DEVELOPMENT OF PILOT-SCALE REACTOR FOR THE PRODUCTION OF ALUMINIUM HYDROXIDE FROM ALUM DERIVED FROM KANKARA KAOLIN FOR ZEOLITE Y SYNTHESIS

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A THESIS SUBMMITED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE (MSc) IN CHEMICAL ENGINEERING

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APRIL, 2015

DECLARATION

I hereby declare that this thesis entitled "Development of pilot-scale reactor for the production of aluminium hydroxide from alum derived from kankara kaolin for zeolite y synthesis" was performed by me in the Department of Chemical Engineering under the supervision of Prof A.S. Ahmed and Dr. A. Hamza. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other institution.

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CERTIFICATION

This thesis titled "DEVELOPMENT OF PILOT-SCALE REACTOR FOR THE PRODUCTION OF ALUMINIUM HYDROXIDE FROM ALUM DERIVED FROM KANKARA KAOLIN FOR ZEOLITE Y SYNTHESIS" by SaniNAKAKANA meets the regulations governing the award of the degree of Master of Science (MSc) of Ahmadu Bello University and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to Almighty Allah (S.W.T).

ACKNOWLEDGEMENT

I thank Allah (SWT) who, in His infinite mercy and blessing, favored me in life, thus giving me the ability to see through the completion of this virtuous work and making my dream a reality.

My heartfelt thanks tomy parents who were responsible for whatever I achieve in life. I will forever extol the roles you played in my life. May Allah (SWT) grant you both Jannatulfirdaus.

My unconditional plaudits go to the one, most prominent, and most beloved pillar in my life, my wife. Only Allah can quantify the deeply felt gratitude I feel for all the years you have stood by my side. May Allah make the recompense for all your efforts the most exalted companionship.

I heartily express my appreciation to my mentor, learned supervisor, and professional father, Prof. A.S. Ahmed for his immeasurable support and tireless supervision. Your advice and constructive criticisms made this work a success. Accordingly, I want to acknowledge the contribution of my minor supervisor, Dr A. Hamza. Your support and kindness is duly appreciated. My special thanks to Dr. I.A. Mohammed-Dabo, Dr. S.M. Waziri, Dr. O.A. Ajayi, DrA.Y.Atta, and Engr. H.F.Akande for their intellectual contributions in the realization of this work.

My profound gratitude goes to the Petroleum Technology Development Fund (PTDF) Chair in Chemical Engineering A.B.U. Zaria for funding this research.

The journey is incomplete without duly acknowledging my colleagues, the research fellows at the PTDF Chair A.B.U. Zaria; Dr. Suleiman Yunusa, Dr.NurudeenSalahudeen, Mr. Solomon G. Bawa, Mallam Mustapha Yusuf and Mr. Kehinde A. Salihu for their incalculable support. Special regards to the PTDF Chair administrative staff, the staff in Chemical Engineering Department A.B.U. Zaria and all my colleagues and friends. Thank you all.

ABSTRACT

This work wasaimed at the design and fabrication of a pilot scale reactor for the production of aluminium hydroxide from aluminium sulphate obtained from Kankara kaolin for use in Zeolite Y synthesis. XRD, XRF and BET analyses were carried out on the aluminium hydroxide first prepared at bench scale and pilot scale. The aluminum hydroxide precipitated on a laboratory bench scale at the pH value of 6 was found to be amorphous while that precipitated at pH value of 7 was found to be a crystalline mix of boehmite and bayerite.The BET surface area of aluminium hydroxide precipitated at the laboratory bench scale was found to be 78.275m^2/g for a pH value of 6 and 209.799m^2/g for a pH value of 7. The effect of temperature on the amountof aluminium hydroxide precipitated was found to be marginal.From the kinetic studies of the precipitation reaction for aluminium hydroxide, the reaction was found to bepseudo-first order with respect to aluminium sulphate. The activation energy and pre-exponential factor of the precipitation reaction were found to be 102kJ/mole and 1.15x10^{14}/sec respectively.Zeolite Y was synthesized using the aluminium hydroxide produced from Kankara kaolin on a laboratory bench scale. A pilot scale semi-batch reactor was designed for the production of aluminium hydroxide and a conversion of 99.98% of aluminium sulphate reactant was obtained. A pilot scale semi-batch reactor with a capacity of 10.448kg per day for the production of aluminium hydroxide was fabricated and test run, and produced good quality aluminium hydroxide with a BET surface area of 97.73m^2/g for the first run and 227.779m^2/g for the second run. The product from the pilot scale reactor was found to be a mixture of crystalline and amorphous phases for the first run, and a purely crystallinemix of bayerite and boehmite for the second run.

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LIST OF ABBREVIATIONS

α	alpha
β	beta
□	gamma
ω	omega
ρ	para
AAS	Atomic absorption spectrometer
Alum	Aluminium sulphate
atm	atmosphere
^{O}C	Degree centigrade
CSTR	Continuous stirred tank reactor
e.g	For example
etc	etcetera (and so forth)
FCC	Fluid catalytic cracking
g	gram
hr	hour
i.e	that is
J	Joule
k	kilo
kgmole	kilogram mole
mol	mole
ODE	Ordinary differential equation
PFR	Plug flow reactor
sec	seconds

CHAPTER ONE

1.0 INTRODUCTION

The need for an increase in the lighter fractions obtained during petroleum processing led to the cracking of the heavy oil fractions gotten from distillation. There are two methods by which this is achieved which are thermal cracking and catalytic cracking. Over the years catalytic cracking has surmounted thermal cracking as the principal process adopted for the cracking of heavier oil fractions. This is due to the effect of the catalyst in catalytic cracking that lowers the activation energy of the chemical reactions, thereby enabling the conversion of the heavy oil fractions at relatively low temperatures of 500-600^{0}C compared to 750-900^{0}C obtained in thermal cracking. Also, there is an improved yield and quality of product obtained by catalytic cracking as compared with thermal cracking.

Catalytic cracking occurs in a fluid catalytic cracking (FCC) unit in the presence of a catalyst. The catalyst is made up of zeolite dispersed in a catalyst matrix, binders and fillers. The catalyst matrix is primarily made up of active alumina. The relative percentages of these components in catalyst formulation affect the performance of the catalyst. These zeolites are incorporated in the matrix because alone they are expensive and catalytically too active to be used in FCC units of practical dimensions due to severe heat transfer requirements.

Alumina is widely used in a variety of industrial fields due to its excellent physical and chemical properties. Aluminas are used in catalysts and as support for catalysts due to their large surface area, superior chemical activity and low cost.

Alumina is obtained commercially from bauxite via the Bayer process which involves the pyrolysis of aluminium hydroxide obtained from bauxite. Non-bauxitic materials, which are more abundant in many countries than bauxite resources, have also been processed in

attempts to develop alternative technologies for alumina production (Hosseini et al, 2011). Some examples of non-bauxitic raw materials include alunite, silimanite, andalusite, kyanite, mica, fly ash, and kaolin.

Kaolin has been found to be a suitable substitute for bauxite due to its considerable alumina content (36-39wt%) and global abundance. It is also next to bauxite in alumina content and purity among the clay family (Aderemi et al, 2001). Also, previous works have shown that the kaolin deposits in Nigeria are a rich alternative source for obtaining alumina (Bawa, 2012). Aluminium hydroxide, the primary precursor used in the production of active alumina can be obtained from kaolin.

This research work is focused on the production of aluminum hydroxide obtained from the calcination, dealumination and hydroxylation of Kankara kaolin, and the construction of a pilot scale reactor for the production of aluminium hydroxide.

1.1 Research Problem

Bauxite, which is the primary precursor in aluminium hydroxide production, is dwindling in quantity globally, and is virtually nonexistent in Nigeria. Gibbsite, which is the primary component of aluminium hydroxide in bauxite is found only in small quantities in Nigeria (Agbaja plateau inLokoja, Kogi State (Mindat.org)). Red mud, a waste product of the bayer process for producing aluminium hydroxide is very hazardous (BBC, 2010). Also, no pilot scale reactor for the production of aluminium hydroxide from Kankara kaolin has been developed.

1.2 Research Scope

The scope of this work covers the laboratory bench scale preparation, pilot-scale production, and characterization of aluminium hydroxide produced from Kankara kaolin clay.

1.3 Research Aim and Objectives

The aim of this work was to design and fabricate a semi-batch reactor for the production ofaluminium hydroxide from Kankara kaolin for Zeolite Y synthesis.

The specific objectives are:

i. To synthesize and characterisealuminium hydroxide from Kankara kaolin for zeolite catalyst synthesis.
ii. To design, fabricate and test-run a semi-batch reactor for the production of aluminium hydroxide from Kankara kaolin.

1.4 Research Justification

1. Enhancement of indigenous technology in aluminium hydroxide production.
2. Production of aluminium hydroxide from Kankara kaolin for zeolite production would be actualized.
3. Conservation of foreign exchange earnings.
4. Creation of job opportunities through increase in investment opportunities.

CHAPTER TWO

2.0 SURVEY OF LITERATURE

2.1 Catalysis

Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself (Lerner,2011). A catalyst may participate in multiple chemical transformations. Catalysts that speed the reaction are called positive catalysts. Substances that slow a catalyst's effect in a chemical reaction are called inhibitors. Substances that increase the activity of catalysts are called promoters, and substances that deactivate catalysts are called catalytic poisons.

Catalytic reactions have a lower rate-limiting free energy of activation than the corresponding uncatalyzed reaction, resulting in higher reaction rate at the same temperature. However, the mechanistic explanation of catalysis is complex. Catalysts may affect the reaction environment favorably, or bind to the reagents to polarize bonds, e.g. acid catalysts for reactions of carbonyl compounds, or form specific intermediates that are not produced naturally, such as osmateesters in osmium tetroxide-catalyzed dehydroxylation of alkenes, or cause dissociation of reagents to reactive forms, such as atomic hydrogen in catalytic hydrogenation.

Kinetically, catalytic reactions are typical chemical reactions; i.e. the reaction rate depends on the frequency of contact of the reactants in the rate-determining step. Usually, the catalyst participates in this slowest step, and rates are limited by amount of catalyst and its "activity". In heterogeneous catalysis, the diffusion of reagents to the surface and diffusion of products from the surface can be rate determining. A Nanomaterial-based catalyst is an example of a

heterogeneous catalyst. Analogous events associated with substrate binding and product dissociation apply to homogeneous catalysts.

Although catalysts are not consumed by the reaction itself, they may be inhibited, deactivated, or destroyed by secondary processes. In heterogeneous catalysis, typical secondary processes include coking where the catalyst becomes covered by polymeric side products. Additionally, heterogeneous catalysts can dissolve into the solution in a solid–liquid system or evaporate in a solid–gas system.

2.1.1 Background of catalysis

The production of most industrially important chemicals involves catalysis. Similarly, most biochemically significant processes are catalysed. Research into catalysis is a major field in applied science and involves many areas of chemistry, notably in organometallic chemistry and materials science. Catalysis is relevant to many aspects of environmental science, e.g. the catalytic converter in automobiles and the dynamics of the ozone hole. Catalytic reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated, as opposed to stoichiometric reactions in which all reactants are consumed and more side products are formed. The most common catalyst is the hydrogen ion (H^+). Many transition metals and transition metal complexes are used in catalysis as well. Catalysts called enzymes are important in biology.

A catalyst works by providing an alternative reaction pathway to the reaction product. The rate of the reaction is increased as this alternative route has a lower activation energy than the reaction route not mediated by the catalyst. The disproportionation of hydrogen peroxide creates water and oxygen, as shown below.

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad (2.1)$$

This reaction is preferable in the sense that the reaction products are more stable than the starting material, though the uncatalysed reaction is slow. In fact, the decomposition of hydrogen peroxide is so slow that hydrogen peroxide solutions are commercially available. This reaction is strongly affected by catalysts such as manganese dioxide, or the enzyme peroxidase in organisms. Upon the addition of a small amount of manganese dioxide, the hydrogen peroxide reacts rapidly. This effect is readily seen by the effervescence of oxygen. The manganese dioxide is not consumed in the reaction, and thus may be recovered unchanged, and re-used indefinitely. Accordingly, manganese dioxide catalyses this reaction (Masel, 2001).

Catalysts generally react with one or more reactants to form intermediates that subsequently give the final reaction product, in the process regenerating the catalyst. The following is a typical reaction scheme, where *C* represents the catalyst, X and Y are reactants, and Z is the product of the reaction of X and Y:

$$X + C \rightarrow XC \quad (1)$$

$$Y + XC \rightarrow XYC \quad (2)$$

$$XYC \rightarrow CZ \quad (3)$$

$$CZ \rightarrow C + Z \quad (4)$$

Although the catalyst is consumed by reaction 1, it is subsequently produced by reaction 4, so for the overall reaction:

$$X + Y \rightarrow Z \qquad (2.2)$$

As a catalyst is regenerated in a reaction, often only small amounts are needed to increase the rate of the reaction. In practice, however, catalysts are sometimes consumed in secondary processes.

