

Chapter 11.1

CLAYS AND CLAY MINERALS FOR POLLUTION CONTROL

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A widespread recognition of the need to develop technologies for pollution control has arisen in only relatively recent times. This has been a result of increased awareness of the effects of pollution on the health and longevity of both human beings and the earth's fragile ecosystems. Therefore it is not surprising to find that clays were not used for environmental protection to any great extent until quite recently. Thus, such an authoritative volume on the practical applications of clays as Grim's *Applied Clay Mineralogy* (Grim, 1962) included only three uses that could be called 'environmental' among the 34 miscellaneous uses that he identified, and none among the 5 major uses that were enumerated. The uses of clays with arguably environmental aspects that Grim (1962) identified over four decades ago were those for radioactive waste disposal, floor adsorbents, and water clarification. The major uses that were identified for clays at that time were for ceramics, foundry-moulding sands, engineering properties, petroleum discovery and recovery, and the refining and preparation of organic materials.

Because of the ubiquitous and widespread occurrence of clays in soils and sediments, it is not surprising that clays were long used for the control of toxic materials albeit at a small scale or only locally. For example, 'Lemnian earth', known only by its location, was used medicinally in ancient Greece and Turkey to counter the effects of snake-bites and poisons, and to cure festering wounds (Robertson, 1986; see also Chapter 11.5). Likewise, Sudanese villagers along the Nile long used a local clay—recently identified as a bentonite—to purify the river's turbid water. As a consequence, these people suffer fewer gastrointestinal disturbances than other

communities nearby. Experiments showed that viruses (Lund and Nissen, 1986), parasites (Olsen, 1987) and many types of bacteria (Madsen and Schlundt, 1989) are removed from the water through addition of the clay, probably acting as both an adsorbent and a flocculant for the disease-bearing organisms.

The undoubted usefulness of clays for pollution control and environmental protection arises from many of the same characteristics that made them so useful industrially and otherwise in human societies for many centuries (e.g., Mackenzie, 1979; Robertson, 1986). Table 11.1.1 gives some of the particular or proposed applications of clays for pollution control and environmental protection, delineates properties of clays that make them useful for these applications, and outlines the requirements for pre-treatment that enhance their effectiveness in each case. Table 11.1.1 also refers to other sections of this chapter where further details of each application are given. Nonetheless, it is important to realise that categorisation, whether within sections of this chapter or into other parts of Chapter 11 is necessarily arbitrary. This is because those properties of clays that are important for pollution control *per se*, such as uptake capacity, also make clays most suitable for specific applications. These include their use for pesticide application and control of excess pesticides (see Chapter 11.2), in liners for waste disposal (see Chapter 11.3) and nuclear waste management (see Chapter 11.4) and also in their application for health (see Chapter 11.5) and to aid the delivery of drugs (see Chapter 11.6). This chapter will focus on the use of natural, mined clays, largely to the exclusion of 'synthetic' clay minerals (see Chapter 4).

Table 11.1.1 and the related detailed discussions specify certain technical characteristics of clays such as their charge, uptake abilities, high-surface areas, colloidal or swelling capacities, among others. Clays are also attractive in comparison with other environmental materials because they are widespread, generally easily mined, and relatively inexpensive. Clays are also naturally occurring materials, generally non-toxic, and have a considerable capacity to adsorb water. Hence, aside from their use for controlling contaminants, they are also useful as adsorbents for water in such modern, and generally urban, applications as in pet litter, although their function in that case may extend beyond that of the simple uptake of water.

11.1.1. CONTROL OF HEAVY METAL CATIONS AND SIMPLE CATIONS

As cation exchangers, clays are effective for the control of cations in solution, although, where only ion exchange is involved, their effectiveness is dictated by the imperative of attaining equilibrium between ions in solution and those on exchange sites. However, clays are most useful for the control of cationic pollutants when the mechanism of uptake extends beyond that of just cation exchange. This is particularly the case for heavy metal ions, on which the following discussion is focussed. The control of heavy metal ions in anionic form is related to that for anions in general (see Section 11.1.4).

Table 11.1.1. Applications of clays for pollution control and environmental protection

Contaminants for control	Status (actual or potential use)	Pretreatments required	Relevant clay properties	Further description
Heavy metal cations and simple cations	Actual, mainly passive, use (e.g., in soils, liners)	Mostly none, some organic and inorganic modification	Charge, surface area, reactive surface groups	11.1.1
Organic and biological cations	Potential for water and wastewater treatment, pesticide control	Generally none, except cation saturation	Charge, surface area, especially interlayer	11.1.2, also 11.2
Non-ionic organic molecules	Actual, for water and wastewater treatment; potential, for pesticide control, waste liners	Cation saturation, organic or inorganic modification	Charge	11.1.3, also 11.2 and 11.3
Anions	Actual, for water and wastewater treatment; potential, for pesticide and nutrient leaching control	Appropriate organic modification	Charge	11.1.4, also 11.2
Turbidity and residual treatment chemicals	Actual, for treatment of potable water and some wastewaters and sewage	Generally none	Colloidal, from size and charge; charge, surface area	11.1.5
Leachates	Actual, for waste liners and radioactive waste storage	Generally none, except cation saturation	Swelling, charge, surface area, reactive surface groups	11.5 and 11.6

A. Practical Applications

As liners in waste repositories clays are used for the control of heavy metal ions, often among other pollutants. Otherwise, clay minerals in soils, along with metal hydr(ox-ides) and organic matter, control the concentrations of heavy metal ions in surrounding and leaching solutions. The relative contribution of each of these soil components to heavy metal ion uptake can vary with the particular heavy metal ion (Elliott et al., 1986; Lumsdon et al., 1995; Tiller, 1996), and solution pH (Metwally et al., 1993;

Lumsdon et al., 1995), among other environmental factors. For example, organic materials removed more Cu^{2+} from solution than pedogenic oxides, and each of these removed more than a montmorillonite (McLaren et al., 1981) from concentrations similar to those in soil solution. By contrast, McLaren et al. (1986) found that a pedogenic oxide was much more effective than organic materials in removing Co^{2+} from solution, with a montmorillonite being the least effective. Furthermore, combinations of soil components, notably clay–organic matter complexes, can strongly influence heavy metal ion uptake (Lumsdon et al., 1995; Petrović et al., 1999). Similarly, heavy metal ion adsorption by clay minerals in soil may occur via hydr(oxides) and/or organic matter coating their surfaces (Swift and McLaren, 1991; Jackson, 1998).

B. Mechanisms of Heavy Metal Ion Uptake

In summarising the uptake of trace and heavy metal ions by clay minerals, Tiller (1996) has concluded that these minerals have a stronger affinity for heavy metal ions than for alkali and alkaline earth cations. Adsorption of heavy metal ions by clays is a complex process, reflecting their strong tendency to form covalent bonds (Jackson, 1998). The extent of uptake is not simply a function of the cation exchange capacity (CEC) of the clay minerals. This is because heavy metal ion uptake involves a variety of processes, including surface complexation—which can be either direct ('inner-sphere') or indirect ('outer-sphere'), simple ion exchange, and surface precipitation (Swift and McLaren, 1991; Scheidegger and Sparks, 1996; Stumm and Morgan, 1996; Jackson, 1998). Some common types of complexes at the mineral/solution interface are illustrated in Fig. 11.1.1.

Surface complexation, constituting specific adsorption, occurs on edge sites. It involves the formation of direct bonds between the metal cations, and surface OH groups and O atoms, that are intermediate in strength between ionic and covalent bonds (McBride, 1991; Swift and McLaren, 1991; Jackson, 1998; Wu et al., 1999). The process is not completely reversible, although this may reflect kinetic effects rather than true irreversibility (McBride, 1991; Scheidegger and Sparks, 1996).

Adsorption of cationic heavy metal ions can occur at different sites on the aluminosilicate structure (Inskeep and Baham, 1983), and the site involved may vary with each particular heavy metal. Using models for adsorption–desorption of copper and cadmium by montmorillonite, Undabeytia et al. (1998, 2002) found that these metal ions can be adsorbed on both edge and interlayer sites. For each of the metal ions the preferred site may depend, in different ways and to different extents, on such factors as ionic strength, pH, and the anions that are present in solution. Cadmium is mostly adsorbed as the uncomplexed cation on planar (interlayer) sites over a wide range of concentrations, and also in potentially complexing chloride solutions (Undabeytia et al., 1998). On the other hand, adsorption of copper is affected by pH and by the presence of Cl^- , when CuCl^+ could form (Undabeytia et al., 2002). Unlike that of Cd^{2+} , desorption of Cu^{2+} shows hysteresis. This would indicate that

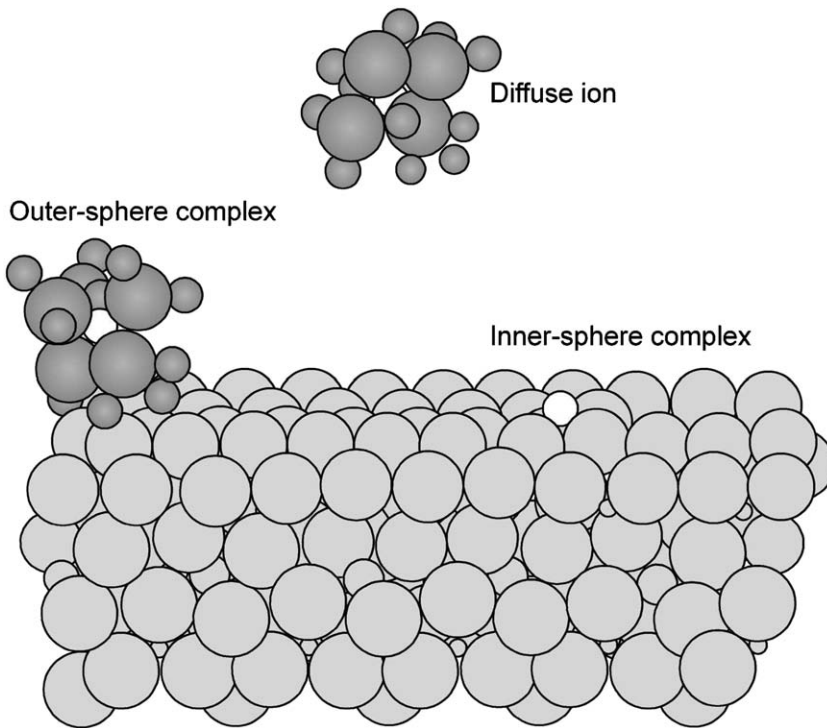


Fig. 11.1.1. The location of inner- and outer-sphere complexes and a diffuse ion relative to an aluminosilicate layer. From Sposito (1992).

adsorption occurs on both edge and planar sites, the former being relatively irreversible while the latter is reversible.

Metal ion hydroxide phases may form as precipitates on mineral surfaces especially when the concentrations of the heavy metal ion are higher than those found in most natural waters, and the pH is close to neutral or alkaline (Jackson, 1998). As Tiller (1996) has pointed out, however, it is difficult to explain the results of solid–solution interactions in terms of precipitation, rather than simple ion exchange, adsorption of the hydroxo-ion, hydrolysis of the simple ion in solution concomitant with its adsorption, or surface complexation. According to McBride (1991), many so-called adsorption isotherms combine the effects of chemisorption and precipitation with those of nucleation of metal hydroxides at surfaces, while Scheidegger and Sparks (1996) suggested that there is a continuum between surface complexation (understood as adsorption) and surface precipitation. The application of high-resolution electron microscopy (HRTEM) and X-ray absorption fine structure spectroscopy (EXAFS) has led Scheidegger et al. (1996) to conclude that Ni^{2+}

preferentially forms a mixed hydroxo-Ni precipitate at the edge surface of pyrophyllite particles, even at low Ni concentrations.

The ambient pH often has a strong influence on the extent of adsorption because it affects the nature of the heavy metal cation (Jackson, 1998; Garcia Sanchez et al., 1999). Generally, high pH favours adsorption through the production of hydroxy cations (Jackson, 1998). For example, lead is only retained strongly by clays as long as the pH is high enough to ensure that precipitation of lead occurs (Yong et al., 1990) although in the case of mercury, an increase in pH causes uptake to decrease (Farrah and Pickering, 1978). High pHs can also result in greater specificity of clay minerals for heavy metal ions relative to alkaline earth ions, probably because of the much greater tendency of heavy metal ions to hydrolyse (McBride, 1991).

In the last several years, synchrotron-based studies aided our understanding of surface complexation and precipitation reactions (see Chapter 12.3). In particular, they shed light on the mechanisms by which surface-induced precipitation can result in the formation of more phases, including oxides, layered double hydroxides (LDHs), and new phyllosilicates (see Chapter 12.3).

