Chapter 1

INTRODUCTION

1.1 Clays and Clay minerals

The term "Clay" is applied to materials having a particle size of < 2μm and also to the family of minerals that has similar chemical compositions and common crystal structural characteristics [Velde 1995]. Clays may be composed of mixtures of finer grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides.

The clay minerals constitute nearly 40% of the minerals in sedimentary rocks of the crust of the earth. Half of these minerals belong to a single species illite. The other half consists of montmorillonite, chlorite and mixed layer chlorite-montmorillonite, kaolinite, septachlorite, attapulgite and sepiolite in the order of relative abundance. Clays and clay minerals are found mainly on or near the surface of the earth.

Clay is defined as an aggregate of minerals and of colloidal substances [Grim, 1962]. Usually the term clay is used in reference to material that becomes plastic when mixed with a small amount of water [Klein and Hurlbut, 1995]. Depending on the physical and refractory properties, the clays are classified into seven different types [Krishnaswamy, 1972]:

1
(i) Pottery Clay is most common form found in all places in black alluvium in river beds and banks, and is used for making pottery.

(ii) China Clay or Kaolin is a product of decomposition of feldspars in granites. This clay creates a colloidal suspension in water with high degree of dispersion.

(iii) Fire-Clay is capable of withstanding very high temperature and is used for making furnaces, etc.

(iv) Lithomarge is a type of residual clay formed in a tropical climate with a poor capability for suspension in water.

(v) Ballclay is highly plastic clay with refractory properties.

(vi) Fuller’s earth has natural bleaching properties and is normally used for removing oil and grease.

(vii) Bentonite is plastic clay of volcanic origin and is made up essentially with the clay mineral montmorillonite. This clay is used in drilling mud in the petroleum industry.

The clay minerals are hydrous aluminosilicates containing a variety of metal ions such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe³⁺, etc. Every clay may contain a number of different clay minerals, the exception being Bentonite, which is predominantly rich in a single clay mineral, montmorillonite. Non-clay minerals like quartz, calcite, feldspar, pyrite, etc., can also be present in the clays. Organic matter in the form of discrete wood particles, leaves, spores, etc., as well as surface absorbed molecules are often present in the clays. Soluble salts and exchangeable ions are also entrapped in clays. Clay minerals, non-clay minerals, organic matter, salts and exchangeable ions present in the clay therefore govern the clay properties.
1.2 **Structural Chemistry of the clay minerals**

The clay minerals have definite crystal structures with the primary constituents Si, Al, O and OH. These primary constituents and a number of other associated cations are arranged in two dimensional structures, which are known as sheets. One of these sheets is a tetrahedral one, while the other is octahedral. The two types of sheets have the following characteristics:

(i) **Tetrahedral Sheet**

This sheet has the general composition $T_2O_5$ where $T$ is a tetrahedral cation, mainly Si but may be also Al or Fe. The basic unit is a tetrahedron with four O atoms at the corners and the Si atom at the centre. The tetrahedrons are connected by sharing of three corners i.e. the three basal O-atoms between two adjacent tetrahedrons. This constitutes a hexagonal network. The fourth O-atom known as the apical-O remains normal to the sheet.

(ii) **Octahedral Sheet**

This sheet consists of a basic unit with an approximately regular octahedral structure. The eight corners of the octahedron are occupied by O-atoms or OH-groups while the octahedral centers are occupied by relatively smaller cations like Mg$^{2+}$, Al$^{3+}$, Fe$^{3+}$, etc. In some clay minerals, the octahedral cation can be Li, Ti, V, Cr, Mn, Co, Ni, Cu and...
Zn. Sharing of oxygen mutually links the octahedrons. The smallest structural unit of the octahedral sheet consists of three octahedrons. If octahedral cations occupy the centers of all the three octahedrons, the sheet is known as trioctahedral sheet. In some clay minerals, only two of the three octahedrons are occupied and in such cases the sheet is called dioctahedral.

The octahedra of the octahedral sheet are linked to the tetrahedral sheet by sharing of the apical-O of the tetrahedrons. In short the apical-O shared by the tetrahedral and the octahedral sheets constitute the plane of junction between the two sheets. The OH-groups of the octahedral sheet also position themselves in this plane of junction with the apical-O atoms but the tetrahedral sheet does not share them. The OH-groups are located at the center of the hexagonal arrangement of the apical-O atoms of the tetrahedral sheet.

The basic octahedral and tetrahedral units and the octahedral and tetrahedral layer structures are depicted in Fig.1.1.

