CHAPTER 1

INTRODUCTION

1.1 Layered Materials:

In the present worldwide search for different advanced materials possessing superior physico-chemical properties, layered materials are considered to be important group of solids bearing enormous application prospects in various fields. These prospects are mainly related to fields like superconductivity, catalysis, photocatalysis, gaseous emission control, development of electro-chemical materials, formulation of lubricants, handling of nuclear materials, development of photo sensors, immobilisation of toxic ions, hydration of cements, preparation of rheological fluids for petroleum exploration, intercalation reactions etc. Layered materials possess a flat two dimensional motif and are composed by different elementary layers of constituting atoms. The elementary layers have definite crystallographic 'a' and 'b' parameters; the 'c' parameters in most of the cases vary. Moreover, mixed layer formation and turbostratic distortion around c direction is also frequently found in this type of materials. This happens because of different stacking arrangement of unit layers. In many of these structures, there are only van der Waals forces between the adjacent layers and as a result they show a pronounced cleavage parallel to the layers. The interlayer space of this type of materials are accessible to
different chemical species\textsuperscript{30,31} through intercalation, and thus amplifies the interest.

Clay minerals are the best known group under the category of layered materials. Out of different types of clays, montmorillonite and kaolinite are the two widely studied species. Kaolinite is an important raw material for ceramic industry. Structurally it has neutral asymmetric layers which bear hydroxyl groups on one of the two layer sites. On the other hand, montmorillonite is a swelling type of clay with a negative layer charge compensated by cations which can be exchanged by various types of cations\textsuperscript{31-33}. Thus, montmorillonite is also called as 'Cationic Clay Mineral'. Due to cation exchangeable properties, it finds use in different fields like catalysis\textsuperscript{34,35}, oil exploration\textsuperscript{36}, environment\textsuperscript{37} etc. In addition to these naturally occurring minerals, there are various other synthetically prepared layered materials like mixed metal layered hydroxides (MMLH) or layered double hydroxides (LDH), zirconium phosphates, vanadyl phosphates, oxyhalides of transition metals, oxocuprates, transition metal dichalcogenides\textsuperscript{10} etc. Among these materials, MMLH have gained recently much interest because of their novelty and important industrial applications.

1.2 Mixed Metal Layered Hydroxides or Hydrotalcites:

MMLH or LDH or Hydrotalcites are charge wise opposite to that of montmorillonites i.e. they possess a positive layer charge. These are
the only known class of ionic layered compounds in which the layers are two-dimensional cations\textsuperscript{38}. The term ‘double’ in LDH was derived from the wrong belief that the structure of these compounds is composed of two layers, a trioctahedral layer of divalent cations within the interlayers of disordered dioctahedral layers of trivalent cations\textsuperscript{39}. However, the actual structure consists of different hydroxidic elementary layers accommodating within the same elementary layer different metal ions like Mg\textsuperscript{2+}, Zn\textsuperscript{2+}, Al\textsuperscript{3+}, Fe\textsuperscript{3+} etc. Bivalent metal ions like Mg\textsuperscript{2+}, Zn\textsuperscript{2+} form the main brucite-like hydroxy framework where isomorphous substitution by trivalent metal ions like Al\textsuperscript{3+}, Cr\textsuperscript{3+}, Fe\textsuperscript{3+} etc. cause the generation of additional charge over the layers which is balanced by interlayer exchangeable counter-anions like Cl\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-}, SO\textsubscript{4}\textsuperscript{2-} etc. Because of the presence of a layer of anions in the interlayer position, these materials are also referred to as “Anionic Clay Minerals”\textsuperscript{40}. Since, hydrotalcite is one of the most prominent minerals of this group found in the nature, therefore, instead of mixed metal layered hydroxides these are also commonly called as hydrotalcite.

\textbf{1.3 Types of mixed metal layered hydroxides:}

There are three main types of MMLH

(1) The crystalline hydrated lithium aluminates with a formula [LiAl\textsubscript{2}(OH)\textsubscript{6}]\textsuperscript{+}X.nH\textsubscript{2}O where monovalent Li\textsuperscript{+} ion is present in the vacancies of aluminium octahedra.
(2) The hydrocalumite \([\text{Ca}_2\text{Al(OH)}_{6.75}](\text{CO}_3)_{0.125}(\text{H}_2\text{O})_{2.5}\) group resembling more to so called hydrotalcite group than crystalline hydrated lithium aluminates, has the variation that the dipositive cation is \(\text{Ca}^{2+}\) and the composition is \([\text{Ca}_2\text{M}^{3+}(\text{OH})_6]^+\ X.n\text{H}_2\text{O}\) (where \(\text{M}\) is a trivalent metal ion; \(\text{Ca}^{2+}: \text{M}^{3+}\) is \(2:3\), \(X\) is an exchangeable anion).

(3) The pyroaurite-sjögrenite mineral with random distribution of bivalent and trivalent metal ions in the hydroxide main layer with a generic formula \([\text{M}_1-x^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x^+}(X^{q_x/q})n\text{H}_2\text{O}\) (where \(\text{M}\) are bi and trivalent metal ions, \(X\) is an exchangeable monovalent anion and \(0.2 \leq x \leq 0.4\), \(n\) is the number of water molecules, generally \(n \equiv 4\) for natural hydrotalcite type MMLH).

Crystalline hydrated lithium aluminates are formed on precipitation of aluminium hydroxide from solution of aluminium salts at alkaline pH in presence of very high amount of \(\text{Li}^+\) ion. Apart from this combination of \(\text{Li}\) and \(\text{Al}\), synthesis of seemingly unusual combination of \(\text{Li}^+\)-\(\text{Ti}^{4+}\) MMLH has also been reported. Many synthetic members of hydrocalumite group are formed during hydration of Portland cement and are represented with the following oxidic formula \(3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaX}_2.n\text{H}_2\text{O}\) (where \(X\) is a monovalent anion). One of the prominent members of this group is so called ‘monochlorohydrate’ \(3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2.n\text{H}_2\text{O}\) which is formed on reaction of \(\text{CaCl}_2\) with ordinary Portland cement. Likewise tetracalcium aluminate \(4\text{CaO}\cdot\text{Al}_2\text{O}_3.x\text{H}_2\text{O}\) or \([\text{Ca}_2\text{Al(OH)}_6]\text{OH}.n\text{H}_2\text{O}\) (where \(n = 19, 13,\)
11 or 7) is another example of a cement hydrational phase having layered structure.