C. Relative Affinities of Clays for Different Heavy Metal Ions

The preference of bentonites for heavy metal ions that adsorb by cation exchange decreases in the order $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+}$ (Lagaly, 1995). From a survey of the literature prior to 1961, Tiller (1996) has deduced that the relative bonding energies to several minerals of some common heavy metals follows the sequence: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} \cong \text{Mn}^{2+}$ which approximates the hydrolysis constants of the metal cations. This suggests the important role played by hydroxocations in adsorption. However, Tiller (1996) has also observed that the order is not invariant in that Co^{2+} and Ni^{2+} could change places. In agreement with McBride (1991), Tiller (1996) concluded that the mechanism of uptake was far from certain. Jackson (1998) has summarised the literature on the relative affinities of different clay minerals for the same divalent cations, and given the following sequences:

montmorillonite	$\text{Ca}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Mg}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$
illite	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Cd}^{2+} > \text{Mg}^{2+}$
kaolinite	$\text{Pb}^{2+} > \text{Ca}^{2+} > \text{Cu}^{2+} > \text{Mg}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$

As already noted, the adsorption capacity of different clay minerals for heavy metal ions does not necessarily follow that of their CEC. Furthermore, their relative affinities can vary with solution concentration of heavy metal ion. For example, illite is more effective than montmorillonite at high concentrations of Cu^{2+} , but the order reverses at low concentrations (Swift and McLaren, 1991). For a single montmorillonite, selectivities may also vary with saturating cation. According to Lagaly (1995), the selectivity of montmorillonite for cations generally depends on the

restriction of interlayer expansion, being minimal for sodium montmorillonites. [Metwally et al. \(1993\)](#) found palygorskite to be more effective than montmorillonite, and very much more effective than kaolinite, for the uptake of Zn^{2+} , at least under the conditions of their experiments (pH 4.5–7.0). Minerals were tailored to remove particular elements (e.g., radioactive species) quite specifically. By this means high affinities for Cu^{2+} and Pb^{2+} ([Kodama and Komarneni, 1999](#)), Sr^{2+} (of importance as ^{90}Sr in radioactive wastes) ([Komarneni et al., 2000](#)), and radium ions ([Komarneni et al., 2001](#)) were obtained with Na^+ -rich micas synthesised from kaolinite. Some natural clays can also show a high selectivity for particular cations, e.g., palygorskite (attapulgite) for radioactive Cs^+ ([Chandra, 1970](#)).

In summary we can say that the laws governing the selective uptake and release of heavy metal ions by clays and clay minerals are so numerous and diverse that they probably cannot be reduced to a universally applicable predictive formula ([Swift and McLaren, 1991](#)). Furthermore, the operation of such factors as the inherent variability of natural minerals, the influence of surface coatings, the variety of surface-binding sites, and the variability of environmental conditions means that there are contradictions between experimental results of different investigators ([Jackson, 1998](#)). More fundamentally, [Scheidegger and Sparks \(1996\)](#) point out that many studies of adsorption processes were limited because they were carried out only at the macroscopic scale. They see considerable hope for future understanding arising from the increasingly common application of molecular and/or surface analytical techniques, including X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), electron spin resonance (ESR), Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), X-ray absorption spectroscopy (XAS), scanning force microscopy (SFM), and HRTEM. These approaches, which are largely microscopic, already showed the great heterogeneity of mineral surfaces and the unique properties of both solid and liquid interfaces relative to their bulk (see Chapter 12.4). An instance of their power is the application of two of these microscopic techniques by [Scheidegger et al. \(1996\)](#) to show surface precipitates of Ni^{2+} on pyrophyllite, as already described.

D. Ease of Displacement of Heavy Metal Ions from Clays

The ease of desorption and the exchange of heavy metal ions, after their uptake by clays, are just as important as their adsorption or absorption. Managers of natural resources and waste depositories usually require materials that hold on to metal ions against desorption and exchange as effectively as is possible. The reviews by [Swift and McLaren \(1991\)](#), [Scheidegger and Sparks \(1996\)](#), and [Jackson \(1998\)](#) show that few studies dealt with the desorption of heavy metal ions from clays. [Churchman \(2002a\)](#) has found that heating a bentonite, following uptake of heavy metal cations, diminishes the ease of their desorption. The immobilisation of small cations (e.g., Cr^{3+}) on bentonite surfaces requires less heating (lower temperatures) as compared with the larger-adsorbed cations (Pb^{2+} , Cd^{2+} , Ni^{2+}).

E. Effects of Clay Modification on Uptake of Heavy Metal Ions

The ability of clays to attract and hold heavy metal ions can be enhanced by suitable modifications of, or at least additions to, the minerals. [Cremers et al. \(1979\)](#) patented a process whereby the addition of a polyamine to clay minerals enhances the removal of heavy metal cations from solution. Similarly, organically modified smectites such as dimethyl dioctadecylammonium (DMDOA)-bentonite can take up considerable amounts of heavy metal ions from aqueous solution ([Lagaly, 1995](#)). The amount of zinc ions adsorbed by DMDOA-bentonite is virtually trebled in the presence of phenol and diethyl ketone, while the uptake of these organic compounds increases synergetically ([Stockmeyer and Kruse, 1991](#)). Lead and chlorobenzene are adsorbed simultaneously by a bentonite that has been modified with hexadecyltrimethylammonium (HDTMA) ([Lee et al., 2002](#)). In recognition of the common association of heavy metal ions with some organic complexing agents, including natural organic compounds ([Krishnamurti et al., 1997](#)), studies were carried out on the uptake of Cd^{2+} -cysteine by montmorillonite and kaolinite. Complexation with cysteine aids the uptake of Cd^{2+} by montmorillonite ([Undabeytia et al., 1998](#)) and, perhaps more surprisingly, also by kaolinite ([Benincasa et al., 2002](#)). Indeed, Cd^{2+} -cysteine can intercalate into kaolinite to some extent, and more so into a less well-ordered than a well-ordered kaolinite. In a procedure developed for the clean-up of galvanic water, [Tarasevich and Klimova \(2001\)](#) showed that grafting polyphosphates on to the edges of kaolinite, metakaolinite, and Al^{3+} (hydr)oxides greatly increases the capacities of these materials to remove Ni^{2+} , Co^{2+} , and Cr^{3+} from solutions through the formation of complexes with the phosphate groups.

Modification of smectites by interlayering with hydroxy-cations and pillaring (see Chapter 7.5) can markedly increase the uptake of heavy metal cations, especially certain specific metal ions. In studying the adsorption of Cu^{2+} on a poly(hydroxo aluminium) interlayered smectite between pH 4.5 and 6.5, [Harsh and Doner \(1984\)](#) found this adsorbent to be much more reactive towards Cu^{2+} than either montmorillonite itself or aluminium (hydr)oxides. Similarly, [Cooper et al. \(2002\)](#) observed that poly(hydroxo iron) or poly(hydroxo iron/aluminium)-interlayered montmorillonites have higher affinities for Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} than the corresponding poly(hydroxo aluminium) compounds.

In investigating the adsorption of some common heavy metal ions (Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+}) by 'clay-aluminium hydroxide complexes' (CALHO), [Keizer and Bruggenwert \(1991\)](#) found that the relative extent of adsorption was strongly affected by the hydroxy interlayering in a manner that particularly reflected pH. The adsorption of Cu^{2+} and Zn^{2+} by CALHO proceeded differently from that of Cd^{2+} and Pb^{2+} . CALHO showed an exceptionally strong affinity for Cu^{2+} and Zn^{2+} , especially at pH 6 (rather than pH 5), but not for Cd^{2+} and Pb^{2+} . Furthermore, Cd^{2+} and Pb^{2+} could be desorbed almost completely without affecting the interlayers, while complete desorption of Cu^{2+} and Zn^{2+} required dissolution of the interlayers. [Keizer and Bruggenwert \(1991\)](#) suggested that Cu^{2+} and Zn^{2+} became

incorporated in the poly(hydroxo aluminium) interlayers while the larger cations Cd^{2+} and Pb^{2+} were excluded from these high energy sites.

There was also a striking comparison to be made between the relative affinities of CALHO and hydrous aluminium oxides for the different heavy metals. Whereas the discrete oxides (of Al, and also Fe) took up the metal ions in the order: $\text{Cu}^{2+} \cong \text{Pb}^{2+} \gg \text{Zn}^{2+} > \text{Cd}^{2+}$ (Kinniburgh et al., 1976), the order of preference for CALHO was $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$, especially at low pH and low concentrations of the heavy metal ions (Keizer and Bruggenwert, 1991). The latter trend was confirmed by Matthes et al. (1999) who studied the adsorption of the same four heavy metals by bentonite that had been interlayered with both poly(hydroxo aluminium) and poly(hydroxo zirconium) ions, and also pillared by calcination of the interlayered materials. On both interlayered and pillared clays, uptake of Zn^{2+} , in particular, increased markedly as the pH was raised from 4.9 to 6.9. Alone among the four heavy metals, Zn^{2+} was adsorbed in excess of the CEC of the various interlayered and pillared clays at pH 6.9. Matthes et al. (1999) attributed the higher and partially non-exchangeable uptake of Zn^{2+} at pH 6.9 to a dominance of surface complexation of Zn^{2+} ions with hydroxyl groups of the Al and Zr (poly)hydroxy cations and the interlayer pillars. The affinity of Zn^{2+} for the Al interlayer species was apparently higher than that for the Zr species. Since the specific adsorption of Zn^{2+} was little influenced by ionic strength, these interlayered clays could be useful for the removal of Zn from saline solutions, wastewaters, and leachates at neutral pH. The results led Matthes et al. (1999) to conclude that the binding of metal cations to oxide and hydroxide surfaces is a complex process, determined by the electrostatic and electron-sharing properties of both adsorbate and solvent.

In general, poly(hydroxy aluminium) smectite can be used to immobilise Cu^{2+} , Zn^{2+} , Cd^{2+} , and also Ni^{2+} , but not Pb^{2+} to any extent. For each metal ion, the most effective immobilisation occurs over a particular pH range: 6–8 for Zn^{2+} and Ni^{2+} ; 4–6 for Cu^{2+} ; and 7–9 for Cd^{2+} (Lothenbach et al., 1997). Vengris et al. (2001) devised a novel route for the production of polycation-modified clays. The clay, a mixture of 2:1 aluminosilicate minerals, is treated with concentrated HCl, and the products are neutralised with NaOH. This latter step results in the re-adsorption of Al, Fe and Mg on the acid-activated clay, giving a material with a high capacity to adsorb Cu^{2+} , Ni^{2+} and Zn^{2+} from water.

11.1.2. CONTROL OF ORGANIC AND BIOLOGICAL CATIONS

Since the majority of clay minerals are negatively charged they would have a strong affinity for organic cations. Although the number of organic species that can acquire a positive charge or act as a base may be limited (Theng, 1974), some of these are important. For example, the pesticides paraquat and diquat present problems as pollutants whereas amines, especially alkylammonium cations, are useful for modifying clay properties, and amino acids, peptides and proteins are biologically

important. Waste proteins from food processing may also be important as pollutants, lending value to their affinity for clays.

A. Practical Applications

The interactions of clays in soil with excess paraquat and diquat, enzymes, and other forms of protein received considerable attention (e.g., [Theng, 1979](#)) but only a limited amount of information is available on the active use of clays for the environmental control of these and other organic cations. [Stansfield \(1986\)](#) reported the contamination of river waters in England by diquat and paraquat, leaking out of plastic storage drums that had melted as a result of a fire. Bentonite was employed to constrain the leakages at their source. The use of bentonite clays to remove excess proteins from wine during its production is a well-established process in the wine industry ([Rankine, 1995](#)). However, this attractive interaction between clays and proteins has not been exploited in the wider environment. [Morris et al. \(2000\)](#) showed that a fine-grained marine sediment, containing kaolinite and montmorillonite, was able to adsorb microcystin-LR. This indicates the potential use of clays to remove this class of potent mammalian liver toxins from drinking waters. As a cyclic heptapeptide ([Moore et al., 1991](#)) microcystin-LR would be expected to adsorb on to clays, in general, provided that the pH of the infected waters are close to the pI of the peptide. [Holo et al. \(1973\)](#) patented a method for reducing the biochemical oxygen demand of sewage, and recovering the protein in sewage by using a clay (either bentonite or kaolin), along with aluminium sulphate and a co-polymer of acrylic acid and acrylic amide. Although the clay here may function partly as a flocculating agent, it is almost certainly responsible for the process of protein recovery within the overall method. [Landau et al. \(2002\)](#) have also experimented with a system for the recovery of protein from water by means of the addition of bentonite that is later removed by fractionation in foam. Similarly, [Churchman \(2002a\)](#) has shown that some bentonites can remove all the proteins from abattoir wastes which otherwise could cause eutrophication of aqueous systems. The use of natural clay by villagers along the Nile River in the Sudan to remove viruses from the river water ([Lund and Nissen, 1986](#)) has already been mentioned. This practice is based on the ability of clay minerals to adsorb viruses (nucleoproteins) in a similar way to proteins ([Theng, 1979](#)). The propensity of clays for taking-up viruses could be exploited further, as demonstrated by the laboratory use of clays for virus removal or concentration ([Barkley and Desjardins, 1977](#); [Simmonds et al., 1983](#); [Sobsey and Cromeans, 1985](#)).