Two types of clay minerals are recognized from the point of view of structure, namely 2-layered and 3-layered. The 2-layered minerals have one tetrahedral layer and one octahedral layer as the repeating unit and the structure can be denoted as – (TO) – (TO) – (TO) –. Kaolinite is a 2-layered clay mineral. On the other hand, clay minerals like montmorillonite and illite have 3-layered structure where the repeating unit is tetrahedral layer followed by octahedral layer followed by tetrahedral layer. Thus, the structural identity of the three layered clay minerals can be depicted through the scheme.
Fig. 1.1 Basic tetrahedral (top) and octahedral (below) structural units and the layer structures of clay minerals [small black and small white circles in the figures at the top represent tetrahedral Si atoms, large white circles represent O atoms in the figures at the top and both O atoms and OH groups in the figures below, large black circles represent octahedral Al atoms in the figures below].
These stacking patterns of the two types of clay minerals as well as other structural features were established over the years by a number of workers [Pauling 1930, Gruner 1932, Brindley et al., 1946, 1961, Bailey 1980, 1988, Grim 1988, Moore and Reynolds 1989]. It has also been established that in the 3-layered clay minerals the two tetrahedral sheets have inverted disposition so that the apical-O atoms of both the sheets face towards the octahedral sheet and are shared.

The space between two layers in a clay mineral is known as the interlayer space. If each layer is electrically neutral, i.e. the charge of the cations are fully neutralized by an adequate number of O-anions or OH-anions, the interlayer space need not contain any chemical species. However, if the layers are not electrically neutral, the interlayer space contains suitable number of additional ions necessary to neutralize the excess charge of the layers. Thus, in many clay minerals, the layers are found to have an excess negative charge and therefore, interlayer cations such as K⁺, Na⁺, Mg²⁺, Ca²⁺, or their hydrated species exist making the clay mineral neutral as a whole. Layer charge may occur due to

(i) Substitution of Si⁴⁺ in tetrahedral position by trivalent (e.g. Al³⁺) or bivalent (e.g. Mg²⁺) cations,
(ii) Substitution of Al³⁺ or Mg²⁺ in octahedral positions by bivalent (e.g. Mg²⁺) or monovalent (e.g. Li⁺) cations,
(iii) Vacancies in the octahedral positions, and
(iv) Dehydroxylation of OH to O [Bailey 1988].
The specific chemical formula unit of a clay mineral is computed on the basis of a unit structure composed of a layer and the interlayer cations. It is found that the unit structure has thickness between 7 – 18 Å for various clay minerals and the basal spacing between two successive units is 7 Å for the 1:1 type, 10 Å for the 2:1 type and 14 Å for 2:1:1 type. The unit structures for a few common clay minerals is shown in Fig. 1.2(a) and (b).

1.3. Clay mineral classification

Depending on the layer type, layer charge and interlayer cations, the clay minerals are divided into eight major groups [Warshaw and Roy 1961, Bailey 1980]. These can again be subdivided on the basis of dioctahedral or trioctahedral sheets and also on the basis of chemical composition or the way in which the individual layers and interlayers superimpose on each other. The general classification is shown in Table 1.1 [Bailey 1980, Baruah 1998]. Besides the above classification there are many other clay minerals which result from mixing of two or more different clay mineral structures. These are called mixed layer clay minerals [Weaver 1956]. One familiar example is rectorite, which has a mixed layer structure of muscovite mica and montmorillonite [Reynolds 1980].

1.4 Structure of kaolinite

Since the present work was carried out on locally available Kaolinite, the structural features of this clay mineral need special attention. The outline of the Kaolinite structure was first proposed by Pauling [1930] and was later developed by successive workers.
Fig. 1.2 (a) Unit structure of Kaolinite (top) and Chlorite (below).
Fig. 1.2 (b) Unit structure of Pyrophyllite (top) and Muscovite (below).
Table 1.1. General Classification of the Clay Minerals

