SMART CLAYS FOR ENVIRONMENTAL PROTECTION AND CLEAN-UP

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Introduction

The release of toxic organic chemicals (e.g., polychlorinated and polycyclic aromatic compounds) into the environment is of growing concern because these compounds are potentially detrimental both to human and ecosystem health. Innovative technologies and affordable products are therefore required for the containment of organic pollutants (before they get into air, water and soil) and for the remediation of contaminated sites. Here we propose to develop surface-modified clays for industrial and environmental applications. We have chosen clays as base materials because they are natural, abundant, inexpensive, and environmentally friendly. Further, the expertise for modifying clays is available in New Zealand (Theng, 1974; Theng et al., 2001; Yuan et al., 2000).

The "Tailor-made smart clays" programme of Landcare Research aims at producing highly selective clay-based adsorbents. These "smart clays" would be superior to such conventional adsorbents as activated carbon (charcoal) in that surface-modified clays have a large propensity to adsorb a wide range and variety of organic pollutants from waste water. By comparison, charcoal is only effective in deactivating small pollutant molecules that occur in low concentration and in the absence of dissolved organic matter (Carter and Weber, 1994).

Principles for Surface Modification of Clays

Clay minerals are layered alumino-silicates with a large surface area. Each layer is made up of an octahedral sheet, sandwiched between two tetrahedral sheets (Fig. 1). The layers are negatively charged because of substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet, and Mg^{2+} (or Fe^{2+}) for Al^{3+} in the octahedral sheet. The net negative layer charge is balanced by sorption of extraneous counterions (e.g., Ca^{2+} and Na^{+}) that are exchangeable with other ions in solution (e.g., heavy metals).

Since clays are essentially hydrophilic (due to the hydration of exchangeable cations), they are ineffective in adsorbing organic pollutants, most of which are hydrophobic. Thus, a principal objective of this programme is to make the clay surface hydrophobic. This can be achieved by replacing the native inorganic counterions with long-chain alkylammonium or quaternary ammonium cations (Fig. 2).

Besides making the clay surface hydrophobic, the intercalated organic cations act as "pillars" propping the clay layers apart. The interpillar space or "gallery" thus created can accommodate a wide range of extraneous organic pollutants. The interlayer space of such clays can also be varied to accommodate organic pollutants of different size and shape, their adsorption capacity can be adjusted to reflect pollutant concentration, and their particle morphology can be altered to facilitate field application. By judicious selection of clay type and organic cation size, we aim to produce "smart clays" to meet specific technological and user requirements.

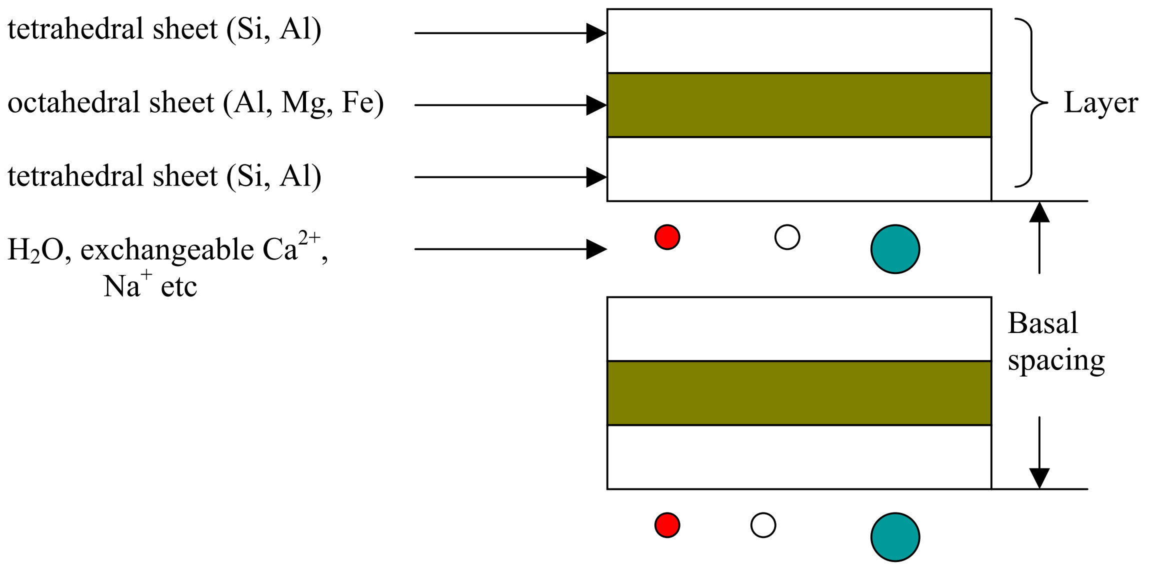

Figure 1. Schematic structure of a montmorillonite clay, showing the arrangement of octahedral and tetrahedral sheets in individual layers. Inorganic cations and water occupy the interlayer space, giving a characteristic basal spacing.

