text{O}_{18}\text{H}_2\text{O} \cdot 4\text{H}_2\text{O}.$$  

Mn-exchanged tobermorite shows poor back exchange capacity. To check the reversibility of the cation exchange
reaction, the Mn-exchanged tobermorite (containing 7.7 wt% of manganese) has been shaken with calcium solution (0.12M) in similar experimental conditions. It could be possible to extract only 0.21 mmols of manganese from 1 g of Mn-exchanged tobermorite. However, almost all the manganese comes out from tobermorite after treatment with 0.1 M Ca-EDTA solution. The 11Å tobermorite can be regenerated by this method.

No marked change has been observed in the thermogravimetric curve of Mn-exchanged tobermorite (Fig. 5.C) in comparison to that of original 11Å tobermorite. Thermogram indicates almost same water content in tobermorite after cation exchange with manganese.

Catalytic Study on Mn-Exchanged 11Å Tobermorite:

The Mn-exchanged tobermorite has also been subjected to investigate its catalytic activity. The reaction studied, is decomposition of hydrogen peroxide in almost neutral medium. Fig. 5.F represents the decomposition of hydrogen peroxide solution with respect to time. This figure clearly indicates the fast decomposition of hydrogen peroxide in presence of Mn-exchanged tobermorite. Kinetics of the catalyzed reaction has been developed at room temperature 303°K (Fig. 5.G) with the help of analytical data obtained at different time intervals. These data have been summarised in Table-5.iv. The reaction follows the first order kinetics with respect to \( [H_2O_2] \) i.e..
\[ \frac{d \left[ H_2O_2 \right]}{dt} \propto \left[ H_2O_2 \right] \] (v)

Average value of rate constant \( k \) observed is \( 5.417 \times 10^{-3} \) \( \text{min}^{-1} \). Kinetics data strongly suggest the fast decomposition of hydrogen peroxide in the presence of Mn-exchanged tobermorite. The rate of reaction observed is fairly fast indicating remarkable catalytic activity of this compound.

This used catalyst has been separated from reaction mixture after completion of the reaction and analysed for the quantity of manganese and its structure. It has been observed that the catalyst remains without significant loss of manganese and with unaffected structure (Table-5.v and Fig. 5.H). This should be noted as a valuable feature of the catalytic activity of Mn-exchanged tobermorite because, the catalyst can be reused without any further treatment. These preliminary studies on catalytic activity of Mn-exchanged tobermorite should thoroughly be investigated in respect of several other chemical reactions which are normally catalysed by manganese.

**Cation Exchange Studies with UO\(^{2+}\)**

As such uranium salts are few and quite unstable but frequently present in some other forms. Uranium can easily be converted in to uranyl and forms several compounds in this form. Uranyl is a bivalent cation (UO\(^{2+}\)) having massive geometry and weight, apart from its complex structure as compared to those
cations studied earlier. The cation exchange is tried with $\text{UO}_2^{2+}$ on 11A tobermorite. These cation exchange experiments were carried out at room temperature with initially 100, 1000 and 2000 ppm (in respect of $\text{UO}_2^{2+}$) aqueous solutions of uranyl nitrate. The analytical data (Table-6.i) reveal that the exchange is comparatively less in case of $\text{UO}_2^{2+}$. As much as only 0.5261 mmols of $\text{UO}_2^{2+}$ could be incorporated to the tobermorite.

The molar ratio of calcium released and $\text{UO}_2$ incorporated is not very appropriate for a bi-bivalent cation exchange (Table-6.i). This ratio is less particularly for higher $\text{UO}_2^{2+}$ concentration. This fact indicates that the adsorption of $\text{UO}_2^{2+}$ on tobermorite's surface is also significant in higher $\text{UO}_2^{2+}$ concentrations. Therefore, in such cases the uptake of $\text{UO}_2^{2+}$ by 11A tobermorite is a result of cation exchange as well as adsorption. Additional proof regarding presence of uranium (in the form of uranyl) inside and on the surface of the crystals of tobermorite was obtained by Electron Probe Microanalysis using CORA; an electron microscope equipped with an energy dispersive analytical system (investigations were carried out on Jeol Electron Microscope - 2000 attached with linked microproseosed system for CORA analysis). The preparation was dispersed on grids using ultrasonics. This study was carried out on sample no. 3 (Table-6.i) having 12.6 wt% of uranyl. Results are presented in Figs. 6.C,D,E,F. These results clearly reveal that the uranium is present on the surface of the crystals of tobermorite (Fig. 6.C) and little in the crystal (Fig. 6.D). However,
uranium is virtually absent in one of the crystals of cation exchanged tobermorite (Fig. 6.E). Some amorphous material is also recognised by this analysis which contains silicon, calcium and uranium as well (Fig. 6.F). Quantitative estimation of uranium could not be possible by this analysis as it was found to be unevenly distributed over the bulk.

It is necessary to check the crystallinity of the exchanger after exchange with such a massive and complex cation. The X-ray diffraction analysis (Fig. 6.B) is performed on the same sample used for electron optical analysis. X-ray powder diffraction data are presented in Table-6.ii. These X-ray diffraction data shows marked difference in the number and positions of crystalline peaks observed for $\text{I11}^0$ tobermorite. This fact suggests that the crystallinity of $\text{I11}^0$ tobermorite is affected after incorporation of $\text{UO}_2^{2+}$. This is also supported by electron optical analysis (Fig. 6.F) showing amorphous phase containing uranium. Effective back exchange is observed in this case, however, the regenerated tobermorite is not as crystalline as it was originally (Table-6.iii).

The uranyl ion shows comparatively poor exchange in tobermorite as well as it also affects the crystallinity of the exchanger. Heavy weight and bigger complex geometry of this cation are probably responsible for this behaviour. The co-ordination of the $\text{UO}_2^{2+}$ with the oxygens (to which releasing calcium ions are linked) is also not feasible as compared to transition metal ions.
GENERAL DISCUSSION (Ion Exchange in Synthetic $^{0}_{\text{IIA}}$ tobermorite):

In this way, the present study on cation exchange behaviour of synthetic normal $^{0}_{\text{IIA}}$ tobermorite, consists of investigations in respect of few different cations, viz. $\text{Zn}^{2+}$, $\text{Fe}^{3+}$, $\text{Pb}^{2+}$, $\text{Mn}^{2+}$ and $\text{UO}_2^{2+}$. In this context, the cation exchange behaviour of $^{0}_{\text{IIA}}$ tobermorite is first investigated in respect of $\text{Zn}^{2+}$, a transition metal bivalent ion. A fairly good exchange capacity of $^{0}_{\text{IIA}}$ tobermorite is observed in respect of $\text{Zn}^{2+}$. The factor mainly responsible for cation exchange is found to be the interlayer calcium content of $^{0}_{\text{IIA}}$ tobermorite which is confirmed by analytical data.

No trivalent cation has so far been studied for cation exchange with $^{0}_{\text{IIA}}$ tobermorite. Cation exchange with $\text{Fe}^{3+}$ was studied to compare it with $\text{Al}^{3+}$, as later ion can easily substitutes $\text{Si}^{4+}$ (at higher temperature) in tobermorite (3,11). Nevertheless, $\text{Fe}^{3+}$ shows normal cation exchange, replacing $\text{Ca}^{2+}$ ions from tobermorite. Mössbauer data confirm the presence of iron in the form of $\text{Fe}^{3+}$ in the spaces vacated by calcium ions of tobermorite. This study also indicates the coordination of $\text{Fe}^{3+}$ with oxygen atoms in almost similar manner in which original calcium ions are present in tobermorite (8).

Ion exchange is generally favoured by smaller size of the exchanging ions. All above described cations are smaller than the $\text{Ca}^{2+}$ which is responsible for charge balance during cation exchange in tobermorite. We observed some interesting results from exchange
study of tobermorite with Pb\textsuperscript{2+}, a bulky cation with greater ionic radius than Ca\textsuperscript{2+}. The exchanger becomes saturated with Pb\textsuperscript{2+} even without release of its all replaceable calcium content. In this way, the cation exchange capacity of IIA tobermorite is comparatively less in case of Pb\textsuperscript{2+}. However, unaffected structure and easy regeneration of tobermorite seems to be promising for its applications in lead removal from industrial waste and polluted water.

The exchange behaviour of \textsuperscript{0}IIA tobermorite with Mn\textsuperscript{2+} is quite similar to that of Zn\textsuperscript{2+} ions. The valuable feature of Mn-exchanged tobermorite is, its remarkable catalytic activity. Manganese does not release from exchanger during catalysis and can be reused without any further treatment.

Apart from these normal cations, UO\textsubscript{2}\textsuperscript{2+} is also investigated for cation exchange in IIA tobermorite. This massive cation which possesses complex structure shows some unusual behaviour. The crystallinity of tobermorite is affected after uptake of UO\textsubscript{2}\textsuperscript{2+}. The adsorption is also found to be significant in this particular case (electron probe microanalysis). This cation shows poor exchange capacity indicating its unsuitability in structurally retaining inside the tobermorite framework.