B. Mechanisms of Uptake of Organic and Biological Cations by Clay Minerals

[Theng \(1974\)](#) has summarised the early literature on the interactions of clay minerals with organic and biological cations, including compounds that can acquire a positive charge via acceptance of a proton in acidic solutions. While electrostatic attraction

leading to exchange for other, generally simple, cations, is perhaps the principal mechanism, other forces also influence the interaction. Even the adsorption by clay minerals of the fully ionised bipyridinium halides, paraquat and diquat, may involve charge transfer between these cations and the negatively charged silicate framework, in addition to the dominant cation exchange process. For larger organic cations such as members of the alkylammonium series, van der Waals attractive forces play a notable role in linking cations to clays. Both [Theng et al. \(1967\)](#) and [Vansant and Uytterhoeven \(1972\)](#) found that the affinity of alkylammonium cations for montmorillonite increases with an increase in the length of the alkyl chains, indicating an increased contribution of van der Waals forces to adsorption energy.

The charge characteristics of biologically important molecules, such as amino acids, peptides and proteins, vary with the pH of the surrounding solution. These molecules have a net positive charge (generally expressed on a nitrogen atom of the amino group) at pH values below their isoelectric point, pI. Early work on the uptake of these molecules by clay minerals ([Theng, 1979](#)) indicated that smectites adsorbed more of these cationic species than clays with lower negative layer charge (e.g., kaolinites). Further, these biological cations entered the interlayer spaces of smectites, and their uptake was enhanced by Na⁺ saturation of the clays. Maximum uptake of proteins commonly occurred at a pH close to their pI, when the proteins are least soluble. At pI > pH proteins tend to be repelled by clays. At least for 'soft proteins' the extent of their spread over clay surfaces increases at pH < pI ([Quiquampoix et al., 1989, 1995, 2002](#); [Quiquampoix and Ratcliffe, 1992](#)). [Fig. 11.1.2](#) supports this mechanism by showing that below the pI the protein (bovine serum albumin) does not displace the exchangeable cations (Mn²⁺) from the mineral surface. The decrease in protein uptake below the pI indicates that the area of surface covered by each protein macromolecule increases with decreasing pH. Protein uptake tends to decrease quite rapidly with pH at pH > pI, when the positive charge on the protein diminishes. Nonetheless, some uptake can still occur at pHs far above the pI, thanks to the non-electrostatic interactions such as hydrogen bonding, van der Waals interactions, hydrophobic forces, and entropy effects ([Theng, 1979](#); [Quiquampoix et al., 1989, 1995](#); [Quiquampoix and Ratcliffe, 1992](#); [Staunton and Quiquampoix, 1994](#)). 'Hard proteins', such as α -chymotrypsin, are less likely to show a conformational change on clay mineral surfaces with pH ([Quiquampoix et al., 2002](#)). Coatings of either natural organic matter (NOM) ([Quiquampoix et al., 1995](#)) or aluminium hydroxide ([Naidja et al., 1995](#); [Violante et al., 1995](#)) tend to decrease protein uptake compared with that by pure Na-saturated clay.

As another class of biologically important molecules, antibiotics may be basic (like paraquat and diquat), or amphoteric (like proteins). Basic antibiotics such as streptomycin, dihydrostreptomycin, neomycin and kanamycin, are taken up and strongly retained by clays. By the same token, amphoteric antibiotics, including bacitracin, auromycin and terramycin, interact strongly with clays at pH values near, or below, their pI ([Theng, 1974](#)). There do not appear to be any reports of the use of clays to control the spread of antibiotics in wastewaters (e.g., from clinics and hospitals), but their use for this purpose seems feasible. The effect of associations of

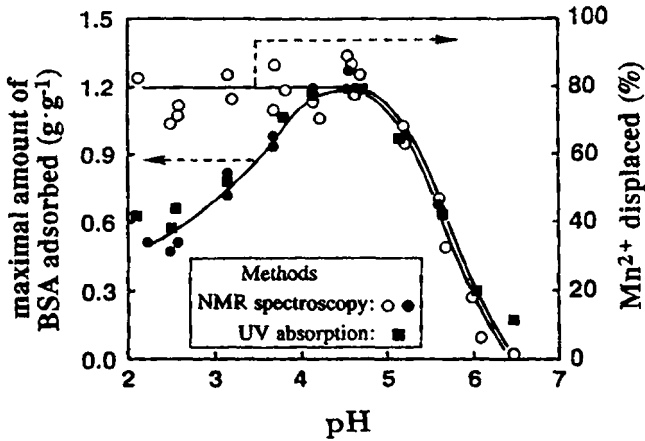


Fig. 11.1.2. Effect of pH on the maximal amount of bovine serum albumin ($pI = 4.7$) adsorbed on montmorillonite and the release of Mn^{2+} displaced by the protein. From Quiquampoix et al. (2002).

enzymes, as proteins, with clays upon their catalytic activity has been discussed at length by Theng (1979) and Quiquampoix et al. (1995, 2002), and is of only indirect interest here. However, following the types of uses cited above, the usefulness of clays for pet litter may derive as much from the deactivation through uptake by the clay of the enzyme urease, which converts urea to ammonia, as by the adsorption of water by the clay (W.P. Moll, personal communication).

Most studies of the association of organic and biological cations with clay minerals focussed on montmorillonite, although early work on proteins also used kaolinite (e.g., McLaren, 1954) and halloysite (Mills and Creamer, 1971). Using sepiolite, Rytwo et al. (2002) showed that the mechanism and also extent of uptake can depend on the charge on the organic cation in a counterintuitive manner, that is, divalent cations are adsorbed less than monovalent cations. The divalent cations paraquat, diquat, and methyl green are adsorbed up to nearly the CEC of the sepiolite, with a maximum uptake being reached between 100% and 140% of the CEC. By contrast, monovalent cations such as methylene blue (Aznar et al., 1992), crystal violet (Rytwo et al., 1998), and TX100 (Alvarez et al., 1987) were adsorbed up to a maximum of 400% of the CEC of sepiolite. The difference is explained by the association of the monovalent cations on neutral sites of the clay mineral, whereas the more highly charged divalent cations do not associate.

C. Ease of Displacement of Organic and Biological Cations

Ease of displacement of organic cations from clays appears to depend upon the size of the organic cation although factors such as clay type and cation shape also play a

role since these latter two factors affect the ease and extent of uptake (Theng, 1974). Thus, large organic cations such as DMDO and dimethyl benzylammonium ions (DMBL) are strongly retained once they are intercalated by smectites. Replacement by simple inorganic cations may not occur to any extent, but one organic cation may be able to replace another (Theng, 1974). Paraquat and diquat, as examples of relatively small organic cations, could be released from complexes with clays by exchange with simple inorganic cations, although their release was less easily achieved from complexes with montmorillonite than from those with kaolinite (Theng, 1974). Proteins could be released by kaolinite when the pH was raised (McLaren, 1954). By contrast, strong treatment with concentrated solutions of both mono- and divalent cations, including very high pH values and severe agitation (prolonged mechanical and ultrasonic), released little protein from proteinaceous complexes of bentonites in waste lees from winemaking (Churchman, 2002a). In general, little desorption of proteins is found to occur from clays (Theng, 1974). As is the case for large quaternary ammonium cations (QACs), it appears that the bonds that form between clays and proteins are not simply electrostatic. Although charge interactions play a large part in holding proteins to the clays, van der Waals interactions and favourable entropy changes contribute to the overall attraction (Theng, 1979; Staunton and Quiquampoix, 1994; Churchman, 2002a; Quiquampoix et al., 2002). Clays are useful for extracting proteins from wastewaters and sewage, for example, but it would be difficult to recycle the clays after usage and so minimise waste and capital costs. Nonetheless, chemical or photo-oxidative methods (Churchman, 2002a), as well as microbial agents, could be employed to destroy the adsorbed protein, without affecting the clay. In stark contrast, Armstrong and Chesters (1964) were able to remove 63% of the protein pepsin ($pI = 2.8$) that had been adsorbed by a bentonite at pH 3.0. They achieved this simply by raising the pH to 5.2 with NaOH. Clearly the ease of protein removal from complexes with bentonite varies with the type of protein.

11.1.3. CONTROL OF NON-IONIC ORGANIC COMPOUNDS

Because of their charge characteristics, clays are naturally hydrophilic. Nevertheless, their high-surface areas and volume of fine pores enable them to adsorb significant amounts of non-ionic substances. There are records of the use of clays for 'fulling', i.e., cleaning grease from wool, that date back before 2000 BC, hence the term 'fuller's earth' (Robertson, 1986). Fuller's earth generally denotes calcium montmorillonite, although it is sometimes used to refer to palygorskite (attapulgite), especially in the USA. Today, clays are used quite widely to adsorb oil and grease, e.g. on floors of workshops (Grim, 1962). Coarser particles are preferred for this purpose, and palygorskite is particularly suitable, while montmorillonite that has been calcined to a sufficiently high temperature to prevent its break-up into small particles is also used. However, clays in their natural state usually effect little uptake

of small non-ionic organic compounds (NOCs) in the presence of water. Despite this drawback, their attractiveness for environmental applications as low-cost, generally non-toxic, high surface-area materials mean that much recent research has gone into the adaptation of clays for the removal of NOCs, which include many substances of concern to environmental and human health.

A. Uptake of NOCs by Organically Unmodified Clay Minerals

In principle, clays and clay minerals could be used to adsorb NOCs from either the vapour or the solution phase. In the absence of water, clay minerals can adsorb significant amounts of non-ionic gases, with amounts adsorbed depending on the surface areas of the clays (Jurinak, 1957; Lee et al., 1990; Sawhney, 1996). However, as NOCs cannot compete well with water, their adsorption as gas by clays diminishes as humidity rises, and only negligible amounts adsorb from aqueous solutions (Lee et al., 1990). Nonetheless, potassium-saturated smectites can show a greater, or at least, similar affinity as soil organic matter for some NOCs, including some pesticides (Sheng et al., 2001). Similarly, Boyd et al. (2001), Johnston et al. (2001), and Sheng et al. (2002) demonstrated that uptake of NOCs by expanding clay minerals was enhanced when the saturating cations are weakly hydrated, such as K^+ and Cs^+ , while the more strongly hydrated cations (Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+}) have the opposite effect. Cations with weaker hydration, i.e., lower enthalpies of hydration: (i) provide larger adsorption domains (Sheng et al., 2001); (ii) form stronger interactions with the $-NO_2$ groups that are common to many of the NOCs studied (Boyd et al., 2001; Johnston et al., 2001); and (iii) minimise swelling, thus enabling the NOCs to interact simultaneously with the opposing pairs of silicate layers, minimising contact with water (Johnston et al., 2001; Sheng et al., 2002). Using two dinitrophenol herbicides, Sheng et al. (2002) also showed that uptake of these NOCs increases as the layer charge of the clay mineral decreases.

B. Organic Modification of Clays and Uptake of NOCs

The capacity of clays to adsorb NOCs is greatly enhanced when the minerals are modified by the uptake of organic cations, rendering the clays hydrophobic and organophilic. QACs were found to be most useful for this purpose. Generally, QACs can easily replace the inorganic cations occupying exchange sites on clays (Xu et al., 1997). However, the degree of hydrophobicity that is attained and the efficiency of uptake of NOCs achieved by these so-called 'organo-clays' depend greatly on the nature of the QACs used, notably on the length of the carbon chains in the QACs.

C. Uptake of NOCs from the Gas Phase by Organo-Clays

Replacement of the inorganic cations in smectite by tetramethylammonium (TMA) and tetraethylammonium (TEA) allows appreciable uptake of gaseous organic

molecules, including hydrocarbons, to take place (Barrer and McLeod, 1955). The organo-clays adsorb organic molecules without the need for any threshold pressure, as is the case for adsorption of simple gases (e.g., N₂ and Ar), on clays or organo-clays. These authors proposed that the intercalation of these short-chain QACs caused the development of pores, creating a zeolite-like structure in the clay interlayer space where NOCs could adsorb. These organo-clays showed a selectivity for the uptake of hydrocarbons that appeared to relate to their molecular shape, a proposition that was confirmed by Lee et al. (1989a). Layer charge also affected uptake of a gaseous NOC (*o*-xylene) by complexes of smectites with TMA. Less of the NOC was adsorbed by the TMA derivative of a high-charge smectite than by the corresponding derivative of a low-charge smectite. This is because the density of packing of TMA cations in the smectite interlayer spaces was relatively low in the low-charge clay mineral, giving rise to more free pore space in its TMA complex than in the derivative of the high-charge clay mineral (Lee et al., 1990).