<table>
<thead>
<tr>
<th>Layer type</th>
<th>Group</th>
<th>Sub-group</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>Kaoline serpentine</td>
<td>Serpentines</td>
<td>Chrysolite, Antigorite, Lizardite, etc.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kaolins</td>
<td>Kaolinite, Dickite, Naercite</td>
</tr>
<tr>
<td></td>
<td>Pyrophyllite-talc</td>
<td>Talcs</td>
<td>Tale</td>
</tr>
<tr>
<td></td>
<td>(x-0)</td>
<td>Pyrophyllites</td>
<td>Pyrophyllite</td>
</tr>
<tr>
<td></td>
<td>Smectite</td>
<td>Dioctahedral</td>
<td>Montmorillonite, Beidellite, Nontronite</td>
</tr>
<tr>
<td></td>
<td>(x-0.2-0.6)</td>
<td>Trioctahedral</td>
<td>Saponite, Hectorite, Sauconite, Stevensite</td>
</tr>
<tr>
<td>2:1</td>
<td>Vermiculites</td>
<td>Dioctahedral</td>
<td>Dioctahedral vermiculite</td>
</tr>
<tr>
<td></td>
<td>(x-0.6-0.9)</td>
<td>Trioctahedral</td>
<td>Trioctahedral vermiculite</td>
</tr>
<tr>
<td></td>
<td>Mica</td>
<td>Dioctahedral</td>
<td>Muscovite, Paragonite, Illite, Glauconite</td>
</tr>
<tr>
<td></td>
<td>(x-1.0)</td>
<td>Trioctahedral</td>
<td>Phlogopite, Biotile, Lepidolite, (Illite)</td>
</tr>
<tr>
<td></td>
<td>Brittle mica</td>
<td>Dioctahedral</td>
<td>Margarite</td>
</tr>
<tr>
<td></td>
<td>(x-2.0)</td>
<td>Trioctahedral</td>
<td>Clinotonite</td>
</tr>
<tr>
<td>2:1:1</td>
<td>Chlorite</td>
<td>Dioctahedral</td>
<td>Donbassite</td>
</tr>
<tr>
<td></td>
<td>(x variable)</td>
<td>Trioctahedral</td>
<td>Chlorite, Clinchlore, Chamosite, Nimite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Di, Trioctahedral</td>
<td>Cookeite, Sudoite</td>
</tr>
<tr>
<td>2:1</td>
<td>Polygorskites</td>
<td>Polygorskites</td>
<td>Polygorskite</td>
</tr>
<tr>
<td></td>
<td>inverted ribbons</td>
<td>Sepiolites</td>
<td>Sepiolite, Xyloite</td>
</tr>
<tr>
<td></td>
<td>(fibrous clays)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(x variable)</td>
<td></td>
<td></td>
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</tbody>
</table>

x = Layer charge per formula unit. x refers to an $O_{10} (OH)_{2}$ formula unit for smectite, vermiculite, mica and brittle mica.
Kaolinite is a 1:1 layered silicate with a tetrahedral Si$_2$O$_5$ sheet and an octahedral sheet with Al$^{3+}$ as the octahedral cation. The tetrahedral sheet is inverted over the octahedral sheet such that the apical-O atoms of the tetrahedral sheet are shared by the octahedral sheet. This is shown in Fig 1.3. The shared layer consists of 2/3rds of O-atom shared by the tetrahedral Si$^{4+}$ and octahedral Al$^{3+}$ ions. The remaining 1/3rd consists of OH-groups coordinated to the octahedral Al$^{3+}$ ions, which are not shared by the tetrahedral sheet. About 1/3rd of the octahedral sites are vacant. The octahedral Al$^{3+}$ cations are placed in such a way that any two Al$^{3+}$ cations are separated from one another by two OH-group, one above and one below. The OH-groups are positioned at the centers of O-hexagons of the basal plane of the tetrahedral layer [Theng 1979]. This is illustrated in Fig 1.4.

In Kaolinite, the charge in each layer is completely balanced and therefore no interlayer ions are necessary for charge balance. However, in some samples of Kaolinite, substitution of octahedral Al$^{3+}$ with Fe$^{2+}$ and/or Ti$^{4+}$ has been reported [Grim 1962, Deer et al. 1985].

The structural formula of Kaolinite is given as Al$_3$Si$_4$O$_{10}$(OH)$_8$ with an average composition of 46.5% SiO$_2$, 39.5% Al$_2$O$_3$, and 14% H$_2$O [Klein and Hurlbut 1985]. Successive layers in Kaolinite are superimposed on each other in a way such that the O-atoms at the base of one layer form pairs with OH-groups at the top of the other layer.
Fig. 1.3 The layer structure of Kaolinite [large white circles represent O atoms, large shaded circles OH groups, large black circles Al atoms, and small black and white circles Si atoms].
Fig. 1.4 Basal plane of the tetrahedral layer of Kaolinite [large circles represent O atoms in the figure at the top. The apical O atoms form a hexagon (bottom figure) with a OH group at the centre].
This arrangement gives rise to a single layered triclinic cell for kaolinite with the following crystallographic dimensions:

\[ a = 5.15 \text{ Å} \]
\[ b = 8.95 \text{ Å} \]
\[ c = 7.39 \text{ Å} \]
\[ \alpha = 91.8^\circ \]
\[ \beta = 104.8^\circ \]
\[ \gamma = 90^\circ \]

There are a few other clay minerals, which have structures identical to that of Kaolinite. These are Dickite, Nacrite, and Halloysite. Despite belong chemically identical, the stacking pattern of the layers in these minerals is different from that of Kaolinite [Deer et al. 1985]. Dickite has a 2-layered structure, Nacrite has a 6-layered structure and Halloysite has a layer of water molecules between the layers (increasing the interlayer distance to 10 Å in Halloysite compared to 7.2 Å in the others). Further in comparison to Kaolinite, these three minerals are very rare in occurrence [Murray et al. 1977, Sudo and Shimoda 1978, Hanson et al. 1981].

