1. INTRODUCTION

1.1 DEFINITION OF CLAYS AND CLAY MINERALS

Agricola, in 1546, first formalized the definition of 'clay' and it has been revised many times up to the date. The term 'clay' in its usage is somewhat ambiguous, because geologist, mineralogist, agronomist, engineers and others use this term in different ways and to remove the ambiguity in the definition of 'clay', the nomenclature committees of the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS) jointly define the 'clay' in following way [1]:

"The term 'clay' refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired. Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fire. Associated phases of clay may include materials that do not impart plasticity and organic matter."

According to their report the definition of 'clay mineral' is as follows:

The term "clay mineral' refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing. Minerals known to produce the property of plasticity are phyllosilicates. Because minerals are not defined according to their crystallite size, appropriate phyllosilicates of any grain size may be considered 'clay minerals'. Likewise, clay minerals are not restricted, by definition, to phyllosilicates. If research reveals that a non phyllosilicate mineral imparts plasticity to a clay and hardens upon drying or firing, this mineral is a 'clay mineral'."

Generally, clays are composed of extremely small crystalline particles of one or more numbers of small groups of minerals, known as clay minerals which can develop plasticity in combination with water. Most of the clay minerals are predominantly hydrous aluminium silicates. The aluminium atoms in some cases are replaced either wholly or partly by Mg or Fe. Some times alkali and alkaline earth metals are also found to be present in some clay minerals.

1.2 GENERAL STRUCTURE OF CLAY MINERALS AND THEIR CLASSIFICATION

It is well known that layer structured clay minerals are formed by the assemblage of tetrahedral sheets of composition T_2O_5 (where T=tetrahedral cations, normally Si^{4+}, Al^{3+}, or Fe^{3+}) and octahedral sheet which consist of octahedral cations Mg^{2+}, Al^{3+}, Fe^{2+}, etc. In tetrahedral sheet, the individual tetrahedra are linked with neighboring tetrahedra by sharing three corners each (the basal oxygen) to form a hexagonal mesh pattern (Figure 1.1.a) [2]. 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 (Figure 1.1.b) [2]. 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. The smallest structural unit contains three octahedra. If all the octahedra are occupied i.e. have octahedral cations at their centres, the sheet is characterized as trioctahedral. If the two octahedral sites are occupied and the third octahedron is vacant, the sheet is characterized as dioctahedral. The assemblage of tetrahedral and octahedral sheet forms a unit layer and the superposition of these unit layers results in an overall structure of clay minerals. If the unit layer is formed by sandwiching an octahedral sheet between two tetrahedral sheets the structure is known as 2:1 layer type materials e.g. montmorillonite, vermiculite, palygorskite (Figure 1.1.c) [2]. If the assemblage formed by linking one tetrahedral sheet with one octahedral sheet is known as a 1:1 layer e.g. kaolinite (Figure 1.1.c) [2]. The main difference arises among these minerals due to the presence of amount of negative layer charges which is generated by the isomorphous substitution of Mg and Fe for Al in the octahedral sheet and to a lesser extent, substitution of Si in the tetrahedral sheet by Al. These negative charges on the layers are balanced by hydrated cations in the interlayer space (usually Mg^{2+}, Na^{+}, Ca^{2+} etc). A typical classification of clay minerals is shown in Table 1.1.