When a long-chain QAC such as DMDOA intercalates into the smectite, it fills a large proportion of the interlayer space. Nonetheless, the derivative is an effective adsorbent for gaseous NOCs when dry (Barrer and Kelsey, 1961). When a different long-chain QAC (hexadecyltrimethylammonium, HDTMA) replaces the inorganic cations on a smectite, partially at first, and then fully (i.e., to satisfy the CEC of the clay mineral), uptake of NOCs tends to increase with the amount of HDTMA (or organic C) in the derivative (Boyd et al., 1988b; Zhu and Su, 2002). In addition, the shape of the adsorption isotherm also changes with the content of HDTMA. At a low content (35% of the CEC) a type II isotherm in Brunauer's classification (Brunauer, 1944) is obtained (similar to that for the uptake of small NOC by Ca²⁺-smectite), while at a HDTMA content corresponding to the CEC, the isotherm is essentially linear. Thus, NOC uptake by the derivative with a low-QAC content occurs, at least partly, by adsorption on to the interlayer surface, while in the fully exchanged HDTMA derivative adsorption takes place by partitioning into the QAC. An analogy is drawn between partitioning of NOCs into QACs in the derivatives with pure clay minerals and that into the organic matter in soils (Chiou et al., 1979, 1983).

D. Uptake of NOCs from Aqueous Solutions by Organo-Clays

Most interest has centred on the use of organo-clays for the control, by uptake, of NOCs occurring as pollutants in aqueous solution. Cowan and White (1962) made a systematic study of the uptake from water of phenol by complexes of montmorillonite with different quaternary ammonium cations. Derivatives with QACs having carbon chains from C = 2 up to C = 18 were effective adsorbents for phenol. In relation to chain length, uptake reached a maximum for C = 12 (dodecylammonium bentonite). Street and White (1963) investigated the uptake from water of a variety of NOCs, although not including hydrocarbons, by dodecylammonium montmorillonite. All could be adsorbed, but to different extents. The implications of these

early findings, as well as those from later studies, for the mechanism of uptake will be discussed below.

Since the late 1980s, there has been a strong revival of interest in the use of clay minerals that were organically modified, mostly by exchange with QACs, but not exclusively. Much of this work has been carried out by Mortland, Boyd and co-workers at Michigan State University (see Xu et al., 1997). The major focus has been on the control by uptake of toxic pollutants that occur in fuel oils, comprising benzene, toluene, ethylbenzene and xylene ('BTEX'). Using phenol, trichlorophenol and pentachlorophenol (PCP), Mortland et al. (1986) and also Boyd et al. (1988c) found that smectites modified with long-chain QACs adsorb more of these NOCs from water than those modified with short-chain QACs. Furthermore, smectites reacted with short-chain QACs can show considerable selectivity of molecules for adsorption, as already noted for hydrocarbons from the gas phase. Molecular shape and size are the principal determinants of the ability of NOCs to be adsorbed by TMA-smectite and, in the extreme, larger molecules such as the herbicide lindane (hexachlorocyclohexane, γ -isomer) can be excluded from sites for adsorption on TMA-smectite (Lee et al., 1989a). There appears to be a distinct difference in mechanism of uptake between smectites modified with either short- or long-chain QACs. This is also reflected by their different effects on the adsorption of gases as discussed below.

While most research on the modification of clay minerals for non-ionic organic contaminant uptake has been carried out on smectites, some has shown the feasibility of this approach for a wide range of clay minerals. Indeed, the enhanced uptake of a number of NOCs by soils containing many different clay minerals besides smectites (Boyd et al., 1988a, 1988b, 1988c) suggested the universal applicability of this approach for clay minerals. A study of uptake of a range of hydrocarbons by the HDTMA derivatives of a variety of clay minerals (Jaynes and Boyd, 1991a) has confirmed the effectiveness of these organo-clays as adsorbents of hydrocarbons. A vermiculite, a high-charge smectite, and an illite each retained more ethylbenzene than a low-charge smectite and a kaolinite. Curiously, this was in spite of the low-charge smectite incorporating more HDTMA than the high-charge type. It would appear that the alignment of the HDTMA in the high-charge smectite is more favourable for partitioning NOCs than that in the low-charge mineral. Xu and Boyd (1995b) also found that HDTMA adsorption by swelling clays was more complex than that by non-swelling clays.

A further curiosity is that an illite incorporated more HDTMA than expected from its CEC, apparently because HDTMA can displace some interlayer K^+ from the illite (Jaynes and Boyd, 1991a). Nonetheless, the uptake of ethylbenzene by the illite is less than that by the high-charge smectite. One possible explanation may arise from the observation that HDTMA-halide salts employed in the modification may be retained by the clay if washing is inadequate. Slade and Gates (2003) found that water-washed HDTMA montmorillonite had greater capacity for toluene uptake than its ethanol-washed counterpart, which contained no HDTMA-Br. The salt may be included in the close-packed structure of the interlayer (Slade and Gates, 2004).

Lee et al. (1989a) showed that TMA-illite could adsorb a large organic molecule (lindane) whereas the TMA-smectite had a much reduced capacity due to steric exclusion of the organic molecule from the interlayer spaces of TMA-smectite. Akcay and Yurdakoc (2000) also observed that smectite modified with a particular QAC was not necessarily superior for the adsorption of organic compounds, although not NOCs in this case. For example, a dodecylammonium-modified sepiolite effected more and stronger adsorption of a range of phenoxyalkanoic acid herbicides (2,4-D, 2,4-DP, 2,4-DB, 2,4,5-T) and MCPA than a smectite modified with the same QAC.

E. Practical Applications of Organo-Clays for Control of NOCs

The preparation of organo-clays formed by reacting clay minerals (generally smectites) with QACs (generally long-chain varieties) and their applications for the removal of organic pollutants from water were described in several patents (e.g., McBride and Mortland, 1973; Kokai, 1975; Beall, 1984, 1985a, 1985b, 1996; Alther, 1999). These organo-clays were used most widely for removing oil and grease from water. They are included in a patent for the specialised task of clearing spills of oil on water (Kemnetz and Cody, 1996). In potable water treatment, they may be used synergistically with more expensive activated carbon, in order to prolong the useful lifetime of the latter material (Alther, 1999). Their use for the removal of trihalo-methanes has been proposed, but not established, to our knowledge at the time of writing. However, a recent patent (Gates and Slades, 2001) describes their use for the removal of microcystin toxins from cyanobacteria (blue-green algae) that accumulated in waterways and water storages. They may also be used to remove waste organic materials from industrial processes, such as tanneries (Cioffi et al., 2001a). Organo-clays were also proposed for use in waste containment barriers (Smith et al., 1990; Sheng et al., 1996a, 1996b). Modelling has shown that small amounts of these materials included in conventional clay barriers would enable effective containment of NOCs for > 100 years (Adu-Wusu et al., 1997). Organo-clays may also be used as adsorption (chemical) barriers in association with landfill liners, where they can increase the useful life of the associated liner by 5–10 years (Voudrias, 2002). They can also be employed as containment barriers for BTEX pollutants around petroleum storage tanks (Jaynes and Vance, 1996; Xu et al., 1997; Sharmasarkar et al., 2000; Lo and Yang, 2001).

Since clays are ubiquitous components of soils and many other earth materials (e.g., sediments and regolith), the knowledge gained from research on organo-clays has found application in the in situ modification of soils for taking-up and immobilising NOCs. Particular uses to which this technology can be put include the immobilisation of leachable pollutants in contaminated land (Boyd et al., 1988a, 1988b; Lee et al., 1989b; Brixie and Boyd, 1994; Xu et al., 1997). This approach can prevent the transport by leaching of pesticides into ground water. To this end, soils, subsoils and aquifer materials are treated with QACs to provide adsorptive zones for

the retardation of pesticide transport (Sheng et al., 1998). The primary concern is with highly water-soluble pesticides that are minimally adsorbed by soil particles and not readily degradable, and hence can move rapidly with infiltrating water. Both Zhao et al. (1996) and Carrizosa et al. (2001) showed that dicamba, a highly soluble herbicide, and so presents these concerns, can be adsorbed by QAC-modified clays. Similarly, Hermosin and Cornejo (1992) demonstrated the effectiveness of QAC-clay as an adsorbent for another soluble herbicide, 2,4-D. Sparingly soluble pesticides like malathion and butachlor are also strongly adsorbed by QAC-clays (Pal and Vanjara, 2001). However, it should be noted that uptake of contaminants may alter important properties of organo-clays. Considerable interlayer swelling of organo-clays can occur as a result of the uptake of both water-immiscible organic contaminants (Sheng et al., 1996b; Singh et al., 2003; Slade and Gates, 2003) and aqueous-miscible solvents (Nzengung et al., 1996; Gates, 2004). Gates et al. (2004) found that such adsorption induces swelling, and decreases the permeability of an organo-modified bentonite to aqueous-miscible solutions by more than three orders of magnitude. Adsorption of pollutants by organo-clays may nonetheless allow their biodegradation. Naphthalene adsorbed by HDTMA-smectite was available to some organisms for degradation directly from the adsorbed state (Crocker et al., 1995), as was the herbicide, fenamiphos, when adsorbed by the same type of organo-clay (Singh et al., 2003). Even when the organism used is unable to access the contaminant (naphthalene) directly, its rapid desorption from the organo-clay meant that biodegradation can occur (Crocker et al., 1995). By contrast, phenanthrene intercalated into a long-chain QAC derivative of montmorillonite is inaccessible to microorganisms. Since the interlayer phenanthrene does not appear to be desorbable, it is not biodegradable, at least within the period of incubation used (Theng et al., 2001). As Sheng et al. (1996a) pointed out, the coupling of immobilisation with in situ biodegradation provides a comprehensive restoration technology to remove target contaminants.

F. Effect of Hydrocarbon Chain Length on Uptake of NOCs by Organo-Clays

Alkylammonium cations are attracted to clays in amounts that increase with the charge on the clays. As noted above in relation to uptake of NOC gases by organo-clays, the influence of the amount of each particular QAC on uptake of NOCs from either aqueous solution or the gas phase, differs according to the length of the alkyl chain (number of C atoms). In the case of short-chain QACs such as TMA, an increase in concentration of QAC on a smectite with increasing layer charge on the mineral, leads to a decrease in the amount of NOC removed from solution (Lee et al., 1990). For long-chain QACs, such as HDTMA, a similar relationship is obtained between the concentration of adsorbed QAC and smectite layer charge but in this case, and in stark contrast, uptake of any particular NOC increases (Jaynes and Boyd, 1991a). Furthermore, adsorption of NOCs by short-chain QAC clay minerals show typical curvilinear isotherms, indicating both high- and low-energy sites (Lee et al.,

1990) (Fig. 11.1.3), whereas long-chain QAC derivatives give essentially linear isotherms, indicating that all sites are equal in energy (Boyd et al., 1988b) (Fig. 11.1.4). Mechanistically, the difference is that short-chain QACs form 'pillars' in the interlayer space, giving rise to pores for the adsorption of NOCs (Fig. 11.1.5), whereas long-chain QACs provide a microscopic organic phase into which NOCs are partitioned (Fig. 11.1.6); that is, they effectively act as a solvent in which NOCs become dissolved (Yariv, 2002). Jaynes and Boyd (1991a) made an extensive study of the retention of eight aromatic NOCs by HDTMA complexes with seven different clay minerals (vermiculites, illites, kaolinites, as well as smectites). They show that the organic matter-normalised adsorption coefficients (K_{OM}), expressed as logarithms, for each adsorbent-adsorbate pair generally parallel the octanol-water partition coefficients (K_{OW}) of the appropriate NOCs. This confirmed that partition is the dominant mechanism for uptake of the NOCs by derivatives of clay minerals with HDTMA.

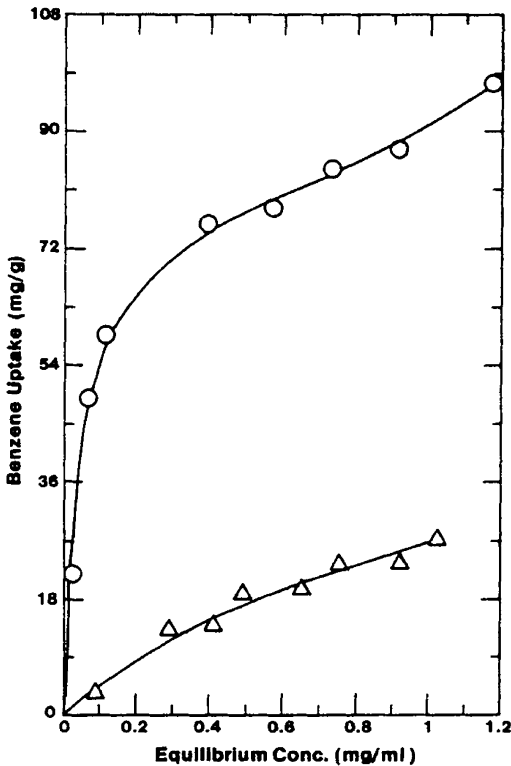


Fig. 11.1.3. Adsorption of benzene from aqueous solution by TMA derivatives of a high-charge smectite, SAz (triangles) and a low-charge smectite, SWy (circles). From Lee et al. (1990).

