Chapter One

INTRODUCTION

Natural aluminas are mostly found as hydrated aluminous material derived through metamorphosis of aluminosilicate minerals. It exists as both monohydrate (Al-O-OH) and trihydrate [Al(OH)₃] forms. Again, each hydrated aluminous form exhibits polymorphism. Monohydrate has two polymorphic forms such as boehmite (γ Al-O-OH) and diaspore (α Al-O-OH) while that of trihydrate as gibbsite [α Al(OH)₃], bayerite [β Al(OH)₃] and nordstrondite [Al(OH)₃]. Crystal habit of monohydrate is orthorhombic and that of trihydrate is monoclinic. Thus water molecules play a vital role in their crystal structure.

Alumina (Al_2O_3) is the major constituent of all aluminous raw materials. Al_2O_3 has very high melting point, high thermomechanical, good electrical and excellent chemical durability properties. The most important hydrated aluminous rock is bauxite which is not a pure mineral but consists of two or more hydrated minerals phases such as gibbsite, boehmite, bayerite, diaspore and tohdite ($5Al_2O_3 \cdot H_2O$). It is often associated with number of mineral impurities like quartz, goethite [FeO(OH)], hematite (Fe_2O_3), anatase (TiO_2), alkali and alkaline earth oxides. It is available in abundant quantities all over the world particularly in North America, South America, Europe, Asia, Africa, and Australia varying in color from white to brown and dull in appearance. The name bauxite was given in mesozoic era when the bauxite was discovered in the village 'Baux' in France. It was formed by chemical weathering of rock in tropical and subtropical climates.Guinea possesses the largest deposit of bauxite rock in the world. In India bauxite is found in Lohardaga, Sourastra etc. with an estimated total reserve of 3.5×10^9 tonnes[1]. Bauxite is an important aluminous raw material for aluminum metallurgy, refractory as well as chemical and ceramic industry[2].

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The physical and technological properties of bauxite rock depend on the mineralogical composition, particle morphology and associated impurities.

Bauxite ore is not only used as major source of Al_2O_3 but also red mud (recovered as by- product after processing of bauxite by Bayer's process). Bauxite also finds several applications such as for water treatment: e.g. removal of phenols[3], heavy metals[4-9], nitrates[10], phosphate[11], dye colors[12], for manufacture of multifarious ceramics products[13-18] and for production of pozzolanic pigments[19].

Gelatinous aluminum hydroxides are of great interest too in preparing sorbents, catalyst and plasticizing additives. Different alumina hydrates can be synthesized with very high purity, high surface area, ultrafine particle size distribution, disorder crystallinity and uniform morphology via a number of chemical, sol-gel, hydrothermal routes. The properties of aluminous materials are greatly governed by the crystal structure of alumina polymorphs present there.

Water molecule is an integral part of hydrated alumina structure and complicated relationship between bauxite rock, alumina gel and water molecule can be explained by the factors such as

I.Size, shape and charge on alumina particles

II.Their lamellar form

III.The adsorption of water molecule on the particles

IV.The high surface tension of water molecule

The gradual expulsion of water molecules occurs during thermal treatment of bauxite and hydrated aluminous minerals leading to the intermediate formation of

several metastable transition alumina phases like Chi (χ), Eta(η), Gamma(γ), Delta (Δ), Iota(ι) Theta(θ), Kappa(κ) and Beta(β) etc. with progressive variation in crystallographic nature, specific surface area and grain morphology until most stable form of alumina, corundum (α-Al_2O_3) is obtained[20-22].

Dehydration involves the loss of physically adsorbed water, interlayer water followed by the loss of hydroxyl groups from the lattice in the form of water. However at still higher temperature, there is no loss in mass.

Various methods of studying the dehydration phenomenon have been employed by different workers.

1.   Equilibrium study:

Heating at a given temperature for sufficient time equilibrium to attain followed by recording the loss in mass. This process is repeated at different temperatures.

2.   Non-equilibrium study:

a)   Heating the sample at different rates and recording the loss in mass with rise of temperature in a thermobalance.

b)   Heating the sample in the thermobalance at the fixed temperature and recording the continuous loss in mass with time.