2.1.2 Catalysis and reaction energetics

Catalysts work by providing an (alternative) mechanism involving a different transition state and lower activation energy as shown in Figure 2.1:

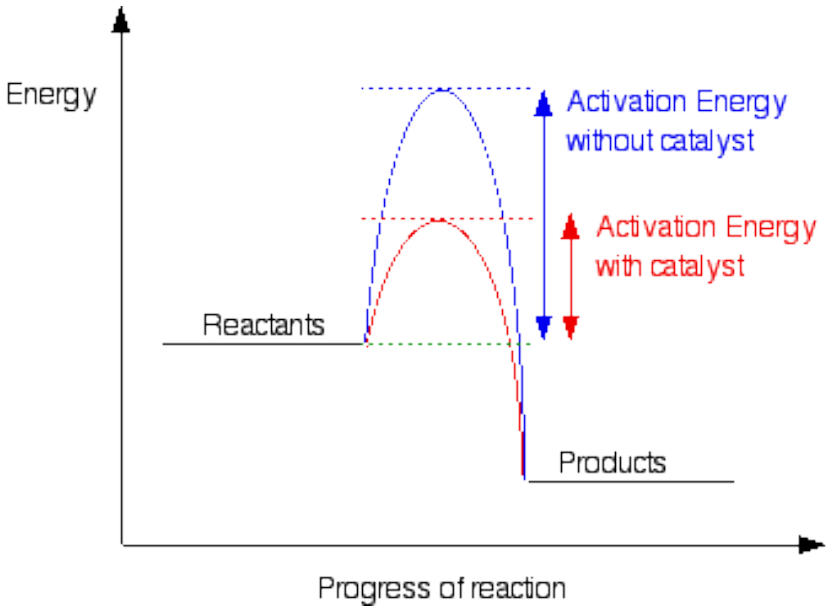


Figure 2.1: Generic potential energy diagram showing the effect of a catalyst in a hypotheticalexothermic chemical reaction (Clark, 2010)

Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be blocked or slowed by a kinetic barrier. The catalyst may increase reaction rate or selectivity, or enable the reaction at lower temperatures. This effect can be illustrated with a Boltzmann distribution and energy profile diagram. In the catalyzed elementary reaction, catalysts do not change the extent of a reaction: they have no effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are both affected. The fact that a catalyst does not change the equilibrium is a consequence of the second law of thermodynamics. If a catalyst

does change the equilibrium, then it must be consumed as the reaction proceeds, and thus it is also a reactant. Illustrative is the base-catalysedhydrolysis of esters, where the produced carboxylic acid immediately reacts with the base catalyst and thus the reaction equilibrium is shifted towards hydrolysis (Robertson, 1970).

The SI derived unit for measuring the catalytic activity of a catalyst is the katal, which is moles per second. The productivity of a catalyst can be described by the turn over number (or TON) and the catalytic activity by the turn over frequency (TOF), which is the TON per time unit. The biochemical equivalent is the enzyme unit. The catalyst stabilizes the transition state more than it stabilizes the starting material. It decreases the kinetic barrier by decreasing the difference in energy between starting material and transition state. It does not change the energy difference between starting materials and products (thermodynamic barrier), or the available energy (this is provided by the environment as heat or light).

2.1.3Typical catalytic materials

The chemical nature of catalysts is as diverse as catalysis itself, although some generalizations can be made. Proton acids are probably the most widely used catalysts, especially for the many reactions involving water, including hydrolysis and its reverse. Multifunctional solids often are catalytically active, e.g. zeolites, alumina, higher-order oxides, graphitic carbon, nanoparticles, nanodots, and facets of bulk materials. Transition metals are often used to catalyze redox reactions (oxidation, hydrogenation). Many catalytic processes, especially those used in organic synthesis, require so called "late transition metals", which include palladium, platinum, gold, ruthenium, rhodium, and iridium.

Some so-called catalysts are really precatalysts. Precatalysts convert to catalysts in the reaction. Precatalysts are easier to store but are easily activated in situ (Arulmurugu*et al*,

2014). Because of this preactivation step, many catalytic reactions involve an induction period.

Chemical species that improve catalytic activity are called co-catalysts (cocatalysts) or promoters in cooperative catalysis.

2.1.4Types of catalysis

Catalysts can be either heterogeneous or homogeneous, depending on whether a catalyst exists in the same phase as the substrate. Biocatalysts (enzymes) are often seen as a separate group.

2.1.4.1Heterogeneous catalysis

Heterogeneous catalysts act in a different phase than the reactants. Figure 2.2 is a simple diagram of a common heterogenous catalyst:

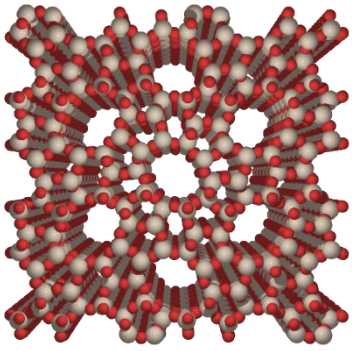


Figure 2.2:Molecular structure of zeolite ZSM-5 (Grabow, 2010)

Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place (Langmuir-Hinshelwood, Eley-Rideal, and Mars-van Krevelen)(Knözinger*et al*, 2003). The total surface area of solid has an important effect on

the reaction rate. The smaller the catalyst particle size, the larger the surface area for a given mass of particles.Heterogeneous catalysts are typically "supported," which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Sometimes the support is merely a surface on which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction. Supports are porous materials with a high surface area, most commonly alumina or various kinds of activated carbon. Specialized supports include silicon dioxide, titanium dioxide, calcium carbonate, and barium sulfate.

2.1.4.2Homogeneous catalysis

Homogeneous catalysts function in the same phase as the reactants, but the mechanistic principles involved in heterogeneous catalysis are generally applicable. Typically homogeneous catalysts are dissolved in a solvent with the substrates. One example of homogeneous catalysis involves the influence of H^+ on the esterification of esters, e.g. methyl acetate from acetic acid and methanol. For inorganic chemists, homogeneous catalysis is often synonymous with organometallic catalysts (Elschenbroich, 2006).

2.1.4.3 Electrocatalysis

In the context of electrochemistry, specifically in fuel cell engineering, various metal-containing catalysts are used to enhance the rates of the half reactions that comprise the fuel cell. One common type of fuel cell electrocatalyst is based upon nanoparticles of platinum that are supported on slightly larger carbon particles. When in contact with one of the electrodes in a fuel cell, this platinum increases the rate of oxygen reduction to water, either to hydroxide or hydrogen peroxide.

2.1.4.4 Organocatalysis

Whereas transition metals sometimes attract most of the attention in the study of catalysis, small organic molecules without metals can also exhibit catalytic properties, as is apparent from the fact that many enzymes lack transition metals. Typically, organic catalysts require a higher loading (amount of catalyst per unit amount of reactant, expressed in mol%amount of substance) than transition metal(-ion)-based catalysts, but these catalysts are usually commercially available in bulk, helping to reduce costs. Organocatalysts are supposed to operate akin to metal-free enzymes utilizing, e.g., non-covalent interactions such as hydrogen bonding.

2.1.5 Significance of catalysis

Estimates are that 90% of all commercially produced chemical products involve catalysts at some stage in the process of their manufacture. In 2005, catalytic processes generated about $900 billion in products worldwide(Busacca*et al*, 2012). Catalysis is so pervasive that subareas are not readily classified. Some areas of particular concentration are surveyed below.

2.1.5.1 Fuel processing

Petroleum refining makes intensive use of catalysis for alkylation, catalytic cracking, naphtha reforming and steam reforming (conversion of hydrocarbons into synthesis gas). Even the exhaust from the burning of fossil fuels is treated via catalysis: Catalytic converters, typically composed of platinum and rhodium, break down some of the more harmful byproducts of automobile exhaust.

$$2\ CO + 2\ NO \rightarrow 2\ CO_2 + N_2 \qquad (2.3)$$

With regard to synthetic fuels, an old but still important process is the Fischer-Tropsch synthesis of hydrocarbons from synthesis gas, which itself is processed via water-gas shift reactions, catalysed by iron. Biodiesel and related biofuels require processing via both inorganic and biocatalysts.Fuel cells rely on catalysts for both the anodic and cathodic reactions.Catalytic heaters generate flameless heat from a supply of combustible fuel.

2.1.5.2 Bulk chemicals

Some of the largest-scale chemicals are produced via catalytic oxidation, often using oxygen. Examples include nitric acid (from ammonia), sulfuric acid (from sulfur dioxide to sulfur trioxide by the chamber process), terephthalic acid from p-xylene, and acrylonitrile from propane and ammonia.

Many other chemical products are generated by large-scale reduction, often via hydrogenation. The largest-scale example is ammonia, which is prepared via the Haber process from nitrogen. Methanol is prepared from carbon monoxide.Bulk polymers derived from ethylene and propylene are often prepared via Ziegler-Natta catalysis. Polyesters, polyamides, and isocyanates are derived via acid-base catalysis.Most carbonylation processes require metal catalysts, examples include the Monsanto acetic acid process and hydroformylation.

2.1.5.3 Fine chemicals

Many fine chemicals are prepared via catalysis; methods include those of heavy industry as well as more specialized processes that would be prohibitively expensive on a large scale. Examples include olefin metathesis using Grubbs' catalyst, the Heck reaction, and Friedel-Crafts reactions.Because most bioactive compounds are chiral, many pharmaceuticals are produced by enantioselective catalysis (catalytic asymmetric synthesis).

2.2 Fluid Catalytic Cracking (FCC)

Fluid catalytic cracking (FCC) is the most important conversion process used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleumcrude oils to more valuable gasoline, olefinic gases, and other products. Cracking of petroleum hydrocarbons was originally done by thermal cracking, which has been almost completely replaced by catalytic cracking because it produces more gasoline with a higher octane rating. It also produces byproduct gases that are more olefinic, and hence more valuable, than those produced by thermal cracking.

The feedstock to an FCC is usually that portion of the crude oil that has an initial boiling point of 340^0C or higher at atmospheric pressure and an average molecular weight ranging from about 200 to 600 or higher. This portion of crude oil is often referred to as heavy gas oil (HGO) or vacuum gas oil (VGO). The FCC process vaporizes and breaks the long-chain molecules of the high-boiling hydrocarbon liquids into much shorter molecules by contacting the feedstock, at high temperature and moderate pressure, with a fluidized powdered catalyst.

In effect, refineries use fluid catalytic cracking to correct the imbalance between the market demand for gasoline and the excess of heavy, high boiling range products resulting from the distillation of crude oil.

As at 2006, FCC units were in operation at 400 petroleum refineries worldwide and about one-third of the crude oil refined in those refineries is processed in an FCC to produce high-octane gasoline and fuel oils (Speight, 2006).

2.2.1 FCC Catalysts

A catalyst is a substance that changes the rate of a chemical reaction without undergoing any chemical changes. Modern FCC catalysts are fine powders with a bulk density of 0.80 to 0.96

g/cc and having a particle size distribution ranging from 10 to 150 μm and an average particle size of 0 to 80 μm (Yang,2003). The design and operation of an FCC unit is largely dependent upon the chemical and physical properties of the catalyst. The desirable properties of an FCC catalyst are:

- Good stability to high temperature and to steam
- High activity
- Large pore sizes
- Good resistance to attrition
- Low coke production

A modern FCC catalyst has four major components: crystalline zeolite, matrix, binder, and filler. Zeolite is the primary active component and can range from about 15 to 50 weight percent of the catalyst. The zeolite used in FCC catalysts is referred to as faujasite or as Type Y and is composed of silica and aluminatetrahedra with each tetrahedron having either an aluminum or a silicon atom at the center and four oxygen atoms at the corners. It is a molecular sieve with a distinctive lattice structure that allows only a certain size range of hydrocarbon molecules to enter the lattice. In general, the zeolite does not allow molecules larger than .8 to 1 nm (i.e., 8 to 10 angstroms) to enter the lattice (Yang, 2003).

The catalytic sites in the zeolite are strong acids (equivalent to 90% sulfuric acid) and provide most of the catalytic activity. The acidic sites are provided by the alumina tetrahedra. The matrix component of an FCC catalyst contains amorphous alumina which also provides catalytic activity sites and in larger pores that allows entry for larger molecules than does the zeolite. That enables the cracking of higher-boiling, larger feedstock molecules than are cracked by the zeolite.The binder and filler components provide the physical strength and integrity of the catalyst. The binder is usually silica sol and the filler is usually clay (kaolin).

2.3 Zeolites

Zeolites are crystalline, microporous, hydrated aluminosilicates of alkaline or alkalineearth metals. The frameworks are composed of [$Si0_4$]4-and [$A10_4$]5-tetrahedra, which corner-share to form different open structures. As of September 2014, 216 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known (International Zeolite Association). Thetetrahedra are linked together to form cages connected by pore openings of defined size; depending on the structural type, the pore sizes range from approximately 0.3-1 nm (Barrer, 1982). The negative charge on the lattice is neutralized by the positive charge of cations located within the material's pores. In the basic zeolites, these are usually univalent and bivalent metals or a combination. The metal cations may be replaced by acidic protons via ion-exchange to ammonium and subsequent calcination. By reason of electrostatic forces it is not possible to make an Al- O-Al bond. They are made up of "T-atoms" which are tetrahedrally bonded to each other with oxygen bridges. Other "T-atoms" such as P, Ga, Ce, B and Be can also exist in the framework. Due to their exceptional properties, zeolites have been widely used in numerous technical applications as catalysts, adsorbents and ion exchangers (Bekkum*et al.,* 1991).