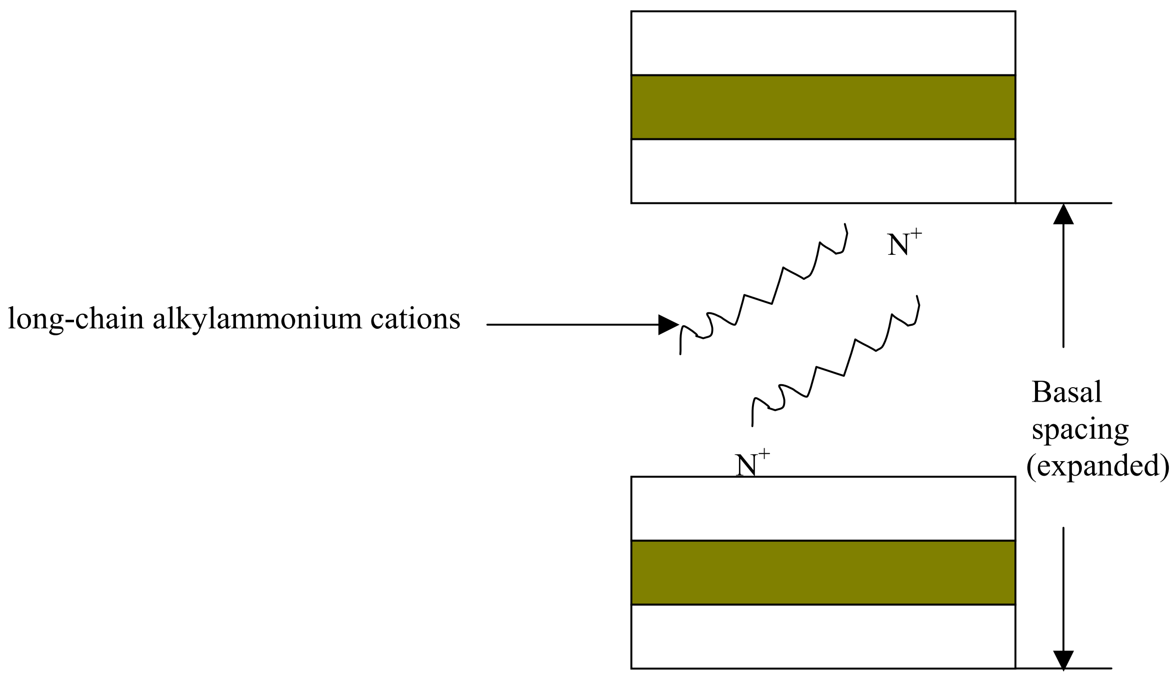

Figure 2. Montmorillonite intercalated with quaternary ammonium cations. Intercalation causes a large expansion of the interlayer space, and increases the capacity of the clay to take up organic pollutants.

Properties of "smart clays" and their potential applications

The organic carbon content and basal spacing of "smart clays" are important factors determining the affinities and capacities for adsorbing organic pollutants. Table 1 shows these properties for three smart clays produced by intercalating different cationic surfactants. Compared with the raw or parent material (Na-montmorillonite), the basal spacings of smart clays are increased, providing extra space to accommodate pollutants. The high content of organic matter provides partition media and adsorptive sites to retain the pollutants.

Table I. Properties of some smart clays

Natural and modified clays		Carbon content (%)	Basal spacing (nm)
Na-montmorillonite		negligible	ca. 1
Smart clays	A-14	18	1.82
	A-18	22	2.11
	B-16	24	1.74

"Smart clays" have the potential to serve as: (1) reliable lining materials for the next generation of landfills by preventing dissolved pollutants from leaking into, and contaminating, ground water; (2) adsorbents for taking up organic pollutants from waste water; (3) porous solids for mopping up oil and chemical spills over land (e.g., petrol stations) and sea (e.g., oil tankers); (4) agents for cleaning up contaminated soils (e.g., by polycyclic aromatic hydrocarbons around disused gas works, and pentachlorophenol near timber-processing plants), and ground water (e.g., by agricultural pesticides). Some examples of the environmental application of modified clays have been published (Brixie and Boyd, 1994; Lo, 1996; Lo and Mak, 1998; El-Nahhal et al., 1999).

References

Brixie, J.M. and Boyd, S.A. 1994. Treatment of contaminated soils with organo-clays to reduce leachable pentachlorophenol. Journal of Environmental Quality, 23:1283-1290.

Carter, M.C. and Weber, W.J. 1994. Modelling adsorption of TCE by activated carbon preloaded by background organic matter. Environmental Science and Technology, 28:614-623.

El-Nahhal, Y., Nir, S. Margulies, L., and Rubin, B. 1999. Reduction of photodegradation and volatilization of herbicides in organo-clay formulations. Applied Clay Science, 14:105-119.

Lo, I.M.C. 1996. Solidification/stabilization of phenolic waste using organo-clay complex. Journal of Environmental Engineering, 122:850-855.

Lo, I.M.C. and Mak, R.K.M. 1998. Transport of phenolic compounds through a compacted organo-clay liner. Water Science and Technology, 38:143-150.

Theng, B.K.G. 1974. The Chemistry of Clay-Organic Reactions. Adam Hilger, London and John Willey & Sons, New York.

Theng, B.K.G., Aislabie, J. and Fraser, R. 2001. Bioavailability of phenanthrene intercalated into an alkylammonium-montmorillonite clay. Soil Biology and Biochemistry, 33:845-848.

Yuan, G., Theng, B.K.G., Parfitt, R.L., and Percival, H.J. 2000. Interactions of allophane with humic acid and cations. European Journal of Soil Science, 51:35-41.