# 1 Introduction

## 1.1 Clay minerals

Clay is a rock term, and like most rocks it is made up of a number of different minerals in varying proportions. Clay also carries the implication of small particle size . Usually the term clay is used in reference to fine-grained, earthy material which becomes plastic when mixed with a small amount of water. With the use of X-ray techniques, clays have been shown to be made up dominantly of a group of crystalline substances known as the clay minerals. They are all essentially hydrous aluminum silicates. In some, magnesium or iron substitute in part of aluminum, and alkalies or alkaline earths may be present as essential constituents(1). The particles of clay minerals may be crystalline or amorphous, platy or fibrous, and, though nearly always small, may vary from colliod dimensions to those above the limit of resolution of an ordinary microscope. The clay minerals vary in their dehydration and breakdown characteristics and in their decomposition products, and they also differ in their cation exchange properties according to the nature of their inter-layer cations and residual surface charges.

The principal clay mineral groups are :

1. Kandite group, including kaolinite, dickite and nacrite, halloysite and mata-halloysite.
2. Illite group, including illite, hydro-micas, phengite, brammallite, glauconite and celadonite.
3. Smectite group, including montmorillonite, nontronite, hectorite, saponite and sauconite.
4. Vermiculite
5. Palygorskite group, including palygorskite, attapulgite and sepiolite(2).

### 1.2 Montmorillonite minerals(3)

Monmorillonite is the name given to a clay mineral found near monmorillonite in France as long ago as 1874. Essentially it had the composition $Al_2O_3.4SiO_2.H_2O + xH_2O$ and was of exceptional stickiness. Many other minerals of similar properties yet with widely differing chemical composition have since been discovered.

A wide range of mineral exists which might be included in the montmorillonite group, but the term montmorillonite now has a more restricted meaning, and impies a compound which is essentially a hydrated alumino-silicate with only little substitution.

Many clays which contain montmorillonite type minerals have been termed ' BENTONITE '. This name has become common usage for commercial grades of montmorillonites.

Montmorillonites have the property of absorbing cations and holding them strongly. As cations are positively charged it is assumed that the layers have a net negative charge, the result of ionic replacements within the lattice. Thus, the replacement of an $Al^{3+}$ by a $Mg^{2+}$ cation in octahedral co-ordination creates a unit deficiency of charge. In the mineral montmorillonite itself magnesium appears to replace aluminium in the appoximate ratio of 1 to 6 and in other minerals of the montmorillonite group ferrous ions can replace, and aluminium ($Al^{3+}$) can take the place of silicon ($Si^{4+}$) in the hexagonal network. The atom in successive sheets of a layer are arranged as shown in Table 1.1. Pyrophyllite is included for comparison.

Table 1.1 The atomic arrangement in successive sheets of montmorillonite and pyrophyllite layers

| montmorillonite | net charge | pyrophyllite | net charge |
|---|---|---|---|
| 3 $O^{2-}$ | -6 | 3 $O^{2-}$ | -6 |
| 2 $Si^{4+}$ | +8 | 2 $Si^{4+}$ | +8 |
| 2 $O^{2-}$+$(OH)^{1-}$ | -5 | 2 $O^{2-}$+$(OH)^{1-}$ | -5 |
| 1.67$Al^{3+}$ + 0.33$Mg^{2+}$ | +5.67 | 2 $Al^{3+}$ | +6 |
| 2 $O^{2-}$+$(OH)^{1-}$ | -5 | 2 $O^{2-}$+$(OH)^{1-}$ | -5 |
| 2 $Si^{4+}$ | +8 | 2 $Si^{4+}$ | +8 |
| 3 $O^{2-}$ | -6 | 3 $O^{2-}$ | -6 |
| sum of positive charge | 21.67 | sum of positive charge | 22 |
| sum of negative charge | 22 | sum of negative charge | 22 |