One of the fascinating subjects of research of the day is the decomposition study of aluminous minerals and aluminosilicate minerals as heat of dehydration appears to be the most important thermodynamic parameter of the thermal dehydration reaction of

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aluminous and related minerals. Fundamental studies on the kinetics of thermal decomposition of alumina bearing minerals showed that magnitude of orientation of water molecule were greatly influenced by the factors such as exchangeable ions, mineralogical composition, crystallographic structure, particle size and shape, nature and content of impurities, packing density etc., therefore, there is wide scope of research work in predicting and elucidating the course of reaction, mechanism of thermal decomposition and accurate energy consumption for conducting such solid state decomposition of useful aluminous minerals in efficient ways.

Because of the diversity of aluminous minerals in terms of disordered structure and existence of different type of bonding water molecules, the alumina bearing materials offer an important system for in depth study of this type of endothermic reaction. A detailed thermal study would provide a deep insight into the effect of heat treatment on the structural changes and elucidating the reaction mechanism under both non-isothermal and isothermal conditions. The relevant data is of immense significance in controlling the course of polymorphic transformation upon dehydration–rehydration reaction, evaluation of the rate constants and activation energies at different stages of heat treatment and elucidation of thermal decomposition mechanism of natural and synthetic hydrated alumina. The results obtained can be compared and analyzed comprehensively to derive the best fitting method and governing kinetic equation for thermal decomposition reaction of different aluminous bearing materials.

The most crucial operative factor in the course of dehydration is the rate of loss of water from the interface between the hydrated and decomposed product and the rate of

diffusion of water molecule through the product under isothermal or non-isothermal conditions.

The basis for understanding of the rate process for isothermal study is the Arrhenius relationship which states that for any process, the logarithm of the reaction rate constant bears a reciprocal relationship with absolute temperature. The relative influences of each factor have been compared through rate curves and kinetic parameter obtained through the isothermal changes, nature of the products through tailoring the kinetic parameters of the thermal treatment.

Keeping in view the variation of water molecule content and their orientation in polymorphic alumina lattice of hydrated alumina minerals or synthesized alumina hydrate gel, the present investigation is aimed at the compressive study on kinetics of thermal decomposition of natural hydrated aluminous mineral like bauxite rock and synthetic alumina hydrate gel under isothermal as well as non-isothermal condition from its thermal analysis TG-DTGA data using different heating rates. The kinetic parameters such as order of reaction, degree of reversibility, values of rate constant, activation energy, validity of 1st order law and pre exponential factor are also determined from thermogravimetric study.

For this purpose, natural bauxite rock of Indian origin (Sourastra) along with synthesized hydrated alumina gel is chosen. The experimental samples are thoroughly characterized by chemical analysis, specific surface area, particle size distribution, FTIR study, TG-DTA analysis, XRD analysis and SEM study.

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Dehydration-rehydration behavior of hydrated alumina samples was being studied in the temperature range 100°C-800°C and relative humidity range 35 % - 100 % respectively. Earlier researchers[23-27] studied extensively the isothermal transformation kinetics of gibbsite, boehmite and bayerite to corundum via series of transition aluminas. It considers the pre-exponential factor as independent of temperature. Nevertheless, conventional method results in ambiguity under linear heating rates if the studied reaction is governed by diffusion controlled kinetic law. In contrast, the dehydration kinetics and transformation mechanism of bauxite ore or synthetic alumina hydrate gel remains still uncertain under non-isothermal condition which is mostly followed in industries. In non-isothermal method, kinetic of decomposition can be computed over the entire temperature range in continuous manner using different sets of heating rate keeping in close agreement with actual calcination conditions followed for aluminous raw materials.

In case of non-isothermal study, integral approximation model of modified Coats and Redfern[28-29], isoconversional FWO model[30-31] and model free Kissinger model[32] were applied individually on the thermogravimetric data obtained at different rates of heating for each sample.

The basic objective of the study is to find out precisely the rate constant, pre exponential factor, activation energy for dehydration-dehydroxylation reaction taking place on two different types of hydrated alumina samples during progressive heat treatment. Attempts have also been made to elucidate the reaction mechanism of thermal decomposition for two types of hydrated alumina sample by Malek method[33-34].

From technological point of view, kinetic study carries a huge importance in predicting the sintering temperature and sintering behavior of aluminous materials. Hence, the kinetic parameters for thermal decomposition of different types of aluminous materials using different methods would be precisely analyzed and optimized.