2.3.1 Zeolite structure

The structural formula of zeolite is based on the crystallographic unit cell:

$$Mx/n\ [(AlO_2)x(SiO_2)y]\ wH_2O \qquad (2.4)$$

where (M) is an alkali or alkaline earth cation, (n) is the valence of the cation, (w) is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and the ratio y/x usually has values of 1 to 5, though for the silica zeolite, y/x can be ranging from 10 to 100.

Zeolites have been well studied in terms of the relations among structure, properties and synthesis. Some of the earlier synthetic zeolites include zeolites A, X, Y, L, ZSM-5 and omega. The Atlas of Zeolite Structure Types (Meier and Olson, 1987) published and frequently updated by the IZA Structure Commission, assigns a three – letter code to be used for a known framework topology irrespective of composition.

Illustrative codes are LTA for Linde zeolite A, FAU for molecular sieves with a faujasitetopology (e.g., zeolites X, Y), MOR for the mordenite topology, MFI for the ZSM - 5 and silicalite topologies and AFI for the aluminophosphate AlPO4-5 topology. The acceptance of a newly determined structure of a zeolite or molecular sieve for inclusion in the official Atlas is reviewed and must be approved by the IZA Structure Commission. The IZA Structure Commission was given authority at the Seventh International Zeolite Conference (Tokyo, 1986) to approve and/or assign the three - letter structure code for new framework topologies (Meier and Olson, 1987).

In most zeolite structures the primary structural units, the AlO_4 or SiO_4tetrahedra, are assembled into secondary building units which may be simple polyhedra, such ascubes, hexagonal prisms or cubo - octahedra. The final framework structure consists ofassemblages of the secondary units. More than 70 novel, distinct framework structures ofzeolites are known. They exhibit pore sizes from 0.3 to 1.0 nm and pore volumes fromabout 0.10 to 0.35 cm^3/g. Typical zeolite pore sizes include: (i) small pore zeolites witheight - ring pores, free diameters of 0.30 − 0.45 nm (e.g., zeolite A), (ii) medium porezeolites with 10 − ring pores, 0.45 − 0.60 nm in free diameter (ZSM - 5), (iii) large porezeolites with 12 − ring pores of 0.6 − 0.8 nm (e.g., zeolites X, Y) and (iv) extra - large porezeolites with 14 -ring pores (e.g., UTD - 1) (McCusker*et al.*, 2001).

2.3.2Zeolite synthesis

The synthetic zeolites are used commercially more often than natural zeolites due tothe purity of crystalline products and the uniformity of particle sizes. The sources for earlysynthesized zeolites were standard chemical reagents. Much of the study of basic zeolitescience was done on natural zeolites. The main advantages of synthetic zeolites incomparison to naturally-occurring zeolites are that they can be engineered with a widevariety of chemical properties and pore sizes and that they have greater thermal stability.The zeolite synthesis involves the hydrothermal crystallization of aluminosilicate gels(formed upon mixing an aluminate and silica solution in the presence of alkali hydroxidesand/or organic bases), or solutions in a basic environment. The crystallization is in aclosed hydrothermal system at increasing temperature, autogenous pressure and varyingtime (few hours to several days). The type of the zeolite is affected mainly by the following factors (Georgiev*et al.*, 2011):

i. Composition of the reaction mixture (silica to alumina ratio; OH-; inorganic cations): Increasing the Si/Al ratio strongly affects physical properties of the zeolites. OH- modifies the nucleation time by influencing transport of silicates from the solid phase to solution.Inorganic cations act as structure directing agents and balance the framework charge.They affect the crystal purity and product yield.
ii. Nature of reactants and their pretreatments: The zeolite synthesis is carried outwith inorganic as well as organic precursors. The inorganic precursors yielded morehydroxylated surfaces whereas the organic precursors easily incorporated the metals intothe network.
iii. Temperature of the process: The rate of crystallization is directly proportional totemperature while the rate of nucleation is inversely proportional to temperature).
iv. Reaction time: Crystallization parameter must be adjusted to minimize theproduction of the other phases while also minimizing the time needed to obtain the desired crystalline phase.

v. pH of the reaction mixture: The process of zeolitization is carried out in alkalinemedium (pH>10).

The synthesis can be carried out on a continuous or semi continuousmode, which enhances the capacity, making it compatible for industrial applications.

The main problem in zeolite research is the availability and cost of raw materialspecifically the silica source. On the other hand, commercial silica (made of sand) which isavailable in gel, sol, fumed or amorphous solid is found to be variable in reactivity andselectivity. The preparation of synthetic zeolites from silica and alumina chemical sourcesis expensive. Yet, cheaper raw materials, such as clay minerals, natural zeolites, coalashes, municipal solid waste incineration ashes and industrial slags, are utilized as startingmaterials for zeolite synthesis. The use of waste materials in zeolite synthesis contributesto the mitigation of environmental problems, generally in the field of water purification,removing heavy metals or ammonium, and turns them into attractive and useful products.

2.3.2.1Kaolin based zeolites

Kaolin is clay mineral whose structure represent SiO_4tetrahedral sheets joined to $Al(O,OH)_6$ octahedral sheets through shared oxygen atoms. Zeolitesprepared from natural kaolin are always contaminated with trace amount of iron, titanium,calcium, magnesium, etc. which are originally present in the natural kaolin. Theseelements may have some influence on the zeolite properties such as brightness,hardness, catalytic activity, electrical properties, etc. Presently, many researchers areworking actively in various aspects on the synthesis of zeolite from kaolin. Clay minerals,such as kaolin, illite, smectite, interstratified illite-smectite, montmorillonite and bentoniteare widely used for synthesis of zeolites. The benefits of using kaolin as an aluminosilicatesource in zeolite synthesis widely known. Studies on thepreparation of various zeolites from kaolin or other ashes have been made with great

progress insynthesis of 4A, mordenite, X, Y zeolites, etc. Kaolin is usually used after calcination attemperatures between 550-950°C to obtain a more reactive phase metakaolin underchemical treatments, with the loss of structural water. Only a small part of AlO_6octahedrais maintained, while the rest are transformed into much more reactive tetra- and penta-coordinatedunits. The conditions of the kaolin calcination strongly influence the reactivityof the obtained solids. The best conditions for obtaining a very reactive metakaolin havebeen discussed by several authors who reported values between 600-800 °C (Rios *et al.,* 2009).

Classical hydrothermal synthesis of zeolites from kaolin include: (i) thermalactivation of kaolinite in order to get metakaolinite; (ii) hydrothermal reaction ofmetakaolinite with various aqueous alkali media;(iii) purification and activation of theresulting zeolite.

Zeolite produced from kaolin is widely reported in literature. The synthesis of zeolite Type NaA from Bulgaria kaolinite by conventional alkalineactivation was investigated by Georgiev*et al*(2011). The low grade Kalabsha kaolin coexisting with quartz, and anatasewas thermally activated between 600 and 1000 °C and treated hydrothermally with 2−8 MNaOH solution with or without added water glass, using water bath or autoclave. Slangen*et al* (1997) produced zeoliteNaA from the synthesis mixture which has a composition of $1SiO_2$:$1Al_2O_3$:$1.5Na_2O$:$6.5H_2O$molar ratios by using a microwave oven. Alkan*et al* (2005) synthesized zeolite NaXfrom locally available natural kaolinite, as metakaolin.

In recent years there has been considerable progress made in the field ofaccelerating the kinetics of low-temperature inorganic synthesis. Several techniques, likesonochemical (acoustic wave stimulation), ionizing and non-ionizing radiation, microwavehydrothermal, hydrothermal process with superimposed electric fields, hydrothermalprocess with

mechanical forces, and mechanochemical, including very high uniaxial pressure and shear have been used (Roy, 1994).

2.3.3 Use of zeolites in thepetrochemical industry

Synthetic zeolites are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydrocracking. Zeolites confine molecules in small spaces, which causes changes in their structure and reactivity. The hydrogen form of zeolites (prepared by ion-exchange) are powerful solid-state acids, and can facilitate a host of acid-catalyzed reactions, such as isomerisation, alkylation, and cracking.

Catalytic cracking uses a reactor and a regenerator. Feed is injected onto hot, fluidized catalyst where large gasoil molecules are broken into smaller gasoline molecules and olefins. The vapor-phase products are separated from the catalyst and distilled into various products. The catalyst is circulated to a regenerator where air is used to burn coke off the surface of the catalyst that was formed as a byproduct in the cracking process. The hot regenerated catalyst is then circulated back to the reactor to complete its cycle.

2.4 Alumina

Aluminium oxide is a chemical compound of aluminium and oxygen with the chemical formulaAl_2O_3. It is the most commonly occurring of several aluminium oxides, and specifically identified as aluminium(III) oxide. It is commonly called alumina, and may also be called aloxide, aloxite, or alundum depending on particular forms or applications. It commonly occurs in its crystalline polymorphicphase α-Al_2O_3, in which it comprises the mineralcorundum, varieties of which form the precious gemstonesruby and sapphire, which owe their characteristic colors to trace impurities.Al_2O_3 is significant in its use to produce

aluminium metal, as anabrasive owing to its hardness, and as a refractory material owing to its high melting point (The A-Z of Materials, 2007).

2.4.1 Properties of alumina

Al_2O_3 is an electrical insulator but has a relatively high thermal conductivity (30 $Wm^{-1}K^{-1}$) for a ceramic material. Aluminium oxide is insoluble in water. In its most commonly occurring crystalline form, called corundum or α-aluminium oxide, its hardness makes it suitable for use as an abrasive and as a component in cutting tools (The A-Z of Materials, 2007).

Aluminium oxide is responsible for the resistance of metallic aluminium to weathering. Metallic aluminium is very reactive with atmospheric oxygen, and a thin passivation layer ofaluminium oxide (4 nm thickness) forms on any exposed aluminium surface (Campbell et al, 1999).This layer protects the metal from further oxidation. The thickness and properties of this oxide layer can be enhanced using a process called anodising. A number of alloys, such as aluminium bronzes, exploit this property by including a proportion of aluminium in the alloy to enhance corrosion resistance. The aluminium oxide generated by anodising is typically amorphous, but discharge assisted oxidation processes such as plasma electrolytic oxidation result in a significant proportion of crystalline aluminium oxide in the coating, enhancing its hardness.

Aluminium oxide is an amphoteric substance, meaning it can react with both acids and bases, such as hydrofluoric acid and sodium hydroxide, acting as an acid with a base and a base with an acid, neutralising the other and producing a salt.

$$Al_2O_3 + 6\ HF \rightarrow 2\ AlF_3 + 3\ H_2O \qquad (2.5)$$

$$Al_2O_3 + 6\ NaOH + 3\ H_2O \rightarrow 2\ Na_3Al(OH)_6 \text{ (sodium aluminate)} \qquad (2.6)$$

2.4.2 Structure of alumina

The most common form of crystalline aluminium oxide is known as corundum, which is the thermodynamically stable form (Brandon and Brandon, 1998). The oxygen ions nearly form a hexagonal close-packed structure with aluminium ions filling two-thirds of the octahedral interstices. Each Al^{3+} center is octahedral. In terms of its crystallography, corundum adopts a trigonalBravais lattice with a space group of R-3c (number 167 in the International Tables). The primitive cell contains two formula units of aluminium oxide.

Aluminium oxide also exists in other phases, including the cubic γ and η phases, the monoclinic θ phase, the hexagonal χ phase, the orthorhombic κ phase and the δ phase that can be tetragonal or orthorhombic (Brandon and Brandon, 1998). Each has a unique crystal structure and properties. Cubic γ-Al_2O_3 has important technical applications.

2.4.3 Production of alumina

Aluminiumhydroxide minerals are the main component of bauxite, the principal ore of aluminium. A mixture of the minerals comprise bauxite ore, including gibbsite ($Al(OH)_3$), boehmite (γ-AlO(OH)), and diaspore (α-AlO(OH)), along with impurities of iron oxides and hydroxides, quartz and clay minerals. Bauxites are found in laterites. Bauxite is purified by the Bayer process:

$$AlO(OH) + H_2O + NaOH \rightarrow NaAl(OH)_4 \quad (2.7)$$

$$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4 \quad (2.8)$$

Except for SiO_2, the other components of bauxite do not dissolve in base. Upon filtering the basic mixture, Fe_2O_3 is removed. When the Bayer liquor is cooled, $Al(OH)_3$ precipitates, leaving the silicates in solution.

$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3 \quad (2.9)$$

The solid $Al(OH)_3$Gibbsite is then calcined (heated strongly) to give aluminium oxide:

$$2 \quad Al(OH)_3 \rightarrow Al_2O_3 + 3 \quad H_2O \quad (2.10)$$

The product aluminium oxide tends to be multi-phase, i.e., consisting of several phases of aluminium oxide rather than solely corundum (Paglia, 2004). The production process can therefore be optimized to produce a tailored product. The type of phases present affects, for example, the solubility and pore structure of the aluminium oxide product which, in turn, affects the cost of aluminium production and pollution control.