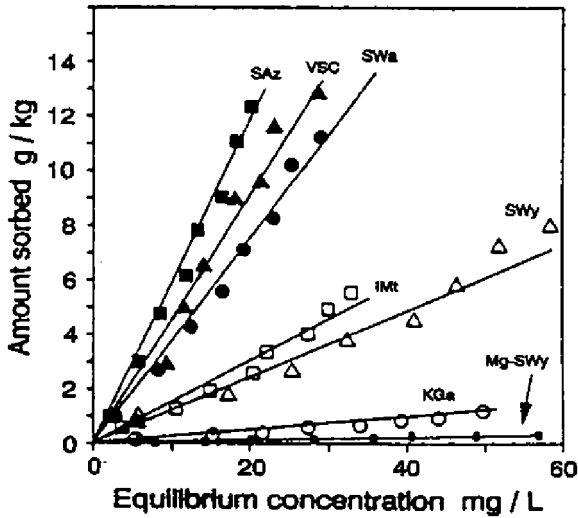


Fig. 11.1.4. Adsorption of ethylbenzene from aqueous solution by HDTMA derivatives of different clay minerals: SAz: high-charge smectite, CEC = 130 cmol(+)/kg; VSC: vermiculite, CEC = 80 cmol(+)/kg; SWa: high-charge smectite, CEC = 107 cmol(+)/kg; IMt: illite, CEC = 24 cmol(+)/kg; SWy: low-charge smectite, CEC = 87 cmol(+)/kg; KGa: kaolinite, CEC = 4 cmol(+)/kg. MG-SWy is the Mg²⁺-saturated low-charge smectite. From Jaynes and Boyd (1991a).

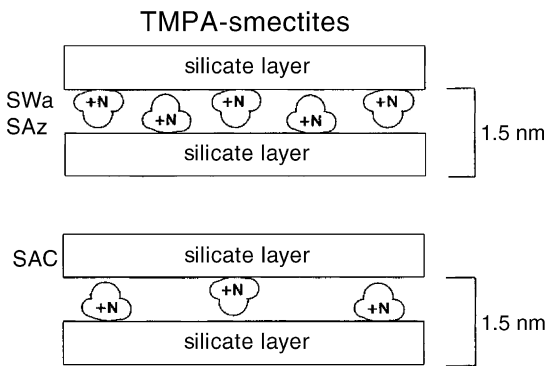


Fig. 11.1.5. Schematic diagram of short-chain QACs, such as TMPA in the interlayer spaces of high-charge smectites (SWa, SAz) and a low-charge smectite (SAC; CEC = 90 cmol(+)/kg). In both instances the basal spacing is about 15 nm. From Jaynes and Boyd (1991b).

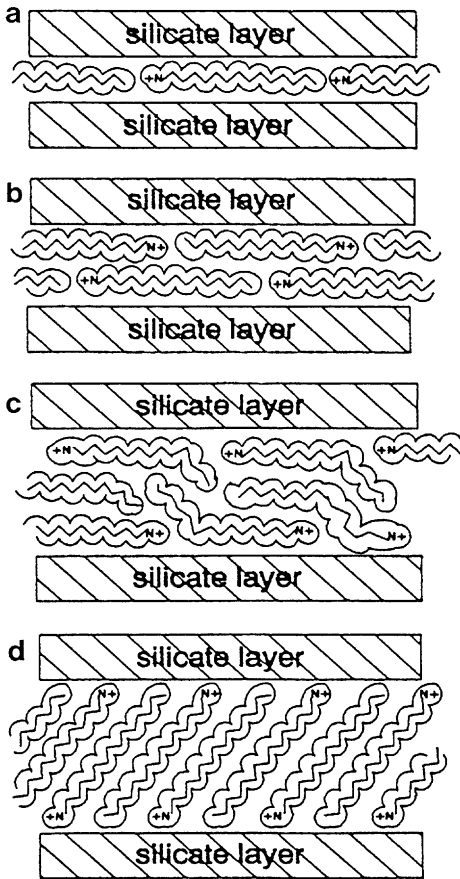


Fig. 11.1.6. Schematic diagram of different possible conformations of long-chain QACs, such as HDTMA in the interlayer space of an expansible clay mineral. (a) monolayer (basal spacing = 1.37 nm); (b) bilayer (basal spacing = 1.77 nm); (c) pseudotrimolecular layer (basal spacing = 2.17 nm); and (d) paraffin-type structure (basal spacing > 2.2 nm). From Lagaly and Weiss (1969); Jaynes and Boyd (1991a).

G. Demarcation between Short-Chain and Long-Chain QACs

As a 'working hypothesis', we may say that the size (length) of the hydrocarbon chain in QACs tends to control whether uptake of NOCs by the corresponding clay mineral derivatives occurs by adsorption or partition. The study by Smith et al. (1990) confirms this view. Derivatives with QACs containing eight or fewer C atoms give rise to

adsorption, while those having more than 14 C atoms show partitioning. QACs containing hydrocarbon groups with between 9 and 13 C atoms were not examined although Jaynes and Vance (1996) showed that clay minerals modified by QACs with 12 C atoms in their hydrocarbon chain take up NOCs by a partitioning mechanism. Smith et al. (1990) also found that the adsorption mechanism (characterised by non-linear isotherms) leads to increased uptake as compared with partition. In the case of adsorption there is competitive adsorption when more than one NOC is present whereas the partition mechanism (giving linear isotherms) shows non-competitive adsorption. However, later work has suggested that the reality is a little more complex. As already noted, some trimethylphenylammonium (TMPA)-like cations, containing one or more aromatic groups, promote uptake by partition, albeit poorly, rather than by adsorption (Jaynes and Vance, 1999). Furthermore, uptake by partition in long-chain QACs can be supplemented by a solvation mechanism for some NOCs and certain clay minerals, causing the isotherm to deviate from linearity through a steadily increasing upward curvature with increasing solution concentration (Jaynes and Vance, 1996; Sheng et al., 1996a; Singh et al., 2003).

H. Influence of Water on Uptake of NOCs by Organo-Clays

For derivatives with short-chain QACs, the presence of water strongly affects their capacity as adsorbents, and especially their selectivity for different NOCs (Lee et al., 1989a). Water molecules shrink the pores in the interlayer spaces of smectites created by the intercalation of short-chain QACs. Depending on their molecular sizes and shapes, NOC molecules may or may not be able to enter these pores. Peaks shifts in the FTIR spectra indicate that in dry derivatives hydrocarbons interact with the QAC pillars, including TMPA and TMA. On the other hand, in aqueous systems water interacts with these pillars in place of the hydrocarbons (Stevens et al., 1996). Nonetheless, hydrocarbons can adsorb on siloxane surfaces in the aqueous systems (Stevens et al., 1996; Stevens and Anderson, 1996). Whether in the absence of water (for gaseous uptake by dry derivatives) or in its presence (for uptake from aqueous solutions), adsorption occurs because the siloxane surfaces of aluminosilicates, specifically those of smectites, are hydrophobic, according to Jaynes and Boyd (1991b). Even when only some, but not all, of the inorganic cations (Ca^{2+}) on a smectite are replaced by TMPA, hydrocarbons are adsorbed by the organo-clay but to a lesser extent (Sheng and Boyd, 1998). It appears that TMPA and remaining Ca^{2+} ions are mixed together within the interlayer spaces, rather than segregated into separate layers. As a result of its exchange behaviour, TMPA does not only replace some Ca^{2+} ions, but also disrupts the network of water molecules associated with the inorganic cations. The 'exposure' of the siloxane surface by TMPA exchange appears to made the environment relatively hydrophobic. By contrast, prior to the introduction of TMPA the interlayer environment of smectite is hydrophilic because of the dominating influence of hydrated exchangeable cations.

I. Cation Properties and Uptake of NOCs by Short-Chain QAC-Clays

In using different QACs (TMPA and the larger trimethylammonium adamantine) and a series of QACs of increasing size from TMA to benzyltrimethylammonium (BTMA), TEA, and benzyltriethylammonium (BTEA), [Sharmasarkar et al. \(2000\)](#) and [Shen \(2002a\)](#) showed that the size of the pillaring organic cation determines the amount of each NOC adsorbed and also the selectivity for adsorption. In each of these studies, uptake of each particular NOC increases to a maximum, and then decreases, as the size of the QAC increases. A variety of aromatic organic cations that are otherwise similar in structure to TMPA are compared to one another and to TMPA as modifiers of hectorite for their efficiency in taking up a mixture of BTEX compounds ([Jaynes and Vance, 1999](#)). Hectorites reacted with the largest cations, and also a highly hydrated cation, are poor adsorbents of BTEX. Furthermore, such adsorption as occurred on these three derivatives occurs by partition, while adsorption prevails with the smaller and/or less strongly hydrated cations tested. Nonetheless, selectivity of adsorption may not depend on the size of the QAC alone. Furthermore, it is the interaction between adsorbent and adsorbate that governs uptake. [Nzengung et al. \(1996\)](#) compared the relative efficiencies of derivatives with TMA and TMPA for the uptake of naphthalene (having two aromatic rings) and diuron with a branched structure on the side of an aromatic ring. Naphthalene uptake is considerably greater on TMPA-clay than on TMA-clay. By contrast, diuron is taken up strongly by clay modified with either TMPA or TMA. In comparing the adsorption of phenols by derivatives of bentonite with TMA and TMPA, [Ceyhan et al. \(1999\)](#) observed that selectivities of adsorption varies with the pillaring QAC, suggesting that the energy of interaction between QAC and NOC affects uptake. [Kukkadapu and Boyd \(1995\)](#) compared the uptake of NOCs by smectite modified by TMA and that with its phosphorus analogue, trimethylphosphonium (TMP). Derivatives with the relatively small TMA cation are more effective adsorbents in the absence of water, while those with TMP are more effective in aqueous solutions. As TMP is less extensively hydrated than TMA, water associated with the organic pillars decreases the area of siloxane surface available for uptake. However, [Sheng and Boyd's \(1998\)](#) study of the effectiveness of only partially exchanged organo-smectites shows that uptake of NOCs actually decreases from a maximum with further addition of the QAC. This would indicate that the space available for NOCs tends to diminish with increasing occupancy of the surface by QAC.

J. Nature of Exchangeable Cations and the Incorporation of Long-Chain QACs into Clays

In the case of derivatives with long-chain QACs, increasing the organic cation content leads to an increasingly hydrophobic material ([Boyd et al., 1988b](#)). The nature of the inorganic cations originally occupying exchange sites affects the way that long-chain QACs are incorporated into expansible clays. Introduction of HDTMA

into a dispersed Na^+ -smectite leads to mixing of Na^+ and HDTMA cations in each layer. On the other hand, a non-dispersed Ca^{2+} -clay produces segregation of inorganic and organic cations into separate layers (Xu and Boyd, 1995b, 1995c). The nature of the exchangeable inorganic cations also influences the rate of uptake of HDTMA into smectite at low concentrations of the organic cation; Na^+ enhances uptake, but there is no effect on the final amount of HDTMA adsorbed (Xu and Boyd, 1995a, 1995b, 1995c).

K. Effect of Amount of Organic Cation on Uptake of NOCs by Long-Chain QAC-Clays

For derivatives with long-chain QACs, the uptake of NOCs, by partitioning into the interlayer organic phase, increases as the extent of that phase increases. This effect may be achieved by increasing the amount of a particular QAC taken up (Boyd et al., 1988b), using high-charge clay minerals (Jaynes and Boyd, 1991a), or increasing the length of the hydrocarbon chain of the QAC (Cowan and White, 1962; Jaynes and Vance, 1996). In expansive clays (smectites and vermiculites), the packing and orientation of the large QACs in the interlayer spaces change with the layer charge on the clay mineral so as to accommodate the amount of organic cation needed to satisfy the CEC of the mineral (Lagaly and Weiss, 1969; Slade et al., 1978; Slade and Gates, 2003, 2004). These changes are reflected by the basal spacings of the organo-clays. In general, the intercalated organic cations tend to maximise their contact with the silicate surface, and hence the basal spacing increases as more QAC cations are accommodated in the interlayer regions (Xu et al., 1997). Thus, while QACs such as HDTMA may intercalate as a monolayer (basal spacing = 1.37 nm) in low-charge smectites, increases in layer charge see their arrangement change to a bilayer (spacing = 1.77 nm), and then a pseudotrimolecular layer (spacing = 2.17 nm) (Lagaly and Weiss, 1969; Jaynes and Boyd, 1991a). When the layer charge further increases, long-chain QACs form paraffin-like arrangements, comprising tightly packed layers inclined at a high angle to the interlayer surface with each QAC lying parallel to one another (spacing > 2.2 nm). Fig. 11.1.6 shows a schematic representation of the different packing and orientation of long-chain QACs in the interlayer spaces of expandible clay minerals.