In all other respects, the structure of montmorillonite show in Fig. 1.1

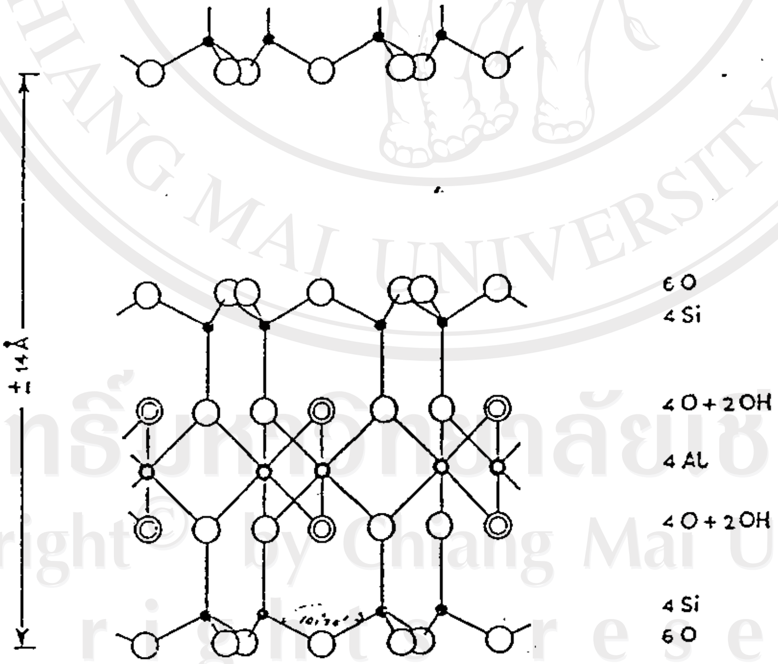


Fig. 1.1 The proposed structures for montmorionite(idealised)(3)

Other absorption properties can be explained in a similar manner. The interesting feature of the Edelman and Favejee concept of montmorillonite is that the layers are electrically neutral and isomorphous replacements resulting in a charge-deficiency are not needed to account for the cationic absorption. The layer may be represented as sheets composed as follows:

| | | | |
|---|---|---|---|
| 1 $(O\text{-}H)^{1-}$ | net charge | -1 | |
| 1 $Si^{4+}$ | " | +4 | Silica hexagonal ring |
| 3 $O^{2-}$ | " | -6 | unit |
| 1 $Si^{4+}$ | " | +4 | with -11and+8 charge |
| 1 $O^{2-}$+2 $(OH)^{1-}$ | " | -4 | |
| 2 $Al^{3+}$ | " | +6 | |
| etc., in reverse order | | | Silica hexagonal ring unit |

sum of negative charges = 22
sum of positive charges = 22

In deducing the structural formula from the chemical composition of the montmorillonite minerals, Ross and Hendricks made several assumptions. These include:

1) That the sum of the charges of all the anions (namely oxygen and hydroxyl) always totals twenty-two in the unit formula; made up usually of ten divalent oxygen and two hydroxyl anions.

2) That the number of cations in tetrahedral co-ordination (namely silicon and aluminium) always totals four.

3) That the exchangeable cations couterbalance the charge deficiency on the layers. The actual determination of this value indicated that the figure was usually about 0.33 positive charge per unit formula, and Ross and Hendricks suggest that this value is constant for all minerals of this type.

Although many cations are present in the structure of montmorillonite minerals, those which occur in appreciable amounts are limited to silicon ($Si^{4+}$), aluminium ($Al^{3+}$), magnesium

($Mg^{2+}$), iron in the ferric ($Fe^{3+}$) and ferrous ($Fe^{2+}$) forms and lithium ($Li^{1+}$).

Alkaline or alkaline earth cations which are absorbed by the layers in montmorillonites must play a large share in the linking of adjacent units. Such ions penetrate between the layers and, although not held firmly in any way, they probably form a bridge between two negative-charged units.

Apparently, in montmorillonites, stacking of successive layers in completely random; some minerals are fibrous in habit, i.e. hectorite, suggesting that the layers may be distored as in halloysite or chrysotile.

Montmorillonites are known to exhibit great plasticity, stickiness and strength in the wet and dry states. This is mainly due to the extremely large spacific surface area which is exposed on dispersion in water.

In addition in their ability inorganic cations and water, montmorillonites are capable of taking up organic molecules in interlamellar positions. Large organic cations such as amines and proteins can replace the exchangeable balancing cations. Mono- and, sometimes, di-molecular layers are adsorbed in this way depending on the size of cation and charge-deficiency in the layers. Organic liquids or solid may also be absorbed where the mechanism is not attributable to base-exchange phenomena. Glycerols, resorcinol, catechol and pyrogallol are only a few examples and it was partly to explain the mechanism by which such compounds are held between montmorillonite plates.

The unusual capacity of montmorillonites for absorbing various components from aqueous media has many interesting aspects in commercial developments. There is none more so than the ability of certain montmorillonites to absorb organic amines and similar derivatives and, in so doing, to change their entire physical chemical nature.