On the basis of earlier studies\textsuperscript{(2)-(27)} and our present investigations on a variety of cations, the cation exchange property of tobermorite needs a mechanism which could explain the exchange phenomenon.
The first mechanism for cation exchange in tobermorite was given by Roy et al. to explain Cs\(^+\) uptake\(^{(23)}\). Although caesium uptake has also been confirmed in other studies\(^{(28)}\), there was disagreement concerning the amount and mechanism of the uptake, however, weak uptake capacity of monovalent cations has been confirmed\(^{(28)}\). It was suggested that caesium exchange occurs as a result of introducing aluminium into the tobermorite structure during synthesis. Aluminium substitutes silicon, while in order to maintain charge deficiency, H\(_3\)O\(^+\) is also introduced. In cation exchange, these H\(_3\)O\(^+\) are replaced by Cs\(^+\). In this way, the Cs\(^+\) uptake in tobermorite was said to be caused by Al\(^{3+}\) substitution with Si\(^{4+}\) i.e. H\(_3\)O\(^+\) subsequently participating in exchange with Cs\(^+\)\(^{(23)}\). It was also suggested later that, since tobermorite is synthesized in alkaline solution in which OH\(^-\) > H\(_3\)O\(^+\), the latter is unlikely to be an important constituent\(^{(22,28)}\). Present investigations on a series of cations, however, have confirmed the release of Ca\(^{2+}\) ions from tobermorite in almost equivalent amount of the cations incorporated. Therefore, charge balance occurs through Ca\(^{2+}\) release during cation exchange. Further, present studies have been carried out on unsubstituted tobermorite in which aluminium is present in trace quantity which is extremely insufficient to explain Si\(^{4+}\) substitution. Thermal studies of the II\(^{0}\)A tobermorite and those of the cation-exchanged derivatives, do not show significant difference in their water content; the theory that the exchange reaction takes place via H\(_3\)O\(^+\) need additional experimental evidence to that effect.
With the help of various investigations made in the present study, we suggest that the factors responsible for cation exchange behaviour of synthetic, normal IIA tobermorite are:

1. Interlayer calcium content of IIA tobermorite.
2. Relative affinity of the cations towards tobermorite "dreierketen".
3. Nature of the cation (i.e. ionic radius, atomic weight).
4. Broken bonds of Ca from the layered lattice and
5. Sorption at the planar surface.

The crystal structure of IIA tobermorite was recently investigated by Hamid (8). According to this structure IIA tobermorite has infinite $\text{Si}_3(\text{O}/\text{OH})_9$ chains running parallel to the $b$-axis and are linked together by calcium atoms. In general, out of five calcium atoms of IIA tobermorite, $\text{Ca}(1)$, $\text{Ca}(2)$, $\text{Ca}(3)$ and $\text{Ca}(4)$ (Fig. 1.4, Ch.1) are almost identically coordinated with seven oxygen atoms forming a tetragonal pyramid. The octahedral coordination of $\text{Ca}(5)$ is very distorted due to weak Ca-O interaction and make possible these calcium atoms to come out easily during cation exchange. Our analytical data of exchange studies confirm the release of $\text{Ca}^{2+}$ from IIA tobermorite in appropriate ratio of charge balance. This is a strong support for calcium replacement from tobermorite. Mössbauer study of iron exchanged tobermorite also suggests the presence of iron in places of released calcium. Electron optical analysis (CORA) of uranyl exchanged derivative indicates that uranyl ions can enter in to the structure of tobermorite. In this way, the interlayer calcium content of IIA
tobermorite (i.e. breaking of bonds of the Ca atoms from the layered lattice framework) is mainly responsible for its cation exchange activity.

The second factor responsible for cation exchange behaviour of IIA tobermorite is also related to its structure. It is established that the interlayer calcium of tobermorite is present in an environment of $\text{Si}_3(0/OH)_9$ chains and coordinated with the oxygens of these silicate units. Therefore, it seems that a cation with capability of attachment with these oxygen atoms of the silicate unit (dreierketten) can easily enter and retain in to the structure of tobermorite. Such cations are also expected to show their stability inside the tobermorite framework. Mössbauer study of iron-exchanged tobermorite confirm the coordination of iron with oxygens of the silicate units in various geometries. Further, we have also observed a fair affinity of transition metal ions towards tobermorite; anticipated by their capacity to allow either six fold or higher coordination with oxygens $^{(29-32)}$. In this connection the comparatively low uptake of $\text{Mg}^{2+}(22)$ in tobermorite can be explained by its ionic structure which is quite unsuitable for its coordination with oxygens $^{(33)}$. Taylor has suggested same reason for the formation of very few number of magnesium silicate hydrates $^{(33)}$. Therefore, it may be suggested that the capacity of cation to adjust in the dreierketten of tobermorite is one of the factors responsible for its cation exchange and selective properties.
A direct relationship is observed between uptake of various cations by $\text{IIA tobermorite}$ and their corresponding ionic radius (Fig. RD-a). Magnesium is an exception and has already been discussed. A similar presentation of the affinity of different cations towards $\text{IIA tobermorite}$ and their size can be shown by plotting free energy of the various exchange reactions of $\text{IIA tobermorite}$ as a function of the ionic radius of corresponding cations (Fig. RD-b). Low exchange capacity of $\text{IIA tobermorite}$ in respect of $\text{Pb}^{2+}$ and $\text{UO}_2^{2+}$ also suggest the influence of the size of exchanging cation on the ion exchange capacity of $\text{IIA tobermorite}$. In this regard the high affinity of $\text{IIA tobermorite}$ towards $\text{Fe}^{3+}$ can be attributed to its very low ionic radius. All these lead us to believe that the ionic radius of a cation significantly affect the cation exchange behaviour of $\text{IIA tobermorite}$.

There are two well known families of silicate cation exchangers namely $\text{clay}$ and $\text{zeolite}$. The ion exchange behaviour of $\text{IIA tobermorite}$ resembles with them in certain respects but marked differences are noted in cation exchange properties of tobermorite. The lattice expansion, usually observed in clays is not significant in $\text{IIA tobermorite}$. $\text{IIA tobermorite}$ also shows the absence of definite sieves or channels in its structure, as these are one of the characteristics of zeolites. In case of zeolites, isomorphous substitution of silicon by aluminium within the lattice gives rise to a net negative charge in the framework. This charge deficiency is counterbalanced by cations, which are responsible for cation exchange in zeolites. The aluminium substituted tobermorites
Metal in solid phase (mmols / g) for 1000 ppm conc.:

RD.a : Relationship between ionic radius of exchanged metal ions and their affinity towards 11 Å Tobermorite.
RD. b: Free energy of the various exchange systems of $\text{IIa}^\circ$ tobermorite as a function of the ionic radius of corresponding cations.
can be better compared with zeolites having aluminosilicate composition and calcium as counter ions. In case of layered silicate minerals the counter ions are present in interlayer spaces and therefore, can easily move apart due to low charge density of the clay framework, which is well dispersed over the sheets of clay. It is interesting to note that the favourable conditions for cation exchange in IIα tobermorite are not dependent on counter ions, since calcium (which comes out during cation exchange) should be considered as a compositional element of tobermorite. In this way, IIα tobermorite belongs to a new category of silicate cation exchangers.

IIα tobermorite is an essential phase of the hydration reaction of Portland cements, therefore, the chemical modification of this compound is also of much importance. Portland cements hydrated at 25°C contain C-S-H phase which is fairly amorphous. When silicious blending agents are added the C-S-H phase may become tobermorite as ageing progresses. It is interesting to note that while C-S-H in unmodified cements show little cation exchange, this capacity may significantly be enhanced on addition of blending agents. Studies on the properties of tobermorite may thus shed new light on the behaviour of hydrogel constituents of blended cements.

It is also notable that the trace quantity of aluminium present in tobermorite is not responsible for its cation exchange activity, whereas substitution of Si by Al is responsible for cation
exchange in clays and zeolites. The crystallinity of the I1A tobermorite remains intact after cation exchange. Therefore, it appears that I1A tobermorite is a new potentially useful cation exchanger, stable in neutral and alkaline medium.

(B) XONOTLITE:

As stated earlier, synthetic Xonotlite is the another calcium silicate hydrate, used for cation exchange studies in the present investigation. The synthetic product is characterised with the help of chemical analysis, infrared spectroscopy, X-ray diffraction and thermal analysis. Chemical analysis (Table-7.1) reveal that the Ca/Si molar ratio observed is 1.03 which closely resembles with the reported value of 1.00\(^{(34,35)}\). This synthetic specimen shows higher water content as compared to the theoretical value, which is based on the crystal structure of xonotlite reported by Mamedov and Belov\(^{(35,36)}\). However, some other workers also reported the higher water content in xonotlite\(^{(34)}\), this is specially discussed by Buckner et al.\(^{(37)}\) and later by Aitken and Taylor\(^{(38)}\).

Synthetic xonotlite shows typical infrared absorption spectrum of calcium silicate hydrate (Fig. 7.1). A clear band observed near 3630 cm\(^{-1}\) is explained as free O-H stretching oscillations which is shifted in xonotlite\(^{(15)}\). Other clear absorptions
due to H-O-H deformation vibrations appeared at around 1640 cm\(^{-1}\) and silicate stretching vibrations absorbed near 1000 cm\(^{-1}\)(9,15).