1.5 The characteristics of clay minerals with special reference to Kaolinite

All clay minerals contain some exchangeable cations and anions on their surfaces, held through the process of adsorption. A few common cations and anions found on clay surface are Ca\(^{2+}\), Mg\(^{2+}\), H\(^+\), K\(^+\), NH\(_4^+\), and Na\(^+\), and SO\(_4^{2-}\), Cl\(^-\), PO\(_4^{3-}\), and NO\(_3^-\) in order
of relative abundance. These ions can be exchanged with other ions relatively easily without effecting the clay mineral structure. The cation exchange capacity (CEC) is different for different clay minerals. Thus, montmorillonite has a very high CEC of 80 – 150 milliequivalent/100g and illite has 10 – 40 milliequivalent/100g, whereas Kaolinite has a very low CEC of 3 – 15 milliequivalent/100g [Grim 1968, Brummer and Herms 1983]. Ma and Eggleton [1999] have shown that exchangeable cations occur mostly on the edges and on the basal (OH) surfaces of the mineral and that permanent negative charge from isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ is insignificant. The ability of the clay minerals to exchange cations in Kaolinite is thought to be mainly due to existence of broken bonds along the edges, which gives rise to unbalanced negative charges on which cations are adsorbed. The large CEC of montmorillonite is however attributed to occurrence of unbalanced negative charges in interlayer positions due to substitution of Si$^{4+}$ with Al$^{3+}$ in the tetrahedral positions or substitution of Al$^{3+}$ with Mg$^{2+}$ and other bivalent cations in the octahedral positions. Another factor responsible for cation exchange may be the replacement of H$^+$ of OH-groups on the surface by cations, which can be freely exchanged with others. Such exposed OH-groups occur along the broken edges of clay minerals. Ma and Eggleton [1999] using High Resolution Transmission Electron Microscopy have recently studied defects in the Kaolinite structure.

Another important property of all clay minerals is their ability to retain water molecules inside the pores on the surfaces along the interlayer positions and also around the edges. Such occluded water molecules are easily lost if the clay mineral is kept at 373 – 423 K for some time. The clay minerals also hold a second type of water molecules known as structural water in the form of OH-group. If the clay minerals are heated above 673K,
the structural water is slowly lost through the process of dehydroxylation. However, complete dehydroxylation is impossible because of simultaneous rehydroxylation. If the clay mineral is heated above 1173K, it is found that the structure is completely destroyed [Grim 1962, Burst 1991].

Worrall [1986], Burst [1991] and Vollet et al. [1994] have shown that heating converts Kaolinite to metakaolin through an endothermic dehydroxylation process between 673K and 923K depending on the exact chemical composition and other factors. On further increase in temperature the metakaolinite is converted to Silicon spinel between 923 to 1253 K through an exothermic phase change. On further heating, another phase change occurs at about 1673 K resulting in the formation of ceramics, mullite and cristobalite. The effect of heating Kaolinite can therefore be represented by the following scheme:

\[
\begin{align*}
\text{Kaolinite} & \xrightarrow{\text{Dehydroxylation}} \text{Metakaolinite} \\
\text{Metakaolinite} & \xrightarrow{\text{Phase Change}} \text{Silicon spinel} \\
\text{Pseudo-mullite} & \xrightarrow{\text{Phase Change}} \text{Mullite} \\
\text{Mullite} & \xrightarrow{\text{Phase Change}} \text{Cristobalite} \\
\end{align*}
\]
Naturally occurring clay minerals also contain a large amount of organic matter. Polar organic molecules easily form complexes with clay minerals and it is found that the clay minerals may have an adsorbed organic layer several molecules thick [Grim 1968].

Clay minerals are known to possess some amount of surface acidity. Tanabe [1981] has shown both Bronsted and Lewis type of acidity in clays by various measuring techniques including IR and NMR spectroscopic methods. The Bronsted acidity arises from $\text{H}^+$ ions on the surface, formed by dissociation of water molecules of hydrated exchangeable metal cations on the surface:

$$\text{[M (H}_2\text{O)}_x]\text{]^n+} \rightarrow \text{[M (OH) (H}_2\text{O)}_{x-1}]^{(n-1)+} + \text{H}^+$$

The Bronsted acidity may also arise if there is a net negative charge on the surface due to the substitution of Si$^{4+}$ by Al$^{3+}$ in some of the tetrahedral positions and the resultant charge is balanced by $\text{H}_2\text{O}^-$ cations. The Lewis acidity arises from exposed trivalent cations, mostly Al$^{3+}$ at the edges, or Al$^{3+}$ arising from rupture of Si-O-Al bonds, or through dehydroxylation of some Bronsted acid sites. The Hammet acidity function, $H_0$ has been shown to have values from $-3.0$ to $-5.6$ for natural Kaolinite, $-5.6$ to $-8.2$ for $\text{H}^+$-Kaolinite, $+1.5$ to $-3.0$ for natural montmorillonite, and $-5.6$ to $-8.2$ for $\text{H}^+$-montmorillonite [Narayanan and Deshpande, 1999].