However, the most widely studied and technologically important MMLH are hydrotalcites. In nature, during the reaction of sea water with basaltic glasses, hydrotalcites are formed as transient minerals. During the process there is a selective dissolution of most of the mobile elements of the basaltic glass forming first a leached SiO$_2$ rich layer followed by precipitation of hydrotalcite like hydroxycarbonates on the modified surfaces. Precipitation of hydroxycarbonates takes place due to local increase of pH near glass surface. CO$_2$ gas assists the reaction. However, the hydroxy carbonates formed undergoes further transformation to form serpentine like phyllosilicates. Besides the formation of hydrotalcites in the natural process of rock and mineral weathering, authigenic formation of hydrotalcite in sediment pore system in lagoons of industrial waste water rich with Al$^{3+}$, NaHCO$_3$ and NaOH has also been reported. 'Green rust' is another type of MMLH formed by Fe$^{2+}$ and Fe$^{3+}$ as an intermediate phase in natural conditions from steels embedded in cement and concrete. Names, composition, unit cell parameters of some MMLH type minerals found in nature are shown in Table 1.1.

In addition to above minerals, some other minerals are found, which exhibit structure similar to that of brucites but with an intermediate layer containing cations apart from anions. These minerals are Motu-
koreaite \[\text{Mg}_{1.82}\text{Al}_{1.12}\text{Mn}_{0.03}\text{Zn}_{0.02}(\text{OH})_{5.15}[(\text{Na}_{0.07}\text{K}_{0.01})(\text{CO}_3)_{0.63}(\text{SO}_4)_{0.4}2.74\text{H}_2\text{O}]\]^67, Wermlandite \[\text{Mg}_{1}(\text{Al}_{0.57}\text{Fe}^{3+}_{0.43})_2(\text{OH})_{18}][(\text{Ca}_{0.6}\text{Mg}_{0.4})(\text{SO}_4)_{2.12}\text{H}_2\text{O}]\]^67, Mountkeithite \[((\text{Mg}_{8.15}\text{Ni}_{0.85}\text{Cu}_{0.02})(\text{Fe}^{3+}_{1.31}\text{Cr}_{1.02}\text{Al}_{0.07})(\text{OH})_{24}][(\text{CO}_3)_{1.11}(\text{SO}_4)_{0.36}(\text{Mg}_{1.76}\text{Ni}_{0.18})(\text{SO}_4)_{1.94}9.39\text{H}_2\text{O}]\]^68, Hydrohonessite \[\text{Ni}^{2+}_{5.4}\text{Fe}^{3+}_{2.5}(\text{OH})_{16}][(\text{SO}_4)_{1.28}0.98\text{NiSO}_46.95\text{H}_2\text{O}]\] etc. The well known clay mineral ‘chlorite’ shows structural similarity of its hydroxidic layer to hydrotalcite type minerals, where anionic layer of hydrotalcites is replaced by talc like alumino-silicate layers\(^70\).

1.4 **Synthetic hydrotalcites:**

The most important precondition for the synthesis of hydrotalcite type MMLH from two different metal ions is near equality of their ionic radii\(^71-73\). Ionic radii, of some of the metal ions which are reported to form MMLH are shown in Table 1.2.

Since \(\text{Cd}^{2+}\) and \(\text{Ca}^{2+}\) have relatively larger ionic radii than the most common trivalent ions (Table 1.2) and therefore they generally do not form exclusively hydrotalcite type MMLH but rather hydrocalumite type structure only\(^16,74\). However, the presence of these ions in combination with other bivalent ions in hydrotalcite like MMLH structure have also been reported\(^41,79\). Apart from substitution of bivalent metal ions in brucitic hydroxy framework by trivalent ions, tetravalent cations like \(\text{Si}^{4+}\) and \(\text{Zr}^{4+}\) have also been reported\(^80,81\) to substitute.
In addition to Cd\(^{2+}\) and Ca\(^{2+}\) ions, Cu\(^{2+}\) ion is another difficult metal ion; incorporation of which to hydrotalcite like MMLH structure is not easy due to various factors like Jahn Teller distortion effect of the octahedra, temperature and pH instability\(^{82-84}\).

Generally, the highest ratio of trivalent to (trivalent + bivalent metal ions) in MMLH structures is \(X = 0.35\) [where e.g. \(X = \frac{Al}{(Al+Mg)}\)], in other words in Mg-Al MMLH structures, Al substitutes randomly for some Mg in the hydroxide main layer up to a maximum of about one in three sites. However, Allmann et al.\(^8^5\) were able to raise the value of \(X\) up to 0.44 by using hydrothermal technique of synthesis.

### 1.5 Crystallographic structure of hydrotalcite type MMLH:

The arrangement of brucitic unit layers accompanied by position of interlayer ions with respect to hydroxide groups of two adjacent layers constitute a major aspect of the deduction of crystallographic unit cell structure of hydrotalcite like MMLH. The major problem in deduction of unit cell structure is scarcity of single crystal XRD data of these materials. Allmann\(^8^6\) from single crystal data obtained by Wiessenberg camera from a mineral sample from Långaban, Sweden has assigned the space group and unit cell data for Sjögrenite \([Mg_6Fe^{3+}Fe^{2+}_2(OH)_{16}] [(CO_3)_2.4H_2O]\) as shown in the Table 1.1. From a separate portion of the same mineral, crystals of Pyroaurite was also isolated. Pyroaurite is a polytype of Sjögrenite, which is formed at higher temperature. Allmann\(^8^8\) has assigned the space group and unit cell data for Pyroaurite as given in the Table 1.1. The two
polytypes differ in stacking sequence of -OH layers; in the rhombohedral 'Pyroaurite' phase, three double layers are present per unit cell with the sequence -BC-CA-AB-BC- and \( c = 3c' \) (\( c' \) = layer thickness), where A, B, C stands for threefold axes in \( xy = 0,0; 2/3, 1/3; 1/3, 2/3 \). Stacking sequence in hexagonal Sjögrenite is -BC-CB-BC- and \( c = 2c' \). Generally, the relation between the cell parameters are \( a_{\text{rh}} = a_{\text{hex}} \) and \( c_{\text{hex}} = 2/3c_{\text{rh}} \). MMLH of rhombohedral Pyroaurite type structure satisfies the condition \((-h+k+l) = 3n^{88}\).

The structure described by Allmann\(^{53}\) explains that the adjacent brucite layers are stacked so that the hydroxide groups on the lower surface of one layer are directly above those on the upper surface of the lower layer. In fact, this arrangement is more closer to a gibbsite structure than a brucite structure. The 2H and 3R subgroups described above represents the two simplest sequences satisfying this condition.