The X-ray powder diffraction pattern of the synthetic xonotlite consists of 28 prominent reflections with d-spacings between 7.48 and 1.53 Å (Table-7.ii and Fig. 7.C). Indexing have been done for an orthorhombic cell with lattice constants \(a = 17.10\) Å, \(b = 7.34\) Å and \(c = 14.06\) Å, characteristic for xonotlite\(^{(6,39,40)}\). Almost all the reflections could be indexed with these constants (Table-7.ii) showing reliability of indexing. The number of molecules per unit cell is 4 and the observed density of the compound is 2.64 g cm\(^{-3}\) which is close to the calculated & reported values\(^{(6,39)}\). X-ray diffraction data of synthetic product fairly matches in intensity and position with reported data on xonotlite and therefore, confirm its identification\(^{(40A)}\).

Xonotlite is a less hydrated, calcium silicate with a chemical composition \(\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2\) or \(\text{Ca}_6\text{Si}_6\text{O}_{18}\), as compared to that of tobermorite \((\text{Ca}_5\text{Si}_6\text{O}_{10}\text{H}_2\cdot4\text{H}_2\text{O})\). This reflects in its thermal decomposition pattern (Fig. 7.B). There is only one clear weight loss step in thermogram of xonotlite, ranging between 770 and 845°C, which corresponds to complete dehydroxylation of xonotlite and recrystallisation to form wollastonite\(^{(37)}\). However, a slow but constant weight loss observed between 270 to 580°C with about 3.5% weight loss, this may be attributed to loss of water which is generally present in xonotlite, in addition to its theoretical chemical formula\(^{(34,37,38)}\).
Cation Exchange Studies with Cu$^{2+}$ and Ni$^{2+}$

The synthetic xonotlite was subjected for cation exchange experiments following batch process, as described earlier. These studies were carried out at room temperature with three different concentrations of Cu$^{2+}$ and Ni$^{2+}$ solutions. The ion exchange data are summarised in Table-8.1 and 9.1. These analytical data show a high uptake of Cu$^{2+}$ as well as Ni$^{2+}$ by xonotlite. As much as 3.4 mmols of copper and 3.5 mmols of Ni$^{2+}$ could be incorporated in 1 g of synthetic xonotlite by shaking it with initially 2500 ppm solution of metal ions. The charge balance in cation exchange is accompanied by calcium release from xonotlite. This is proved by the release of appropriate amount of calcium from xonotlite (Table-8.1 & 9.1). Hence, the cation exchange reaction of xonotlite for these bivalent cations can be represented as follows:

\[
\text{Ca}_{\text{Xonotlite}}^{2+} + M_{\text{Solution}}^{2+} \rightleftharpoons \text{Ca}_{\text{Solution}}^{2+} + M_{\text{Xonotlite}}^{2+} \quad (\text{vi})
\]

where M represents the Cu$^{2+}$ or Ni$^{2+}$.

In this way, the cation exchange phenomenon in xonotlite with respect to these bivalent cations, seems to be similar to that in IIA tobermorite. However, the uptake of metal ions in xonotlite is very high. The distribution coefficient $K_d$ observed, has a maximum value of 19880 for Cu$^{2+}$ exchange and 17141 for Ni$^{2+}$ exchange showing high affinity of xonotlite towards these cations.
After such a high uptake of exchanged cation, there may be some damage in crystal structure of exchanger, which subsequently renders its reuse or regeneration. The X-ray powder diffraction data of copper (Table-8.ii) and nickel exchanged xonotlite (Table-9.ii), however, ruled out the possibility of crystal damage at such a high concentrations of exchanging cations. X-ray powder diffraction studies (Fig. 8.B, 9.B) have been carried out on samples obtained from 2500 ppm cation solutions. These data show characteristic reflections of xonotlite and almost same lattice constants (Table-7.ii) which suggest the unaffected crystallinity of the exchanger.

Xonotlite is considered as typical crystalline calcium silicate derived from wollastonite\(^{(79,40)}\). Presence of double dreierkette or double metasilicate chains in xonotlite makes its structure rigid and stable\(^{(7,40)}\) which may prevent the lattice change during cation exchange. Though the X-ray diffraction pattern of nickel exchanged xonotlite contains less number of peaks, yet most of these intense peaks are characteristic for xonotlite.

Both, copper-and nickel-exchanged xonotlite show very poor back exchange. As much as only 0.4 mmols of copper could be removed from Cu-xonotlite (derived from 2500 ppm Cu\(^{2+}\) solution) after treatment with a 10,000 ppm Ca\(^{2+}\) solution. However, almost all the copper can be removed from Cu-xonotlite by treatment with
Ca-EDTA solution. The X-ray powder diffraction data of regenerated xonotlite (Table-8.iii and Fig. 6.C) resembles with that of original synthetic xonotlite.

Thermogravimetric analysis of copper and nickel exchanged xonotlite (Figs. 8.A & 9.A) show some interesting results. A clear weight loss step observed between 265 and 555°C in case of Cu-xonotlite. This consists about 7.6 wt% loss in addition to those 2 wt% loss up to 200°C and about 1.5 wt% loss around 750°C. Xonotlite shows only one major weight loss step around 770°C with 3.2 wt% loss. In case of Ni-xonotlite first weight loss step ranges between 60 to 210°C with ~3.7 wt% loss. Second main weight loss step (between 220 and 750°C) shows ~10 wt% loss while, third step observed around 770°C with ~1.5 wt% loss. These marked additional weight loss in case of copper and nickel exchanged xonotlite may be incorporated with the uptake of water alongwith cations during ion exchange. Xonotlite contains less water and when exchanged cations enter in its structure, it is supposed that they may brought water of hydration and water of coordination as well. This subsequently, enhance the water content in cation-exchanged xonotlite. For such a significant water uptake, xonotlite should possess sufficient spaces in its structure. If this prediction is true, xonotlite may be tried for intercalation of some bigger molecules, which is not possible in IIÅ tobermorite$^{22,41}$.

Xonotlite possesses double chain structure, these double chain or dreierkette are perfect and made up of SiO$_4$ units$^{40}$. 
The silicon atoms are attached with calcium. The double chain also produce a degree of condensation in the silicate anion which is also supposed in case of Al-substitution for silicon (7). All these factors together seems to be responsible for high cation exchange capacity of xonotlite as compared to that of tobermorite (21,22), which is a hydrated calcium silicate with single chain structure (8).

Komarneni and Roy et al. studied the cation exchange behaviour of Al-substituted tobermorites and reported its high exchange capacity (23-25). This is attributed to the better stabilized structure of tobermorite and other steric changes brought about due to Al-substitution (25).

Xonotlite may also be compared with Al-substituted tobermorite as its structure is stabilized by double chains which may easily remove structural calcium. The higher calcium content of xonotlite and its easy removal from double chain stable structure probably cause, such a high uptake of metal ions during cation exchange.

Though at this stage it is too early to predict industrial applications of this family of silicate minerals in cation exchange processes but the crystalline stable structure, high exchange capacity, easy and cheap synthesis of these materials are some of the factors which promise potential applications in various areas where hydrated calcium silicates like tobermorites and xonotlite may find myriad applications and importance. The cation exchange and other properties of these compounds, therefore, need
to be further explored in applied point of view. This study may also serve as a background to investigate other calcium silicate minerals like nekoite, okenite which are structurally related to tobermorite and xonotlite.

Further, recently it has been found that it is possible to make about 12 mole% substitution for Si⁴⁺ by (Al + Na) in tobermorite. The ion exchange capacity is found to be enhanced by this substitution in respect of Cs⁺ and other alkali metal cations. (41A) Thus, it may be predicted that tobermorite can be modified for its applications in ion exchange and ion selective separation, actinide separation, ion seiving, catalysis, waste disposal and related fields.
Part II: MONTMORILLONITE CLAY MINERAL

The clay mineral montmorillonite is made up of negatively charged silicate layers and has a typical composition \( \text{Al}_4\text{Si}_8\text{O}_{20} - (\text{OH})_4 \cdot n\text{H}_2\text{O} \) along with interlayer cations, compensating the positive charge deficiency of silicate layers. (42,43) The clay sample used in the present investigation has an empirical formula: 

\[
(Ca^{0.09}Na^{0.16}K^{0.03})(Al^{1.48}Fe^{0.13}Mg^{0.40})(Si^{3.99}Al^{0.01})_10(\text{OH})_2 \cdot 5\text{H}_2\text{O}
\]

(Table-10.1). The charge deficiency of silicate layers in montmorillonite is mainly due to the isomorphous substitution of \( Si^{4+} \) by \( Al^{3+} \) and, to some extent, by other cations of lower valency like \( Mg^{2+} \). (42,43) This charge deficiency is compensated by counter cations which are present between structural layers of montmorillonite and in general, are exchangeable (42,43). In the present montmorillonite sample the exchangeable cations are mainly \( Ca^{2+} \) and \( Na^+ \). As stated earlier, clay minerals possess the ion exchange capacity but found less applications as ion exchangers in comparison to those of zeolites and resins which are of course better exchangers. However, the interlayer spacings of the montmorillonite (where exchangeable cations are present along with water molecules) are expandable (Fig. 1.6 & 1.7), permitting it to act as a host compound. (42-44) Therefore, it is possible to prepare intercalation (between two layers) compounds of montmorillonite. (42-46)

As an application of the cation exchange and intercalation phenomenon in silicate minerals, the author has prepared fourteen
Intercalated coordination compounds of exchanged Cu(II) and Ni(II) in montmorillonite clay mineral. The various nitrogen containing organic ligands used are 1,2-diaminoethane, 1,2-diaminopropane, diethylenetriamine, 2,2'-bipyridyl, 1,10-phenanthroline, 8-hydroxyquinoline and dimethylglyoxime. The metal ions Cu$^{2+}$ and Ni$^{2+}$ were introduced in montmorillonite by cation exchange and intercalated coordination compounds of these exchanged cations were then prepared by inclusion of organic ligands in the interlayer spaces. These intercalated coordination compounds were characterised and studied on the basis of elemental analysis, IR-spectral studies, magnetic measurements, X-ray diffraction and thermal analysis.