For its application as an electrical insulator in integrated circuits, where conformal growth of thin film is a prerequisite and the preferred growth mode is atomic layer deposition, Al_2O_3 films were prepared by the chemical exchange between trimethylaluminum $Al(CH_3)_3$ and H_2O:

$$2\ Al(CH_3)_3 + 3\ H_2O \rightarrow Al_2O_3 + 6\ CH_4 \quad (2.11)$$

H_2O in the above reaction was subsequently replaced by ozone (O_3) as the active oxidant and the following reaction took place:

$$2\ Al(CH_3)_3 + O_3 \rightarrow Al_2O_3 + 3\ C_2H_6 \quad (2.12)$$

The Al_2O_3 films prepared using O_3 show 10–100 times lower leakage current density compared with those prepared by H_2O.

Known as alundum (in fused form) or aloxite in the mining, ceramic, and materials science communities, aluminium oxide finds wide use. Annual world production of aluminium oxide

is approximately 45 million tonnes, over 90% of which is used in the manufacture of aluminium metal (The A-Z of Materials, 2007). The major uses of specialty aluminium oxides are in refractories, ceramics, and polishing and abrasive applications. Large tonnages are also used in the manufacture of zeolites, coating titania pigments, and as a fire retardant/smoke suppressant.

2.4.4 Applications of alumina

The great majority of aluminium oxide is consumed for the production of aluminium, usually by the Hall–Héroult process. Other applications are:

2.4.4.1 Filler

Being fairly chemically inert and white, aluminium oxide is a favored filler for plastics. Aluminium oxide is a common ingredient in sunscreen and is sometimes present in cosmetics such as blush, lipstick, and nail polish.

2.4.4.2 Catalysis

Aluminium oxide catalyses a variety of reactions that are useful industrially. In its largest scale application, aluminium oxide is the catalyst in the Claus process for converting hydrogen sulfide waste gases into elemental sulfur in refineries. It is also useful for dehydration of alcohols to alkenes.

Aluminium oxide serves as a catalyst support for many industrial catalysts, such as those used in hydrodesulfurization and some Ziegler-Natta polymerizations.

2.4.4.3 Purification

Aluminium oxide is widely used to remove water from gas streams.

2.4.4.4 Abrasive

Aluminium oxide is used for its hardness and strength. It is widely used as an abrasive, including as a much less expensive substitute for industrial diamond. Many types of sandpaper use aluminium oxide crystals. In addition, its low heat retention and low specific heat make it widely used in grinding operations, particularly cutoff tools.

2.4.4.5 Paint

Aluminium oxide flakes are used in paint for reflective decorative effects, such as in the automotive or cosmetic industries.

2.4.4.6 Composite fiber

Aluminium oxide has been used in a few experimental and commercial fiber materials for high-performance applications (e.g., Fiber FP, Nextel 610, Nextel 720). Alumina nanofibers in particular have become a research field of interest.

2.5 Bauxite

Bauxite is an aluminiumore and is the main source of aluminium. This form of rock consists mostly of the mineralsgibbsite $Al(OH)_3$, boehmite γ-AlO(OH), and diaspore α-AlO(OH), in a mixture with the two iron oxidesgoethite and hematite, the clay mineral kaolinite, and small amounts of anatase TiO_2. Bauxite was named after the village Les Baux in southern France, where it was first recognised as containing aluminium and named by the French geologist Pierre Berthier in 1821.

2.5.1 Bauxite formation

Lateritic bauxites (silicate bauxites) are distinguished from karst bauxite ores (carbonate bauxites). The early discovered carbonate bauxites occur predominantly in Europe and Jamaica above carbonate rocks (limestone and dolomite), where they were formed by lateritic weathering and residual accumulation of intercalated clays or by clay dissolution residues of the limestone.

The lateritic bauxites are found mostly in the countries of the tropics. They were formed by lateritization of various silicate rocks such as granite, gneiss, basalt, syenite, and shale. In comparison with the iron-rich laterites, the formation of bauxites depends even more on intense weathering conditions in a location with very good drainage. This enables the dissolution of the kaolinite and the precipitation of the gibbsite. Zones with highest aluminium content are frequently located below a ferruginous surface layer. The aluminium hydroxide in the lateritic bauxite deposits is almost exclusively gibbsite.

In the case of Jamaica, recent analysis of the soils showed elevated levels of cadmium suggesting that the bauxite originates from recent Mioceneash deposits from episodes of significant volcanism in Central America.

2.5.2 Production trends of bauxite

In 2010, Australia was the top producer of bauxite with almost one-third of the world's production, followed by China, Brazil, India, and Guinea. Increased aluminium recycling, which has the advantage of lowering the cost in electric power in producing aluminium, will considerably extend the world's bauxite reserves. Table 2.1 gives the total bauxite production and reserves in various countries (USA geological survey, 2012).

Table2.1: Total global proven bauxite reserves (x1,000 tonnes) (2010)

Country	Mine production		Reserves	Reserve base
	2010	2011 (est.)		
Guinea	17,400	18,000	7,400,000	8,600,000
Australia	68,400	67,000	6,200,000	7,900,000
Vietnam	80	80	2,100,000	5,400,000
Jamaica	8,540	10,200	2,000,000	2,500,000
Brazil	28,100	31,000	3,600,000	2,500,000
Guyana	1,760	2,000	850,000	900,000
India	18,000	20,000	900,000	1,400,000
China	44,000	46,000	830,000	2,300,000
Greece	2,100	2,100	600,000	650,000
Iran	—	500	—	—
Suriname	4,000	5,000	580,000	600,000
Sierra Leone	1,090	1,700	180,000	?
Kazakhstan	5,310	5,400	160,000	450,000
Venezuela	2,500	4,500	320,000	350,000
Russia	5,480	5,800	200,000	250,000
United States	NA	NA	20,000	40,000
Other countries	2,630	2,600	3,300,000	3,800,000

World total (rounded) 209,000 220,000 29,000,000 38,000,000

2.6Aluminium hydroxide

Aluminium hydroxide, $Al(OH)_3$, sometimes erroneously called hydrate of alumina, is found in nature as the mineral gibbsite (also known as hydrargillite) and its three, much more rare polymorphs: bayerite, doyleite and nordstrandite. In addition, two aluminum oxide–hydroxides, AlO(OH),boelimite and diaspore, have been clearly defined, differing only by loss of water. These compounds together are the major components of the aluminiumorebauxite.

These compounds are true hydroxidesand do not contain water of hydration. Several forms are known; a general classification is shown in Figure 2.3:

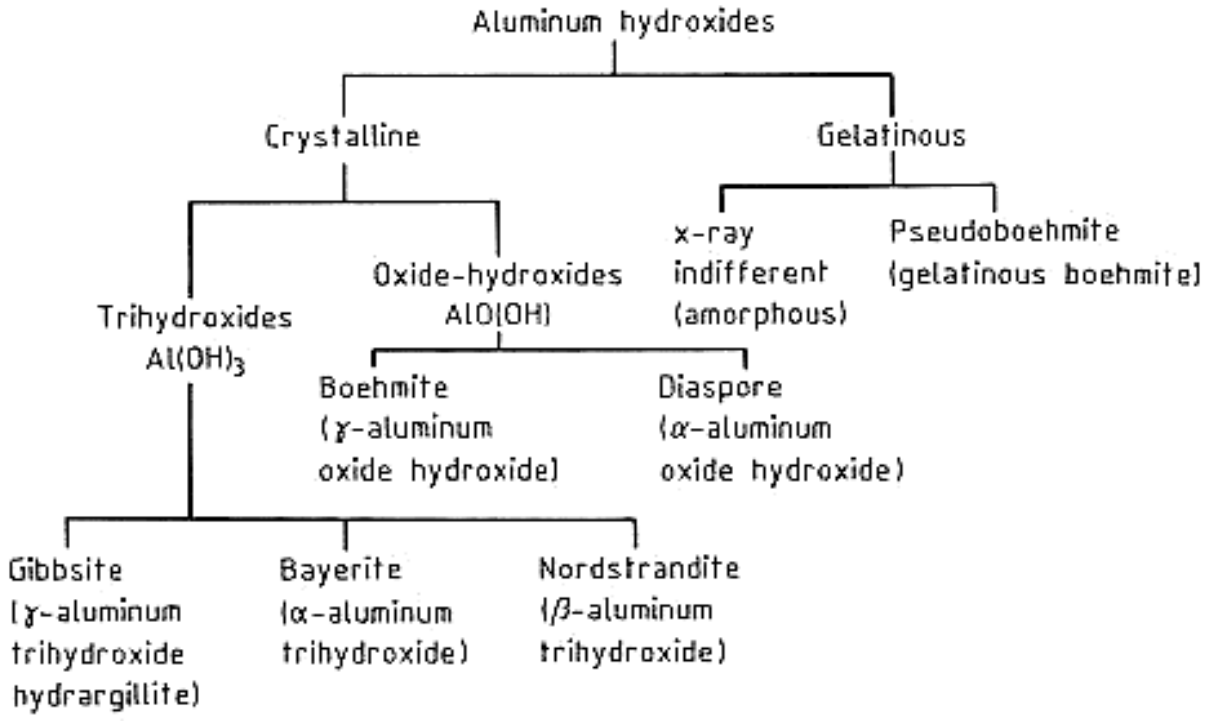


Figure 2.3: The classification of aluminum hydroxides. (Hudson*et al*, 2012)

Freshly precipitated aluminium hydroxide forms gels, which is the basis for application of aluminium salts as flocculants in water purification. This gel crystallizes with time.

Aluminium hydroxide gels can be dehydrated (e.g., using water-miscible non-aqueous solvents like ethanol) to form an amorphous aluminium hydroxide powder, which is readily soluble in acids. Aluminium hydroxide powder which has been heated to an elevated temperature under carefully controlled conditions is known as activated alumina and is used as a desiccant, an adsorbent, in gas purification, as a Claus catalyst support, water purification, and an adsorbent for the catalyst during the manufacture of polyethylene by the Sclairtech process.

2.6.1 Properties of aluminium hydroxide

Four polymorphs of aluminium hydroxide exist, all based on the common combination of one aluminium atom and three hydroxide molecules into different crystaline arrangements that determine the appearance and properties of the compound. The four combinations are:

i. Gibbsite
ii. Bayerite
iii. Nordstrandite
iv. Doyleite

All polymorphs are composed of octahedral layers of aluminium hydroxide molecules with the aluminiumatom in the centre and the hydroxyl groups on the sides, with hydrogen bonds holding the layers together. The polymorphisms vary in how the layers stack together, with the arrangements of the molecules and layers determined by the acidity, presence of ions (including salt) and the surface of the minerals the substance forms on. Under most

conditions gibbsite is the most chemically stable form of aluminium hydroxide. All forms of $Al(OH)_3$ crystals are hexagonal (Karamalidis and Dzombak , 2010).

As a case study, Gibbsite has a typical metal hydroxide structure with hydrogen bonds. It is built up of double layers of hydroxyl groups with aluminium ions occupying two-thirds of the octahedral holes between the two layers(Wells, 1975).Aluminium hydroxide is amphoteric. It dissolves in acid, forming $[Al(H_2O)_6]^{3+}$ (hexaaquaaluminium) or its hydrolysis products. It also dissolves in strong alkali, forming $[Al(OH)_4]^-$ (tetrahydroxidoaluminate).

2.6.2 Production of aluminium hydroxide

Virtually all the aluminium hydroxide used commercially is manufactured by the Bayer processwhich involves dissolving bauxite in sodium hydroxide at temperatures up to 270°C (Hind *et al*, 1999). The remaining solids, which is a red mud, is separated and aluminium oxide is precipitated from the remaining solution. This red mud is damaging to the environment and highly toxic. It is usually stored in large artificial lakes, this is what led to the Ajka alumina plant accident in 2010 in Hungary, killing nine people and injuring 122. The dam holding back the red mud burst allowing it to contaminate large areas of land and waterways (BBC, 2010). The aluminium oxide that is produced can be converted to aluminium hydroxide through reaction with water.

Other methods of commercial production of aluminium hydroxide include the production of gelatinous aluminum hydroxide, involving the neutralization of aluminum sulfate or ammonium alum by ammonia or sodium hydroxide, or by the neutralization of a sodium aluminate solution by acids, $NaHCO_3$,or CO_2.

U.S aluminum hydroxide production capacity was nearly 940 x 10^3t in 1997.About 90% of world production came from the Bayer process. Although many alumina plants

possessthecapability to make the normal Bayer-grade hydroxide, specialty grade aluminumhydroxides for the chemical industry are generally produced in aluminarefining plantsdedicated tononmetallurgical alumina products. In 2000, 1 x 10^3t of aluminum hydroxide were consumed in the U.S.; 960 x 10^3t were consumed in Western Europe, and 430 x 10^3t were used in Japan (Suresh *et al*, 2001).

2.6.3 Uses of aluminium hydroxide

Annual production is abouta 100 million tonnes, over 90% of which is converted to aluminium oxide (alumina) that is used in the manufacture of aluminium metal.The major other uses of aluminium hydroxide is as a feedstock for the manufacture of other aluminium compounds: specialty calcinedaluminas, aluminium sulfate, polyaluminium chloride, aluminium chloride, zeolites, sodium aluminate, activated alumina, and aluminium nitrate.