Similar to Mg-Al MMLH, in Zn-Al MMLH the Zn/(Zn+Al) ratio has been raised to 0.44 from 0.35\(^{68, 88}\). As ionic radii of \( Al^{3+} \) is smaller than \( Mg^{2+} \), therefore, below the level of 0.35, the in plane unit cell ‘a’ dimension decreases with increasing isomorphous substitution of \( Mg^{2+} \) by \( Al^{3+} \). However, above the value of 0.35 of \( Al/(Al+Mg) \) ratio, the crystallographic \( a_0 \) value remains constant at 3.04 Å\(^{90}\). This is because for values \( X \leq 0.35 \), each \( Al(OH)_3 \) octahedron is surrounded by six \( Mg(OH)_2 \) octahedra and for \( X > 0.35 \), \( Al(OH)_3 \) octahedra must be directly adjacent to each
other. Thus at $x > 0.35$ the expected reduction in unit cell parameter in crystallographic 'a' direction due to smaller ionic radii of $\text{Al}^{3+}$ ion is compensated by the increased electrostatic repulsion within the brucite like layers by $\text{Al(OH)}_3$.

In the above said structural descriptions where Mg-Al type MMLH are indexed with 'a' value around $3.1 \text{ Å}$, the overall distribution of bivalent and trivalent metal ions in the structure is random. However, in some cases the ordering of these cations resulting in crystallographic 'a' value $\sqrt{3}$ times that of basic value $3.1 \text{ Å}$ ($\sqrt{3} \times 3.1 = 5.3 \text{ Å}$) is also reported.

Apart from the structure of main layer, the stereochemical characteristics of various interlayer anions play vital role in the chemical and physical properties of MMLH. Of particular interest is the cause of exceptional stability of $\text{CO}_3^{2-}$ ion in the interlayer position of hydrotalcite like MMLH. The oxygen sites of $\text{CO}_3^{2-}$ groups and $\text{H}_2\text{O}$ molecules are accommodated in a single set of sites (Fig. 1.1). Each group of oxygen has six possible sites and only one of it is occupied at a time. The oxygen sites are distributed closely around those symmetry axes that pass through the hydroxyl ions of adjacent brucite layers. Interestingly the three oxygen sites from adjacent groups are occupied in a particular way that they are in exactly the right places to form a horizontal $\text{CO}_3^{2-}$ ion with
C atom in the center. Because of such exceptional stereochemical stability of \( \text{CO}_3^{2-} \) ions, it is very difficult to drive it out from the interlayer positions. In some occasions, presence of carbonate ion in the interlayer helps in formation of layered hydroxide\(^8\). On the other hand, if there is an oxygen atom from a water molecule, it can form reasonably good tetrahedral configuration by forming hydrogen bonds to other oxygen atoms in the interlayer and to hydroxyl groups in adjacent brucite layers. NMR study has shown that there is an ordering of interlayer carbonates and water molecules due to hydrogen bonding between the hydrogen atoms of the main layer and oxygen atoms of the interlayer molecules. During the ordering, the interlayer water molecules possess a rotational freedom around \( C_2 \) molecular axis. Molecular symmetry axes of both carbonate (\( C_3 \)) and water (\( C_2 \)) are oriented parallel to the crystallographic \( c \)-axis of hydrotalcite\(^9\). Apart from the said surface water which is bound to intragallery and external basal planes, there are other water molecules condensed between aggregated crystal platelets also.

Drits et al.\(^{50,92,93}\) in the course of an extensive study have reported different possible diverse polytypes of hydrotalcite like MMLH differing in construction of interlayers, position of octahedral layers with respect to its neighbouring layers and number of layers per unit cell. Besides two and three layer polytypes, a theoretical descriptions has been given\(^9\) about the possible existence of polytypes of six layers per unit cell. In
fact many synthetic analogues have been indexed with larger than three layered unit cell. Rietveld analysis of synthetic MMLH with different type of anions with various c parameters has also been reported.

1.6 Crystallographic structure of hydrocalumite and Li-Al type MMLH:

Similar to ordered arrangement of bivalent and trivalent ions in some hydrotalcite type MMLH, a superstructure formation with a larger unit cell is also found in hydrocalumite type Ca-Al MMLH. Since in comparison to the size of Mg\(^{2+}\) ion, Ca\(^{2+}\) ion is larger therefore there arises three different distortions of Portlandite Ca(OH)\(_2\) layers. The OH\(^-\) ions are drawn in towards the Al\(^{3+}\) ions, so that the layers could alternatively be described as consisting of Ca\(^{2+}\) ion and [Al(OH)\(_3\)]\(^3-\) octahedra. These octahedra are then rotated around an axis normal to the plane of the layer, and the Ca\(^{2+}\) ions are displaced parallel to the axis; half of them in one direction, and the other half in the other direction. The net result of these distortions is to render the CaO\(_6\) octahedra very open on one side forming a bowl so that a water molecule from the interlayer can form bond with Ca\(^{2+}\) and as a result Ca\(^{2+}\) becomes seven coordinated.

The crystalline hydrated lithium aluminates with a formula [LiAl\(_2\)(OH)\(_6\)]\(^+\)X\(^-\)·nH\(_2\)O containing monovalent Li\(^+\) ions in the vacancies of gibbsite like Al(OH)\(_3\) octahedra were initially indexed with a hexagonal cell of superlattice parameters a=5.32 and c=15.24 indicating a
cation ordered structure. However, later on it has been suggested that the unit cell can be better described by a C-centered monoclinic system with the cell parameters as $b=\sqrt{3}a$ and $\cos \beta = -a/3c$ ($a=5.097$ Å, $b=8.829$ Å, $c=7.741$ Å and $\beta=103.0^\circ$).

1.7 Thermal properties of MMLH:

The thermal properties of this group of materials require special attention due to formation of immense number of oxidic phases like non-stoichiometric oxides, segregated spinels, nanometer sized oxide particles etc. on calcination. During the process of heating, MMLH undergoes various weight loss and phase changes; the exact nature and temperature of change depends upon the composition of MMLH. Generally, the interparticle condensed water from the solid is liberated first at around 60°C, followed by loss of intragallery surface water in the temperature range 120-150°C. At this stage there is a pronounced shrinkage of basal planes, which however is reversible up to 70% of the original value upon rehydration. After the stage of dehydration, the next important thermal change that occurs at around 450°C is dehydroxylation, whereby hydroxy groups of framework hydroxide and interlayer anionic groups like $\text{CO}_3^{2-}$ and $\text{Cl}^-$ etc. begins to decompose giving rise to certain layered nonstoichiometric mixed metal oxides. These oxides exhibit a 'rock-salt' like crystallographic structure. This is actually a solid
solution of MgO and Al₂O₃ which on rehydration gives back the parent MMLH structure, provided that the calcination temperature does not exceed 550-600°C. The solid state ²⁷Al MAS NMR studies conducted under in situ heating condition at a slow heating rate of 1°C/min. on Mg-Al type MMLH shows that the interlayer CO₃²⁻ begins to decompose even at temperature as low as 250°C, which is considerably lower than the decomposition temperature of MgCO₃. At a temperature above 900°C the mixed oxide segregates to MgO, MgAl₂O₄ and a trace of γ-Al₂O₃.