In almost all the cases, the colour of the metal-exchanged montmorillonite significantly changed after treatment with various ligands. These colours are the indication of complex formation.

The chemical analysis of montmorillonite clay is given in Table-I0.i. On the basis of chemical analysis of intercalated compounds (Chapter-III), the metal to ligand molar ratios were calculated (Table-RD.i & RD.ii). It is observed that in the compounds of Cu(II)-montmorillonite, this ratio is 1:2 for all the cases. In the compounds of Ni(II)-montmorillonite with 1,2-diaminoethane and 1,2-diaminopropane this ratio is found as 1:3 while in remaining compounds it is again 1:2.

In most of the cases, some metal content is released from montmorillonite during formation of these intercalated compounds.
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Metal</th>
<th>Ligand</th>
<th>Magnetic Susceptibility ($\sim$27°C) $X_g \times 10^{-6}$ (cgs unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)-montmorillonite</td>
<td>54.10</td>
<td>-</td>
<td>6.23</td>
</tr>
<tr>
<td>1,2-Diaminoethane-Cu(II)-montmorillonite</td>
<td>53.62</td>
<td>100.0</td>
<td>5.98</td>
</tr>
<tr>
<td>1,2-Diaminopropane-Cu(II)-montmorillonite</td>
<td>52.36</td>
<td>99.28</td>
<td>5.80</td>
</tr>
<tr>
<td>Diethylenetriamine-Cu(II)-montmorillonite</td>
<td>49.09</td>
<td>97.31</td>
<td>5.71</td>
</tr>
<tr>
<td>2,2'-Bipyridyl-Cu(II)-montmorillonite</td>
<td>46.42</td>
<td>85.65</td>
<td>5.29</td>
</tr>
<tr>
<td>1,10-Phenanthroline-Cu(II)-montmorillonite</td>
<td>36.19</td>
<td>67.80</td>
<td>4.13</td>
</tr>
<tr>
<td>8-Hydroxyquinoline-Cu(II)-montmorillonite</td>
<td>41.23</td>
<td>78.21</td>
<td>4.92</td>
</tr>
<tr>
<td>Dimethylglyoxime-Cu(II)-montmorillonite</td>
<td>45.47</td>
<td>90.66</td>
<td>5.31</td>
</tr>
</tbody>
</table>
Table-RD.ii: CHEMICAL AND MAGNETIC DATA FOR Ni(II)-MONTMORILLONITE COMPOUNDS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Metal</th>
<th>Ligand</th>
<th>Magnetic Susceptibility (27°C) $\chi_g \times 10^{-6}$ (cgs unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)-montmorillonite</td>
<td>61.32</td>
<td>-</td>
<td>8.69</td>
</tr>
<tr>
<td>1,2-Diaminoethane-Ni(II)-montmorillonite</td>
<td>54.11</td>
<td>157.05</td>
<td>7.89</td>
</tr>
<tr>
<td>1,2-Diaminopropane-Ni(II)-montmorillonite</td>
<td>54.69</td>
<td>152.32</td>
<td>7.82</td>
</tr>
<tr>
<td>Diethylenetriamine-Ni(II)-montmorillonite</td>
<td>50.95</td>
<td>100.01</td>
<td>7.90</td>
</tr>
<tr>
<td>2,2'-Bipyridyl-Ni(II)-montmorillonite</td>
<td>44.30</td>
<td>87.77</td>
<td>6.96</td>
</tr>
<tr>
<td>1,10-Phenanthroline-Ni(II)-montmorillonite</td>
<td>33.36</td>
<td>61.23</td>
<td>6.17</td>
</tr>
<tr>
<td>8-Hydroxyquinoline-Ni(II)-montmorillonite</td>
<td>48.89</td>
<td>98.62</td>
<td>6.76</td>
</tr>
<tr>
<td>Dimethylglyoxime-Ni(II)-montmorillonite</td>
<td>41.74</td>
<td>85.36</td>
<td>diamagnetic</td>
</tr>
</tbody>
</table>
It is concluded from the analytical data (Table-RD.i & RD.ii) that the amines prefer to form the complexes with metal inside the interlayer spaces of montmorillonite clay, while other ligands extract some amount of the metal from montmorillonite. This is probably due to high selectivity of the metals towards these ligand molecules and steric hindrance which may brought in coordination with some ligands. This effect is specially significant in the case of 1,10-phenanthroline adducts.

**INFRARED ABSORPTION STUDIES**:

The infrared spectral studies are important to understand the chemical composition as well as structure of clay minerals. These investigations are also very useful in deciding the actual sites of coordination of ligand to the metal and the nature of the coordinate bond present in the complexes. In the present study, there are sufficient prominent bands observed in the infrared absorption spectra of intercalated compounds of Cu(II) and Ni(II)-exchanged montmorillonite. These are interpreted in a view to investigate the coordination of the ligands with exchanged metal ions.

The infrared spectrum of montmorillonite clay mineral is well established and described by several earlier workers. (47-57) In the IR-spectra of the present sample of montmorillonite clay (Fig.10.A) and its Cu(II) (Fig.11.A) and Ni(II)-exchanged derivatives (Fig. 19.A), the absorption bands are observed in three different
frequency regions and show marked similarity with its parent mineral pyrophyllite. The O-H stretching vibrations are observed near 3600 cm⁻¹ as a sharp peak. This corresponds to structural OH groups in montmorillonite, which are linked with aluminium ions in octahedral sites and with silicon ions in tetrahedral sites (Fig.1.6, Ch.1)(42,43) The coupling occur between two hydroxyl groups and give rise to frequency of vibration which is responsible for the origin of this infrared absorption band.(13). In the second frequency region, one significant absorption band observed at 1630 cm⁻¹, which is due to the H-O-H deformation vibrations(58). Third frequency region which ranges from 1150 to 400 cm⁻¹ is specially important in the study of silicates, because of the occurrence of lattice vibrations. Characteristic Si-O stretching band is observed near 1000 cm⁻¹ as a broad but intense band. This is significantly different as in pyrophyllite, indicating that the silicate layers in montmorillonite has a different geometry in comparision to its parent mineral pyrophyllite.(58) Since this is one of the characteristic vibrations of the silicate structure, its frequency might reasonably be expected to get influenced by the nature of the cations in octahedral layers and interlayer constituents of montmorillonite as well.(57,58) IR-spectra of Cu(II)-and Ni(II)-exchanged montmorillonite also show the presence of coordinated water. A comparatively weak band is appeared at 750 cm⁻¹ indicating the coordination of interlayer water with exchanged metal ions.
The IR-spectroscopy found important applications in coordination chemistry. The infrared absorption depends on the arrangement of atoms in space, their masses, bond lengths and bond angles. Whenever a ligand is coordinated with a metal, this metal ion is introduced into the vibrating system of the ligand. Thus, the bond lengths, bond angles and interatomic forces within the ligand are expected to alter. In this way, the infrared spectrum of the coordinated ligand differs from that of the free ligand. The infrared absorption spectra of the present series of intercalated compounds of montmorillonite have been assigned various modes of vibrations by analogy to the spectra of known complexes with similar composition. These spectra have also been compared with those of the corresponding free ligands, in order to investigate the coordination sites.

Three chelating amines i.e. 1,2-diaminoethane, 1,2-diaminopropane and diethylenetriamine were used in the present study. The former two act as bidentate ligands while later as tridentate. The IR-spectra of these amine adducts with both Cu(II) and Ni(II)-exchanged montmorillonite have been studied with the references of other reported complexes which give consistently similar spectra\(^{(59,60)}\).

