Chapter Four

PLAN OF THE WORK

Bauxite is a solid solution of a number of hydrated aluminum oxides in varying proportions. Gibbsite, boehmite and diaspore are the main constituents of bauxite rock and laterite minerals, with gibbsite often being the predominant component and diaspore being the minor component. Different alumina hydrates can also successfully be synthesized by various methods like solution-precipitation, organic gel assisted citrate complexion (modified Pechini process), sol-gel or hydrothermal routes. However, the degree of crystallinity and nature of crystalline phases in synthetic alumina hydrates are greatly influenced by the conditions of synthesis such as initial concentration of the reactants, nature of the precipitating medium, final pH of the solution, aging technique used etc. Bauxite rock and all other alumina hydrates assume various polymorphic phases on progressive heat treatment. The main endothermic process during such heat treatment comprises mainly dehydration and dehydroxylation reactions which lead to the development of precursor materials of Al_2O_3-H_2O system.

Present investigation was undertaken to study systematically the equilibrium dehydration-rehydration behavior of bauxite rock and synthetic alumina hydrate followed by kinetics of thermal dehydration and dehydroxylation process under isothermal and non-isothermal conditions.

For this purpose, Sourastra bauxite, the best variety high alumina rock available in India containing gibbsite as the major mineral phase and a synthetically prepared alumina hydrate were selected. The raw bauxite rock was at first ground to fine powder. The loose powder of bauxite rock was then fractionated into three different size fractions such as -20+50, -50+80 and -80+120 meshes (British Standard Sieve) by sieving process and stored in a constant temperature incubator (36±1°C) in order to

maintain constant free moisture content. Synthetic alumina hydrate was prepared by hydrolysis of dilute solution of aluminum iso-propoxide in iso-propanol in presence of HNO_3 acid as peptizing agent at pH 4.0 followed by refluxing at 70°C and aging for 24 hours. The formed gel was then processed as in case of bauxite rock. The different size fractions of the bauxite rock and synthetic alumina hydrate in powder form were chosen as the starting materials for thermal study from which various kinetic relationships have been derived as embodied in the present investigation.

Initially, physico-chemical characterizations of the different fraction of bauxite and synthetic alumina hydrate were carried out through chemical analysis, differential thermal analysis, particle size analysis, surface area, X-ray diffraction and infrared spectroscopy analysis. Equilibrium dehydration-rehydration study related to structural flexibility on progressive heat treatment was recorded by taking a definite weight of the sample and heating at a definite temperature up to equilibrium mass loss. The temperature range of the heat treatment varied from 100°C to 800°C at an interval of 100°C. The heat treated sample at each temperature were then equilibrated successively at 35%, 55%, 75% and 100 % relative humidity for studying the reversibility of the dehydration-rehydration process which is in other ways related to structural stability.

Water molecule is an essential part of bauxite rock and synthetically prepared alumina hydrate. Expulsion of structural water from the lattice takes place in the temperature range 200-500°C. The important parameters which control the dehydroxylation process are particle size, crystallinity, rates of heating and heating environment etc.

Another part of the investigation deals with the study on the kinetics of dehydroxylation process of bauxite rock and synthetically prepared alumina hydrate under isothermal and non-isothermal condition. The important factors controlling the dehydroxylation process are thought to be the rate of loss of water molecules from the interface between the hydrates and its derived products and the rate of diffusion of water molecules through the solid product.

Isothermal dehydration kinetics was carried out in thermo-balance where all the experimental condition affecting the heat transfer was kept fixed. All the experiments were conducted on the samples in the form of loose powder. From the results of the isothermal study, reaction rate constants, equilibrium mass loss, applicability of the 1^{st} order kinetic law and finally activation energies at both the initial and final stages of dehydroxylation was determined applying Guggenheim and ICTAC methods.

Non isothermal dehydration and dehydroxylation kinetics was carried out by TG-DTG analysis using a high temperature Netzsch simultaneous thermal analyzer (Model-409) at three different heating rates from 5.0, 7.5 and 10°C min^{-1}.The bauxite rock and synthesized alumina hydrate sample were taken in the form of loose powder for thermal analysis and pure α-alumina powder as reference sample. From the results of the non-isothermal study, activation energy, pre-exponential factor and mechanism of dehydration process were determined applying FWO, modified Coats-Redfern, Kissinger and Malek methods.

Finally, the kinetic parameters obtained by different techniques would be thoroughly examined, correlated and optimized.