2.7 Gibbsite

Gibbsite, $Al(OH)_3$, is one of the mineral forms of aluminium hydroxide. It is often designated as γ-$Al(OH)_3$, but sometimes as α-$Al(OH)_3$(Greenwood and Earnshaw, 1997). It is also sometimes called hydrargyllite. It is an important ore of aluminium in that it is one of three main phases that make up the rock bauxite.

Gibbsite has three named structural polymorphs or polytypes: bayerite (designated often as α-$Al(OH)_3$, but sometimes as β-$Al(OH)_3$), doyleite, and nordstrandite. Gibbsite and bayerite are monoclinic, whereas doyleite and nordstrandite are triclinic forms. The crystal structures of Gibbsite, Bayerite and Nordstrandite are shown in Figure 2.4 below:

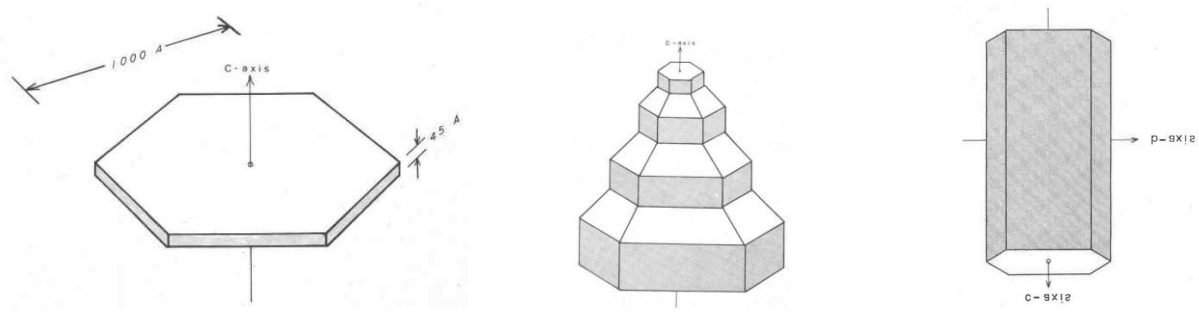


Figure 2.4: Crystal structure of Gibbsite, Bayerite and Nordstrandite respectively (Schoen and Roberson, 1970)

2.7.1 Structure of gibbsite

The structure of gibbsite is interesting and analogous to the basic structure of the micas. The basic structure forms stacked sheets of linked octahedrons of aluminium hydroxide. The octahedrons are composed of aluminium ions with a +3 charge bonded to six octahedrally coordinated hydroxides with a -1 charge. Each of the hydroxides is bonded to only two aluminium atoms because one third of the octahedrons are vacant a central aluminium. The result is a neutral sheet since +3/6 = +1/2 (+3 charge on the aluminiums divided by six hydroxide bonds times the number of aluminiums) and -1/2 = -1/2 (-1 charge on the hydroxides divided between only two aluminiums); thus the charges cancel. The lack of a charge on the gibbsite sheets means that there is no charge to retain ions between the sheets and act as a "glue" to keep the sheets together. The sheets are only held together by weak residual bonds and this results in a very soft easily cleaved mineral.

Gibbsite's structure is closely related to the structure of brucite, $Mg(OH)_2$. However the lower charge in brucite's magnesium (+2) as opposed to gibbsite'saluminium (+3) does not require that one third of the octahedrons be vacant of a central ion in order to maintain a neutral sheet. The different symmetry of gibbsite and brucite is due to the different way that the layers are stacked.

It is the gibbsite layer that in a way forms the "floor plan" for the mineral corundum, Al_2O_3. The basic structure of corundum is identical to gibbsite except the hydroxides are replaced by oxygen. Since oxygen has a charge of -2 the layers are not neutral and require that they must be bonded to other aluminiums above and below the initial layer producing the framework structure that is the structure of corundum.

Gibbsite is interesting for another reason because it is often found as a part of the structure of other minerals. The neutral aluminium hydroxide sheets are found sandwiched between silicate sheets in important clay groups: the illite, kaolinite, and montmorillonite/smectite groups. The individual aluminium hydroxide layers are identical to the individual layers of gibbsite and are referred to as the gibbsite layers (The Mineral Gibbsite, 2014).

2.8Boehmite

Boehmite is an aluminium oxide hydroxide (γ-AlO(OH)) mineral, a component of the aluminium ore bauxite. It is dimorphous with diaspore. It crystallizes in the orthorhombicdipyramidal system and is typically massive in habit. It is white with tints of yellow, green, brown or red due to impurities. It has a vitreous to pearly luster, a Mohs hardness of 3 to 3.5 and a specific gravity of 3.00 to 3.07. It is colorless in thin section, and optically biaxial positive.

Boehmite occurs in tropical laterites and bauxites developed on alumino-silicate bedrock. It also occurs as a hydrothermal alteration product of corundum and nepheline. It occurs with kaolinite, gibbsite and diaspore in bauxite deposits; and with nepheline, gibbsite, diaspore, natrolite and analcime in nephelinepegmatites (Handbook of Mineralogy).

It was first described by J. de Lapparent in 1927 for an occurrence in the bauxites of Mas Rouge, Les Baux-de-Provence, France, and namedfor the Bohemian-German chemist Johann

Böhm (1895–1952) who carried out X-ray studies of aluminium oxide hydroxides in 1925 (and not for the German geologist Johannes Böhm (1857–1938) as often stated).

2.9Pseudoboehmite

Pseudoboehmite is an aluminium compound with the chemical composition AlO(OH). It consists of finely crystalline boehmite. However, the water content is higher than in boehmite.Calvet et al. in 1952 coined the name 'pseudoboehmite' when they synthesized pure aluminiumhydroxyde gel (de Souza Santos, 2009). Its XRD pattern is similar to that of boehmite but the relative intensities of the peaks differ.

2.9.1 Morphology of pseudoboehmite

Pseudoboehmite is essentially finely crystalline boehmite which consists of the same or similar octahedral layers in the xz plane but lacks three-dimensional order because of a restricted number of unit cells in y direction (Tettenhorst and Hofmann, 1980). It consists of a significant number of crystallites which contain a single unit cell along y or single octahedral layers. It contains more water which is commonly intercalated between octahedral layers, normally randomly arranged, but sometimes regularly.

The water content consists of adsorbed and chemically bound water. The higher water content compared to boehmite can be explained by a smaller crystallite size (Baker and Pearson, 1974). While boehmite consists of relatively long AlOOH chains that have terminal H_2O groups, the chains in pseudoboehmite are significantly shorter. This translates into a significantly higher specific water content due to the terminal water groups as shown in Figure 2.5:

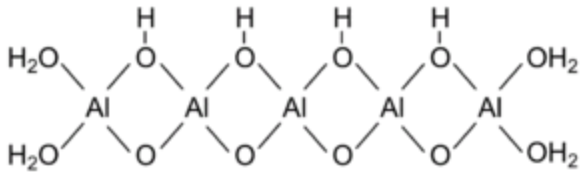


Figure 2.5: Chemical structure of pseudoboehmite (Luyken, 2012)

It is a "poorly crystallized" Al^{3+}compund with the composition Al_2O_3 x H_2O ($1.0 < x < 2.0$) with interplanarspacings increased in the [020]-direction to 0.67 nm in comparison with 0.617 nm for boehmite.

At higher temperatures pseudoboehmite is transformed to γ-alumina but the pore size distribution remains unchanged up to 1000 °C (Nogi*et al*, 2007). At around 1100 °C however, specific area significantly decreases because of sintering related to a transformation to α-Al_2O_3.

2.9.2 Synthesis of pseudoboehmite

Pseudobohemite can be synthesized by aging non-crystalline aluminium hydroxide gels at pH values between 5.0 and 7.4 (Vieira Coelho *et al*, 2008).

2.9.3 Uses of pseudoboehmite

Pseudoboehmite is used as binder for FCC catalysts and adsorbents. It is also a raw material for activated alumina.

2.10 Clay Minerals

Clay minerals are hydrous aluminiumphyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations. Clays form flat hexagonal

sheets similar to the micas. Clay minerals are common weathering products (including weathering of feldspar) and low temperature hydrothermal alteration products. Clay minerals are very common in fine grained sedimentary rocks such as shale, mudstone, and siltstone and in fine grained metamorphic slate and phyllite.

Clay minerals are usually (but not necessarily) ultrafine-grained (normally considered to be less than 2 micrometres in size on standard particle size classifications) and so may require special analytical techniques for their identification/study. These include x-ray diffraction, electron diffraction methods, various spectroscopic methods such as Mössbauer spectroscopy, infrared spectroscopy, and SEM-EDS. These methods can be augmented by polarized light microscopy, a traditional technique establishing fundamental occurrences or petrologic relationships.

Clay minerals include the following groups:

- Kaolin group which includes the minerals kaolinite, dickite, halloysite, and nacrite (polymorphs of $Al_2Si_2O_5(OH)_4$). Some sources include the kaolinite-serpentine group due to structural similarities (Bailey, 1980).
- Smectite group which includes dioctahedralsmectites such as montmorillonite and nontronite and trioctahedralsmectites for example saponite.
- Illite group which includes the clay-micas. Illite is the only common mineral.
- Chlorite group includes a wide variety of similar minerals with considerable chemical variation.
- Other clay types exist such as sepiolite or attapulgite, with long water channels internal to their structure (Moore and Reynolds Jr, 1997).

2.10.1 Structure of clay minerals

Like all phyllosilicates, clay minerals are characterised by two-dimensional sheets of corner sharing SiO_4tetrahedra and/or AlO_4octahedra. The sheet units have the chemical composition $(Al,Si)_3O_4$. Each silica tetrahedron shares 3 of its vertex oxygen atoms with other tetrahedra forming a hexagonal array in two-dimensions. The fourth vertex is not shared with another tetrahedron and all of the tetrahedra "point" in the same direction; i.e. all of the unshared vertices are on the same side of the sheet.

In clays the tetrahedral sheets are always bonded to octahedral sheets formed from small cations, such as aluminium or magnesium, coordinated by six oxygen atoms. The unshared vertex from the tetrahedral sheet also form part of one side of the octahedral sheet but an additional oxygen atom is located above the gap in the tetrahedral sheet at the center of the six tetrahedra. This oxygen atom is bonded to a hydrogen atom forming an OH group in the clay structure.

Bonding between the tetrahedral and octahedral sheets requires that the tetrahedral sheet becomes corrugated or twisted, causing ditrigonal distortion to the hexagonal array, and the octahedral sheet is flattened. This minimizes the overall bond-valence distortions of the crystallite.

Depending on the composition of the tetrahedral and octahedral sheets, the layer will have no charge, or will have a net negative charge. If the layers are charged this charge is balanced by interlayer cations such as Na^+ or K^+. In each case the interlayer can also contain water. The crystal structure is formed from a stack of layers interspaced with the interlayers.

2.10.2 Formation of clay minerals

Clay minerals are typically formed over long periods of time by the gradual chemical weathering of rocks, usually silicate-bearing, by low concentrations of carbonic acid and

other diluted solvents. These solvents, usually acidic, migrate through the weathering rock after leaching through upper weathered layers. In addition to the weathering process, some clay minerals are formed by hydrothermal activity. Clay deposits may be formed in place as residual deposits in soil, but thick deposits usually are formed as the result of a secondary sedimentary deposition process after they have been eroded and transported from their original location of formation. Clay deposits are typically associated with very low energy depositional environments such as large lakes and marine basins (Wilson, 1999).Primary clays, also known as kaolins, are located at the site of formation. Secondary clay deposits have been moved by erosion and water from their primary location.

2.10.3 World production of clays

Global reserves are large and distributed throughout many countries, but country specific data are not available. Table 2.2 gives the clay production and sales for various countries (USA geological survey, 2014):

Table 2.1: World mine production of clays (x1,000 tonnes) (2012)

	Mine production			
	Kaolin		Bentonite	
Country	2012	2013 (est.)	2012	2013 (est.)
United States (Sales)	5,980	5,950	4,980	4,950
Brazil (Beneficiated)	1,950	2,050	567	570
Czech Republic(crude)	3,320	3,300	221	220
Germany (Sales)	4,900	4,500	375	350

Italy	640	640	110	100
Mexico	163	160	54	50
Spain	303	300	115	110
Turkey	1,200	2,000	400	400
Greece	—	—	800	1200
Ukraine	1,300	1,600	210	210
United Kingdom (sales)	900	900	—	—
Uzbekistan (crude)	7,000	7000	15	15
Other countries	8,540	8,600	2100	2100
World total (rounded)	36,200	37,000	9,950	10,300

Resources of all clays are extremely large.

2.11 Kaolinite

Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygenatoms to one octahedral sheet of aluminaoctahedra. Rocks that are rich in kaolinite are known as kaolin or china clay (Pohl, 2011).

The name is derived from Kao-ling, a village near Jingdezhen, Jiangxi province, China. The name entered English in 1727 from the French version of the word: "kaolin", following Francois Xavier d'Entrecolles's reports from Jingdezhen (Harper, 2014). In Africa, kaolin is sometimes known as kalaba (in Gabon and Cameroon), calaba, and calabachop (in Equatorial Guinea).