Like Mg-Al MMLH, Ni-Al type MMLH also undergoes conversion to a rock-salt type mixed metal oxide at 300°C, and converts to NiO and NiAl₂O₄ at 700-1000°C. The temperature at which mixed metal oxide forms depend upon the composition of the MMLH, e.g. Ni-Al MMLH converts to NiO and NiAl₂O₄ at around 920°C, while in Ni-Cr MMLH NiCr₂O₄ is formed only at around 580°C. This is because of difference in crystal field stabilization of metal ions involved in the spinel structure, which is higher for Cr in NiCr₂O₄ as the structure is a spinel one while it is lower for Al in NiAl₂O₄ as the structure is an inverse spinel.

1.8. Methods of synthesis of different MMLH:

MMLH are prepared by various methods like (i) Coprecipitation from aqueous solution at alkaline pH; (ii) Precipitation at constant pH by induced hydrolysis; (iii) Synthesis from hydrolysis of alkoxides; (iv) High temperature solid state reactions; (v) Chimie-douce method; (vi)
Electrochemical precipitation; (vii) Acid phase hydrolysis of metal oxides etc. Salient points of these different synthetic approaches are described below.

(i) Coprecipitation method: Different approaches are adopted to prepare hydrotalcite like MMLH at alkaline pH and they are - titration method, slow precipitation, fast precipitation etc. Size of MMLH crystals synthesised by different method also depends upon post-precipitation-hydrothermal condition applied for ageing the precipitates. Generally, big crystals are formed after heating at 180°C for 10 hours\textsuperscript{105,20}. The coprecipitation method can be further divided to following three methods,

(a) Titration method: To a dilute solution of bi and trivalent metal ion, NaOH and/or Na\textsubscript{2}CO\textsubscript{3} solution is added to increase the pH to a range where coprecipitation takes place. As different ions precipitate in hydroxide form at different pH therefore in many cases pure product is not obtained. A single component hydroxide precipitates first than the mixed hydroxide e. g. in a mixture of Mg and Al salts, the precipitation of Al(OH)\textsubscript{3} and Mg(OH)\textsubscript{2} take place at pH of 4.0-4.5 and 9.5\textsuperscript{41} respectively.

(b) Slow precipitation: In this method, coprecipitation is carried out at a slow rate from a mixture of concentrated solutions of bivalent and trivalent salts by slow addition at a constant pH\textsuperscript{106}. The pH for precipitation is maintained constant by adding alkali slowly in a
continuous stream. This is the most commonly practised method for synthesis of hydrotalcite like MMLH as in this method solids with better crystallinity is obtained due to rate of nucleation being higher than the rate of crystal growth. In this method by maintaining a slow rate of precipitation, MMLH with a distribution of interlayer mesopores in the range 50-300 Å is obtained and is higher than the value of ~20 Å obtained by other methods of synthesis. Report has been made about the synthesis of Mg-Ga MMLH by this method.

(c) Fast precipitation: In this method the salt solution and the alkali are brought into contact with each other quickly at a desired pH for precipitation. The precipitates obtained by this way are however less crystalline. Report has been made about synthesis of 'Green Rust' by this method. Another method used for synthesis of Al containing MMLH at a faster rate is aluminate method. In this method, Mg-Al MMLH is prepared by adding MgCl₂ solution in stoichiometric amounts to aluminate solution (pH >13), at a faster rate and final pH is maintained at 10. However, Al³⁺ substitution is lower in this type of synthesis than in slow precipitation method.

(ii) Precipitation at constant pH by induced hydrolysis: In this method, Hydrotalcite type MMLH is synthesised by a hydrolysis reaction involving a cation in the solution state and a cation in fully hydrolysed or precipitated hydroxide state. The method has been named as induced
hydrolysis because the fully hydrolysed cation causes complete hydrolysis of the second cation present in the solution state. The second cation is required to be kept in the solution state at a pH slightly lower than the level at which it generally precipitates as hydroxide, e.g. CoCl₂ begins to precipitate at pH 7.7 as hydroxide and therefore it is kept at pH 7.4. Thus the first cation is selected in such a way that it precipitates at a pH lower than the second cation. As Al³⁺ precipitates as Al(OH)₃ at a pH 4.0-4.5, a Co²⁺ - Al³⁺ MMLH was prepared by this method from a suspension of Al(OH)₃ and CoCl₂ in aqueous medium by maintaining the pH at a value of 7.4 for more than 7 hours. Similarly, several other hydrotalcite like MMLH, involving metal ion combination like Ni²⁺-Al³⁺, Mg²⁺-Al³⁺, Co²⁺-Al³⁺, Co²⁺-Fe³⁺, Mg²⁺-Mn³⁺ have been synthesised by this method.

(iii) **Synthesis from hydrolysis of alkoxides:** Synthesis of Mg-Al and Li-Al type MMLH have been reported to be carried out by hydrolysis of alkoxides at room temperature at proper metal ion ratios in ionic and non ionic media. However, the products obtained contained impurities like boehmite AlO(OH)⁰⁸,¹¹²,¹¹³.

(iv) **High temperature solid state reactions:** Synthesis of Mg-Al, Mg-Fe, Ni-Fe, Ni-Al, Ca-Al, Cd-Al, Li-Al type MMLH have been carried out by hydrothermal conditions¹⁶,¹¹⁴ which transforms amorphous or small crystallites of MMLH into larger and well crystallised ones. Mg-Al type
MMLH was first synthesised by this method starting from a mechanical mixture of MgO and Al₂O₃ in an autoclave at temperatures lower than 325°C (with a total pressure ranging from 13789.6 to 137896 kPa).³⁰

(v) **Chimie-douce method**: Redox ‘Chimie-douce’ or soft chemistry approach is relatively a new non-classical approach used by solid state chemists to synthesise novel compounds. It has been utilized to synthesise Ni-Co MMLH also. Since oxidation-reduction process is involved in the synthesis, the metal ions taking part should be from transition metals as they can show multiple oxidation states. It is claimed that the method has advantage over other methods as it can give bivalent : trivalent ratio in a wide range which would depend upon the M²⁺/M³⁺ solid solution range of precursor NaM²⁺₁₋ₓ M³⁺ₓO₂ phase. The synthesis involves two steps - first the synthesis of precursor NaM²⁺₁₋ₓ M³⁺ₓO₂ phase by classical high temperature solid state reaction involving Na₂O, Co₃O₄ and NiO etc. Second step is ‘Chimie-douce’ step of oxidising hydrolysis of NaM²⁺₁₋ₓM³⁺ₓO₂ by selective reduction of higher valent Ni to divalent state and conversion of γ-oxyhydroxide formed to MMLH.