Principal IR-absorptions of the intercalated compounds containing various amines have been listed in Table RD.iii and RD.iv. The free amines normally show IR-absorptions due to amino
<table>
<thead>
<tr>
<th>Assignments</th>
<th>1,2-Diaminoethane-Cu(II)-montmorillonite</th>
<th>1,2-Diaminopropane-Cu(II)-montmorillonite</th>
<th>Diethylenetriamine Cu(II)-montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretching</td>
<td>3600 (vs)</td>
<td>3600 (vs)</td>
<td>3580 (vs)</td>
</tr>
<tr>
<td>NH stretching</td>
<td>3320 (s)</td>
<td>3325 (br)</td>
<td>3340 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3240 (s)</td>
<td>3250 (s)</td>
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<tr>
<td></td>
<td></td>
<td>3120 (m)</td>
<td></td>
</tr>
<tr>
<td>C-H stretching</td>
<td>2940 (m)</td>
<td>2940 (s)</td>
<td>2980 (s)</td>
</tr>
<tr>
<td></td>
<td>2890 (w)</td>
<td>2885 (s)</td>
<td>2920 (s)</td>
</tr>
<tr>
<td>H-O-H bending</td>
<td>1635 (m)</td>
<td>1620 (s)</td>
<td>1615 (vs)</td>
</tr>
<tr>
<td>NH₂ bending</td>
<td>1585 (s)</td>
<td>1580 (s)</td>
<td>1575 (s)</td>
</tr>
<tr>
<td>C-N stretching</td>
<td>1450 (m)</td>
<td>1470 (m)</td>
<td>1460 (vs)</td>
</tr>
<tr>
<td>CH₂ wagging</td>
<td>1380 (w)</td>
<td>-</td>
<td>1385 (s)</td>
</tr>
<tr>
<td>Si-O stretching</td>
<td>1210-890 (br)</td>
<td>1150-790 (br)</td>
<td>1200-800 (br)</td>
</tr>
</tbody>
</table>
### Table RD.iv: Infrared Absorptions (in cm$^{-1}$) of Amine Complexes of Ni(II)-Montmorillonite

<table>
<thead>
<tr>
<th>Assignments</th>
<th>1,2-Diaminoethane-Ni(II)-montmorillonite</th>
<th>1,2-Diaminopropane-Ni(II)-montmorillonite</th>
<th>Diethylenetriamine Ni(II)-montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretching</td>
<td>3600 (vs)</td>
<td>3575 (vs)</td>
<td>3605 (s)</td>
</tr>
<tr>
<td>NH stretching</td>
<td>3300 (s)</td>
<td>3320 (s)</td>
<td>3330 (m)</td>
</tr>
<tr>
<td></td>
<td>3220 (w)</td>
<td>3205 (s)</td>
<td>3190 (vs)</td>
</tr>
<tr>
<td>C-H stretching</td>
<td>2945 (m)</td>
<td>2940 (s)</td>
<td>2930 (m)</td>
</tr>
<tr>
<td></td>
<td>2890 (w)</td>
<td>2885 (s)</td>
<td>2880 (w)</td>
</tr>
<tr>
<td>H-O-H bending</td>
<td>1625 (s)</td>
<td>1630 (vs)</td>
<td>1625 (m)</td>
</tr>
<tr>
<td>NH$_2$ bending</td>
<td>1585 (m)</td>
<td>1585 (s)</td>
<td>1580 (s)</td>
</tr>
<tr>
<td>C-N stretching</td>
<td>1460 (s)</td>
<td>1455 (s)</td>
<td>1450 (m)</td>
</tr>
<tr>
<td>CH$_2$ wagging</td>
<td>1390 (w)</td>
<td>1390 (s)</td>
<td>1375 (w)</td>
</tr>
<tr>
<td></td>
<td>1330 (m)</td>
<td>1370 (w)</td>
<td>1340 (s)</td>
</tr>
<tr>
<td>Si-O stretching</td>
<td>1190-805 (br)</td>
<td>1180-830 (br)</td>
<td>1185-830 (br)</td>
</tr>
<tr>
<td>NH$_2$ rocking</td>
<td>-</td>
<td>800 (w)</td>
<td>820 (m)</td>
</tr>
</tbody>
</table>
group in the four regions, $\sim 3300, \sim 1600, \sim 1300$ and $\sim 800 \text{ cm}^{-1}$. In the free ligand, the uncoordinated amino group shows two to three absorption bands between 3340 and 3160 cm$^{-1}$ due to N-H stretching vibrations. $^{(64)}$ The NH$_2$ bending is appeared very close to 1580 cm$^{-1}$. In the present intercalated compounds the stretching and bending vibrations of amino groups occur at $\sim 20 \text{ cm}^{-1}$ (stretching band) and $\sim 10 \text{ cm}^{-1}$ (bending mode) on the lower energy side respectively (Table-RD.iii and RD.iv). This shows the weakening of the N-H bonds and can easily be explained as resulting due to the electrons drainage from the nitrogen atoms (of amino groups) because of their coordination with the metal $^{(65,66)}$ (exchanged metal ions, present in the interlayer spaces of the montmorillonite). The symmetric deformation absorption is not observed while the NH$_2$ rocking mode could not be traced in most of the cases because this is mixed with Si-O stretching band and give a broad bump in the region 1200-800 cm$^{-1}$. However, a band near 810 cm$^{-1}$ is appeared due to this mode in pn and dien adducts of Ni(II)-montmorillonite. An intense band is observed at $\sim 2950 \text{ cm}^{-1}$ due to C-H stretching vibrations $^{(67)}$. A sharp band near 1450 cm$^{-1}$ is observed, which corresponds to C-N stretching vibrations. $^{(67,68)}$ Absorptions due to CH$_2$ wagging vibrations are appeared around 1380 cm$^{-1}$ in case of Cu(II)-montmorillonite while two bands due to this mode are observed near 1380 and 1335 cm$^{-1}$ in the amine adducts of Ni(II)-montmorillonite.

The IR-spectra of 2,2'-bipyridyl and 1,10-phenanthroline
adducts of Cu(II) and Ni(II)-montmorillonite (Figs.-15.A, 16.A, 23.A, 24.A) have number of absorption bands corresponding to pyridine and benzene ring. These are quite complicated and assignments of the important bands have been made by analogy to other reported complexes (Table-RD.v)\(^{69-71}\).

In the present intercalated compounds, the C=C, C=N and ring stretching vibrations are observed in the region 1605-1500 cm\(^{-1}\). Three bands due to these modes are found in the spectrum of 2,2'-bipyridyl-Ni(II)-montmorillonite. These most typical bands are: first close to 1605 cm\(^{-1}\), the second at 1575 cm\(^{-1}\) and third around 1530 cm\(^{-1}\). Bipy adduct of Cu(II)-montmorillonite shows similar absorptions except the absence of band near 1530 cm\(^{-1}\). Compounds having 1,10-phenanthroline show almost similar spectra, with little change in band positions. However, the absorption near 1560 cm\(^{-1}\) is absent in case of 1,10-phenanthroline-Ni(II)-montmorillonite. On comparison with those of the free ligands, it is noted that the bands due to these modes are shifted towards higher energy side. This indicates the tightening of the ring on coordination through the nitrogen atoms of the bidentate ligand.\(^{72-77}\) A negative shift is observed in the bands correspond to C–H out of plane deformation due to three hydrogen atoms and out of plane ring deformation bands, which are positioned at \(\tilde{\nu}\) 770 and \(\tilde{\nu}\) 730 cm\(^{-1}\) respectively.\(^{76}\) These negative shift also indicates the coordination through the nitrogen atoms of the ligands.\(^{76}\)
<table>
<thead>
<tr>
<th>Assignments</th>
<th>2,2'-Bipyridyl-Cu(II)-montmorillonite</th>
<th>2,2'-Bipyridyl-Ni(II)-montmorillonite</th>
<th>1,10-Phenanthroline-Cu(II)-montmorillonite</th>
<th>1,10-Phenanthroline-Ni(II)-montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretching</td>
<td>3600 (s)</td>
<td>3600 (s)</td>
<td>3595 (vs)</td>
<td>3590 (vs)</td>
</tr>
<tr>
<td>H-O-H bending</td>
<td>1630 (m)</td>
<td>1635 (s)</td>
<td>1650 (s)</td>
<td>1630 (s)</td>
</tr>
<tr>
<td>C=C, C=N and ring stretching</td>
<td>1595 (w)</td>
<td>1605 (s)</td>
<td>1595 (m)</td>
<td>1585 (s)</td>
</tr>
<tr>
<td>Si-O stretching</td>
<td>1200-840 (br)</td>
<td>1190-810 (br)</td>
<td>1210-830 (br)</td>
<td>1100-830 (br)</td>
</tr>
<tr>
<td>C-H out of plane deformation due to three adjacent hydrogens</td>
<td>765 (s)</td>
<td>770 (s)</td>
<td>785 (s)</td>
<td>760 (m)</td>
</tr>
<tr>
<td>Out of plane ring deformation</td>
<td>730 (w)</td>
<td>-</td>
<td>-</td>
<td>725 (s)</td>
</tr>
<tr>
<td>H-O-H (coord) rocking</td>
<td>-</td>
<td>700 (m)</td>
<td>-</td>
<td>710 (m)</td>
</tr>
</tbody>
</table>
The infrared absorption spectra of the intercalated compounds containing 8-hydroxyquinoline (Figs.-17.A & 25.A) have been studied in the following regions:

The first ranges from 1600 – 1300 cm\(^{-1}\) which consists of C = C and C = N stretching vibrations. These are found to be absorbed at 1565 \(\pm\) 5 and 1485 \(\pm\) 5 cm\(^{-1}\) respectively (Table-RD.vi). These bands are slightly shifted towards higher energy side in comparison of free oxine.\(^{(74,78-80)}\) In addition to these, two more intense bands are noted near 1450 and 1340 cm\(^{-1}\). These can frequently be assigned to ring stretching vibrations.\(^{(79,81)}\) The former band is absent in case of Ni(II)-montmorillonite adduct.