L. Size of Organic Cation and Uptake of NOCs by Long-Chain QAC-Clays

Cowan and White (1962) showed that increases in the number of C atoms in the QAC tend to lead to increased uptake of a given NOC by the resulting clay derivative, up to a point at which the number of C atoms is so large as to decrease the amount of the QAC that is adsorbed by the clay. Following on Cowan and White (1962), Jaynes and Vance (1996) made derivatives from different expandible clay minerals with each of 5 QACs containing C atoms/molecule in the range from 15 (cyclododecyl trimethylammonium, CDTMA, molecular weight (Mw) = 226 and

dodecyl trimethylammonium, DTMA, $M_w = 228$) to 38 (dioctadecyl trimethylammonium, DODMA, $M_w = 551$). There was a general increase in uptake of BTEX hydrocarbons as the C content of the QAC increased. However, comparison of CDTMA and DTMA showed that the former QAC, having straight-chain alkyl groups, was much more effective in taking up BTEX than the latter, containing cyclic groups with the same number of C atoms and almost identical M_w . The derivative with QAC of $M_w = 383$ (didodecyl dimethylammonium, DDDMA, 26 C atoms/molecule) was the most efficient adsorbent for BTEX molecules, while the derivative with the largest QAC (DODMA) was less efficient.

M. Co-adsorption and Uptake of NOCs by Long-Chain QAC-Clays

Jaynes and Vance (1996) also showed that NOCs, after adsorption, can increase the capacity of the organic phase for further molecules. In particular, they observe that the adsorption of individual BTEX components (from a mixture of BTEX compounds) is enhanced relative to that from solutions of the pure component. This process of co-adsorption, by which one or more NOCs generally produce a synergistic effect on the uptake of others, gives rise to an isotherm that curves upwards from a straight line. Similarly, Sheng et al. (1996a) reported that nitrobenzene and, to a lesser extent, carbon tetrachloride, enhance uptake of trichloroethylene (TCE) by an HDTMA-smectite. Likewise, chlorobenzene enhances the uptake of TCE and dichlorobenzenes (Sheng et al., 1996b; Sheng and Boyd, 2000), while Gao et al. (2001) found that the uptake of chlorobenzene by an HDTMA-soil is enhanced by the presence of nitrobenzene. Co-adsorption may be employed to increase uptake of NOCs generally, or else to encourage the uptake of particular NOCs (Jaynes and Vance, 1996). The adsorption of an organic compound can even enhance its own uptake. Isotherms for the uptake by HDTMA-clays of aromatic hydrocarbons and chlorohydrocarbons, as well as interlayer swelling shown by X-ray diffraction (XRD), suggested that, especially for high-charge smectites, the rate of uptake of these NOCs with increasing solution concentration is increased as a result of HDTMA solvation (Sheng et al., 1996b). Aromatic molecules, in particular, interact strongly with interlayer HDTMA, because of their planar shape and delocalised π -bonds. As a result, the alkyl chains of HDTMA adopt a more vertical orientation and the basal spacing increases. These changes occur more easily, although not exclusively, with high-charge smectites, creating space for the uptake of more of the aromatic molecules. Where enhancement of adsorption of one NOC by another occurs by co-adsorption, as described above, this may also occur as a result of solvation of the QAC by one of the co-adsorbates. For example, enhanced uptake of TCE in the presence of nitrobenzene (Sheng et al., 1996a) or chlorobenzene (Sheng et al., 1996b) could occur because these aromatic compounds solvate interlayer HDTMA, and thereby promote intercalation of HDTMA. Slade and Gates (2003) found that NOCs replace water on HDTMA, enhancing swelling. Although

carbon tetrachloride enhances the uptake of TCE by HDTMA-smectite this apparently affects only HDTMA located specifically on external surfaces and hence obtains to a lesser extent than for the aromatic benzenes (Sheng et al., 1996b). By way of exception, ethyl ether actually suppresses TCE uptake by the HDTMA-smectite, apparently by decreasing the capacity of HDTMA for TCE (Sheng et al., 1996a).

N. Bonding Modes of Long-Chain QAC in Organo-Clays

Although the bulk of a QAC may be held strongly by the aluminosilicate layer via electrostatic forces, a part of the organic cation may be held by van der Waals attraction (Sheng et al., 1998). One result of this van der Waals bonding is that, while QACs are generally very strongly retained by clay minerals, the fractions that are bound by van der Waals forces may be easily desorbable (Xu and Boyd, 1995a; Xu et al., 1997; Lee and Kim, 2002; Slade and Gates, 2003). These particular fractions usually only develop when the amount added exceeds the CEC of the minerals (Xu and Boyd, 1995a; Xu et al., 1997).

O. Properties of NOCs and their Uptake by Organo-Clays

The factors controlling the relative affinities of different NOCs for organo-clays were also investigated. We have seen earlier that QACs, acting as pillars, promote adsorption of NOCs. However, some NOCs may be prevented from entering the pores within the interlayer spaces because of the size and/or shape of the NOC. Apart from this 'gateway' condition, other factors that affect the affinities of NOCs for organo-clays, in general, include the solubility of the NOCs in the relevant solvent, specific interactions of the organo-clay with the solvent, the C content of the NOC, its structure, especially in relation to that of the QAC on the clay, and its polarity.

According to Street and White (1963), the solubility of NOCs in water has an over-riding influence on the extent of their adsorption by octadecyl trimethylammonium montmorillonite. The dissolved portions of the NOCs with the lowest solubility in water are taken up most completely by the organo-clay. Jaynes and Boyd (1991a) also found an inverse relationship between the solubility in water of eight different aromatic NOCs and their retention by HDTMA derivatives of a vermiculite, an illite, a kaolinite and smectites. These results show that the QAC phase and water compete for uptake of NOCs. In most studies, interest has focussed on uptake from water. However, in recognition that wastes to be controlled by organo-clay liners may contain substantial proportions of organic solvents, Nzungung et al. (1996) studied the uptake of two NOCs from mixed solutions of methanol and water. They found that the organo-clays swelled to different extents in methanol and that swelling enhanced uptake of the NOCs because the interlayer organic phase became both more organophilic and more accessible. In comparing TMPA- and TMA-montmorillonite for their ability to take up two molecules with contrasting aromaticities, Nzungung et al. (1996) suggested that the more aromatic molecule

(naphthalene) is more strongly attracted to TMPA-clay than to TMA-clay because TMPA contains an aromatic group, but not TMA. Similarities between the structures of QAC and NOCs appear to promote the uptake of the latter by clay minerals containing the former. The polarity of NOCs can also influence their uptake by clay minerals containing long-chain QACs (Sheng and Boyd, 2000). Generally, adsorption is enhanced by a high-solute polarity and the effect is most pronounced at large interlayer separations. Sheng and Boyd (2000) demonstrated the effect of polarity by comparing the uptake by HDTMA derivatives of a high- and low-charge smectite and an illite of *o*-, *m*- and *p*-dichlorobenzene (DCB) where the order of polarities was *o*-DCB > *m*-DCB > *p*-DCB. All were intercalated, leading to interlayer expansion, by the high-charge smectite derivative, but only the *o*- and *m*- forms were intercalated by the low-charge smectite derivative, and then only at high concentrations of the compounds. Intercalation led to a double-sigmoid isotherm, indicating two different mechanisms for uptake. The differences could be explained by solvation of HDTMA with the more polar forms, leading to interlayer expansion. This did not happen with the less polar forms, and hence the interlayer spaces were not expanded by these compounds.

P. Mechanisms of Uptake of NOCs by Organo-Clays

It is clear from the foregoing discussion that there are many factors affecting the uptake of different NOCs by derivatives of various clays with the range of QACs. As a result, a variety of mechanisms are involved. Indeed, for many studies these mechanisms cannot be deduced with certainty because of the possible combinations of adsorbate and adsorbent involving an enormous range of NOCs and a considerable range of QACs as well as the many subtleties of composition and structure that can affect clay behaviour. Table 11.1.2 provides a summary of the knowledge and understanding that we gleaned on the likely mechanisms for the uptake of NOCs by organo-clays.

Q. NOC Uptake by Long-Chain QAC-Clays and Organic Matter

Several workers have compared the effectiveness of organo-clays with soil organic matter for the uptake of NOCs. Lee et al. (1989b) showed that modification of two different subsoils, containing mainly vermiculite and illite, by addition of HDTMA, increased the uptake from aqueous solution of individual BTEX compounds by over two orders of magnitude. The relevant coefficients of adsorption for benzene and TCE were 5–10 times higher for HDTMA-smectite than common values obtained with soil organic matter (Boyd et al., 1988b). Smith et al. (1990) determined coefficients for the adsorption of tetrachloromethane (TCM) by a smectite that had been modified by five different long-chain QACs with different chain lengths, and with or without aromatic substituent groups. They found that QACs with 12, 14 and 16 C atoms in their hydrocarbon chain were actually less effective in adsorbing

Table 11.1.2. Summary of factors involved and the mechanisms proposed for the uptake of non-ionic compounds (NOCs) by derivatives of clays with quaternary ammonium cations (QACs)

Type of cation	Short-chain	Long-chain	Key References*
Hydrocarbon C atoms (number)	1–8 [†]	12 or more [†]	Smith et al. (1990) ^{sc} ; Jaynes and Vance (1996) ^{lc}
Influence of amount of QAC on NOC uptake	Increases to maximum, then decreases	Generally increases	Sheng and Boyd (1998) ^{sc} ; Boyd et al. (1988b) ^{lc}
Influence of QAC size on NOC uptake	Uptake decreases with increase in QAC size	Uptake increases with increase in QAC size	Jaynes and Vance (1999) ^{sc} ; Sharmasarkar et al. (2000) ^{sc} ; Jaynes and Vance (1996) ^{lc}
Effect of water on NOC uptake	Tends to decrease uptake	Appears to decrease uptake	Lee et al. (1990) ^{sc} ; Boyd et al. (1988b) ^{lc}
Effect of other NOCs	Competitive—decrease uptake	Most are synergistic—increase uptake	Smith et al. (1990) ^{sc} ; Jaynes and Vance (1996) ^{lc} ; Sheng et al. (1996a) ^{lc}
Influence of clay type	Apparently ineffective with non-expansile clays	Effective with all, most effective with expansible clays	Ceyhan et al. (1999) ^{sc} ; Jaynes and Boyd (1991a) ^{lc}
Influence of higher layer charge on clay	Can decrease uptake, depending on NOC size and shape	Increases uptake	Lee et al. (1990) ^{sc} ; Jaynes and Boyd (1991a) ^{lc}
Effect of NOC properties on uptake	Size and shape critical, to enable NOCs to fit	Enhanced by low solubility; high polarity, and similar groups as on QAC	Lee et al. (1990) ^{sc} ; Nzungu et al. (1996) ^{sc} ; Sheng and Boyd (2000) ^{lc}
Role of QAC	Pillaring between layers in expandible clays	Organophilic phase between layers or on edges	Lee et al. (1989a) ^{sc} ; Mortland et al. (1986) ^{lc}
Mechanism of NOC uptake	Adsorption on to siloxane surface	Partitioning into QAC, with possible solvation	Jaynes and Boyd (1991b) ^{sc} ; Boyd et al. (1988b) ^{lc} ; Sheng et al. (1996a) ^{lc}

*References for short-chain QACs denoted by 'sc', those for long-chain QACs by 'lc'.

[†]Information lacking on QACs with hydrocarbon C from 9 to 12, to our knowledge.

TCM, in relation to percent C content, than was soil organic matter. However, 2 QACs with 12 and 16 C atoms containing an aromatic group could partition TCM as effectively as soil organic matter.

Of course, the usefulness of an organo-clay or a competing adsorbent in a particular situation is ultimately determined by its cost. A competitor that may not be as effective as an adsorbent may be preferred for its relatively low cost. Thus, shales that can adsorb appreciable amounts of two chlorohydrocarbons and a ketone but less than some QAC-bentonites, may be preferred as barrier materials because of their much lower cost (Gullick and Weber, 2001). On the other hand, organo-clays may be preferred over more effective adsorbents because they are cheaper. Activated carbon can adsorb much more benzene than a bentonite modified with either a short-chain QAC, BTEA, or HDTMA (Redding et al., 2002). Nevertheless, the organo-clays may be preferred to activated carbon as barriers for wastes involving organic liquids because organo-clays swell in non-polar liquids, and show low permeability (Gates et al., 2004). In addition, they are less likely to be saturated and 'poisoned' by adsorbates than activated carbon (Alther, 1999).

R. Alternatives to QAC Clay Minerals for Control of NOCs

In order to enhance their capacity for taking up NOCs, clays may be modified ('activated') by other methods besides the simple addition of quaternary ammonium cations (QACs). These include addition of (i) other organic cations; (ii) non-cationic organic materials; and (iii) inorganic (acids) and mixed inorganic/organic materials. Clays can also serve as carriers of catalysts to break down NOCs.