(vi) **Electrochemical precipitation**: In this method base is generated electrochemically over cathodic surface by reduction of anions and the metal hydroxide thus produced can either be unary or mixed-metal type hydroxide based upon the system selected. Ni-Al, Ni-Mn, Mg-Al, Mg-Cr type MMLH are produced from mixtures of nitrate salt solutions of...
these metal ions. Reduction of $\text{NO}_3^-$ to $\text{NO}_2^-$ at the cathode surface gives a high concentration of $\text{OH}^-$ and $\text{H}_2$ gas. $\text{OH}^-$ produced is then consumed by the corresponding metal ions to precipitate the crystalline MMLH. Although the product obtained is poorly crystalline yet there is an advantage of being free from $\text{CO}_3^{2-}$ ion, which is a serious problem in synthesis of these materials.

(vii) Acid phase synthesis from metal oxides: This method is in use for a long time to prepare different metal hydroxides involving a single bivalent, two different bivalent ions and a bivalent - trivalent metal ion combination i.e. a hydrotalcite type MMLH. In the pioneering works on MMLH type hydrotalcite by Feitknecht$^{119}$ syntheses were done by this method. The method basically involves the reaction of a bivalent metal oxide with an aqueous solution of a salt of a trivalent metal ion at low temperature. Since the pH involved in this type of synthesis is acidic but hydrotalcite type MMLH are produced mainly in alkaline medium, therefore, the mechanism of formation is complicated. Bivalent oxides form a local excess of $\text{OH}^-$ ions around the metal oxide surfaces in aqueous medium thereby facilitating the deposition of hydrotalcite type MMLH by reaction with trivalent metal ions present in the solution phase. Although not all the possible members of hydrotalcite type MMLH can be synthesised by this method but some important members like Zn-Al$^{120}$, Zn-Cr$^{121}$, Cu-Cr$^{121,122}$ type are easily synthesised by this method. Like electro-
chemical precipitation method, this method also provides a route to synthesise $\text{CO}_3^{2-}$ free hydrotalcite type MMLH. Synthesis of Ni-Al type MMLH from reaction of alumina with Ni amine complexes at neutral pH has also been reported\textsuperscript{1,23}

1.9 Nature of interlayer anions:

In MMLH a wide variety of anions can be intercalated, which can compensate the positive charge of the brucite-like sheets. The only difficulty in obtaining different intercalated species under ordinary laboratory conditions is the preoccupancy of interlayer position by $\text{CO}_3^{2-}$ ions which cannot be removed through ordinary ion exchange\textsuperscript{1,24} Using various synthetic techniques, different hydrotalcite like MMLH have been prepared involving the following groups of anions -

(a) Inorganic monomeric anions like $\text{F}^-$, $\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$, $\text{ClO}_3^-$, $\text{ClO}_4^-$, $\text{IO}_3^-$, $\text{BrO}_4^-$, $\text{OH}^-$, $\text{SO}_4^{2-}$, $\text{PO}_4^{3-}$, $\text{S}_2\text{O}_3^{2-}$, $\text{WO}_4^-$, $\text{CrO}_4^{2-}$, $\text{NO}_3^-$, $\text{AsO}_4^{3-}$, $\text{BO}_3^{3-}$, $\text{SiO}_4^{4-}$, $\text{MnO}_4^{2-}$, $\text{HGaO}_3^{2-}$, etc.

(b) Inorganic polymeric anions like $[\text{V}_{10}\text{O}_{28}]^{6-}$, $[\text{Mo}_{27}\text{O}_{44}]^{6-}$, $[\text{Ta}_{6}\text{O}_{18}(\text{OH})]^{7-}$, $[\text{Nb}_{6}\text{O}_{18}(\text{OH})]^{7-}$, $[\text{PMo}_6\text{W}_6\text{O}_{40}]^{6-}$, $[\text{PMo}_6\text{V}_6\text{O}_{40}]^{5-}$, $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$, $[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{NaPW}_{30}\text{O}_{62}]^{8-}$, $[\text{P}_2\text{W}_{10}\text{O}_{62}]^{8-}$, $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, $[\text{NiW}_6\text{O}_{24}\text{H}_6]^{4+}$, $[\text{SiW}_8\text{V}_3\text{O}_{40}]^{7-}$, $[\text{Cr}_2\text{O}_7]^{2-}$, $[\text{PCuW}_{11}\text{O}_{39}(\text{H}_2\text{O})]^{5-}$, $\alpha$-$[\text{SiW}_{11}\text{O}_{39}]^{6-}$, $\alpha$-$[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$, $\text{C}_{60}$ fullerene anions etc.
(c) Organic species like: micron size carbon powders\textsuperscript{138}, adipic, acetic, propionic, n-butyric, n-valeric\textsuperscript{139}, oxalic, succinic, malonic, sebacic\textsuperscript{141}, capric\textsuperscript{142}, 1,12 dodecandicarboxylic acid, hexanoic\textsuperscript{142}, myristic acid\textsuperscript{142}, terephthalic acid, chloro-cinnamic acid, p-toluene sulphonnic acid, trans-cinnamate, 1-naphthocarboxylate, 9-anthracene-carboxylate\textsuperscript{143}, styrene sulphonnic acid, benzoic acid, polyvinyl alcohol, polydimethyldiallyl ammonium chloride\textsuperscript{144}, poly(N,N-dimethylbutylammonium iodide), polyaniline\textsuperscript{145}, alkyl halides, dodecyl glycol ether sulphate, alkyl sulphates\textsuperscript{146}, trichlorophenol, trinitrophenol, naphthalene carboxylate ions, tetra (4-sulphonatophenyl) porphyrin, tetra (4-carboxyphenyl) porphyrin, indigo carmine dye, potassium indigo tetratsulfonate\textsuperscript{147}, new coccine dye, naphthoyl yellow dye\textsuperscript{148}, indolinespirobenzopyran, adenosine monophosphate, 9,10-Anthraquinonedisulfonates\textsuperscript{149}, poly (dibutylammonium chloride)\textsuperscript{148}, l-ascorbic acid\textsuperscript{150}, dodecylsulphate\textsuperscript{148}, nucleic acid\textsuperscript{150}, D & L-histidines\textsuperscript{151} etc.