In the second frequency region two sharp bands have been observed near 1230 and 1120 cm\(^{-1}\) in case of oxine-Ni(II)-montmorillonite. These are due to ring vibrations. The former band is found to be absent in the spectrum of oxine-Cu(II)-montmorillonite.

In the lower frequency region three different bands could be assigned.\(^{(78-81)}\) Absorptions correspond to out of plane C-H deformation due to two and three adjacent hydrogens are observed near 820 and 780 cm\(^{-1}\) respectively while, out of plane ring deformation band lie at \(\sim\) 740 cm\(^{-1}\).

The IR absorption spectra of the intercalated compounds with dimethylglyoxime (Figs.-18.A & 26.A) were investigated in the light of reported data on dmg complexes.\(^{(82-84)}\) The important absorption bands are summed up in Table-RD.7 with their
Table-RD.vi: INFRARED ABSORPTIONS (in cm\(^{-1}\)) OF 8-HYDROXYQUINOLINE COMPLEXES OF Cu(II)-AND Ni(II)-MONTMORILLONITE

<table>
<thead>
<tr>
<th>Assignments</th>
<th>8-Hydroxyquinoline-Cu(II)-montmorillonite</th>
<th>8-Hydroxyquinoline-Ni(II)-montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretching</td>
<td>3595 (vs)</td>
<td>3590 (vs)</td>
</tr>
<tr>
<td>H-O-H bending</td>
<td>1620 (s)</td>
<td>1615 (vs)</td>
</tr>
<tr>
<td>C=C, C=N and ring stretching</td>
<td>1565 (s)</td>
<td>1570 (m)</td>
</tr>
<tr>
<td></td>
<td>1485 (s)</td>
<td>1490 (s)</td>
</tr>
<tr>
<td></td>
<td>1450 (s)</td>
<td>1355 (s)</td>
</tr>
<tr>
<td></td>
<td>1340 (m)</td>
<td></td>
</tr>
<tr>
<td>Ring vibrations</td>
<td>1115 (s)</td>
<td>1230 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1120 (m)</td>
</tr>
<tr>
<td>Si-O stretching</td>
<td>1090-880(br)</td>
<td>1050-830(br)</td>
</tr>
<tr>
<td>C-H out of plane deformation due to</td>
<td>820 (m)</td>
<td>825 (m)</td>
</tr>
<tr>
<td>two adjacent hydrogens</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H out of plane deformation due to</td>
<td>780 (s)</td>
<td>785 (w)</td>
</tr>
<tr>
<td>three adjacent hydrogens</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Out of plane ring deformation</td>
<td>740 (m)</td>
<td>745 (w)</td>
</tr>
<tr>
<td>H-O-H (coord) rocking</td>
<td></td>
<td>700 (m)</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Assignments</th>
<th>Dimethylglyoxime–Cu(II)–montmorillonite</th>
<th>Dimethylglyoxime–Ni(II)–montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H stretching</td>
<td>3590 (s)</td>
<td>3600 (vs)</td>
</tr>
<tr>
<td>H–O–H bending</td>
<td>1620 (s)</td>
<td>1630 (vs)</td>
</tr>
<tr>
<td>C=N stretching</td>
<td>1570 (s)</td>
<td>1565 (s)</td>
</tr>
<tr>
<td>C–CH₃ bending</td>
<td>1365 (s)</td>
<td>1370 (s)</td>
</tr>
<tr>
<td>N–O stretching</td>
<td>1230 (s)</td>
<td>1235 (m)</td>
</tr>
<tr>
<td>N–O' stretching</td>
<td>1175 (w)</td>
<td>1190 (s)</td>
</tr>
<tr>
<td>Si–O stretching</td>
<td>1130–750 (br)</td>
<td>1100–775 (br)</td>
</tr>
</tbody>
</table>
assignments. The C=N stretching band observed at \( \approx 1570 \text{ cm}^{-1} \) in both the compounds containing dmg. A sharp absorption near 1365 cm\(^{-1}\) is assigned to C-CH\(_3\) bending vibrations. The absorption at \( \approx 1230 \text{ cm}^{-1} \) is due to N-O stretching while the band near 1180 cm\(^{-1}\) corresponds to N-O' stretching vibrations. These are quite clear in both the spectra.

IR absorption spectra of Ni(II)-montmorillonite compounds with bipy, O-phen and oxine show the presence of coordinated water. A relatively weak absorption is noted between 800-650 cm\(^{-1}\) which corresponds to the rocking mode of coordinated water.

Apart from these ligand absorptions, the absorptions of montmorillonite clay itself, are also observed in the IR spectra of various intercalated compounds, discussed above (Tables-10-26). All the compounds show a sharp band at \( \approx 3600 \text{ cm}^{-1} \) which is due to O-H stretching vibrations,\(^{(42,43)}\) while an absorption of various intensity is noted between 1650 - 1610 cm\(^{-1}\) in different compounds, corresponds to H-O-H deformation vibrations.\(^{(58)}\) A remarkable feature of the IR absorption spectra of almost all the intercalated compounds, is the broadening of characteristic Si-O stretching absorption band in comparison to that of montmorillonite and metal-exchanged montmorillonite (Chapter-III). As this absorption is directly related to the composition and structure of silicate layers in montmorillonite, this is expected to alter with the effect on silicate layers.\(^{(13,58,85)}\) The exchanged cations (in the present
case Cu$^{2+}$ and Ni$^{2+}$) are present on the interlayer surfaces of the montmorillonite.$^{(42,43,45)}$ Our chemical and IR absorption studies suggest the formation of coordination compounds of these metals. Therefore, we may predict the formation of coordination compounds of exchanged metal ions in the interlayer spaces of montmorillonite, which consequently influence the IR absorptions of silicate layers.

**MAGNETIC MEASUREMENTS**

The magnetic data are often found to be very useful in the determination of stereochemistry of the coordination compounds. The present series of compounds have been investigated for their magnetic behaviour. These data are summed up in Table-RD.i & RD.ii.

The montmorillonite clay itself is paramagnetic in nature. The magnetic susceptibility value for Cu(II)-montmorillonite is $6.23 \times 10^{-6}$ cgs unit. This increase in the magnetic susceptibility value (in comparison of montmorillonite clay, Table-20, Ch.III) should be due to the introduction of Cu$^{2+}$ ions in montmorillonite. We know that copper has electronic configuration (A) (3d)$^{10}$(4s)$^1$. The electronic configuration of divalent copper is (A) (3d)$^9$. The magnetic moments of simple Cu(II) complexes are generally lie in the range 1.75 - 2.20 B.M. regardless of their stereochemistry because, the Cu(II)-complexes whether octahedral, square planar or tetrahedral almost always contain one unpaired electron.$^{(86-95)}$
All the prepared coordination compounds of Cu(II)-montmorillonite are found to be paramagnetic in nature. Their magnetic susceptibility values are in the range of $5.98 - 4.13 \times 10^{-6}$ cgs unit. Analytical data (Table-RD.1) inferred that the metal to ligand ratio is 1:2 in these compounds. Since all the ligands used (in the present series of intercalated coordination compounds) normally show bidentate behaviour, the copper can be considered to possess the coordination number four. Square planar is the favourable geometry between two possible orientations of Cu(II) complexes with tetracoordinated copper.\(^{(96)}\) Therefore, the present intercalated Cu(II) complexes of montmorillonite clay may be considered to have square planar geometry. Few earlier studies on intercalation behaviour of montmorillonite, also suggest the flat, parallel orientations of organic molecules present inside the interlayer spaces of the clay mineral structure.

Except that of the dimethylglyoxime-Ni(II)-montmorillonite, all the prepared intercalated compounds of Ni(II)-montmorillonite show paramagnetic behaviour. Their magnetic susceptibility values generally ranges between $7.90 - 6.17 \times 10^{-6}$ cgs unit at room temperature. It is well known that two unpaired electrons are present in Ni(II), when it is in octahedral field.\(^{(100,101)}\) Most of the bivalent nickel complexes may be divided into three distinct categories:\(^{(102-104)}\)

1. Six covalent, octahedral paramagnetic complexes.
2. Four covalent, square planar diamagnetic complexes.
3. Four covalent, tetrahedral, paramagnetic complexes.
In this way, in paramagnetic Ni(II)-montmorillonite compounds the possibility of square planar geometry is ruled out. In case of 1,2-diaminoethane and 1,2-diaminopropane adducts of Ni(II)-montmorillonite, the metal to ligand molar ratio is observed as 1:3 while analytical data confirm the 1:2 metal to ligand ratio in diethylenetriamine-Ni(II)-montmorillonite thereby suggesting the six coordination number of Ni(II) in these compounds. In the intercalated compounds of Ni(II)-montmorillonite with 2,2'-bipyridyl, 1,10-phenanthroline and 8-hydroxyquinoline, the observed metal to ligand ratio, is 1:2, however, some coordinated water is found to be present in these compounds. This has been inferred with the help of IR and TG studies. The hexacoordinated Ni(II) may thus be considered in all these intercalated compounds of montmorillonite clay mineral. The most common Ni(II) complexes are six covalent, octahedral and paramagnetic in nature. Therefore, these intercalated Ni(II) complexes are also appear to possess octahedral geometry with hexacoordinated Ni(II).

