ABSTRACT

Chapter 1: The present work has been designed and carried out by keeping in mind the proliferation of interest over the chemistry of "Mixed Metal Layered Hydroxides" (MMLH) in recent times. These materials are used in various fields 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. Introduction chapter provides a thorough background with an extensive literature survey of these materials.

In the context of the present work, various aspects like synthesis of MMLH through different techniques, crystallographic characterisation of synthesised products, solid-liquid, solid-gas adsorption for combating pollution and rheology of clay-water systems containing MMLH were studied.

Chapter 2: In the synthesis part, mainly two types of syntheses of MMLH were concentrated - the alkaline pH precipitation and the acidic pH oxide hydrolysis methods. In the alkaline pH synthesis, the effects of shaking and non-shaking conditions on crystallinity were studied. Additionally, the effect of starting pH on bi : tri-valent metal ion ratio in the product 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 (≈4) salt solutions. For successful synthesis of
MMLH in acidic pH through hydrolysis of metal oxides, the oxide must have an extremely low solubility in water.

**Chapter 3:** Crystallographic unit cell parameter for unreported Cu-Cr-CI MMLH phase synthesised by oxide hydrolysis have been calculated from XRD data by computer aided interpretational softwares. A set of ordered unit cell parameters was assigned with \( a = 5.3902 \) Å and \( c = 46.5149 \) Å of a hexagonal crystal system. The ordered arrangement of \( \text{Cu}^{2+} \) and \( \text{Cr}^{3+} \) ions in the lattice is ascribed to (a) change of volume of \( \text{Cu}^{2+} \) octahedra due to their \( d^9 \) Jahn-Teller distorted structure and (b) higher Trivalent/ (Trivalent+Bivalent) ratio in Cu-Cr MMLH. Like Cu-Cr-CI MMLH, the Zn-Cr-CI MMLH synthesised by similar method also crystallises with a six layered ordered structure with the following unit cell parameters \( a = 5.4047 \) Å, \( c = 46.6800 \) Å and a hexagonal system. It has also been shown for the first time that synthesis of Cu bearing MMLH viz. Cu-Cr MMLH is highly sensitive to temperature e.g. above 45°C, \( \text{Cu}_2(\text{OH})_3\text{Cl} \) is the only phase formed.

Ternary MMLH constituted by \( \text{Zn}^{2+} - \text{Cr}^{3+} - \text{Al}^{3+} \) ions have been synthesised by acid phase hydrolysis method. Thermal degradation of different synthesised binary and ternary MMLH at different temperatures were also studied. 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 made to overcome the difficulty. Thermal decomposition of Cu-Cr-CI MMLH at 900°C produces Cu$_2$Cr$_2$O$_4$ by conversion of Cu$^{2+}$ to Cu$^{1+}$. Intimate physical mixture of equal portions of Cu-Cr-CI MMLH and Zn-Cr-CI MMLH heated at 650°C gives CuO and ZnCr$_2$O$_4$ due to the reaction of ZnO with decomposition product of Cu-Cr-CI MMLH. Zn-Cr-Al MMLH produces ZnCr$_2$O$_4$ spinel at 650°C. The indication of formation of ZnAl$_2$O$_4$ type spinel is obtained only at 750°C.

Thermal stability study of hydroxyl-aluminium chloride, another positively charged metal hydroxy species, was carried out by high temperature XRD under a dry atmosphere. It has been shown that the crystalline structure of hydroxyl-aluminium chloride undergoes a transition to a semi-crystalline state at a temperature above 80°C. Indexing of powder XRD pattern of the compound gives a unit cell with the following cell parameters, system = Triclinic P, $a = 9.16\text{Å}$, $b = 11.50\text{Å}$, $c = 24.31\text{Å}$, and $\alpha = 107.26^\circ$, $\beta = 94.31^\circ$, $\gamma = 105.52^\circ$.

Chapter 4: Adsorption of toxic anions like Cr$_2$O$_7^{2-}$ and AsO$_4^{3-}$ by MMLH has been carried out. Emphasis was given to determine the nature of adsorption phenomenon, rate of adsorption and stability of adsorbed species, suitability of different MMLH for the adsorption etc. It has been established that adsorption of Cr$_2$O$_7^{2-}$ through ion exchange in uncalcined MMLH is slower in rate and smaller in amount than in calcined one where the adsorption takes place via rehydration. Calcined Mg-Al MMLH with
higher Al$^{3+}$ content in the precursor structure shows higher adsorption capacity. Adsorption of Cr$_2$O$_7^{2-}$ in Mg-Al MMLH is higher than in Zn-Cr and Ni-Al MMLH. The kinetics for Cr$_2$O$_7^{2-}$ adsorption in Mg-Al MMLH is two stepped first ordered. The rate of first stage of adsorption is approximately 20 times faster than the second stage. The pH of initial Cr$_2$O$_7^{2-}$ solution in the pH range 5 to 11 have no influence on adsorption of Cr$_2$O$_7^{2-}$ by calcined Mg-Al MMLH. The adsorption phenomenon obeys a Freundlich type adsorption isotherm. Presence of CO$_3^{2-}$ anion in the liquid phase enhances the release of adsorbed of Cr$_2$O$_7^{2-}$ from the adsorbed system. Calcined Mg-Al MMLH is a better adsorbent for AsO$_4^{3-}$ than calcined Ca-Al MMLH.