(d) Anionic metal complexes like: \([\text{Co(CN)}_6]^3-\), \([\text{Fe(CN)}_6]^3-\), \([\text{Fe(CN)}_6]^4-\)\textsuperscript{152}, \([\text{Fe(CN)}_5\text{NO}]^2-\), \([\text{IrCl}_3]^3-\), \([\text{Mo(CN)}_9]^4-\)\textsuperscript{6}, \([\text{Fe(III) EDTA}]^2-\), \([\text{Ni(II) EDTA}]^2-\), \([\text{Cu(II) EDTA}]^2-\), \([\text{Zn(II)EDTA}]^2-\), \([\text{Co(pcts)}]^4-\) (pcts = Phthalocyanine)\textsuperscript{2}, \([\text{MoO}_2(\text{O}_2\text{CC(S)}\text{Ph}_2)]^2-\), \([\text{Ru}(4,7\text{-diphenyl-1,10-phenanthroline-sulfonate})_3]^4+\), Ni(II)phthalocyaninetetrasulfonate\textsuperscript{153}, \([\text{Ru(CN)}_6]^4-\)\textsuperscript{7} etc.
1.10 Applications of MMLH:

MMLH are attaining the status of a most versatile group of inorganic materials by finding an increased number of applications in different fields. Some of the applications are as follows -

(A) Medical and related applications:

Application of hydrotalcite like MMLH begins from the world famous antacid product Talcid of M/S Bayer, Germany, which is a Mg-Al type MMLH. These hydroxidic materials elevates the pH of the gastric content of human intestine by neutralising the intestinal hydrochloric acid to a value of pH above 4 to control the peptic activities. The effectiveness of hydrotalcite suspensions have been increased by combining it with other ingredients like dimethicone e.g. Altacite (Hoechst Marion Russel), Gastrocote (Boehringer, Mannheim), Asilone (Boots) etc. Cl-form of Mg-Al type MMLH is suggested as substitute of aluminium hydroxide gel for effectively binding phosphate for controlling hyperphosphatemia, which is induced during hemodialysis for patients with severe renal disease. MMLH are also commonly added to tablets as fillers, to cosmetics for pH balancing of skin, to toothpastes for destruction of plaques etc.

(B) Adsorbents:

Application of MMLH as adsorbent for various types of inorganic anions are distributed over a wide range of literatures. Toxic anions like \( \text{Cr}_{2}\text{O}_7^{2-} \), \( \text{CrO}_4^{2-} \), \( \text{AsO}_4^{3-} \), \( \text{SeO}_4^{2-} \), trinitrophenoxide, trichloro-
phenoxide etc. are effectively removed from aqueous medium by the hydrotalcite like MMLH. For this, basically calcined hydrotalcite like MMLH having a non stoichiometric oxidic composition are taken, which gives back the layered hydroxide on rehydration in aqueous medium by an effect which is termed in vogue as 'Memory Effect'. During the process of rehydration it intercalates in the interlayer positions the toxic anions present in the medium.

(C) **Toxic gas remover:**

Apart from toxic anions, MMLH are used to prepare different adsorbents for gases like SO₂, H₂S etc. Mg-Al based spinels derived from hydrotalcites works as an effective sorbent for SO₂ gas from hydrocarbon processing units. Similarly ZnO based adsorbents derived from Zn-Cr or Zn-Al type MMLH are good adsorbents for H₂S gas. Mg-Al type MMLH has been used to decompose greenhouse gas N₂O to N₂ and O₂.

(D) **Catalysts and catalyst precursors:**

Catalytic application of MMLH have been reported for various type of important reactions e.g.:

**a) Solid base catalysis:** MMLH structures act as solid base catalysts with very high basicity, which can be decreased to certain extent by calcination. MMLH has been successfully utilized to synthesise citronitril from ethyl cyanoacetate and benzylacetone by a Knovenagel
type condensation. Dehydrogenation and dehydration of 2-propanol to ketone and propylene, alkylation of phenol by methanol, aldol condensation like conversion of acetone to crotonaldehyde and 3-hydroxybutanol\textsuperscript{158} etc. are also reported to occur in presence of such basic catalysts.

b) **Reformation catalysis**: Reformation reactions involve following reactions:

a) \(C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2\)

b) \(CO + H_2O \rightarrow CO_2 + H_2\)

c) \(CO + H_2 \rightarrow CH_4 + H_2O\)

Calcined catalysts based upon precursors like Ni-Al MMLH or Cu-Zn-Al MMLH\textsuperscript{159} prepared by coprecipitation method and subsequently reduced with \(H_2\) find use in this reaction.

c) **Hydrogenation reactions**: MMLH based catalysts with the following metal ions in different ratios \(Co:Mn:Al = 5.5:0.5:2\) were found as effective catalysts for conversion of Nitrobenzene to Aniline\textsuperscript{160}. Similarly, Ni-Mg-Al type MMLH were effective catalyst for conversion of acetonitrile to amines\textsuperscript{161}. Apart from hydrogenation of ‘Syngas’ to \(CH_3OH\), MMLH containing Cu has also been used for conversion of ‘Syngas’ to \(CH_3OH\)-higher alcohol mixtures and hydrocarbons\textsuperscript{162-164}.

d) **Oxidation reactions**: Metal oxide catalysts derived from polyoxometallate intercalated MMLH have been tested as an oxidation catalyst
for conversion of o-xylene to o-tolualdehyde and photoxidation of isopropyl alcohol. Mg-Al MMLH has been found as a suitable catalyst for Baeyer-Villiger oxidation of ketones by use of oxygen to lactones and esters. Also report has been made about the use of calcined MMLH for oxidation of benzylic hydrocarbon\textsuperscript{165}. Catalytic Partial Oxidation (CPO) of CH\textsubscript{4} have been studied by using hydrotalcites of Ni/Mg/Al type\textsuperscript{166}. In addition to these, other important chemical reactions viz. Meerwin-Pondorf-Verley reduction\textsuperscript{167}, Phenol hydroxylation\textsuperscript{168} etc. have also been performed through catalysis by MMLH.

\textbf{e) Halide exchanger reactions:} Halide ions intercalated in interlayer positions of MMLH undergoes exchange reactions or in other words nucleophilic substitution occurs with alkyl halides e. g. reaction between alkyl bromides in toluene solution and halide ions in gallery space of MMLH has been reported,

\[
[Zn_2Cr(OH)_{8}]Cl + RBr \rightarrow [Zn_2Cr(OH)_{6}]Br + RCl
\]

Similarly, halide exchange reaction of alkyl bromide (or iodide) and benzyl chloride in toluene ( or DMF) through the intermediacy of Cl or Br intercalated MMLH as catalyst has also been reported. The halide exchange reaction between alkyl bromides and halide ion intercalated as a ligand bound to an anionic complex e. g. [NiCl\textsubscript{4}]\textsuperscript{-} is also possible\textsuperscript{169}.

\textbf{f) Support for biomimetic reaction:} Biomimetic catalyst molecules like phthalocyanins and metalloporphyrins when immobilised in the interlayers
of MMLH enhances the reactivity about two times than their analogous homogenous catalytic reactions. Oxidation of 2,6-di-tert-butyl phenol to the corresponding benzoquinone and diphenooquinone and oxidation of thiols to tetrasulfonates have been reported. This type of catalytic performance makes MMLH an exceptionally promising class of support for immobilisation of metallomacrocycles for various applications.