Most of the clays expand when put in a polar solvent. This property is known as swelling. Due to this, interlayer space expands and many large molecules can be accommodated in the interlayer space. This property of the clays has been utilized in catalysis.
The clays can be activated by treatment with a mineral acid. The acid treatment results in replacement of interlayer cations with H\(^+\) and in leaching of Al\(^{3+}\) from the octahedral layers. The dealumination gives rise to mesoporosity in the layers and increases the overall surface area while the H\(^+\) ions enhance acidity. Prolonged acid treatment, however, leads to complete dealumination and conversion of the clay mineral into a silica matrix.

It has already been pointed out that continuous dehydroxylation by heating the clay above 473 K gradually destroys the clay structure. To improve the thermal stability of the clay minerals, the interlayer cations can be exchanged with bulky polyhydroxy cations followed by calcination. This is known as pillaring of the clay. Pillaring results in formation of strong covalent bonds by interaction between the pillaring species and the dehydroxylated OH-groups of the clay layer which in turn enhances the thermal stability up to 1023 K. Further pillaring expands the interlayer space and increases the possibility of larger molecules entering into the interlayer space and interacting in the clay surface. [Narayanan and Deshpande, 1999]. Komori et al. [1999] have shown that kaolinite has a higher intercalation ability for a wider variety of guest molecules than previously thought of, if appropriate intermediates are used. Suitably modified Kaolinite can adsorb Cd\(^{2+}\) and Cu\(^{2+}\) from aqueous solution [Suraj et al. 1998].

1.6 Utilisation of Clay minerals

The plasticity of clays with water has been made use of in manufacturing potteries, earthenwares and other ceramic goods from very early times. Bricks, tiles, porcelain and
various refractory materials are made from clays. The metallurgical industry uses molding sand, made from clay and sand, for casting metals. Kaolinite is used in paper coating, in fillers for paints and plastics, etc.

Clay minerals namely Kaolinite, Smectite, and Polygorskite have found wide use in chemical and other industries [Grim 1968]. Originally the clays were used as catalyst for purification of vegetable oil and also cracking of hydrocarbons. Their use has been discontinued because of the relative ease with which the clay catalysts become deactivated. However, recent works have generated renewed interest in the use of clays as catalysts and adsorbents. Particularly, the mesoporous nature of clay has been found to be useful for cracking higher hydrocarbons [Jasra et al. 1999]. Pillared clays and acid-activated clays have been found to be efficient catalysts for alcohol dehydration, petroleum cracking, and preparation of fine chemicals. These have been used as acidic catalysts in a large number of organic syntheses [Adams et al. 1984, Laszlo and Luchetti 1984, Adams and Clapp 1986, Vougen 1988, Lalithambika et al. 1999]. Clays are also utilized in the synthesis of zeolite catalysts [Somani et al. 1987, Pinnavaia et al. 1989, Dimotakis and Pinnavaia, 1990, Murray 1991, Sabu and Sukumar, 1993].

Other areas of clay utilization are: -
(i) In improving water retention capacity, strength and plasticity of mortars,
(ii) In removing impurities from water by adsorbing colloidal and other turbid matter, foul odour and taste-causing substances and hardness.
(iii) In removing colloidal impurities from urine, beer, and other beverages,
(iv) In manufacturing adhesives for paper and cement industries,
(v) In the disposal of radio-active wastes by adsorbing the radio-active material on clay surface and then transforming it to an inescapable, cemented form with the clay by calcination above 1273 K,

(vi) In the manufacture of white portland cement and other special cements,

(vii) For cotton and linen finishing in textile mills in the form of very fine (2 to 5\(\mu\)) powder,

(viii) In the fertilizer industry as diluent and prilling material,

(ix) In the manufacture of water and heat resistant, superior quality grease,

(x) In the manufacture of printing ink,

(xi) As useful material in the leather industry, medicinal, pharmaceutical and cosmetics industry and also in the manufacture of pesticides, plastics and resins and in rubber industry,