Kaolinite has a low shrink-swell capacity and a low cation exchange capacity (1-15 meq/100g). It is a soft, earthy, usually white mineral (dioctahedralphyllosilicateclay), produced by the chemical weathering of aluminiumsilicate minerals like feldspar. In many

parts of the world, it is colored pink-orange-red by iron oxide, giving it a distinct rust hue. Lighter concentrations yield white, yellow or light orange colors. Alternating layers are sometimes found, as at Providence Canyon State Park in Georgia, USA. Commercial grades of kaolin are supplied and transported as dry powder, semi-dry noodle or as liquid slurry.While the most common chemical notation for kaolin is $Al_2Si_2O_5(OH)_4$, in ceramics applications the formula is typically written in terms of oxides, thus the formula for kaolinite is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Cement chemist notation is even terser: AS_2H_2, with the oxides represented as $A = Al_2O_3$, $S = SiO_2$, $H = H_2O$.

2.11.1 Structural transformations of kaolin

Kaolinite group clays undergo a series of phase transformations upon thermal treatment in air at atmospheric pressure. Endothermic dehydroxylation (or alternatively, dehydration) begins at 550–600^{0}C to produce disordered metakaolin, $Al_2Si_2O_7$, but continuous hydroxyl loss (-OH) is observed up to 900^{0}C and has been attributed to gradual oxolation of the metakaolin. Because of historic disagreement concerning the nature of the metakaolin phase, extensive research has led to general consensus that metakaolin is not a simple mixture of amorphous silica (SiO_2) and alumina (Al_2O_3), but rather a complex amorphous structure that retains some longer-range order (but not strictly crystalline) due to stacking of its hexagonal layers (Bellotto*et al*, 1995).

$$2\ Al_2Si_2O_5(OH)_4 \rightarrow 2\ Al_2Si_2O_7 + 4\ H_2O \qquad (2.13)$$

Further heating to 925–950 °C converts metakaolin to an aluminium-silicon spinel, $Si_3Al_4O_{12}$, which is sometimes also referred to as a gamma-alumina type structure:

$$2\ Al_2Si_2O_7 \rightarrow Si_3Al_4O_{12} + SiO_2 \qquad (2.14)$$

Upon calcination to ~1050 °C, the spinel phase ($Si_3Al_4O_{12}$) nucleates and transforms to mullite, $3\ Al_2O_3 \cdot 2\ SiO_2$, and highly crystalline cristobalite, SiO_2:

$$3\ Si_3Al_4O_{12} \rightarrow 2\ Si_2Al_6O_{13} + 5\ SiO_2 \qquad (2.15)$$

2.11.2 Occurrence of kaolin

Kaolinite is one of the most common minerals; it is mined, as kaolin, in Brazil, Bulgaria, France, United Kingdom, Iran, Germany, India, Australia, Korea, the People's Republic of China, the Czech Republic and the United States (MinDat.org, 2009).

2.11.2.1 Predominance in tropical soils

Kaolinite clay occurs in abundance in soils that have formed from the chemical weathering of rocks in hot, moist climates—for example in tropical rainforest areas. Comparing soils along a gradient towards progressively cooler or drier climates, the proportion of kaolinite decreases, while the proportion of other clay minerals such as illite (in cooler climates) or smectite (in drier climates) increases. Such climatically-related differences in clay mineral content are often used to infer changes in climates in the geological past, where ancient soils have been buried and preserved.

2.11.3Uses of kaolin

The largest use is in the production of paper, including ensuring the gloss on some grades of paper.

The US Naval Medical Research Institute announced the successful use of a kaolinite-derived aluminosilicatenanoparticle infusion in traditional gauze, known commercially as QuikClot Combat Gauze (Rowe, 2008).

Kaolin is or was also used as a component in the following:

- Ceramics: It is generally the main component in porcelain.
- Toothpaste.
- Light diffusing material in white incandescent light bulbs.
- Cosmetics.
- Paint to extend titanium dioxide (TiO_2) and modify gloss levels.
- Rubber: for its semi-reinforcing properties.
- Adhesives to modify rheology.
- Production of common smoking pipes in Europe and Asia.
- Organic farming:As a spray applied to crops to deter insect damage, and in the case of apples, to prevent sun scald.
- Whitewash in traditional stone masonry homes in Nepal. The most common method is to paint the upper part with white kaolin clay and the middle with red clay. The red clay may extend to the bottom, or the bottom may be painted black.
- Filler in Edison Diamond Discs.
- Indicators in radiological dating since kaolinite can contain very small traces of uranium and thorium.
- Dyspepsia drugs: To soothe an upset stomach, similar to the way parrots (and later, humans) in South America originally used it. More recently, industrially-produced kaolinite preparations were formerly common for treatment of diarrhea; the most common of these was Kaopectate, which abandoned the use of kaolin in favor of

attapulgite and then (in the United States) bismuth subsalicylate (the active ingredient in Pepto-Bismol).

- Facial masks or soap.

2.12 Chemical Reactors

In chemical engineering, chemical reactors are vessels designed to contain chemical reactions. One example is a pressure reactor. The design of a chemical reactor deals with multiple aspects of chemical engineering. Chemical engineers design reactors to maximize net present value for the given reaction. Designers ensure that the reaction proceeds with the highest efficiency towards the desired output product, producing the highest yield of product while requiring the least amount of money to purchase and operate. Normal operating expenses include energy input, energy removal, raw material costs, labor, etc. Energy changes can come in the form of heating or cooling, pumping to increase pressure, frictional pressure loss (such as pressure drop across a 90° elbow or an orifice plate) or agitation. Figure 2.6 shows a cutaway view of a stirred tank reactor.

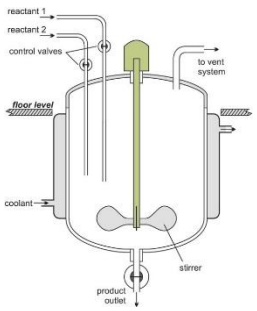


Figure 2.6: Cut-away view of a stirred-tank chemical reactor with a cooling jacket (The Essential Chemical Industry Online, 2013)

There are a couple of main basic vessel types:

- A tank
- A pipe or tubular reactor

Both types can be used as continuous reactors or batch reactors, and either may accommodate one or more solids (reagents, catalyst, or inert materials), but the reagents and products are typically fluids. Most commonly, reactors are run at steady-state, but can also be operated in a transient state. When a reactor is first brought into operation (after maintenance or inoperation) it would be considered to be in a transient state, where key process variables change with time.

There are three main basic models used to estimate the most important process variables of different chemical reactors:

- Batch reactor model (batch),
- Continuous stirred-tank reactor model (CSTR), and
- Plug flow reactor model (PFR).

Furthermore, catalytic reactors require separate treatment, whether they are batch, CST, or PF reactors, as the many assumptions of the simpler models are not valid.

Key process variables include:

- Residence time (τ,)
- Volume (V)
- Temperature (T)
- Pressure (P)
- Concentrations of chemical species (C_1, C_2, C_3, ... C_n)
- Heat transfer coefficients (h, U)

A chemical reactor, typically tubular reactor, could be a packed bed. The packing inside the bed may have catalyst to catalyze the chemical reaction. A chemical reactor may also be a fluidized bed.

Chemical reactions occurring in a reactor may be exothermic, meaning giving off heat, or endothermic, meaning absorbing heat. A chemical reactor vessel may have a cooling or heating jacket or cooling or heating coils (tubes) wrapped around the outside of its vessel wall to cool down or heat up the contents.

2.12.1 Types of chemical reactors

We have a few main types of reactors, some of which are:

2.12.1.1Continuous Stirred-Tank Reactor (CSTR)

In a CSTR, one or more fluid reagents are introduced into a tank reactor (typically) equipped with an impeller while the reactor effluent is removed. The impeller stirs the reagents to ensure proper mixing. Simply dividing the volume of the tank by the average volumetric flow rate through the tank gives the residence time, or the average amount of time a discrete quantity of reagent spends inside the tank. Using chemical kinetics, the reaction's expected percent completion can be calculated. Some important aspects of the CSTR:

- At steady-state, the mass flow rate in must equal the mass flow rate out, otherwise the tank will overflow or go empty (transient state). While the reactor is in a transient state the model equation must be derived from the differential mass and energy balances.

- The reaction proceeds at the reaction rate associated with the final (output) concentration, since the concentration is assumed to be homogenous throughout the reactor.

- Often, it is economically beneficial to operate several CSTRs in series. This allows, for example, the first CSTR to operate at a higher reagent concentration and therefore

a higher reaction rate. In these cases, the sizes of the reactors may be varied in order to minimize the total capital investment required to implement the process.

- It can be demonstrated that an infinite number of infinitely small CSTRs operating in series would be equivalent to a PFR.

The behavior of a CSTR is often approximated or modeled by that of a Continuous Ideally Stirred-Tank Reactor (CISTR). All calculations performed with CISTRs assume perfect mixing. If the residence time is 5-10 times the mixing time, this approximation is considered valid for engineering purposes. The CISTR model is often used to simplify engineering calculations and can be used to describe research reactors. In practice it can only be approached, particularly in industrial size reactors in which the mixing time may be very large.

2.12.1.2Plug Flow Reactor (PFR)

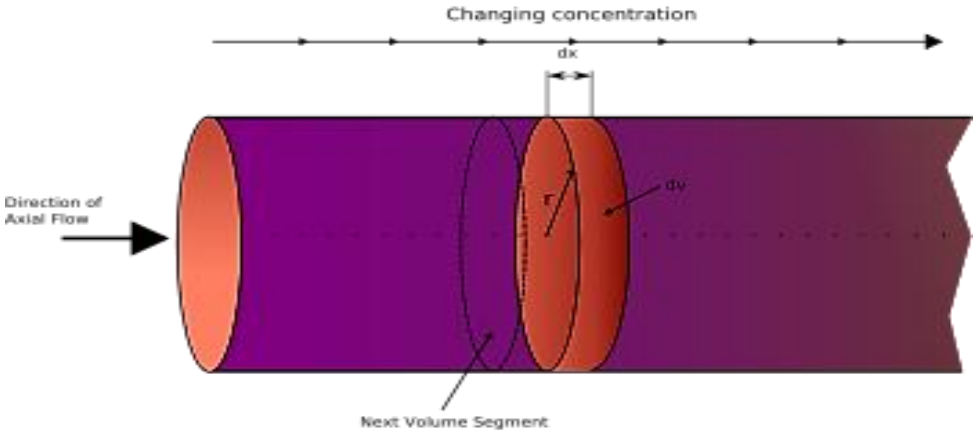


Figure 2.7: Simple diagram illustrating plug flow reactor model

Asshown in Figure 2.6, in a PFR, one or more fluid reagents are pumped through a pipe or tube. The chemical reaction proceeds as the reagents travel through the PFR. In this type of

reactor, the changing reaction rate creates a gradient with respect to distance traversed; at the inlet to the PFR the rate is very high, but as the concentrations of the reagents decrease and the concentration of the product(s) increases the reaction rate slows. Some important aspects of the PFR:

- All calculations performed with PFRs assume no upstream or downstream mixing, as implied by the term "plug flow".
- Reagents may be introduced into the PFR at locations in the reactor other than the inlet. In this way, a higher efficiency may be obtained, or the size and cost of the PFR may be reduced.
- A PFR typically has a higher efficiency than a CSTR of the same volume. That is, given the same space-time (or residence time), a reaction will typically proceed to a higher percentage completion in a PFR than in a CSTR. This is not always true for reversible reactions.

For most chemical reactions of industrial interest, it is impossible for the reaction to proceed to 100% completion. The rate of reaction decreases as the reactants are consumed until the point where the system reaches dynamic equilibrium (no net reaction, or change in chemical species occurs). The equilibrium point for most systems is less than 100% complete. For this reason a separation process, such as distillation, often follows a chemical reactor in order to separate any remaining reagents or byproducts from the desired product. These reagents may sometimes be reused at the beginning of the process, such as in the Haber process. In some cases, very large reactors would be necessary to approach equilibrium, and chemical engineers may choose to separate the partially reacted mixture and recycle the leftover reactants.

Continuous oscillatory baffled reactor (COBR) is a tubular plug flow reactor. The mixing in COBR is achieved by the combination of fluid oscillation and orifice baffles, allowing plug flow to be achieved under laminar flow conditions with the net flow Reynolds number just about 100.

2.12.1.3Catalytic reactor

Although catalytic reactors are often implemented as plug flow reactors, their analysis requires more complicated treatment. The rate of a catalytic reaction is proportional to the amount of catalyst the reagents contact, as well as the concentration of the reactants. With a solid phase catalyst and fluid phase reagents, this is proportional to the exposed area, efficiency of diffusion of reagents in and products out, and efficacy of mixing. Perfect mixing usually cannot be assumed. Furthermore, a catalytic reaction pathway often occurs in multiple steps with intermediates that are chemically bound to the catalyst; and as the chemical binding to the catalyst is also a chemical reaction, it may affect the kinetics. Catalytic reactions often display the so-called falsified kinetics, i.e. the apparent kinetics differ from elementary chemical kinetics due to physical transport effects.

The behavior of the catalyst is also a consideration. Particularly in high-temperature petrochemical processes, catalysts are deactivated by sintering, coking, and similar processes.

A common example of a catalytic reactor is the catalytic converter following an engine. However, most petrochemical reactors are catalytic, and are responsible for most of industrial chemical production in the world, with extremely high-volume examples such as sulfuric acid, ammonia, reformate/BTEX (benzene, toluene, ethylbenzene and xylene) and alkylate gasoline blending stock.

