1. INTRODUCTION

1.1 Preliminary considerations

It is now well established that clays are essentially composed of extremely small crystalline particles of one or more numbers of a small group of minerals. All clay minerals are predominantly hydrous aluminium silicates. The aluminium atoms in some minerals are replaced either wholly or partly, by Mg or Fe. Sometimes alkali and alkaline earth metals are also found to be present in some clay minerals. From the standpoint of size, clays are defined as fine grained earthy materials with particle size generally less than 2μ. Most of the clay minerals of wide occurrence and profound industrial importance are characterised by layer structures which are built up by a regular stacking of two dimensional lattice layers, each one of which is composed of two basic component layers known as octahedral and tetrahedral respectively. Clay minerals play an important role in various fields of scientific and technological interest. The study of clay minerals is of great interest to the agriculturists and soil scientists. The occurrence and properties of clay minerals govern the soil fertilization, plant nutrition and water retention capacity of the soil to a large extent. Hence such a study of the clay minerals present in the soil is of special importance in agriculture. Besides agriculture, such study is also useful to the construction engineers. The physical properties of a soil largely depend on the prevalence and kind of clay minerals present in the soil. Therefore the nature of the clay minerals present in the soil and their properties, will largely be responsible for the stability and strength of the structures built on it. Clays are also very important in certain industries. In oil industry, certain clays have important catalytic activity. They are also used as drilling muds. It is widely used in foundary industry for moulding purposes. But of all industrial uses of clays, the use in ceramic industry stands first. It is the most essential and important raw material of ceramic industry.

In most of the cases of industrial uses of clays, they are either subjected to heat treatment or to simple dehydration at ordinary conditions. In view of these facts, dehydration and the effect of heat treatment on clay minerals as well as products thereof are considered to constitute an important field of study. Hence a study of dehydration or more precisely the effects of heat treatment and the consequent changes in their structural and physical properties are of great importance to the user of clays. In fact considerable amount of work has already been done and is still being carried out by a host of workers in the field of ceramic technology. The results of such investigations are very much useful in understanding the behaviour of the clays and consequently to adjust the industrial operations involved in their uses.

It is also well known that the end products of heat treatment of these minerals are also affected by the rate and range of heat treatment at intermediate stages. Therefore the study of the different intermediate stages and the associated structural transformations also constitute a significant branch of study for proper understanding of the continued transformation mechanism leading to the final products.

1.2 Layer structure of clay minerals

It is well established that most of the clay minerals have layer structures which are characterized by weak interlayer forces. Each unit layer is built up by the superposition of two basic unit layers or sheets viz. a tetrahedral and an octahedral layer. The tetrahedral silicate layer is the most basic and stable layer. It consists of continuous two dimensional tetrahedral sheets of composition X_2O_5 (X = tetrahedral cation, viz Si, Al or Fe^{+++}) in which individual tetrahedra are linked with neighbouring tetrahedra by sharing three corners each (the basal oxygens) to form an hexagonal mesh pattern (Fig. 1.1.a). The fourth tetrahedral corner (the apical oxygen) points in a direction normal to the sheet and at the same time forms part of an immediately adjacent octahedral sheet in which individual octahedra are linked laterally by sharing octahedral edges (Fig. 1.1.b). The common plane of junction between the tetrahedral and octahedral sheets consists of the shared apical oxygens plus unshared (OH) groups that lie at the centre of each tetrahedral six fold ring at the same z - level as the apical oxygens. F may substitute for OH in some species. The octahedral cation in most of the clay minerals is Al. However, Mg, Fe^{2+} and Fe^{3+} also occupy the octahedral sites in several minerals. Some medium sized cations such as Li, Ti, V etc. also occur in some species. The smallest structural unit contains three octahedra. If all three octahedra are occupied i.e. have octahedral cations at their centres, the sheet is characterized as trioctahedral. If only two octahedral sites are occupied and the third octahedron is vacant, the sheet is characterized as dioctrahedral.

Depending on the number of the tetrahedral and octahedral sheets forming the unit, there may be layer structure of several types. The assemblage formed by linking one tetrahedral sheet with one octahedral sheet is known as a 1:1 layer. In such layers, the upper most, unshared plane of anions in the octahedral sheet consists entirely of OH groups. A 2:1 layer links two tetrahedral sheets with one octahedral sheet. In order to accomplish this linkage the upper tetrahedral sheet must be inverted so that its apical oxygen points down and can be shared with the octahedral sheet below (Fig. 1.1.c). Both octahedral anion planes then are of the same O, OH composition. If the 1:1 or 2:1 layers are not electrostatically neutral, the excess layer charge is neutralized by various interlayer materials, including individual cations hydrated cations and hydroxide octahedral groups and sheets. The total assemblage of a layer plus interlayer is referred to as a structure unit or unit layer. It contains one or more chemical formula units (Z) in a structural unit.

Thus structurally all the layer silicate clay minerals having 1:1 or 2:1 layer structure, will be built up of parallel lattice layers stacked regularly in direction normal to the layer themselves. The layer by themselves will behave as a perfect two-dimensional gratings of lattice points or atoms which are held bound by strong interatomic forces within the layer, but the interlayer forces holding the corresponding atoms in successive layers are relatively weak. The successive layers are held by weak Vander Waals forces and long hydrogen bond forces. Consequently, in these type of clay minerals the probability of a layer being displaced or rotated with respect to adjacent layer is quite high. A further contributory factor which facilitate this effect in layer silicate clay minerals is the highly symmetrical arrangement of the oxygen atoms and the hydroxyl groups in the uppermost planes of the unit layer composed of the superposition of the component octahedral and tetrahedral sheets of atoms as explained earlier.

In the present study of layer silicate clay minerals, the most widely used clay mineral namely kaolinite, has been selected as a representative of 1:1 layer type while nontronite and hectorite have been chosen to represent 2:1 layer structure.

1.3 Structure of kaolinite

It has been already mentioned that kaolinite falls under the category of 1:1 layer type clay minerals formed by the combination of one tetrahedral with one octahedral sheet. It is built up by superposition of a single basic unit layer, called kaolin layer composed of 1:1 tetrahedral-octahedral layer which has the structural formula $Al_4Si_4O_{10}(OH)_8$ or in terms of oxide $2\,Al_2O_3.\ 2\,SiO_2.2\,H_2O$. Kaolinite exhibits a nearly perfectly ordered sequence of the layer and triclinic symmetry and is the simplest member of the kaolin family consisting of one layer per unit cell. The number of unit layers and their relative arrangements vary from member to member of the kaolin family.