

## 6. SUMMARY AND CONCLUSIONS

The experimental montmorillonites were selected on the basis of CEC and iron-content to study its effect on intercalation. Montmorillonites from India contained very high iron (~12% Fe<sub>2</sub>O<sub>3</sub>) in comparison to ~3% for the commercially available pure montmorillonite. But no well-crystalline iron-containing mineralogical phases were detected in X-ray diffraction of these clays. By FTIR spectroscopy, location of Fe<sup>3+</sup> was assigned to octahedral lattice of the iron-rich clays. The cation exchange capacity of the iron-rich montmorillonites was found less than its low-iron variety. Study on intercalation of these iron-rich, low CEC variety of montmorillonites with a higher CEC and low-iron reference montmorillonite, was carried out with a range of cationic surfactants viz., alkylammonium cations of varying chain length and chain number.

In case of intercalation with *n*-alkylammonium cation, montmorillonite with highest CEC always led to greater extent of intercalation than the iron-rich, low-CEC montmorillonites, in terms of basal spacing and organic loading. Extent of intercalation always followed the order of CEC of the individual clays. Small alkylammonium cations (C<sub>10</sub>, C<sub>12</sub>) could not replace significant amount of exchangeable cations during intercalation. With increasing alkyl chain length almost complete intercalation took place for all montmorillonites. The difference in organic loading and interlayer expansion of intercalated montmorillonite is prominent with small chain intercalants. The evolution of structure of the clay-organic hybrids depends mostly on CEC and marginally on iron-content. Basal spacing was always higher for the high-CEC clay, than iron-containing varieties, most possibly due to the effect of CEC. Also, no obvious correlation was found between basal spacing and the CEC, among the iron-rich clays. Intercalation of montmorillonite converted the clay surface organophilic which was observed by easy dispersion of intercalated clays in organic medium. The swelling behaviour of intercalated clays was proportional to CEC and reached maximum with intermediate chain length of surfactant, with no correlation with iron-content of montmorillonite.

Intercalation of montmorillonites of different CEC with dialkylammonium cations followed similar trend of increasing basal spacing with increasing alkyl chain length like *n*-alkylammonium cations. But unlike *n*-alkylammonium cations, the interlayer arrangement started from bilayer for shorter alkyl chain and finally reached paraffinic arrangement for the longest alkyl chains in case of all the clays. Due to this arrangement large interlayer expansion was obtained with the longest dialkyl ammonium intercalated clays. Here also highest CEC clay led to greater interlayer expansion. Like *n*-alkylammonium intercalated clays dialkylammonium intercalated clays showed more dependence on CEC rather than iron content in case of basal spacing.

When surfactant configuration was changed with increasing alkyl chain numbers for a particular chain length, some interesting observations were made. Basal spacing gradually increased with increasing alkyl chain numbers. Thus basal spacing increased in the order tri>di>mono alkylammonium intercalated clays. The interlayer arrangement changed from nearly bilayer arrangement for monoalkyl ammonium surfactant-intercalated clays to paraffinic arrangement for trialkyl ammonium surfactant-intercalated clays. The gradual increase in basal spacing with increasing alkyl chain numbers resulted from gradual increase in molecular volume of the intercalants. From mono- to trialkyl-ammonium intercalation however, CEC of the clay had a prominent effect on basal spacing. But CEC effect was more prominent in dialkylammonium cation intercalated clays than that of the mono and trialkyl ammonium intercalated clays. The correlation can be found from the respective organic loading values. The maximum organic loading value was obtained from dialkylammonium cations among the three intercalants when intercalated within the clay interlayer. Organic loading was found less for trialkyl ammonium intercalated clays from both two varieties may be due to the difficulty in intercalation for higher space size intercalant.

FTIR study showed that, with increasing alkyl chain length of the surfactant irrespective of the intercalant's architecture (mono or di), CEC or iron- content of the clay, interlayer conformation of the surfactants became more ordered. But

molecular ordering of the intercalated surfactants changed in a different manner with increasing alkyl chain numbers of a particular chain length. Here, the most ordered conformation of the intercalated surfactant was obtained for dialkyl ammonium cation intercalated clay than trialkyl ammonium cation intercalated clays. This may be attributed to the greater packing density of the dialkyl ammonium cation as a consequence of its greater organic loading than that of the trialkylammonium cation in the clay interlayer.

An important aspect of this study is that the experimental montmorillonites were intercalated without exceeding the CEC value of clay. Previous studies on intercalation mostly dealt with addition of intercalant over CEC. From technological point, excess addition of expensive intercalants increases the cost of intercalated clays and also, removal of excess adsorbed intercalant requires large amount solvent and time for washing process- which increases the cost of the intercalated clay. This excess adsorbed intercalant lowers the thermal stability of the composite, since the onset of degradation temperature of this excess adsorbed intercalant is lower than that of the ionically exchanged intercalant.

Since structural iron present in octahedral lattice of the iron-rich montmorillonites cannot account for such a high amount (~12%  $\text{Fe}_2\text{O}_3$ ), the presence of iron in cation exchange sites of the montmorillonites was also studied for its effect on intercalation. Experimental montmorillonites were exchanged with  $\text{Fe}^{3+}$  and then intercalated with cationic surfactants. It was observed that  $\text{Fe}^{3+}$  in exchange position hinders intercalation. And interestingly, this inhibiting effect is independent on whether  $\text{Fe}^{3+}$  occupies the cation exchange sites of montmorillonites- partly or fully. Hindering action of  $\text{Fe}^{3+}$  on intercalation was more prominent in low- iron-containing montmorillonite. This may be due to leaching of  $\text{Fe}^{3+}$  from iron-rich montmorillonites during reaction and subsequent attachment to the cation exchange sites.

Overall, irrespective of architecture of the intercalant (mono, di, tri), chain length, type of exchangeable inorganic cations in the clay interlayer,

montmorillonite with low-CEC, high-iron exhibited effective intercalation with less basal spacing and organic loading in comparison to the high-CEC, low-iron-containing reference montmorillonite. This systematic study of structural evolution and comparable swelling nature of intercalated montmorillonites for low-CEC, high-iron-variety surmise its potential industrial application at par with high-CEC montmorillonite.

### **Scope for further investigation**

Intercalated clays, studied in this investigation may be compounded to form polymer composites as filler. The effect on mechanical, thermal, rheological and barrier properties of the composite may be studied with respect to CEC, organic loading and iron –content and polymer matrix.