Among other cationic organic compounds that were used are positively charged polyelectrolytes or polycations (Breen and Watson, 1998; Breen, 1999, Churchman, 2002a, 2002b). The effectiveness of polycation-clay complexes in adsorbing NOCs depends on their structure and the degree of loading of the clay (Breen and Watson, 1998; Churchman, 2002b). The advantage of polycations over QACs is likely to be economic and also acceptability for human health, especially when used to help clean potable water. This is because polyelectrolytes such as poly(diallyldimethylammonium) chloride (poly DADMAC), are commonly used as coagulants for potable water treatment (Churchman, 2002b). Other organic cations that may be reacted with clays to enhance their uptake of NOCs include pyridinium ions, which affect clay properties in a similar fashion to QACs (Jaynes and Vance, 1999) and cationic dyes. Among the many cationic dyes in common use are methyl green, acraflavine, thioflavin-T, methylene blue, crystal violet, and rhodamine-B. Borisover et al. (2001) studied the latter two dyes as candidates for the modification of a smectite to enhance NOC uptake from aqueous solutions. The capacity of smectite modified with crystal violet CV or rhodamine-B for the uptake of naphthalene, phenol and the herbicide, atrazine was similar to that of some QAC-smectites. However, the isotherms were non-linear and adsorption was competitive from mixed NOC solutions,

suggesting adsorption rather than partition. This is consistent with the dye molecules forming rigid structures on the clay surface (see Chapter 12.3).

Shen (2001) has described the formation of organo-clays with high C contents using non-ionic surfactants that intercalate into smectite and are held by hydrogen bonding. To our knowledge, however, these materials were not tested for their uptake of NOCs. Cowan and White (1962) have prepared derivatives of clays with tertiary amines that could adsorb phenol to an extent depending on a balance between hydrophilicity and hydrophobicity. Khalil and Abdelhakim (2002) showed that fatty acids can become physically adsorbed by smectites, rendering the minerals organophilic, but tests of the adsorption of NOCs by these materials were apparently not carried out. Churchman and Anderson (2001) took out a patent for the use of the waste products (comprising organic materials mixed with clays and/or acid-activated clays) from food industries as adsorbents for fuel oil.

Acid-activated clays were long used industrially for decolourising or bleaching raw-cooking oils and animal fats to produce acceptable products for edible use (Anderson and Williams, 1962). Acid activation also increased the uptake of gases by smectites, as well as increasing their selectivity for some gases (SO₂ and CO₂) in relation to others (CH₄ and O₂) (Volzone and Ortiga, 2000; Venaruzzo et al., 2002). The capacity and selectivity of even kaolinite for gas adsorption can be improved by acid activation, followed by mechanical and thermal treatments (Churchman and Volzone, 2003). Treatment of smectites with hot concentrated acids greatly increases their surface acidity, surface areas, and volume of meso-pores (2–10 nm), while the materials become more siliceous (Anderson and Williams, 1962). Some naturally acidic clays can decolourise fats and oils, but not to the same extent as acid-activated clays (Theng and Wells, 1995). The decolourisation process involves the adsorption of large, generally polyaromatic, non-polar molecules, and carotenoids, especially β-carotene, but also xanthophylls, chlorophyll, pheophytin, tocopherols and gossypol and their degradation products, as well as phospholipids, soap and trace metals (Sarier and Güler, 1988; Christidis et al., 1997). Acid-activated clays are also used as adsorbents for neutral polyaromatic leuco dyes that become positively charged and coloured on adsorption, and are used in carbonless copying papers. The XRD patterns indicated that adsorption of leuco dyes led to a reordering of the aluminosilicate layers (Fahn and Fenderl, 1983). Acid-activated clays can serve as carriers for fungicides and insecticides, and can be used to regenerate organic fluids for dry cleaning. It seems surprising, therefore, that acid-activated clays are not used more widely as adsorbents for NOCs (Lagaly, 1995).

Modifying clays with hydr(oxides), and subsequent heating, can also provide materials ('pillared clays') with an enhanced capacity for taking-up NOCs. Zielke and Pinnavaia (1988) suggested that PCP was adsorbed on clays pillared with Al₂O₃ (and Cr₂O₃ but to a lesser extent), through direct association with the oxides rather than with the faces or edges of the aluminosilicate layers. The enhanced uptake of PCP by delaminated pillared clays apparently reflects a greater availability of oxide-treated surfaces. The inorganic pillars themselves appear to act as adsorbents for

NOCs whereas the silicate surface appears to be the main adsorbent for NOCs in organically pillared clays. Neither the hydroxy-interlayered nor oxide pillared clays adsorb as much PCP as organo-clays, let alone activated carbon. However, a poly(hydroxo aluminium) smectite was shown to be a powerful adsorbent for polychlorinated dibenzo dioxins (PCDDs) and polychlorinated biphenyls (PCBs) (Srinivasan et al., 1985), and was as effective as activated carbon for binding the more hydrophobic pollutants (Srinivasan and Fogler, 1986a, 1986b). Similarly, Matthes and Kahr (2000) found that Al- and Zr-hydroxy interlayered, and pillared smectites, could completely remove atrazine and chloranilines at ppm levels from water. Of these sorbents, the pillared smectites were more effective than the hydroxy-interlayered minerals and the Zr-pillared smectites were the most effective of all. They suggested that increased acidity of the intercalated species enhances the adsorption of organic bases. Like Zielke and Pinnavaia (1988), Nolan et al. (1989) suggested that the poly(hydroxo aluminium) material adsorbs dioxin through electrostatic forces.

Subsequently, a series of materials has been devised that constitute variations on pillaring, to produce a class of materials generally described as 'inorgano-organo-clays'. Srinivasan and Fogler (1990) produced a material of this kind by adsorbing a cationic surfactant (in particular, cetylpyridinium) on a smectite clay exchanged with polyvalent inorganic cations (either poly(hydroxo aluminium) cations, or La^{3+}). This composite clay mineral can strongly adsorb highly hydrophobic molecules (PCP and benzo(a)pyrene) with the latter apparently being held more strongly than by activated carbon. The partition coefficients for these two essentially insoluble hydrophobic compounds into the inorgano-organo clay were at least two orders of magnitude greater than those for the organo-clay (cetylpyridinium-smectite) itself. A more water-soluble, hence less hydrophobic, compound (3,5-dichlorophenol) is adsorbed by the composite material but is not held any more strongly than by the cetylpyridinium-smectite. Another variant of an inorgano-organo-clay is obtained by incorporating a non-ionic surfactant during the synthesis of pillars in a smectite with aluminium hydroxide, but without calcination to produce oxides (Michot and Pinnavaia, 1991). Incorporation of surfactant around pillars in the interlayer increased the uptake of phenols and chlorinated phenols from aqueous solution. Notably there was much greater uptake of PCP by this material (recyclable by heating) than what Zielke and Pinnavaia (1988) obtained with alumina-pillared smectite. Bouras et al. (2001, 2002) used a similar approach, but with surfactants included in poly(hydroxo iron) smectites, for the removal of PCP from water. A further approach involves the addition to smectites of surfactants, both cationic and non-ionic, together with Si and/or Al in solution forms, followed by calcination, to produce the so-called 'porous clay heterostructures' (Galarneau et al., 1995). Although these materials were generally tailored to produce highly acidic catalysts, their large porosity and surface areas mean that they could be very useful as adsorbents (Zhu et al., 2002a).

Catalysts based on clays can also be used to control pollutants in both gas and aqueous phases, generally by enhancing their decomposition. A common approach

has been through the attachment to clays of titanium dioxide, which is pre-eminent as a catalyst for the photo-oxidation of refractory organic pollutants in water and air. TiO_2 can be incorporated into clays either as a pillar by adding Ti as an acid sol-gel to a smectite with NaOH (Sun et al., 2002), or as solid dispersions with the clay formed by adding a Ti gel to a smectite in the presence of a polyethylene oxide surfactant (Zhu et al., 2002b). The resulting materials are effective catalysts for the photo-degradation of various dyes (Li et al., 2002; Sun et al., 2002; Zhu et al., 2002b) and phenol (Zhu et al., 2005) and also, in association with V_2O_5 , for the reduction of NO by NH_3 (Chae et al., 2001). As an alternative approach, emphasising prevention of pollution rather than its amelioration, Pinnavaia (1995) has suggested that clay minerals, principally smectites, modified by oxide pillaring or by the exchange with QACs, as well as LDH ('anionic clays'), could be used to promote 'green chemistry', a process that achieves complete conversion of reagents to products while avoiding the production of pollutant by-products.

11.1.4. CONTROL OF ANIONS

A. Uptake of Anions by Unmodified Clays

As clay minerals are predominantly negatively charged, they have only a small capacity for taking-up anions. Anion exchange generally occurs on the edges of the aluminosilicate layers and is pH-dependent. The anion exchange capacity (AEC) of clays increases with decreasing pH but its magnitude is never high, being < 5 cmol/kg for smectites (Borchardt, 1989) and apparently not more than 2 cmol/kg for kaolinites (Dixon, 1989). Some anions, notably phosphates, may be adsorbed, at least partially irreversibly, to layer silicates (Dixon, 1989; McLaren and Cameron, 1996). However, layer silicates may be modified to give materials that can take up substantial amounts of anions. Even though these materials tend to have much lower capacities for anions than many LDH, they may offer advantages from the point of view of economics because they can be prepared in situ from clays in soils or sediments, or because they are more stable in particular environments.

B. Anion Uptake by Clays Modified with Organic Cations

The studies by Bors and co-workers (Bors, 1990; Bors and Gorny, 1992; Dultz and Bors, 2000; Riebe et al., 2001) showed that iodide (which, as radioiodide, is a dangerous component of radioactive waste), and also pertechnetate (TcO_4^-) can be adsorbed by clay minerals, particularly smectites, that were modified with long-chain QACs. The adsorption data are consistent with different types of binding of the QAC (generally hexadecylpyridinium, HDPy) for different levels of loading of the clay. The HDPy⁺ cation was dominant, in exchangeable form, at low loadings. At intermediate loadings, the chloride salt (HDPyCl) became associated with the clay

mineral, while micelles were formed at high loadings. This suggests adsorption of the anions occurring by a variety of mechanisms. Nonetheless, caution is advised when interpreting uptake of simple anions by organo-modified clays, as large amounts of organo-salts can remain associated with the intercalate in aqueous solutions (Slade et al., 1978; Lee and Kim, 2002; Slade and Gates, 2003, 2004) (also see Section 11.1.3.D).

Li (1999) has shown that addition of HDTMA, in amounts sufficient to satisfy the plateau for adsorption, to a kaolinite, an illite and a smectite, enabled the uptake of chromate and nitrate anions from aqueous solutions. Krishna et al. (2001) showed that the adsorption of chromate by HDTMA-clays, which included montmorillonite, pillared montmorillonite, and kaolinite, was strongly dependent upon pH, the amount adsorbed decreasing from pH 1 to ~ 8 , when it became negligible. This reflected the form of chromium in solution.

Undoubtedly, the development of positively charged areas on the clay is a prime requirement for the uptake of anions. Xu and Boyd (1995b) showed that the electrophoretic mobility of a Na^+ -smectite, treated with HDTMA, changed abruptly from negative to positive as the CEC of the clay was exceeded. Since electrophoretic mobility reflects the charge on the external surfaces little, if any, of the QAC was found on these surfaces until the amount that satisfied the layer charge (CEC) was intercalated. Changes in zeta potential also occur as cationic polymers are added to clays. However, these appear to be more complex than shown by Xu and Boyd (1995b) for the addition of HDTMA to clay. Instead, a gradual decrease in the magnitude of the negative zeta potential occurs prior to the point at which a more abrupt change occurs to a positive value (Billingham et al., 1997; Churchman, 2002b) (Fig. 11.1.7). This reflects the adsorption of some polycation to external sites, as well as their incorporation into interlayer spaces, even at low concentrations of polyelectrolyte. Ueda and Harada (1968) found that the AEC of the product gradually increased while its CEC decreased as polycation was added to a smectite. They attributed the origin of the AEC to the loops and tails on the adsorbed cationic polymer. These extended away from the clay mineral surface while the trains of the polymer were held close to the surface. As the surface coverage of the polymer increased, the proportion of its loops and tails, the segments for anion uptake, increased relative to its train segments. Similarly, Kleinig et al. (2003) reported that more phosphate was adsorbed (at comparable concentrations) on a smectite when it was complexed with poly DADMAC of high-molecular weight than of one with low-molecular weight. They explained the difference by the higher proportions of loops on the high-molecular weight variant of the polycation. From an electrostatic interaction viewpoint, the mechanism by which associated polycations can enable clays to adsorb anions is thought to involve positive patches that are formed on clay surfaces because the centres of positive charge on the polycations are closer together than the centres of negative charge on the clays, so localities of excess positive charge develop (Durand-Piana et al., 1987; Denoyel et al., 1990; Breen and Watson, 1998). It seems probable that positively charged areas occur alongside negatively charged

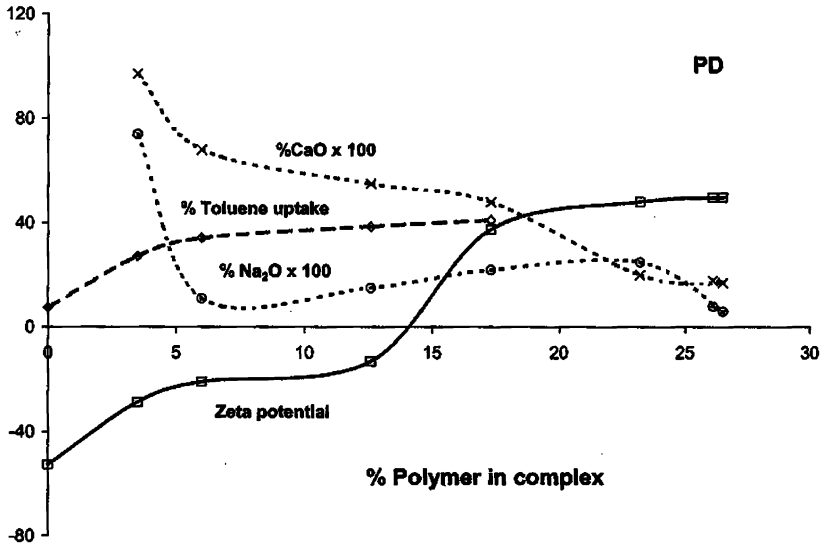


Fig. 11.1.7. Zeta potential, percentage removal of toluene from solution and percentages of both Ca^{2+} and Na^+ , expressed as oxide (and multiplied by 100), plotted simultaneously against changes in the actual percentage of the polymer (polydiallyldimethylammonium chloride; poly DADMAM) in the polymer-smectite. From Churchman (2002b).

areas, so that adsorption of anions and of cations can occur together, as shown by Ueda and Harada (1968). For clays modified with long-chain QACs (Dultz and Bors, 2000; Riebe et al., 2001) as for polycation-modified clays (Billingham et al., 1997; Churchman, 2002b), exchangeable inorganic cations can remain while the net charge of the clay derivative has reversed and the material has become an adsorbent for anions.