E. Anion exchangers:

MMLH also find use as inorganic anion exchangers; as they can exchange the interlayer anions with different type of anions. The selectivity sequence for most of the commonly available anions for anion exchange in the interlayer positions is given as below,

\[
\text{CO}_3^{2-} \rightarrow \text{SO}_4^{2-} \rightarrow \text{Cl}^{-} \rightarrow \text{ClO}_4^- \rightarrow \text{NO}_3^- \rightarrow \text{CH}_3\text{COO}^{-}
\]

Due to very high selectivity of CO$_3^{2-}$ ion for interlayer positions, application of MMLH as an anion exchanger is extremely limited as in most of the cases CO$_2$ from atmosphere contributes for the formation of CO$_3^{2-}$ ion in the interlayer positions, which once formed is never released by other anions under ordinary condition.

Hydrotalcites are used to make high grade PVC materials for windows, doors etc. These type of PVC materials are prone to degradation caused by exposure to direct sunlight. Addition of Mg-Al MMLH of CO$_3$ form during manufacture effectively traps the degrading material HCl formed in the PVC by action of sunlight.
F. Host for chemical reactions:

Although due to certain difficulties like high charge density and limitation of gallery swelling, the galleries of MMLH are not as facile as smectites for intracrystalline reactions, yet they provide ample opportunities as supported anionic reagents\textsuperscript{170}. In order to provide excellent sites for organic reactions, hydrophobisation of interlayer hydroxidic groups by reaction with esters has also been reported\textsuperscript{148,171}. Oxidation-reduction reactions like oxidation of interlayer I\textsuperscript{-} ion to I\textsubscript{2}, S\textsubscript{2}O\textsubscript{6}\textsuperscript{2-} to SO\textsubscript{4}\textsuperscript{2-} by H\textsubscript{2}O\textsubscript{2}, reduction of interlayer IO\textsubscript{3}\textsuperscript{-} to I\textsuperscript{-} ion by N\textsubscript{2}H\textsubscript{4} has also been reported\textsuperscript{175}. Redox reactions between two interlayer anions like SO\textsubscript{3}\textsuperscript{2-}/MnO\textsubscript{4}\textsuperscript{2-} to SO\textsubscript{4}\textsuperscript{2-}/MnO\textsubscript{2} have also been reported\textsuperscript{172}. Styrene sulphonic acid has been polymerised to polystyrene sulphonate\textsuperscript{173} within the interlayers of MMLH. Similarly 'Chimie-douce' type polymerisation of aniline intercalated in Cu-Cr type MMLH to polyaniline has also been reported\textsuperscript{173}.

G. Ionic conductors:

MMLH are found as effective solid ion conductors with conductivities as high as 10\textsuperscript{-3} \( \Omega \text{ cm} \)\textsuperscript{-1} at 17\textdegree C for Zn-Cr-Cl type MMLH. This is because of a 'quasi-two dimensional' electrolyte type behaviour of solvated ions in layered host lattices\textsuperscript{174,178}. Such properties enhance the prospects of these materials as hydrogen sensors, humidity sensors\textsuperscript{179} etc.
H. Clay viscosity modifier:

MMLH due to their +ve layer charge interacts with montmorillonite type clays with -ve layer charge in aqueous medium and finds application as oil well drilling fluid viscosity increaser additive. Similarly oleophilised MMLH are also used to increase the viscosity of non aqueous fluids containing oleophilic clays.
Table 1.1 Chemical composition and unit cell parameters of some MMLH type minerals.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical composition</th>
<th>Unit cell parameters (Å)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrotalcite</td>
<td>Mg₆Al₂(OH)₁₆[(CO₃)₂.4H₂O]</td>
<td>a = 3.054, c = 7.603×3 = 22.81 (3R)</td>
<td>Allmann &amp; Jepsen⁵¹</td>
</tr>
<tr>
<td>Manasseite</td>
<td>Mg₆Al₂(OH)₁₆[(CO₃)₂.4H₂O]</td>
<td>a = 3.10, c = 7.8×2 = 15.6 (2H)</td>
<td>Taylor⁵²</td>
</tr>
<tr>
<td>Pyroaurite</td>
<td>Mg₆Fe³⁺₂(OH)₁₆[(CO₃).4.5H₂O]</td>
<td>a = 3.109, c = 7.804×3 = 23.41 (3R)</td>
<td>Allmann⁵³</td>
</tr>
<tr>
<td>Sjögrenite</td>
<td>Mg₆Fe³⁺₂(OH)₁₆[(CO₃).4.5H₂O]</td>
<td>a = 3.113, c = 7.805×2 = 15.6 (2H)</td>
<td>Allmann⁵³</td>
</tr>
<tr>
<td>Coalingite</td>
<td>Mg₆Fe³⁺₂(OH)₂₄[(CO₃).2H₂O]</td>
<td>a = 3.12, c = 12.5×3 = 37.5 (3R)</td>
<td>Mumpton et al.⁵⁴</td>
</tr>
</tbody>
</table>

*continued*
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>a</th>
<th>c</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meixnerite</td>
<td>[Mg₆Al₂(OH)₁₆][(OH)₂.₄H₂O]</td>
<td>3.046</td>
<td>7.64×3=22.92</td>
<td>Koritnig and Süssé 56</td>
</tr>
<tr>
<td>Stichtite</td>
<td>[Mg₆Cr₂(OH)₁₆][(CO₃).₄H₂O]</td>
<td>3.10</td>
<td>7.8×3=23.4</td>
<td>Taylor 56, 57</td>
</tr>
<tr>
<td>Barbertonite</td>
<td>[Mg₆Cr₂(OH)₁₆][(CO₃).₄H₂O]</td>
<td>3.10</td>
<td>7.8×2=15.6</td>
<td>Taylor 52 &amp; Drits et al 56</td>
</tr>
<tr>
<td>Takovite</td>
<td>[Ni₆Al₂(OH)₁₆][(CO₃,OH).₄H₂O]</td>
<td>3.025</td>
<td>7.53×3=22.59</td>
<td>Bish &amp; Brindley 57 &amp; Bish 56</td>
</tr>
<tr>
<td>Reevsite</td>
<td>[Ni₆Fe²⁺₂(OH)₁₆][(CO₃).₄H₂O]</td>
<td>3.10</td>
<td>7.8×3=23.4</td>
<td>White et al. 59</td>
</tr>
</tbody>
</table>