Dmg-Ni(II)-montmorillonite is observed to be diamagnetic in nature. The simple Ni-dmg complex has also been reported to possess diamagnetic behaviour\(^{(105,106)}\). The square planar geometry of the complex is suggested.\(^{(105,106)}\) In this way the intercalated nickel-dmg is almost similar to that of normal complex.

Thus, it may be concluded that the present intercalated compounds show fair similarity with those of the reported normal complexes of Cu(II) and Ni(II) with similar composition.
**THERMOGRAVIMETRIC ANALYSIS:**

Thermogravimetric analysis gives the information regarding thermal stability and composition of the compound. This also describes the decomposition pattern for a particular product. TGA data of the present intercalated compounds have been summarised in Table-10-26 (Ch.III).

The thermogram of montmorillonite clay mineral (Fig.10.B) consists of two major weight loss steps. First sharp weight loss step ranges from 60 to 135°C. The montmorillonite lost 18.5% of its initial weight between this temperature range. This can be frequently attributed to the loss of water which is normally present in the interlayer spaces as well as on the surface of the montmorillonite clay mineral.\(^{(42,43)}\) The second weight loss step with 4.5% weight loss is located in the temperature range 540 - 720°C. This weight loss at such a high temperature should be due to the loss of structural OH groups.\(^{(16,43,108-116)}\) An oxides mixture is reported to be formed after this thermal decomposition.\(^{(107)}\) The metal exchanged montmorillonites also show similar two step decomposition patterns (Figs. II.B & 19.B). However, first weight loss step is observed to be extended up to \(\sim 180^\circ\)C. This indicates the **coordination** of interlayer **water** molecules with exchanged Cu(II) and Ni(II) ions in montmorillonite.\(^{(107)}\) Structural dehydroxylation appeared in a wide range of 470-740°C with about 3.5 wt% loss.
The thermograms of the intercalated compounds of Cu(II) and Ni(II)-montmorillonite (Ch.III) are in general consist of three weight loss steps. In most of the compounds first weight loss observed in a temperature range of 60 – 130°C. In case of bipy, O-phen and oxine adducts of Ni(II)-montmorillonite, this weight loss step appeared up to 200°C. In such compounds the interlayer water molecules appear to be coordinated with the metal ions and therefore, they are lost at comparatively higher temperature. The second weight loss step vary with the intercalated compound in a wide temperature range of 180-800°C. In this major weight loss step, decomposition of ligand takes place. In this way, this weight loss corresponds to the quantity of the ligand present in the intercalated compounds.

These thermal data agree with the chemical compositional data (Table-12-26) which are derived from the elemental analysis of various intercalated compounds of Cu(II) and Ni(II)-montmorillonite. Third weight loss step is mostly observed near 780°C which again corresponds to structural decomposition. (16,43,107,108)

The following conclusions may be drawn from the thermogravimetric studies.

1. In the Cu(II) and Ni(II) exchanged montmorillonite the coordinated water is present which is lost above 150°C. Coordinated water also present in bipy, O-phen and oxine adducts of Ni(II)-montmorillonite.
2. The interlayer water content of Cu(II) and Ni(II)-montmorillonite is found to be significantly decreased after formation of intercalation compounds with various ligands. This indicates that the ligands replace the water molecules from interlayer spaces. In Cu(II)-montmorillonite compounds, it is noted that the interlayer water content decreases with the increasing size of the ligand molecules, e.g. the water content in en and pn compounds is found to be about 7 wt% whereas, in intercalated compounds with bipy, 0-phen and oxine, the water loss is only ~ 4 wt%.

3. Some of the present compounds show remarkable thermal stability. Compounds of Cu(II)-montmorillonite with oxine and those of Ni(II)-montmorillonite with bipy, 0-phen and oxine are observed to be thermally more stable as compared to the normal complexes of Cu(II) and Ni(II) with these ligands. (121, 122)

The general scheme of decomposition patterns for different compounds are as follows:

(a) Two step decomposition of montmorillonite and its metal exchanged derivatives:

1. \[ \text{MNT}_{s}^{H} \xrightarrow{60 - 135^\circ C} \text{MNT}_{s} \xrightarrow{540 - 720^\circ C} \text{MNT} \]

\[ \text{MNT}_{s}^{H} = \text{Montmorillonite clay mineral.} \]

\[ \text{MNT} = \text{Residue after structural dehydroxylation.} \]

\[ \text{MNT}_{s} = \text{Montmorillonite without interlayer water.} \]
2. \[ \text{CuMNT}_{\text{H}_{\text{c}}} \underset{60 - 175^\circ C}{\longrightarrow} \text{CuMNT}_{\text{s}} \underset{470 - 740^\circ C}{\longrightarrow} \text{CuMNT} \]
\[ \text{NiMNT}_{\text{H}_{\text{c}}} \underset{60 - 185^\circ C}{\longrightarrow} \text{NiMNT}_{\text{s}} \underset{540 - 740^\circ C}{\longrightarrow} \text{NiMNT} \]

\( \text{CuMNT}_{\text{H}_{\text{c}}} \) = Cu(II)-montmorillonite

\( \text{H}_c \) denotes coordinated water.

\( \text{NiMNT}_{\text{H}_{\text{c}}} \) = Ni(II)-montmorillonite.

(b) Three step decomposition of intercalated compounds of Cu(II)- and Ni(II)-montmorillonite:

1. Cu(II)-montmorillonite compounds:

\[ \text{CuL}_2\text{MNT}_{\text{H}_{\text{c}}} \underset{60 - 140^\circ C}{\longrightarrow} \text{CuL}_2\text{MNT}_{\text{s}} \underset{185 - 740^\circ C}{\longrightarrow} \]
\[ \text{CuMNT}_{\text{s}} \underset{420 - 950^\circ C}{\longrightarrow} \text{CuMNT} \]

L = corresponding ligand used.

(subscript 2 denotes ligand to metal ratio).

2. Ni(II)-montmorillonite compounds without coordinated water:

\[ \text{NiL}_{(2-3)}\text{MNT}_{\text{H}_{\text{c}}} \underset{60 - 150^\circ C}{\longrightarrow} \text{NiL}_{(2-3)}\text{MNT}_{\text{s}} \underset{190 - 690^\circ C}{\longrightarrow} \]
\[ \text{NiMNT}_{\text{s}} \underset{590 - 920^\circ C}{\longrightarrow} \text{NiMNT} \]

3. Ni(II)-montmorillonite compounds with coordinated water:

\[ \text{NiL}_2\text{MNT}_{\text{H}_{\text{c}}} \underset{60 - 200^\circ C}{\longrightarrow} \text{NiL}_2\text{MNT}_{\text{s}} \underset{380 - 810^\circ C}{\longrightarrow} \]
\[ \text{NiMNT}_{\text{s}} \underset{725 - 900^\circ C}{\longrightarrow} \text{NiMNT}. \]
Four step decomposition of Cu(II)-montmorillonite compounds:

\[
\begin{align*}
\text{CuL}_2\text{MNTH}_s & \quad 60 \text{ -} 130^\circ\text{C} \hspace{1cm} \text{CuL}_2\text{MNTH}_s & \quad 185 \text{ -} 604^\circ\text{C} \hspace{1cm} \text{CuLMNTH}_s \\
340 \text{ -} 788^\circ\text{C} \hspace{1cm} \text{CuMNTH}_s & \quad 592 \text{ -} 950^\circ\text{C} \hspace{1cm} \text{CuMNT}.
\end{align*}
\]

X-RAY DIFFRACTION STUDIES:

We know that the montmorillonite clay is an excellent host compound having expandable interlayer spaces suitable for several incoming molecules. Normally water is present in these interlayer spaces along with exchangeable cations. The quantity of water reflects in the basal spacings of montmorillonite structure which varies from \(\sim 9.0\AA\) for a fully collapsed cell to a very large value \(\sim 23\AA\) which observed in wetted samples.\(^{(16,43,44)}\) This lattice parameter \(c\) for a monoclinic cell of the montmorillonite is found to be dependent on the size of interlayer molecules and a significant change in \(c\) is reported with different intercalated compounds.\(^{(45,46,123-131)}\) The X-ray diffraction technique is found to be very useful to measure the change, which may brought in the lattice parameters of montmorillonite after formation of intercalated compounds. Such data are also useful to investigate the orientations of intercalated molecules.

In the present study, all the intercalated compounds were subjected for X-ray powder diffraction investigation. The reflections in the diffractograms of various compounds (Chapter. III) were indexed and the \(\sin^2 \theta\) values are determined.\(^{(132-135)}\) These
observed values are in good agreement with the calculated \( \sin^2 \theta \) values. In this way, the crystal system and lattice parameters for all the prepared compounds have been determined. These indexed X-ray diffraction data are presented in Chapter (III).