2.12.1.4 Batch reactor

The batch reactor is the generic term for a type of vessel widely used in the process industries. Its name is something of a misnomer since vessels of this type are used for a variety of process operations such as solids dissolution, product mixing, chemical reactions, batch distillation, crystallization, liquid/liquid extraction and polymerization. In some cases, they are not referred to as reactors but have a name which reflects the role they perform (such as crystallizer, or bio reactor).Figure 2.8 is an illustration of a simple batch reactor.

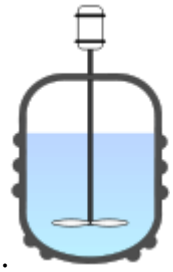


Figure 2.8: Simple Batch reactor

A typical batch reactor consists of a tank with an agitator and integral heating/cooling system. These vessels may vary in size from less than 1 litre to more than 15,000 litres. They are usually fabricated in steel, stainless steel, glass lined steel, glass or exotic alloy. Liquids and solids are usually charged via connections at the top cover of the reactor. Vapors and gases also discharge through connections at the top. Liquids are usually discharged out of the bottom.

The advantages of the batch reactor lie with its versatility. A single vessel can carry out a sequence of different operations without the need to break containment. This is particularly useful when processing toxic or highly potentcompounds.

The usual agitator arrangement for a batch reactor is a centrally mounted driveshaft with an overhead drive unit. Impeller blades are mounted on the shaft. A wide variety of blade designs are used and typically the blades cover about two thirds of the diameter of the reactor. Where viscous products are handled, anchor shaped paddles are often used which have a close clearance between the blade and the vessel walls.

Most batch reactors also use baffles. These are stationary blades which break up flow caused by the rotating agitator. These may be fixed to the vessel cover or mounted on the interior of the side walls.

Despite significant improvements in agitator blade and baffle design, mixing in large batch reactors is ultimately constrained by the amount of energy that can be applied. On large vessels, mixing energies of more than 5 Watts per litre can put an unacceptable burden on the cooling system. High agitator loads can also create shaft stability problems. Where mixing is a critical parameter, the batch reactor is not the ideal solution. Much higher mixing rates can be achieved by using smaller flowing systems with high speed agitators, ultrasonic mixing or static mixers.

Products within batch reactors usually liberate or absorb heat during processing. Even the action of stirring stored liquids generates heat. In order to hold the reactor contents at the desired temperature, heat has to be added or removed by a cooling jacket or cooling pipe. Heating/cooling coils or external jackets are used for heating and cooling batch reactors. Heat transfer fluid passes through the jacket or coils to add or remove heat.

Within the chemical and pharmaceutical industries, external cooling jackets are generally preferred as they make the vessel easier to clean. The performance of these jackets can be defined by 3 parameters:

- Response time to modify the jacket temperature
- Uniformity of jacket temperature
- Stability of jacket temperature

It can be argued that heat transfer coefficient is also an important parameter. It has to be recognized however that large batch reactors with external cooling jackets have severe heat transfer constraints by virtue of design. It is difficult to achieve better than 100 Watts/litre even with ideal heat transfer conditions. By contrast, continuous reactors can deliver cooling capacities in excess of 10,000 W/litre. For processes with very high heat loads, there are better solutions than batch reactors.

Fast temperature control response and uniform jacket heating and cooling is particularly important for crystallization processes or operations where the product or process is very temperature sensitive. There are several types of batch reactor cooling jackets:

The single jacket design consists of an outer jacket which surrounds the vessel. Heat transfer fluid flows around the jacket and is injected at high velocity via nozzles. The temperature in the jacket is regulated to control heating or cooling.

The single jacket is probably the oldest design of external cooling jacket. Despite being a tried and tested solution, it has some limitations. On large vessels, it can take many minutes to adjust the temperature of the fluid in the cooling jacket. This results in sluggish temperature control. The distribution of heat transfer fluid is also far from ideal and the heating or cooling tends to vary between the side walls and bottom dish. Another issue to consider is the inlet temperature of the heat transfer fluid which can oscillate (in response to the temperature control valve) over a wide temperature range to cause hot or cold spots at the jacket inlet points.

The half coil jacket is made by welding a half pipe around the outside of the vessel to create a semi-circular flow channel. The heat transfer fluid passes through the channel in a plug flow fashion. A large reactor may use several coils to deliver the heat transfer fluid. Like the single jacket, the temperature in the jacket is regulated to control heating or cooling.

The plug flow characteristics of a half coil jacket permits faster displacement of the heat transfer fluid in the jacket (typically less than 60 seconds). This is desirable for good temperature control. It also provides good distribution of heat transfer fluid which avoids the problems of non-uniform heating or cooling between the side walls and bottom dish. Like the single jacket design however, the inlet heat transfer fluid is also vulnerable to large oscillations (in response to the temperature control valve) in temperature.

The constant flux cooling jacket is a relatively recent development. It is not a single jacket but has a series of 20 or more small jacket elements. The temperature control valve operates by opening and closing these channels as required. By varying the heat transfer area in this way, the process temperature can be regulated without altering the jacket temperature.

The constant flux jacket has very fast temperature control response (typically less than 5 seconds) due to the short length of the flow channels and high velocity of the heat transfer fluid. Like the half coil jacket the heating/cooling flux is uniform. Because the jacket operates at substantially constant temperature however the inlet temperature oscillations seen in other jackets are absent. An unusual feature of this type jacket is that process heat can be measured very sensitively. This allows the user to monitor the rate of reaction for detecting end points, controlling addition rates, controlling crystallizatione.t.c.

Applications of batch reactors: Batch reactors are often used in the process industry. Batch reactors also have many laboratory applications, such as small scale production and inducing fermentation for beverage products. They also have many uses in medical production. Batch

reactors are generally considered expensive to run, as well as variable product reliability. They are also used for experiments of reaction kinetics, volatiles and thermodynamics. Batch reactors are also highly used in waste water treatment.

2.12.1.5 Semi-batch reactor

A semi-batch reactor is operated with both continuous and batch inputs and outputs. A fermenter, for example, is loaded with a batch of medium and microbes which constantly produce carbon dioxide that must be removed continuously. Analogously, driving a reaction of gas with a liquid is usually difficult, since the gas bubbles off. Therefore, a continuous feed of gas is injected into the batch of a liquid. One chemical reactant is charged to the vessel and a second chemical is added slowly (for instance, to prevent side reactions). Semi-batch (semi-flow) reactors operate much like batch reactors in that they take place in a single stirred tank with similar equipment. However, they are modified to allow reactant addition and/or product removal in time. A normal batch reactor is filled with reactants in a single stirred tank at time=0 and the reaction proceeds. A semi-batch reactor, however, allows partial filling of reactants with the flexibility of adding more as time progresses. Stirring in both types is very efficient, which allows batch and semi-batch reactors to assume a uniform composition and temperature throughout.

Advantages of semi-batch reactors: The flexibility of adding more reactants over time through semi-batch operation has several advantages over a batch reactor. These include:

i. Improved selectivity of a reaction

Oftentimes a particular reactant can go through parallel paths that yield two different products, for which only one is desired as shown by the simple example below:

A→V (desired product) (2.16)

A→W (undesired product) (2.17)

The rate expressions are:

$$\frac{dC_v}{dt} = k_1 C_A^{\alpha} \quad (2.18)$$

$$\frac{dC_w}{dt} = k_2 C_A^{\beta} \quad (2.19)$$

Selectivity of the desired product is defined as:

$$S = \frac{dC_v}{dC_w} = \frac{k_1}{k_2} C_A^{\alpha-\beta} \quad (2.20)$$

If$\beta > \alpha$, the concentration of the reactant should be kept at a low level in order to maximize selectivity. This can be accomplished using a semibatch reactor.

ii. Better control of exothermic reactions

Exothermic reactions release heat, and ones that are highly exothermic can cause safety concerns. Semibatch reactors allow for slow addition of reactants in order to control the heat released and thus, temperature, in the reactor.

iii. Product removal through a purge stream

In order to minimize the reversibility of a reaction one must minimize the concentration of the product. This can be done in a semibatch reactor by using a purge stream to remove products and increase the net reaction rate by favoring the forward reaction.

2.12.2 Design of a semi-batch reactor

For an elementary liquid-phase reaction, take an irreversible reaction between A and B to give C:

$$A + B \rightarrow C \tag{2.21}$$

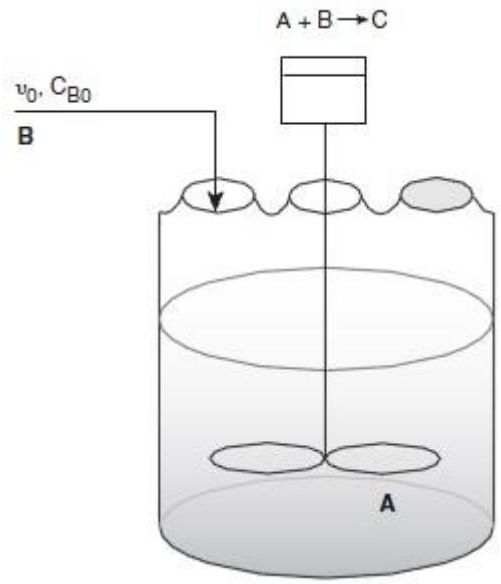


Figure 2.9: Semibatch reactor (Fogler, 2006)

A mole balance of species A yields:

$$\begin{bmatrix} Rate \\ in \end{bmatrix} - \begin{bmatrix} Rate \\ out \end{bmatrix} + \begin{bmatrix} Rate\ of \\ generation \end{bmatrix} = \begin{bmatrix} Rate\ of \\ accumulation \end{bmatrix} \tag{2.22}$$

$$0 \quad - \quad 0 \quad + \quad r_A V(t) \quad = \quad \frac{dN_A}{dt}$$

Three variables can be used to formulate and solve semibatch reactor problems: the concentrations, C_j, the number of moles, N_j, and the conversion, X.

Recalling that the number of moles of A, N_A, is just the product of concentration of A, C_A, and the volume, V, Equation (2.19) can berewrittenas

$$r_A V = \frac{d(C_A V)}{dt} = \frac{V dC_A}{dt} + C_A \frac{dV}{dt} \tag{2.23}$$

We note that since the reactor is being filled, the volume, V, varies with time. The reactor volume at any time t can be found from an overall mass balanceof all species:

$$\begin{bmatrix} Rate \\ in \end{bmatrix} - \begin{bmatrix} Rate \\ out \end{bmatrix} + \begin{bmatrix} Rate\ of \\ generation \end{bmatrix} = \begin{bmatrix} Rate\ of \\ accumulation \end{bmatrix} \tag{2.24}$$

$$\rho_0 v_0 \quad - \quad 0 \quad + \quad 0 \quad = \quad \frac{d(\rho V)}{dt}$$

For a constant-density system, $\rho = \rho_0$, and

$$\frac{dV}{dt} = v_0 \tag{2.25}$$

with the initial condition $V = V_0$ at $t = 0$, integrating for the case of constant volumetric flow rate v_0 yields

$$V = V_0 + v_0 t \tag{2.26}$$

Substituting Equation (2.25) into the right-hand side of Equation (2.23) and rearranging will give

$$-v_0 C_A + V r_A = \frac{V dC_A}{dt} \tag{2.27}$$

The balance on A [i.e., Equation (2.27)] can be rewritten as

$$\frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A \tag{2.28}$$

A mole balance on B that is fed to the reactor at a rate F_{B0} is

$$\begin{bmatrix} Rate \\ in \end{bmatrix} - \begin{bmatrix} Rate \\ out \end{bmatrix} + \begin{bmatrix} Rate\ of \\ generation \end{bmatrix} = \begin{bmatrix} Rate\ of \\ accumulation \end{bmatrix} \quad (2.29)$$

$$F_{B0} \quad - \quad 0 \quad + \quad r_B V \quad = \quad \frac{dN_A}{dt}$$

Rearranging,

$$\frac{dN_B}{dt} = r_B V + F_{B0} \quad (2.30)$$

$$\frac{d(VC_B)}{dt} = C_B \frac{dV}{dt} + V \frac{dC_B}{dt} = r_B V + F_{B0} = r_B V + v_0 C_{B0} \quad (2.31)$$

Substituting Equation (2.26) in Equation (2.31) in terms of V and differentiating, the mole balance on B becomes

$$\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V} \quad (2.32)$$

At time $t = 0$, the initial concentration of B in the vat is zero, $C_{Bi} = 0$. The concentration of B in the feed is C_{B0}. If the reaction order is other than zero- or first-order, or if the reaction is nonisothermal, we must use numerical techniques to determine the conversion as a function of time. Equations (2.28) and (2.32) are easily solved with an ODE solver (Fogler, 2006).

2.13 Related Works

A number of researchers have done some work on the production of aluminium hydroxide and subsequently alumina from various precursors. Anderssonand Hansson (2000) worked on the precipitation of a reactive aluminium hydroxide from an acidic aluminiumsulphate solution by addition of sodium hydroxide. The main thrust of the work was to produce aluminium hydroxide that was readily soluble in hydrochloric acid and easy to dewater. It

was observed that for an aluminium hydroxide with good filterabilty to be produced, a high stirring rate and low base addition rate were required, which were the factors of largest influence on filterability.