*continued*
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Cell Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desautelsite</td>
<td>$[\text{Mg}_6\text{Mn}^{3+}<em>2\text{(OH)}</em>{16}] [(\text{CO}_3) \cdot 4\text{H}_2\text{O}]$</td>
<td>$a = 3.114$ c = $7.79 \times 3 = 23.39$ (3R)</td>
<td>Dunn et al. 60</td>
</tr>
<tr>
<td>Iowaite</td>
<td>$[\text{Mg}<em>{4.63}\text{Fe}^{3+}</em>{1.32}\text{OH}<em>{12}] [(\text{Cl}</em>{22} 1.95\text{H}_2\text{O})]$</td>
<td>$a = 3.119$ c = $8.08 \times 3 = 24.25$ (3R)</td>
<td>Kohls &amp; Rodda 61</td>
</tr>
<tr>
<td>Honnesite</td>
<td>$[\text{Ni}_6\text{Fe}<em>2\text{(OH)}</em>{16}]\text{[SO}_4.4\text{H}_2\text{O]}$</td>
<td>$a = 3.083$ c = $8.90 \times 3 = 26.71$ (3R)</td>
<td>Bish &amp; Livingstone 64 &amp; Nickel &amp; Wildman 65</td>
</tr>
<tr>
<td>Stratlingite</td>
<td>$[\text{Ca}_2\text{Al}(\text{OH})_6] [(\text{Al} \text{ Si} \text{ O}_3 \text{ (OH)}_2) \text{ or Ca}_2\text{Al}_2\text{SiO}_5\text{I} 8\text{H}_2\text{O} \text{ or Ca}_2\text{ASH}_8 \text{ phase}$</td>
<td>$a = 5.747$ c = $37.64$ (3R)</td>
<td>Kuzel 66</td>
</tr>
</tbody>
</table>
### Table 1.2 Ionic radii (Å) of some cations*

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Cu</th>
<th>Ni</th>
<th>Co</th>
<th>Zn</th>
<th>Mn</th>
<th>Cd</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bivalent</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>0.69</td>
<td>0.72</td>
<td>0.74</td>
<td>0.74</td>
<td>0.80</td>
<td>0.97</td>
<td>0.98</td>
</tr>
<tr>
<td><strong>Trivalent</strong></td>
<td>Al</td>
<td>Ga</td>
<td>Ni</td>
<td>Co</td>
<td>Fe</td>
<td>Mn</td>
<td>V</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.62</td>
<td>0.62</td>
<td>0.63</td>
<td>0.64</td>
<td>0.66</td>
<td>0.74</td>
<td>0.69</td>
</tr>
</tbody>
</table>

*Ref: 16,71-80.*
Fig 1.1: Layer sequence in MMLH (Pyroaurite/Sjögrenite type). Thick lines represent brucite like layers. A. The location of $CO_3^{2-}$ group and $H_2O$ molecules in the interlayer is shown in a plan view. Oxygen sites are arranged in a group of 6, open circles represent empty sites. B. Spacial relationship between $OH^-$ groups in two consecutive layers and oxygen sites in the interlayer, where dotted line represent the H-bond.
1.11 Aim and Purpose of the Present Work:

The aim and purpose of the present work has been outlined mainly keeping in view the following important developments in the chemistry of "Mixed Metal Layered Hydroxides"

(1) Mixed Metal Layered Hydroxides of the general type $[\text{M}^{\text{II}}_{1-x} \cdot \text{M}^{\text{III}}_x (\text{OH})_2]^n \cdot x^{-} \cdot n\text{H}_2\text{O}$ (where M are bi and trivalent metal ions, X is an exchangeable anion and $0.2 \leq x \leq 0.4$, n is the number of water molecules) are currently under investigation as a primary class of support for various type applications e.g. (A) Medical and related applications; (B) Adsorbents; (C) Toxic gas remover; (D) Catalysts and catalyst precursors; (E) Anion exchangers; (F) Clay viscosity modifier etc.

In addition to above, the physico-chemical characteristics of these materials are novel, flexible and such materials exhibit a variety of important properties which could be modified for commercial exploitation.

To extend these developments further, various aspects like synthesis through new techniques, crystallographic characterisation, solid-liquid, solid-gas adsorption for combating pollution and rheology of systems containing MMLH are required to be studied. The purpose of the present study was to carry out extensive investigation on these aspects which concerned mainly on synthesis and applications.

In the synthesis part of the work mainly two types of synthesis of MMLH were concentrated - the alkaline pH precipitation method and the
acidic pH oxide hydrolysis method. In the alkaline pH synthesis, the effect of shaking and non-shaking conditions on crystallinity was studied. The effect of starting pH on bi:tri-valent metal ion ratio was studied by carrying out the precipitation by lowering the pH to 10 from high pH (=13) aluminate solutions and also by increasing the pH to 10 from low pH salt solutions.

Regarding acidic pH oxide hydrolysis for synthesis of MMLH, a proper reaction mechanism has not been reported so far. In the present work, attempt has been made to establish the criteria to select the suitable starting oxide for such reactions. It has also been shown for the first time that some of these reactions are highly sensitive to temperature.

In many occasions, during characterisation of synthesised MMLH, a simple mixture of two different binary MMLH are wrongly identified as ternary MMLH. In the present work, a simple thermal approach was tried to get rid of such difficulty. Apart from this, it is intriguing to know the nature of crystallographic unit cell of different MMLH bearing characteristic metal ions like Cu$^{2+}$, Ca$^{2+}$, Cd$^{2+}$ etc. In the present work, it was tried to calculate the crystallographic unit cell parameters of a Cu-Cr MMLH synthesised in acidic pH. A set of ordered unit cell parameters was assigned which have been explained on the basis of distorted $d^9$ configuration of Cu$^{2+}$ ion.
For solid-liquid system a detail study was designed and carried out on adsorption of \( \text{Cr}_2\text{O}_7^{2-} \) species by MMLH, the study included investigation of different factors like bi:tri-valent metal ion ratio in MMLH, effect of calcination, pH, combination of various bi and tri-valent metal ions, rate of adsorption, nature of adsorption isotherm and rate of release of adsorbed species etc. Suitability of different MMLH in respect of adsorption of more lethal toxic anions like \( \text{AsO}_4^{3-} \) has also been studied.

Suitability of MMLH-montmorillonite composite to synthesise novel active oxide surfaces to work as efficient adsorbent / catalysts for solid-gas systems have not been reported so far. In the present work it have been established that these systems act as efficient adsorbent for toxic gases like hydrogen sulphide.

A rheological model for montmorillonite aqueous suspensions extended by MMLH is not available. The envisaged model must be so constituted, which can account the high thixotropy and shear stress-shear rate rheogram shown by these systems. Apart from this aspect of rheological behaviour of MMLH-montmorillonite interactions, further studies of stability of these suspensions in different concentrations of commonly encountered cations like \( \text{Na}^+ \) and \( \text{Ca}^{2+} \) etc. and rheological behaviour of MMLH hectorite / attapulgite have not been reported so far. Present study was designed to cover thoroughly these aspects.
Various instrumental techniques like XRD, DTA-TGA, SEM-EDXA, AAS, IR, UV-VIS spectroscopy etc. were used to characterise the products. Interactive PC based softwares like JCPDS-PDF CDROM database, POWD and XPAS were also used for interpretation of XRD results. In addition to these for analysis and presentation of results programs like PLOTIT for Windows, GWBASIC etc. were used.