1.7 Role of Clays in the Environment

Clays have been assigned a role in the environment from prehistoric times. It is believed that the clays played an important role in generation of prebiotic components and in biological evolution as a whole [van Olphen 1977]. The large surface area of the natural clays accounts for their excellent capacity of the clay minerals to adsorb pollutants. The particle size of clay mineral is typically below 2 \(\mu\) while the internal surface area may be as large as 800 m\(^2\)/g for montmorillonite [Greenland 1965]. This is nearly equal to the surface area of about 1000 m\(^2\)/g for activated carbon [Cadena 1989].
In the natural environment, clays in soil and river sediments always play the role of a scavenger for the pollutants. The edges and the faces of clay particles can adsorb anions, cations, non-ionic and polar contaminants from natural water. These contaminants accumulate on clay surface and are retained through the processes of ion exchange, coordination, or ion-dipole interactions. Sometimes the pollutants can be held through H-bonding, van der Waals interactions or hydrophobic bonding effects. In other cases, the pollutants may be held through weak or strong adsorptive interactions. The strength of such interactions is determined by the particular structural and other features of the clay mineral [Bedding et al., 1983].

The role of the clay minerals in the environment can be categorized into the following four types [van Olphen 1977]:

(i) The clay mineral can behave as a strong Bronsted acid, due to interaction of cations with adsorbed or interlayer water molecules. The strength of the acid sites is determined by the type of cation, its position on the surface and the water content of the clay,

(ii) In absence of adsorbed water molecules [e.g. a calcined clay], the clay mineral behaves as a weak Lewis acid.

(iii) In presence of ions like Fe$^{3+}$ in octahedral positions or adsorbed oxygen, the clay mineral behaves as an oxidizing agent.

(iv) In presence of ions like Fe$^{2+}$ in octahedral positions the clay mineral behaves as a reducing agent.
The clay minerals in the environment interact with air, water and soil, thereby regulating the occurrence and distribution of a large number of pollutants. All clays contain metals like Mg, Fe, Ti, Cr, and Zr with trace amounts of Be, V, Mn, Co, Ni, Zn, Mo, Ag, Cd, Sn, Tl, Pb, Bi as well as Cu, As, and Se [Wedepohl 1991, Alloway and Ayres 1993]. The metals remain adsorbed to the clay surface and their release to the environment (air, water, soil) depends on factors like pH, temperature, precipitation, etc. Natural weathering processes through clay-water, clay-air interactions and other physical changes are responsible for the transport of contaminants between clay and environment [Trangmar et al. 1985, Adriano 1986, Wopereis et al. 1988, Schmitt and Sticher 1991]. Different types of clay minerals have been evaluated as adsorbents for metal ions and the results are very encouraging [Raymahashay 1987, Donnert et al. 1990, Atanassova 1999]. Compared to clay-metal interactions, the clay-organic matter interactions are likely to be much more complex and are governed by various structural and stereochemical considerations besides the usual environmental conditions. People have also suggested use of clay as a liner in water purification plants to remove heavy metal and other contaminants [Lo et al. 1995].

1.8 Role of Clays in Removing Organic Pollutants

The role of clays in regulating metallic contaminants by ion exchange and other processes has received wide attention. The clay in soil serves as a filter retaining metals in runoff water. Thus the leachate from clay-rich soil which receives wastes contaminated with metals has been found to be free from metal contamination [Wentick and Etzel 1972, Jermett and Linnemann 1977, Shuman 1975, 1977, Griffin and Au,
1977]. Thus the clay in soil helps in preventing ground water contamination and it is suggested that clay liners in land fill pits can be effective in preventing the release of contaminated leachates.

Clays also play a very important role in the treatment of industrial wastes [Huang and Rhoades 1989, Gupta et al. 1991]. Treatment of coloured effluent discharged by industries like textile mills can be done successfully with clays. Basic compounds like ammonia, amines, pyridines, etc., could be removed by adsorption on acidic sites of clay minerals [Parker et al. 1985].

Of the clay minerals, montmorillonite has been known to have the highest adsorption capacity due to its large surface area and other properties. Montmorillonite is followed by illite, chlorite and kaolinite in that order [Mehrotra 1990]. However depending on the adsorbate properties, the clay minerals often show different behaviour. Generally the adsorption process is dependent on pH and temperature of the medium, the type and the nature of the clay mineral, the presence of organic matter in the clay mineral, and the type and the nature of the adsorbate [Raymahashay 1987, Sharma et al. 1991] including its polarity [Sheng and Boyd 2000].

When clay minerals as part of the soil structure take part in the removal of organic contaminants, the general concept was that the humic substances present in soil play a major role compared to the clay minerals themselves. Natural soil contains 20 – 40 % clay minerals compared to 0 – 5 % humic matter and therefore the contribution of the clay fraction can not be neglected. Thus, Rebhun et al. [1992] have demonstrated that
pure bentonite as well as mixtures of sand and bentonite can remove substantial amounts of large organic compounds like fluoranthene, di- and tri- chlorobenzene, indole, etc.