**Chapter 5: Suitability of MMLH-montmorillonite composite to synthesise novel active oxide surface to act as efficient adsorbent / catalyst for solid-gas systems has not been reported so far. In the present work, it has been attempted to synthesise highly reactive metal oxide particles projected like display boards over a ceramic matrix. This was achieved by a process of self-exfoliation of MMLH to discrete layers by montmorillonite through intimate contact, hydration and subsequent drying and calcination of hydrated mixture. Surface active ZnO supported particles obtained from Zn-Cr MMLH-montmorillonite composite has been shown to absorb H$_2$S gas at 500°C. The active oxide may be regenerated easily by thermal treatment. Apart from ZnO, in order to obtain other active metal oxide
surface-clay composite, any suitable MMLH from a combination of transition / non-transition metals like Ni, Co, Mn, Mg, Ca, Li etc. may be utilized.

Chapter 6: The flow behaviour of different swelling clays extended by different MMLH have been studied and a flow model has also been proposed. The proposed model can account for the high thixotropy and shear stress-shear rate rheogram shown by the MMLH-montmorillonite systems. Rotational viscometer data suggest a shear rate(x) - shear stress(y) relationship of Herschell-Bulkley model \( y = ax^n + b \), where \( n \) decreases and \( b \) increases with increasing dosage of MMLH. However, at higher MMLH concentrations (0.6% w/v) the shear rate-shear stress curve becomes almost parallel to shear rate \( (x) \) axis. The increase in rheological parameters of montmorillonite suspensions with increasing dose of MMLH is accompanied by a constancy of capillary suction timer values which suggest that action of crystalline MMLH solids on neat clays strengthen the gel formation. It has also been shown that higher the positive charge in MMLH, higher is the rise in viscosity of MMLH-montmorillonite suspensions.

The rheological behaviour of MMLH- hectorite / attapulgite systems has also been reported for the first time. Hectorites, inspite of lower negative charge in it, show a substantial increase of rheological parameters with lower dosage of MMLH treatment. Attapulgite containing
system does not show any viscosity build up on treatment with MMLH. Thus, it has been shown that negative layer charge over the layers of the clay is essential for the MMLH (having positive layer charge) to act as viscosifier.

The rheological properties like apparent viscosity, yield point, capillary suction time of MMLH-clay suspensions decrease with increasing dose of Na\(^+\) or Ca\(^{2+}\) ion due to partial neutralisation of negative charge on the interacting layer surfaces of clay.

In order to accomplish these studies various instrumental techniques like XRD, DTA-TGA, SEM-EDXA, AAS, IR, UV-VIS spectroscopy, rotational co-axial cylindrical viscometer etc. were used to characterise different products and intermediates. Interactive PC based softwares like JCPDS-PDF CDROM database, POWD and XPAS were also used for interpretation of XRD results. In addition, for analysis and presentation of results programs like PLOTIT for Windows, GWBASIC etc. were used.

**Future plan:**

1) Further experiments on the topic of adsorption of anions by MMLH is planned to develop some economically viable material for immobilisation of AsO\(_4\)\(^{3-}\) anion. The planned work includes immobilisation of the toxic species in Ca-Al, Mg-Al, Zn-Al etc. MMLH and conversion of
the adsorbed species to stable mineral forms by thermal or hydrothermal treatments.

2) Experiments are also planned to develop active oxide surfaces supported on ceramic base from MMLH-montmorillonite composites for environmental applications like decomposition of CO, SO₂ and N₂O etc. gases.

3) Experiments are also planned to intercalate anionic species like [Co(EDTA)₂]²⁻, [Cr(SCN)₄(NH₃)₂]⁻, [Fe(CN)₆]³⁻, [Co(NO₂)₆]³⁻ etc. in MMLH structures, so that ligand exchange reactions by strategic ligands like CN⁻, CO can be carried out in the interlayers. This would enable intercalation of metal carbonyls or nitrosyls in the interlayers. Such intercalated complexes may find important industrial end use.