C. Alternative Methods of Modifying Clays for Anion Adsorption

Clays that are pillared with inorganic hydroxy cations can promote the adsorption of anions. Polubesova et al. (2000) demonstrated the effectiveness of hydroxy-Al pillared clay for the uptake of an anionic herbicide, sulfometron, as well as of sulphate, acetate, and chloride. They suggested that the association between the anions and the pillars was electrostatic. In a later paper, these authors compared a poly(hydroxo aluminium) pillared smectite and a positively charged derivative of the smectite with crystal violet (CV) for their relative abilities as adsorbents of the herbicide imazaquin, which is anionic under the experimental conditions used. Both materials are similarly effective, but desorption and also displacement by other anions are more difficult from the clay-CV derivative than from the pillared clay (Polubesova et al., 2002). Bouras et al.

(2002) showed that an inorgano-organo clay prepared from a smectite by the co-adsorption of the cationic surfactant hexadecyltrimethylammonium (i.e., HDTMA) chloride and poly(hydroxo titanium) cations can decolourise a solution containing the anionic textile dye, sulfacid brilliant pink.

11.1.5. CONTROL OF TURBIDITY AND RESIDUAL TREATMENT CHEMICALS

A. Control of Turbidity in Water Treatment

The addition of clays, and particularly bentonite (i.e., smectite, as mined), as an aid to flocculation/coagulation during the treatment of water or wastewater is a well-established technology. Its historical use in the Sudan to clean pathogenic organisms from river water has already been observed. Bentonite was included, along with the soluble cationic polymeric flocculant, ferric chloride, and aluminium sulphate (alum) for use in a water filtration plant planned for Los Angeles (McBride et al., 1982). Bentonite can reduce the need for soluble flocculants by 1.5–2 times and has the added advantage of being non-toxic (Akhundov et al., 1983). It can also give a greater reduction of phosphate in water, when used in conjunction with aluminium sulphate, than either aluminium sulphate alone or calcium hydroxide (Jorgensen et al., 1973).

Dissolved NOM is one of the major causes of turbidity in drinking water. It is also a pollutant insofar as it produces poisonous trihalomethanes upon chlorination. Coagulation with cationic electrolytes can remove NOM but only partially unless suspended solids are present (Bolto et al., 2001). Apparently solids are required to adsorb NOM, with the solid-NOM combination being flocculated by the added polycation. Bolto et al. (2001) found that a high-surface area kaolinite, ball clay, was more effective than smectites for aiding NOM removal, while illite and palygorskite were also more effective than smectites for removing NOM. The superiority of kaolinite is consistent with its stronger affinity for humic acid as compared with smectite, and reflects the aluminous and less hydrated surface of kaolinite (Parazak et al., 1988). Curiously, bentonite is also used in a completely contrasting process proposed for the treatment of highly turbid waters, this time as a flotation aid with (QAC) surfactants (Grieves, 1967). Bentonite is also useful for removing mercury from water in treatment (Logsdon and Symons, 1973; Hatch, 1975) where it acts as an adsorbent that is itself coagulated with alum, ferric sulphate, or a polyelectrolyte.

B. Control of Turbidity in Wastewater Treatment

Clays, especially bentonite, proved to be particularly useful as flocculation aids in the treatment of effluent from pulp and paper mills. Additions of bentonite effected the removal from these effluents of starch (Gillespie et al., 1970), ammonium-base spent

sulphite liquor (Scherler, 1972), basic dyes (Mobius and Gunther, 1974), and colour and fines generally (Potskhersvili et al., 1977; Ciba-Geigy, 1978; Delaine, 1978), in processes that also involve coagulating agents such as alum, polymers, sulphuric acid and/or lime, usually in combinations. The bentonite could serve the dual roles of adsorbent and nucleation solid for flocculation in these processes. Dilek and Bese (2001) found that colour removal efficiency was improved over that from using alum alone when sepiolites, and Ca^{2+} - or Na^{+} -bentonites were added to wastewaters along with alum, as were the settling characteristics of the sludge produced. Compared with virgin Na^{+} -bentonite, acid-activated bentonite greatly improved the sludge settling characteristics.

Clays can also be used as flocculant/coagulant aids in some treatments of sewage designed to reduce their biological oxygen demand, principally by the removal of protein (Holo et al., 1973; Ogedenge, 1976). Treatment of acid-cracked waste liquor from wool scouring can also be assisted by the addition of bentonite to aid flocculation (Heisey, 1975, 1977). Many different clays were more effective than either alum, polyaluminium chloride and 4 organic flocculants for the removal by flocculation of red-tide and brown-tide organisms (Sengco et al., 2001).

C. Control of Residual Treatment Chemicals

Clays may further act as scavengers for chemicals used in certain wastewater treatments in order to remove these after the treatment is complete. For example, the presence of surfactants in water, whether cationic or non-ionic, and also polyelectrolytes, can result in the poisoning of marine organisms as many of these organic molecules are very toxic. However, addition of bentonite can remove both surfactants (Cary et al., 1987) and polyelectrolytes (Carberry et al., 1977) by adsorption (see Section 11.1.3.R). In some cases, treatment of sewage to remove pathogenic organisms is aided by dye-sensitisers, such as methylene blue. After treatment, bentonite can be added to adsorb the excess dye (Acher and Juven, 1977; Acher and Rosenthal, 1977).

11.1.6. CONCLUDING REMARKS AND FUTURE PROSPECTS

The use, and enhancement of the utility, of clays, for the control of each of the different classes of pollutants has reached its own particular stage of maturity or development. This point will be discussed, along with research which shows promise for new targets for the environmental use of clays and also for overcoming some of the problems raised in their environmental applications to date.

A. Heavy Metal Ions and Simple Cations

Clays provide an in situ, or low-cost method of attenuating and/or immobilising heavy metal ions. Although their applicability was established decades ago, our

understanding of the mechanisms involved in the uptake of different heavy metal cations by clays is still incomplete. Modern, sophisticated surface analytical techniques are poised to greatly aid our understanding of the clay–heavy metal ion interaction. Even so, enough work has been done on various modification methods for the enhancement of heavy metal ion uptake to suggest that organic complexation as well as hydroxyl interlayering and pillaring can improve the adsorption capacity of clays for metal cations in general.

B. Organic and Biological Cations

There has been interest for many years in the interactions of clays with both permanently charged organic cations and amphoteric molecules that are positively charged under ambient conditions. There is now enough knowledge to provide the basis for the use of clays as low cost, non-toxic adsorbents for the removal of waste proteins, biological toxins, antibiotics, and biological entities such as viruses, from water.

C. Non-Ionic Organic Molecules

The late 1980s and the 1990s saw an explosion of scientific interest in the use of clays, and particularly organically modified clays, for the control of NOCs in the environment. Most of the research on this topic has concentrated on modifying clay minerals by exchange and intercalation of a few quaternary ammonium cations in order to exploit their large surfaces as organophilic adsorbents. Much is now known about the procedures involved, enabling organo-clays to be put to relevant environmental uses, such as water clean-up, in barriers, and for the prevention of leaching of contaminants to groundwater and sensitive surface water bodies. The procedure for producing organophilic clays *in situ* through the addition of an appropriate cation that is available as a surfactant or coagulant is particularly useful for the modification of soils for environmental protection.

As people become more sensitive to the probable toxicity of chemicals in everyday use, the protective use of appropriately treated clays on a personal, household, workplace or even vehicle scale may increase. There may be particular opportunities to extend the use of modified clays for the control of gas-phase pollutants and also to expand the scope of these. There may also be opportunities for cross- and interdisciplinary work, in which organic chemists and even biochemists associate with clay mineralogists in testing a wide range of organic and biological cations for modifying and tailoring clays for environmental protection and remediation. Cost will almost always remain a decisive factor influencing the use of modified clays and clay minerals. Further, public sensitivities to the use of synthetic chemicals, even when they are bound by clay, could force a re-think of the conventional approach to organo-clays. For these reasons, research that is aimed to re-use clay-based wastes may become particularly valuable. For example, spent bleaching earths constitute a

waste that is rich in clays. Although such clays are altered, their activation can actually enhance their adsorption qualities, as also may their association with organic compounds from the oil-bleaching process. It is an abundant waste material as the edible oil industry world-wide uses almost 1 million tonnes of clays annually (Crossley, 2001). Pollard et al. (1992) showed that spent bleaching earth could be chemically activated to produce a char that adsorbs phenols from water, while Tsai et al. (2002) demonstrated how this waste material could be activated by controlled heating to produce a mesoporous material that can adsorb paraquat.

D. Anions

It has long been known that the charge on clays can be reversed in sign by appropriate organic modification. However, the implications of charge reversal for the uptake and possible immobilisation of anions were hardly explored. Yet anions, in run-off and leaching water following the application of fertilizers and some pesticides, and also as dyes (e.g., in wool processing), are common environmental contaminants. Although positively charged organo- and polymer-clays may not be competitive with LDH in terms of their anion uptake capacity, the ability to produce such clays in situ means that they may have a cost advantage over LDH. Their main rivals among natural materials are hydr(oxides) particularly of ferric iron, as these are positively charged in weakly acidic environments such as those of natural waters. However, organo- and polymer-clays are likely to be more stable than either LDH in acidic environments, or ferric hydr(oxides) in reductive environments.

E. Turbidity and Use of Colloidal Characteristics

The well-established use of clays as flocculation aids offers prospects for future environmental uses because of the colloidal properties of certain clays. Recent work has shown that these properties may be exploited in such diverse applications as reducing fouling by oil of ultrafiltration membranes used to clean up wastewater from car washes (Panpanit and Visvanathan, 2001). Bentonite is effective in this application partly because it promotes aggregate formation, thereby enhancing the flux. This characteristic of bentonites can also be used in newspaper recycling to avoid ink speck formation (Philippakopoulou et al., 2002).

F. Exploitation of Mixtures of Properties

Organo-clays can be both hydrophilic and organophilic at the same time. They can therefore be tailored to retain some CEC while organic contaminants can be adsorbed on organophilic sites, as already discussed. Furthermore, the usefulness of organo-clays can be enhanced if their interaction with contaminants involves more than one useful characteristic of the clay derivative. For example, phenol could be removed from water through the application of a short-chain surfactant cation

(benzyltrimethylammonium) to the contaminated water containing pre-dispersed bentonite to bring about flocculation of the bentonite on complex formation through cation exchange (Shen, 2002b). Phenol may then be removed by a combination of adsorption and flocculation.

G. Waste Removal and Disposal

Flocculation enables the pollutant, associated with the adsorbent, to be separated from water. However, since the clay materials often remain in suspension, the contaminant may be immobilised but is not removed from the system. In this case, other means of withdrawing the dispersed phase from the liquid phase need to be devised. Oliveira et al. (2003) proposed the use of magnetic clay–iron oxide composites for this purpose. These synthetic adsorbents are re-usable as Taylor and Churchman (1998) showed for magnetised alumina. Adsorbed contaminants may be degraded by microorganisms, as already discussed. However, if the adsorbed contaminants are not bioavailable, recalcitrant, or highly toxic, their leaching may be prevented through solidification in cements. This seems feasible in the case of clay minerals modified with quaternary ammonium ions (Montgomery et al., 1988; Lo, 1996; Cioffi et al., 2001b), whereas free organic matter in cements generally causes difficulties with hardening and strength.

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