Kaolinite itself was shown to be very effective in removing detergent contamination like that of alkylbenzene sulfonate from water [Fink et al. 1972, Raymahashay et al. 1984]. Kaolinite and other clays have also been shown to be good adsorbents for pigments, solvents like glyce. 1, acetone, trichloroethylene, carbon tetrachloride, benzene and xylene [Sethuraman and Raymahashay 1975, Green et al. 1983, Raymahashay 1987]. Clays have therefore become important adsorbents for removal of a very large number of organic contaminants from water including pesticides and their residues. This has been attributed to the small particle size [<2μ], unusual intercalation capacity and large surface area of the clay minerals [Pinnavaia 1983, Sanchez-Camazano and Sanchez-Martin 1991, Hermosin et al. 1991].

Jamrah et al. [1993a] has shown that the cation exchange capacity (CEC) of the clay plays a very important role in the uptake of an adsorbate. According to these workers, the mechanism of adsorption is dominated by ion exchange if the uptake is below CEC and adsorption takes place by mechanism of hydrophobic bonding if the uptake is more than CEC. In their experiments with surfactants such as tetramethylammonium chloride, hexadecyltrimethylammonium bromide and hexadecylbenzyldimethylammonium chloride on montmorillonite, it is shown that the adsorption increases the basal spacings of the clay and there is strong interaction between the negatively charged montmorillonite surface and the positively charged surfactant molecules. When the
surfactant dose is \(<\text{CEC}\), the surfactant molecules are adsorbed with the head groups oriented towards the clay surface. Above \text{CEC}, more surfactant molecules adsorb on to other molecules already adsorbed on the surface by lateral interaction among the hydrophobic groups. In this case there is no change in the basal spacing of the clay and the head groups are pointed away from the surface. The same group of workers [Jamrah et al. 1993b] has shown that an organic clay prepared by interacting montmorillonite with hexadecyltrimethylammonium bromide is very effective for removal of 2,4,6-trichlorophenol from drinking water. Stapleton et al. [1994] have found that the adsorption of pentachlorophenol on montmorillonite modified with adsorption of hexadecyltrimethylammonium bromide is dependant on pH as well as the ionic strength of the medium.

Earlier, Cadena [1989] has shown that the presence of water molecules associated with exchangeable cations in clays hinders adsorption of organic substances, which are mostly hydrophobic in nature. If the inorganic exchangeable cations are replaced with quaternary ammonium ions, the adsorption of organic compounds is immediately enhanced. Under such conditions the adsorption is very rapid and also pH-dependent being more favourable at lower pH values.

Compared to montmorillonite, the adsorption measurements on Kaolinite are limited. This is obviously due to the small CEC and less surface area of Kaolinite. Phukan et al. [1993] have investigated the acidic nature of the Kaolinite by adsorbing ammonia and pyridine on it. It is shown that ammonia adsorption was in the range of 35 – 55 millimoles/100g in the temperature range 300 – 593 K and the pyridine adsorption was
in the order of 30.6 millimoles/100g at 473 K. Calcination of the clay improved
adsorption of the bases.

Organic contaminants in natural water are responsible for imparting undesirable taste
and odour and therefore, selective removal of these compounds has received attention of
the workers throughout the world. Bottero et al. [1994] have shown that organoclays
prepared from hectorite by exchanging the interlayer Na$^+$ and Ca$^{2+}$ cations with
dimethyldistearylammonium chloride or dimethylbenzylammonium chloride are very
effective in removing specific organic micro-pollutants in presence of a large number of
other organic compounds. Dentel et al. [1995] have studied the adsorption of tannic
acid, phenol and 2,4,5-trichlorophenol on montmorillonite-based adsorbents and found
that the adsorption capacity increased after surfactant treatment. The order of adsorption
was phenol < Tannic acid < Trichlorophenol exactly in the order of increasing
hydrophobicity of the organic compounds. The adsorption was favourable at lower pH
in conformity with hydrophobicity consideration. These results are in agreement with
Soundararajan et al. 1990].