*Bentones* is the commercial name give to this class of treated montmorillonite type minerals. Wyoming bentonite was the prototype source, hence the etymological derivation of the name. In these materials, the clay minerals have absorbed amines from solution to such an extent that the product has acquired a hydrophobic character, i.e. it is water repellent. As such bentones have and affinity for organic non-polar species such as oils and greases. which they absorb freely and often preferentially.

The whole field of organic derivatives of montmorillonites offers exciting possibilities. By their means, the extraction of essential oils from natural products is easier, more efficient and cheaper. They are finding increasing applications in a wide range of industries ranging from industrial effluent disposal, oil refining, preparation of foodstuffs, to perfume extraction.

## 1.3 Transition metal

Nickel and cobalt occour in transition group VIII of the periodic table. In simple salts of cobalt and nickel the oxidation state is usually +2, usually $Co^{2+}$ and $Ni^{2+}$. Simple compounds of both metals, in the oxidation state of +3, are less common, the stable complex compounds of cobalt are those in which the metal is in this state. The cobaltic ion $Co^{3+}$, is a strong oxidizing agent(4). Some physical properties of cobalt and nickel are given in Table 1.2(5).

Table 1.2 Physical constants of cobalt

| Physical constants | Cobalt | Nickel |
|---|---|---|
| Atomic number | 27 | 28 |
| Atomic weight | 58.933 | 58.71 |
| Valency electrons | $3d^7 4s^2$ | $3d^8 4s^2$ |
| Density, $g/cm^3$ | 8.9 | 8.9 |
| Melting point,°C | 1493 | 1453 |
| Boiling point,°C | 3100 | 3000 |

## 1.4 Chemistry of Cobalt(III), Cobalt(II) and Nickel(II)

### 1.4.1 Cobalt(III) and Cobalt(II)

The most commom cobalt(II) complexes may be either octahedral or tetrahedral. There is only a small difference in stability and both types, with the same ligand, may be in equilibrium. Thus for water there is a very small but finite concentration of the tetrahedral ion.

$$[Co(H_2O)_6]^{2+} \;=\; [Co(H_2O)_4]^{2+} + 2H_2O$$

Addition of excess $Cl^-$ to pink solutions of the aqua ion readily gives the blue tetrahedral species(6,7)

$$[Co(H_2O)_6]^{2+} + 4Cl^- \;=\; [CoCl_4]^{2-} + 6H_2O$$

or $$2[Co(H_2O)_6]^{2+} + 4Cl^- \;=\; Co^{2+} + [CoCl_4]^{2-} + 12H_2O$$

Cobalt(III) complexes are synthesized by the oxidation of $Co^{2+}$ in solution in the presence of the ligands. Oxygen or hydrogen peroxide and a catalyst, such as activated charcoal, are used. For example,

$$4Co^{2+} + 4NH_4^+ + 20NH_3 + O_2 \rightarrow [Co(NH_3)_6]^{3+} + 2H_2O$$

$$4Co^{2+} + 8en + 4en{\cdot}H^+ + O = 4[Coen_3]^{3+} + 2H_2O$$

Here, diagram concluded of the pink aquo-cation(A) cannot be oxidised to the +3 state (B) in aqueous solution, since B would itself oxidise water to give oxygen(8). Replacement of the water ligands by chloride alters the shape, colour and redox potential, but again oxdation of C to D is not possible. However, replecement of water ligands by ammonia to give E allows easy oxidation to the stable +3 complex F. Replecement of water by cyanide would be expected to give G; in fact this is immediately oxidised by the solvent water to the +3 complex H.