The X-ray diffraction data of montmorillonite and its Cu(II)-exchanged derivatives were reported by earlier workers. The lattice parameters observed for montmorillonite clay in the present study are \( a = 5.07\,\AA, \text{ } b = 9.12\,\AA \text{ } \text{ and } \text{ } c = 10.28\,\AA \text{ } \text{ with } \beta = 98^\circ \) for a monoclinic crystal system. These values are in good agreement with the reported values, however, the \( c \) spacing of montmorillonite depends on its water content and vary sample to sample. No significant change is observed in the \( a \) and \( b \) lattice parameters of Cu(II)- and Ni(II)-exchanged montmorillonite while, \( c \) value is observed as 12.10\,\AA \text{ for Cu(II)-montmorillonite and 11.93\,\AA } \text{ for Ni(II)-montmorillonite, thereby indicating the presence of water inside the interlayer spaces. This is also supported by TGA data (Table-II & 19, Ch.III).}

With the help of various studies, it is concluded that in the present intercalated compounds the organic ligand molecules which are of different shape and size, form coordination compounds with Cu(II) and Ni(II), present in the interlayer spaces of montmorillonite. These complexes are obviously of various shape and comparatively bigger size and therefore, may need expansion in the interlayer spaces of montmorillonite for their accommodation.
All the prepared intercalated compounds of montmorillonite are found to be crystalline in nature. These compounds possess the same monoclinic crystal system with almost unchanged \( a, b \) lattice parameters and \( \beta \) as well. The lattice parameter \( c \) which is a function of interlayer spaces was found to vary with the intercalated compound. In general, the \( c \) values lie in the range \( 15 - 23 \text{Å} \) for intercalated compounds. Efforts have been made to interpret these structural data in correlation with the size of intercalated complex compounds.

8-hydroxyquinoline-Cu(II)-montmorillonite has a \( c \) value of 20.45\( \text{Å} \) (P.156). There are two possible orientations for Cu(Oxine)\(_2\) complex which is sought to be formed in the interlayer spaces of montmorillonite. The complex may be oriented in such a manner that their planes are vertical to the silicate layers and with their functional groups near the midway plane in the interlayer spaces.

In this case the basal spacing of the montmorillonite should be \( \approx 20.19 \text{Å} \) (i.e. 12.10 + 8.09) where, 12.10\( \text{Å} \) is the height of the Cu(II)-montmorillonite sheet and 8.09\( \text{Å} \) is the length of oxine molecule.\(^{(130)}\) The observed \( c \) value is in good agreement with this calculated value, thereby suggesting, that the Cu(II) ions are located on the interlayer surfaces of montmorillonite and having the square planar geometry with oxine molecules (Fig. RD.c). This is also supported by magnetic study.

The observed value of \( c \) spacing for Ni(oxine)\(_2\) adduct of
FIGURE 3: SCHEMATIC PRESENTATION OF INTERCALATED Cu-OXINE COMPLEX IN MONTMORILLONITE
montmorillonite is $15.30\text{"}(P.173)$. This value is not appropriate with same orientation of oxine molecules as considered in Cu(II)-montmorillonite, because Ni(II)-montmorillonite itself has a $c$ spacing value of $11.93\text{"}$. Another probable orientation of oxine molecules may be considered with that the molecules lie flat with their planes parallel to the sheets of montmorillonite (Fig.-RD.d). In such case, the basal spacings should be $15.73\text{"}(11.93 + 3.80\text{"})$ for 8-hydroxyquinoline-Ni(II)-montmorillonite. Where $3.8\text{"}$ is the thickness of oxine molecule. This calculated value is in good agreement with the observed value ($15.30\text{"}$), therefore, this is the most probable orientation of oxine molecules in Ni-oxine complex situated in the interlayer spaces of montmorillonite clay.

The structure of dimethylglyoxime and Nickeldimethylglyoximinate are established. The reported data on Ni(dmg)$_2$ complex reveal that the unit cell parameters of the compound are $a = 16.68$, $b = 10.44$, $c = 6.49\text{"}$ and $n = 2$, where $n$ is the number of molecules per unit cell. It is also reported that the molecules are linear and lie parallel to the $c$ axis. In the present dimethylglyoxime-Ni(II)-montmorillonite, if we predict that the Ni(dmg)$_2$ complex is parallel to the interlayer surfaces of montmorillonite then the $a$ lattice parameter of this complex will be responsible to effect the $c$ spacing of montmorillonite. The Ni-Ni distance in Ni(dmg)$_2$ complex is $3.25\text{"}$ therefore, the anticipated $c$ spacings of the dimethylglyoxime-Ni(II)-montmorillonite will be $11.93 + 6.715 = 18.645\text{"}$. Which is close to the observed value of $c$
FIG. RD. d: SCHEMATIC PRESENTATION OF INTERCALATED Ni-OXINE COMPLEX IN MONTMORILLONITE
for this compound (p. 175). This suggest the parallel orientation of Ni(dmg)$_2$ complex in the interlayer spaces of montmorillonite.

The observed value of c spacing for dimethylglyoxime-Cu(II)-montmorillonite is 18.01Å. If we consider the same parallel orientation of Cu(dmg)$_2$ complex in the interlayer spaces of montmorillonite, the effective c value for the compound will be 12.10 + 6.715 = 18.815Å. This calculated value closely resembles with the observed c value for dimethylglyoxime-Cu(II)-montmorillonite, thereby suggesting same parallel orientation of Cu(dmg)$_2$ as in the case of dmg-Ni(II)-montmorillonite. Magnetic data of both these dmg adducts also suggest the similar square planar geometry of the intercalated complex.

The crystal structure of 2,2'-bipyridyl is fully understood.\(^{138}\) Lattice parameters for a monoclinic cell of 2,2'-bipyridyl are a = 5.51Å, b = 6.24Å and c = 13.68Å with β = 120° and n = 2. It is a coplanar molecule, therefore, in the Cu(bipy)$_2$ and Ni(bipy)$_2$ complexes, the c parameter of bipyridyl molecule will be expected to effect the interlayer spacings of montmorillonite clay. As per this consideration the anticipated enhanced c spacing for 2,2'-bipyridyl-Cu(II)-montmorillonite will be 18.94Å. Similarly, the 2,2'-bipyridyl-Ni(II)-montmorillonite will have a c value of 18.77Å. The observed c value for 2,2'-bipyridyl-Cu(II)-montmorillonite is 18.70Å and 18.60Å for 2,2'-bipyridyl-Ni(II)-
montmorillonite. These values are very close to the calculated c values, considering the parallel orientation of co-planar 2,2'-bipyridyl molecules in the interlayer spaces of Cu(II)-montmorillonite and Ni(II)-montmorillonite.

The observed c values for monoclinic cells of the compounds 1,10-phenanthroline-Cu(II)-montmorillonite and 1,10-phenant-hroline-Ni(II)-montmorillonite are 15.21 and 15.04Å respectively. These comparatively low values suggest flattened parallel orientations of the 1,10-phenanthroline molecules in the interlayer spaces of Cu(II)-and Ni(II)-montmorillonite.

Amines are comparatively smaller molecules but significant expansion have been observed in the c spacings of amine adducts of Cu(II)- and Ni(II)-montmorillonite. The observed c spacings for 1,2-diaminoethane, 1,2-diaminopropane and diethylenetriamine adducts of Cu(II)-montmorillonite are 16.36, 16.62 and 17.88Å respectively. (139) These values show slight increase with the increasing size of the amine molecules.

The Ni(II)-montmorillonite compounds with 1,2-diaminoethane, 1,2-diaminopropane and diethylenetriamine are having the c values of 22.30, 23.46 and 17.44Å respectively. The comparatively high c values of the 1,2-diaminoethane and 1,2-diaminopropane compounds might be due to the stoichiometry of the complexes of Ni(II) with these ligands in which three molecules of these amines are found to be coordinated with nickel (Table-RD.ii).
Obviously these complexes will require more spaces in the inter-layer gap of Ni(II)-montmorillonite than the diethylenetriamine intercalated compound of Ni(II)-montmorillonite clay.

With the help of these X-ray diffraction data, it can be concluded that the coordination compounds of Cu(II) and Ni(II) are present in the interlayer spaces of montmorillonite clay structure. These intercalated complexes can retain their normal geometries by expanding the interlayer spaces of the clay.

Owing to the large scale applications of the intercalation and coordination compounds in catalysis, N-fixation and other areas of industrial importance, the intercalation compounds of cation exchanged clays deserve attention of many more workers in future. Such compounds promise their applications as nitrogen immobilising and microencapsulating agents. On the basis of this work fixation of the N and O containing organic molecules in the clay mineral structure could be undertaken to investigate their structure-property relationship and possible applications in fixing hazardous chemicals in clay minerals, after introduction of suitable cations. The remarkable thermal stability of some intercalated coordination compounds of Cu(II)- and Ni(II)-montmorillonite may be exploited in extensive industrial applications.
REFERENCES (CHAPTER-IV)


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