While adsorption on granulated activated carbon (GAC) or powdered activated carbon
(PAC) has been a favourite method for removal of micropollutants, clays have received
attention because of their easy availability, low cost and their important role in the
natural purification process by being a constituent of soil. A large number of different
contaminants have been tried on clays to evaluate the effectiveness of the adsorption
process. For example, Oberoi [1990] has found that the cationic pesticides, diquot and
paraquat, absorb on both Kaolinite and Montmorillonite in concentrations of 1 to 11x $10^{-5}$ M aqueous solutions giving good Langmuir and BET plots. Similarly organoclays prepared from bentonite have been found to be effective in treating coloured waste water [Bhalala et al. 1996] and also in removing ethylene diamine contaminant [Bhatt and Pandya 1996]. Barakat et al. [1995] had tried to adsorb linear alkylbenzene sulphonates on Kaolinite and found encouraging results. Ganjidoust et al. [1995] have investigated adsorption of coloured effluents from textile industries on several adsorbents including Kaolinite and found that the adsorption capacity was as much as 40%. The adsorption of dyes on Kaolinite was shown to be exothermic by these workers with $\Delta H^0$ value of about $-5$ kJ mol$^{-1}$.

The organoclays prepared by treating a clay mineral, mostly montmorillonite with quaternary ammonium compounds have received special attention due to exhaustive work done by Mortland et al. [1986], Dentel et al. [1995, 1998], Boyd et al. [1988a, 1988b, 1991], Lee et al. [1989, 1990], Xu et al. [1997], Lawrence et al. [1998] and others. Thus, many organic compounds particularly the toxic chlorohydrocarbons like 1,2,4-trichlorobenzene have been found to absorb very well on organoclays. Zhao and Vance [1998] have similarly investigated the adsorption of trichloroethylene on organoclays. It must be recognized that the clay itself should be sufficiently active to retain quaternary ammonium compounds on its surface which in turn increases the effectiveness of the clay for adsorption of other organic substances. Chlorinated phenols from aqueous solution can also be removed by adsorption on montmorillonite pillared with aluminum [Danis et al. 1998]. Singh and Singh [1999] have shown that phenol can be very effectively removed from water if the soil has substantial clay content and a
lower sand content. In a very recent work, Konstantinou et al. [2000] have obtained 70 – 98.5% removal of the herbicides, atrazine, propazine, prometryne, propachlor, propanil and molinate from aqueous solutions by using pillared clays. Earlier, Barriuso [1994] investigated atrazine adsorption – desorption on smectite clays. Torrents and Jayasundera [1997] have studied adsorption of non-ionic pesticides on clays, where as Michot and Pinnavaia [1991] have reported on adsorption of chlorophenols on modified clays from aqueous solution.

Clays present naturally in soil often act as a scavenger of various inorganic and organic contaminants present in surface, sub-surface and ground water. The exchangeable cations present on clay surface such as Na+, K+, Ca2+, Mg2+ are strongly hydrated in water producing a hydrophilic environment on the clay surface. This surface is normally effective towards adsorption of non-polar, non-ionic organic compounds in water. The transformation of the clay surface to an organophilic environment by replacing the inorganic cation with organic cations like [(CH₃)₃NR]+ or [(CH₃)₂ NR₂]⁺ where R is large alkyl hydrocarbon [>C₁₂] has already been discussed [Boyd et al. 1988, Jaynes and Boyd 1990, 1991a, 1991b, Jaynes and Vance 1996, Smith and Galam 1995, Stevens et al. 1996, Sheng et al 1997, Sheng and Boyd 1996, 1998]. In a recent work, Jaynes and Vance [1999] have shown that hectorite clays exchanged with aromatic organic cations can adsorb benzene, toluene, ethylbenzene and xylene compounds giving good fit with Langmuir isotherm indicating the process to be largely taking place at the surfaces. Such studies with Kaolinite are rare. It was thought that Kaolinite was a nonexpandable clay mineral. However it was shown by Wada [1961] that Kaolinite could be expanded using potassium acetate and other appropriate organic salts. It was latter found that
organic molecules like dimethylsulphoxide, hydrazine, urea, formamide, etc., could be inserted between the 1:1 layers of Kaolinite [Olejnik and Quirk 1970, Kristof et al. 1997]. These molecules are held by hydrogen bonding with the OH-groups of the octahedral sheet or with the O-atoms of the adjacent tetrahedral sheet as well as by weak van der Waals interactions. The intercalation of Kaolinite has often being influenced by the amount of water present and the pH of the medium. In a resent work, Frost et al. [1999] has described the use of Raman and FTIR spectroscopy in the study of kaolinites intercalated with formamide. It is shown that the formamide molecules are held on to the Kaolinite surface by hydrogen bonding with OH-groups attached to octahedral Al.

1.9 Conclusion

The literature search reveals the following:-

(i) Most of the adsorption experiments for removal of organic contaminants from water have been confined to montmorillonite clays.

(ii) The recent trend is to prepare organoclays by replacing the exchangeable inorganic cations with quaternary ammonium cations and then using them as adsorbents for other organics.

(iii) Not much work has been done on adsorptive properties of Kaolinite or its modified varieties.