1. INTRODUCTION

Smectite clay minerals constitute a family of expandable 2:1 phyllosilicate minerals having permanent layer charge between 0.2 - 0.6 charges per half unit cell. Montmorillonite (Mt) clay is the most important member of smectite clay group, which possess unique combination of interesting properties like high cation exchange capacity, swelling behavior, surface chemistry, submicron lateral dimension with thickness of few nanometers. Intense academic research and product development studies explored these properties of the clay mineral resulting in useful products. These applications involve cationic surfactant intercalated Mt as reinforcements in polymer nanocomposites, rheology control agents in cosmetics, paints, drug delivery system, substrates for nanopatterning, in removal of organic pollutants from waste water.

It is interesting to note that, most of these applications exploit the cation exchange capacity (CEC) of Mt, for intercalating organic cations into the basal plane. The CEC of Mt is a consequence of excess negative octahedral layer charge arising from isomorphous lattice substitution of Al^{3+} by Mg^{2+} in the octahedral sheet, which is compensated by basal surface adsorption of cations (Na^+, K^+, Li^+ and Ca^{2+}). During intercalation reaction, these cations are replaced by cationic surfactants to form clay-surfactant hybrid commonly known as intercalated clay or organoclay. This intercalation process has been studied intensively and it was found that the properties of the intercalated Mt clay mostly depend on CEC of the clay, nature of organic cation and extent of intercalation. Insertion and attachment of bulky organic moiety during intercalation lead to increase in separation of adjacent Mt layers (increase of basal spacing) and development of organophilicity.

Bentonite clays are commercial minerals rich in Mt. An inherent problem associated with development of Mt-based products is the variability of mineralogical composition, layer charges and texture across different origins, which affect the properties of intercalated Mt. Compositional heterogeneity of the bentonite is a result of heterogeneity of the microenvironment during their formation.

India has several bentonite deposits. Total resource of bentonite in India is about 531 million tonnes out of which 25 million tonnes are categorized as reserves. Rajasthan, 423 million tonnes (80%) and Gujarat, 97 million tonnes (18%) possess the majority of the total resources. Indian bentonites are generally high swelling type and contain more than 10% Fe_20_3. These clays find application in foundry, drilling, sealant, geosynthetic liner, as adsorbent, rheological modifier etc. Apart from these conventional low-cost applications, it can be used as a precursor for nanomaterial. But, the high cost of purification and separation of Mt phase is a deciding factor in the techno-economic success of the intercalated Mt. Iron –rich bentonites are abundant in nature and can be used as a cheaper source of Mt but numbers of such detailed scientific studies are less than conventional Mt. Although the effect of layer charge (and CEC) on crystallographic structure (basal spacing) of intercalated clays is well studied for phase pure Mt with low iron content, remaining factors like mineralogical composition and impurity and texture, makes it difficult to prepare intercalated clays with predictive properties.

In this perspective systematic studies on the intercalation of Mt with high-iron content and low-CEC are insufficient. A comprehensive understanding of the structure of resultant intercalated clay from this abundant and cheaper resource is scientifically and technically useful. Keeping this in mind, we studied the intercalation of iron-rich and low-CEC Mt along with a reference Mt having higher CEC, with different alkylammonium cations. The intercalated clay of this reference Mt (high-CEC and low-iron) are useful in different applications. A comparative study of intercalation behaviour of low-CEC and high-iron Mt clays with this reference Mt might be helpful to exploit possibility of developing intercalated clays for various end uses like polymer nano composites, as rheology modifier in paints, cosmetics, in waste water treatment etc.

Effect of iron on intercalation also have been investigated by exchanging the interlayer cations with Fe^{3+} followed by intercalation. Because of complex interplay of population of cation exchange sites, degree of exchange, mutual interaction between alkyl chains and morphology of clay platelets, impurities present in the clay structure this study can provide fundamental understanding of the intercalation process.