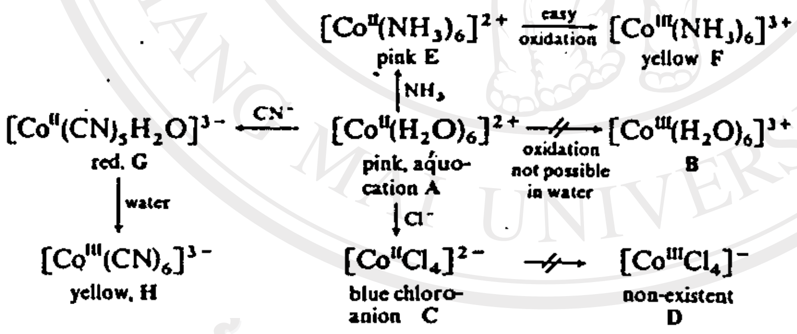


Fig. 1.2 Digram of cobalt complexes reaction

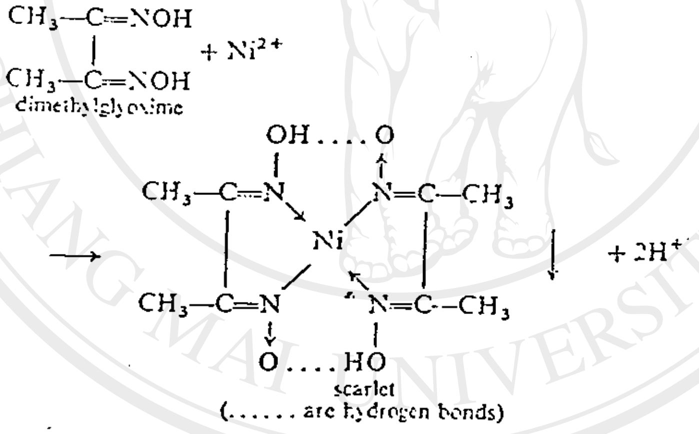
The chlorides can be obtained in the anhydrous condition by heating the respective metal in chloride, or by treating a suspension of the hydrated acetate, in benzene, with acetyl chloride:

$$Co(CH_3COOH)_2 + 2CH_3COCl + 2H_2O \rightarrow CoCl_2\downarrow + 4CH_3COOH$$

### 1.4.2 Nickel(II),$d^8$(4,6)

The commonest of six-coordinate species is the green aquo ion $[Ni(H_2O)_6]^{2+}$ which is formed on dissolution of Ni, NICO etc., in acids and gives salts like $NiSO_4 \cdot 7H_2O$. The water molecules in the aquo ion can be readily displaced especially by amines to give complexes such as trans-$[Ni(H_2O)_2(NH_3)_4]^{2+}$, $[Ni(NH_3)_6]^{2+}$ or $[Nien_3]^{2+}$. These amine complexes are usually blue or purple because of shifts in absorption bands when $H_2O$ is replaced by a stronger field ligand.

Planar complexes of Ni(II) are thus invariably diamagnetic. They are frequently red, yellow, or brown. Probably the best known example is the red bis(dimethylglyoximato)nickel(II), $Ni(DMGH)_2$, which is use for the gravimatric determination of nickel; it is precipitated on addition of ethanolic $DMGH_2$ to ammonical nickel(II) solutions.



Cobalt(II) ion give no precipitate with dimethylglyoxime and the reaction provides a means of separating cobalt from nickel and also of estimating the latter.

### 1.5 Health and safety factors(9)

#### 1.5.1Cobalt

Cobalt salts in sufficiently large doses can irritate the gastrointestinal tract and cause nausea, vomiting, and diarrhea. In man single oral doses as low as 500 mg of the chloride have provided nausea and vomiting; however, dosages as high as 1200 mg/d over a period of 6 wk have been given to individuals, where tolerated, without evidence of toxic symptoms.

Cobalt salts are used in the treatement of anemia, in some cases together with iron or manganese salts. The oral dosage range has been estimated at approximately 0.25-1.0 mg elemental cobalt per kg body weight. In infants and children, much larger doses(up to 12.5 mg/kg) have not produce recognized toxic effects.

Externally, cobalt may produce dermatitis. It is also suspected as a carcinogen of the connective tissue and lungs.

#### 1.5.2 Nickel

Some aqueous solutions of nickel are irritating on contact with the eye, eg, nickel sulfate and nickel chloride. Face shields, eye protection, and safety showers should be used where there is a possibility of splashes with nickel containing solutions.

Nickel and nickel compounds, particularly in aqueous solution, may cause allergic dermatitis in some wokers. Nonoccupational dermatitis has occurred in individuals and has resulted from skin contact with nickel in jewelry and in nickel-plated articles. Health studies have demonstrated that 4-13 % of patients with skin disease are sensitive to nickel on patch testing. In contrast to nonoccupational exposure, allergic dermatitis in nickel-exposed workers is not a significant problem. Nevertheless, care should be tacken to prevent skin contact with aqueous solutions containing nickel by means of protective clothing. Surface wounds that may be contaminated with nickel should be cleansed with mild soap and water before treatment.

**Aims of this research**

The main aims of this research project were:

1. to study the method used to synthesis complexes of nickel and cobalt occured on clay surface, including their characterizations
2. to study the role of ligands to metal on clay surface, for example, type of ligands used, the effect of concentration of ligands on complex formation, acid-base properties of ligand.