INTRODUCTION

Clays are the oldest ceramic raw materials and are most important among the widely distributed geologic sediments. According to the clay-mineral concept, clay materials are essentially composed of extremely small crystalline particles of one or more members of a small group of minerals that are commonly known as clay minerals. These minerals are essentially hydrous aluminium silicates. The introduction of X-ray technique has led to the elucidation of the majority of clay minerals and whilst refinement of technique may result in some revision and elaboration, the basis appears sound. Clay minerals fall under the group of layer lattice structures where three oxygen atoms of each silica tetrahedron \((\text{SiO}_4)^4\) are linked to similar units. One oxygen of each group of four is not fully satisfied electrically and requires to be linked to external cations. The sheet of silicon-oxygen atoms is capable of extension in two directions at right angles. Therefore, mineral structure within this group is invariably platey. Definite layers are formed which are stacked one above the other and the bonds between each layer are relatively weak. Each mineral layer or plate is an independent unit and must be electrically balanced and each cation co-ordinated with anions in a way dependent on their size ratio.

In some cases the layers are not balanced within themselves (montmorillonite) and invite ions to be adsorbed on the surface of the layers.
Besides plastic property for which clay is indispensable, the pyrochemical changes whereby the phase composition is completely altered are of great significance in many industries. Clays are used as ingredients in a vast number of products and also as agents in many processes, for example, water purification and as a source of desired material e.g. aluminium.

Many clays contain as much as 30 to 40 per cent of alumina and consequently are potential ores of aluminium. Much research has been done on a variety of processes for extracting alumina from clays\(^1\). Generally no specific clay has been mentioned, but the context of the patent often suggested kaolin. There is no information available indicating whether or not clay minerals other than kaolinite would be better, or in some cases worse.

The chemical reactions to which ceramic materials are subjected at ordinary temperature are chiefly due to water, acids and alkalis. Water has no rapid chemical effect upon most ceramic materials at ordinary temperature. Most silicates, when subjected to action of water for very long periods of time, tend to hydrolyse and although some change fairly rapidly, the reaction of most can be observed only on geological age. Probably the most important effect of water on clay is its ability to form ions from soluble components. The cation exchange capacity is of great importance in clay because it can greatly influence the texture. Acid may come into contact with ceramic materials in a variety of ways. Organic acids are produced by bacterial action on carbonaceous
constituents and can directly attack clays with which they are in contact. Many acids will dissolve certain substances in clays and will alter their chemical composition as well as their physical form. Alkalies usually combine with acid substances, but their actions in cold upon silicates and alumino silicates are slight and is very feeble in case of crystalline silicates, of course the concentration of alkali is very important towards the attack.

The effect of reagents on most ceramic materials is not usually very distinct on account of the heterogeneous nature of the latter and the limited extent to which they may be attacked. Only in isolated instances can one mineral be separated from the rest, as before one is completely dissolved others will have began to decompose. The production of new chemical and physical states when clays are heated often results in a material with a very different chemical reactivity from that of the original form.

Thus clay minerals which appear to be physically rigid, are decomposed by heat treatment above certain temperature as well as in aqueous phase by some chemical agents. In the physical treatment all the constituents remain intact, only the phase composition changes, but in the chemical leaching process the constituents are preferentially dislodged from the structure and the chemical composition of the residual phase is completely different from the parent material.

Various work has been done on the structure and the physicochemical characteristics of clay minerals which definitely reveal
some important attributes of clay minerals. The migration characteristics of different structural constituents of clay minerals in aqueous phase are the subject matter of the present thesis. Although the complexity of clay structure i.e. heterogeneity in bonding as well as various types of reaction occurring during the course of clay-aqueous phase reaction drew the attention of scientists but the literature with respect to the systematic study of solubility is extremely meagre. The solubility of clay minerals in acids and alkalies is important fundamentally because it also reflects some of the characteristic features of the structure which may not be available from other studies. Besides application in ceramic industries clays are used in various industries as important ingredients. Thus from the practical point of view solubility characteristics are important in determining the utility of various clay minerals as sources of aluminium and its compounds. Such study will also give an idea about the bonding of refractories in acid medium, in the fixation of certain materials in soils, in the manufacture of catalysts etc. Moreover the relative resistivity towards chemical agents, data of different clay minerals will be very much helpful to their utilisation under various experimental conditions.

Considering the importance of the subject the present work was undertaken. Comparative solubility study was performed taking different types of clays. The important parameters which usually affect this type of quasi-heterogeneous phase reaction such as nature of the clay minerals, nature and concentration of leaching
agents, temperature, particle size were studied for purified kaolinite and bentonite. Heat treatment brings about a drastic change towards the mineralogical composition of clay minerals, it passes through various unstable and stable phases on progressive heat treatment. This effect was clearly reflected through the solubility measurement. Finally the kinetics of the decomposition of clay minerals in aqueous phase was studied in order to throw some light on the decomposition of the process. All the isothermal experiments were carried out in batchwise process and the corresponding rate curves were plotted.