Xuelian*et al* (2009) worked to determine the influence of pH on the microstructure and phase transformation of aluminium hydroxide prepared by chemical precipitation from an $Al(NO_3)_3$ solution. It was found that the pH value affected not only thecomposition, structure, morphology, phase transformation, andthermal behavior of the precipitated aluminum hydroxides but alsothe microstructures of their final thermo-decomposition products.With an increasing pH value from 5 to 11, the aluminum hydroxidesprecipitated from the solution varied from amorphous aluminumhydroxide through γ-AlOOH to α-$Al(OH)_3$.The aluminium hydroxidesprecipitated at different pH values had different transformationsequences toward α-$Al_2O_3$and different formationtemperatures of α-Al_2O_3.

Saukkoriipi's (2010) work focused on the molecular-level chemistry of the solvation of aluminium salts.It was observed that the most important variable in the aquatic chemistry of aluminium is the pH. Itstrongly affected the overall speciation of the mononuclear and polynuclearaluminium hydroxides.In the near neutral pH range (5 <pH < 8), aluminum trihydroxide ($Al(OH)_3$), also known as gibbsite andbayerite, started to precipitate.Depending on time and conditions, aluminumtrihydroxide can give one water molecule off forming pure Boehmite (AlO(OH)). In the basic range (pH > 7) the predominant mononuclear form was thealuminate anion ([Al(OH)4]). It was also noted that the hydrolysis of aluminum was not simply a mononuclear process but also involved polynuclearaluminium complexes.

Hosseini*et al* (2011) worked on the production of gamma alumina from kaolin. In this work, *γ*-alumina powders were successfully synthesized by alumina extraction processes through reaction of meta- kaolin with H_2SO_4 solution. Direct precipitation in ethanol was found to be

a crucial step for the synthesis of γ-alumina. It concluded that kaolin can be used aspromising material for the preparation of γ-alumina.

Finally, Bawa (2012) was successful in producing gamma alumina from kaolin for potential use as a catalyst support. It involved the production of gamma alumina by the processing of calcined kaolin (metakaolin) with the aid of H_2SO_4 and ammonium sulphate, and subsequent calcination at various temperatures and soaking time. The gamma alumina produced had a large surface area, making it potentially suitable for use as a catalyst support.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

The major materials used in the course of this work were:

Kaolin clay from Kankara, Katsina State, 98wt% sulfuric acid, Distilled water, 98wt% sodium hydroxide, Barium chloride.

3.2 Apparatus

The apparatus used in this work were:

Beakers (1000ml and 500ml), Pyrexconical flasks (500ml), Pyrexmeasuring cylinders (1000ml, 500ml, 10ml), Pyrexcrucibles, Laboratory mortar and pestle, Tyler mesh sieve (70µm), Spatula, Plastic spoons, Buchner flask (1 litre), Sinter glass filter funnel (Quickfit TM), Plastic bucket, Glass rod stirrer, Magnetic stirrer rod, Desiccator (dry seal type, Jencons), Plastic sample containers, Plastic pipes, Plastic fittings, Plastic valves, Stainless steel sheets, Stainless steel rod, Teflon rod, Teflon plates, Teflon tank (50L).

3.3 Equipment

The list of equipment used in this work are given in Table 3.1:

S/No	Name	Model	Manufacturer
1	Weighing scale (0-100kg Range)	1455T 18	WEDA, Holland
2	Oven	TM OV-420 (0-260^{0}C)	Gallenkamp, England
3	Analytical balance	AB 204 (0-180g)	MettlerToledo, Switzerland
4	High vacuum pump	ES-100	Edwards, England
5	Refrigerator	C1202	Thermocool, England
6	Distilled water machine	Aquatron A4000	Stuart, England
7	Atomic absorption spectrometer	iCE 3300	Thermo Scientific, USA
8	X-ray fluorescence spectrometer	Minipal 4	PANalytical, Holland
9	X-ray diffractometer	Empyrean	PANalytical, Holland
10	BET surface area analyser	V-Sorb 2800P	GAPP, China
11	Electric motor	KMER 71G4	Bauer, Germany
12	Magnetic stirrer/hotplate	MS300	AMTAST, China

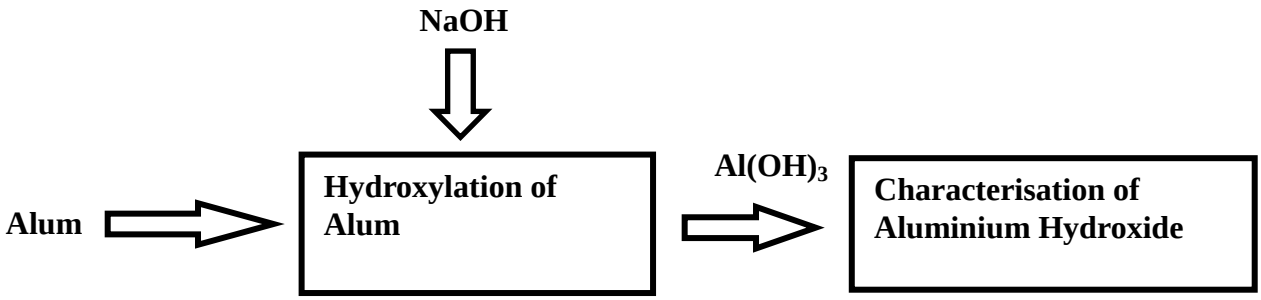
Table 3.1: List of equipment

3.4 Experimental Procedure

The following procedure was followed in the course of this work:

3.4.1 Hydroxylation of the aluminiumsulphate using sodium hydroxide

Aluminium hydroxide was precipitated from the reaction betweenaluminiumsulphate obtained by the method established by Aderemi et al (2010)and sodium hydroxide until a pH of between 6 and 9 was reached. The temperature of the reaction was varied by the use of a water bathfor five runs. The temperature range applied was from ambient temperature (25^oC) to 100^oC.After precipitation, the mixture was washed with distilled water to remove the sodium sulphate solution produced from the reaction. Barium chloride was used to check for the complete removal of sodium sulphate. The aluminium hydroxide precipitate formed was then dried in an oven for 3 to 5 hours at 105^0C.



Hydroxylation of alum

$$Al_2(SO_4)_3 + \mathbf{6}NaOH \rightarrow \mathbf{2}Al(OH)_3 + \mathbf{3}Na_2(SO_4) \quad (3.1)$$

Figure 3.1: Block diagram of laboratory synthesis of aluminium hydroxide

3.4.2 Characterisation of aluminium hydroxide prepared

3.4.2.1 Chemical composition

The chemical composition of the samples of aluminium hydroxide prepared were determined using a Minipal 4, Panalytical X-ray fluorescence analyser at the Nigerian Geological Survey Agency, Kaduna State.

3.4.2.2 Mineralogical composition

The crystal phases present in the samples of aluminium hydroxide produced were determined using an Empyrean,panalytical X-ray diffractometer at the Nigerian Geological Survey

Agency, Kaduna State. The patterns were recorded from Bragg angles of 0^0 to 70^0, using CuKα target X-ray radiation.

3.4.2.3 Surface area determination

The BET surface area of the samples of aluminum hydroxide produced were determined using a V-Sorb 2800P Surface Area and PorosimetryAnalyser working with Nitrogen Absorption at National Research Institute for Chemical Technology (NARICT), Zaria, Kaduna State. The time for pre-treatment was 16 hours.

3.4.3 Design of pilot scale reactor

The activation energy and pre-exponential factor were determined by carrying out kinetic studies on the reaction between aluminiumsulphate and sodium hydroxide. The reaction between aluminiumsulphate and sodium hydroxide was carried out at various times for three temperature conditions. A plot of temperature against concentration was then made and subsequently a plot of rate constant against temperature was then made from the results obtained.

The pilot scalesemi-batch reactor was designed using numerical methods (MATLAB software). The operating conditions were taken to be as follows: reaction temperature of 79^oC, pressure of 1 atm, flow rate of NaOH of 0.3225L/hr, volume of $Al_2(SO_4)_3$ of 32.2469L, activation energy of 102.2373kJ/mol and pre-exponential factor of $1.153509 \times 10^{14}\ sec^{-1}$.

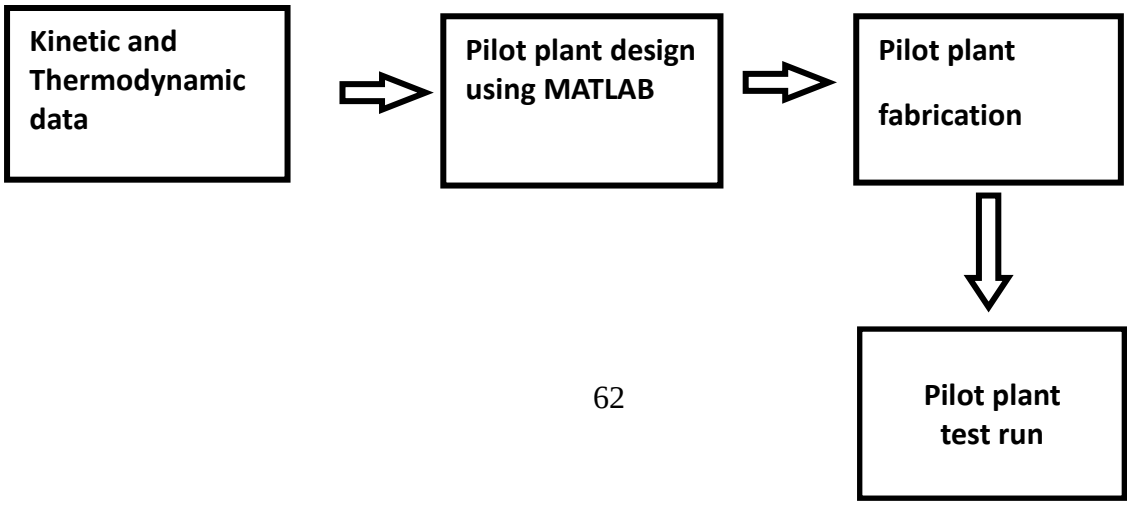


Figure 3.2: Block diagram of the development of a pilot scale reactor

3.4.4 Fabrication of pilot scale reactor

The pilot scale reactor was drawn for construction using AUTOCAD 2013 version. The pilot scale reactor was fabricated using stainless steel of rating Schedule 80, ANSI 304 SS for the external surfaces and polypropylene for the internal reactor tank. Plastic fittings and pipes were chosen all through the reactor. A pre-fabricated electric motor was installed on the reactor top. A reinforced Teflon road was used as the shaft of the impeller. The impeller blades were made of Teflon.

3.4.5 Test –run of pilot scale reactor

The pilot scale reactor was test–run in two batches, for 30 minutes each. The operating conditions were taken to be the same as those for the design of the reactor.

3.4.6 Determination of kinetic parameters for aluminium hydroxide production

Using the power law model for homogenous reactions,from the Stoichiometric equation:

$$Al_2(SO_4)_3 + \mathbf{6}NaOH \rightarrow \mathbf{2}Al(OH)_3 + \mathbf{3}Na_2(SO_4), \quad (3.2)$$

The reaction is written as

$$A + 6B \rightarrow 2C + 3D \quad (3.3)$$

Where

A=$Al_2(SO_4)_3$

B=NaOH

C=$Al(OH)_3$, and

D=$Na_2(SO_4)$,

The rate law is

$$-r_A = kC_B^m C_A^n \quad (3.4)$$

For very large C_B that doesn't change appreciably i.e. $C_B \cong C_{B0}$,

Equation 3.4 can be written as

$$-r_A = k'C_A^n \quad (3.5)$$

Where $k' = kC_B^m$

Taking the natural log of both sides,

$$\ln(-r_A) = \ln\left(\frac{dC_A}{dt}\right) = lnk' + nlnC_A \quad (3.6)$$

Data for C_A with time was plotted using the polynomial fit by differential method of analysis to get $-r_A$, then ln($-r_A$) was plotted with lnC_A to get n, and ln k'.

From Arrhenius equation

$$k' = Ae^{\frac{-E}{RT}} \quad (3.7)$$

Taking the natural log of both sides, it is written as

$$\ln k' = lnA - \frac{E}{RT} \tag{3.8}$$

The plot of ln k' with 1/T is made and the slope was obtained as E/R with an intercept of ln A

3.4.7 Specific design of the semi-batch pilot scale reactor

Basis = 10.448 Kg of$Al(OH)_3$per day (6 batches of 4 hours each)

Substituting the rate law from Equation 3.5 in Equations 2.28 and 2.32 gives

$$\frac{dC_A}{dt} = -k'C_A^n - \frac{v_0}{V}C_A \tag{3.9}$$

$$\frac{dC_B}{dt} = -k'C_A^n + \frac{v_0}{V}(C_{B0} - C_B) \tag{3.10}$$

Similarly for C and D, it was gotten as

$$\frac{dN_C}{dt} = r_C V = -r_A V \tag{3.11}$$

$$\frac{dN_C}{dt} = \frac{d(C_C V)}{dt} = V\frac{dC_C}{dt} + C_C\frac{dV}{dt} = V\frac{dC_C}{dt} + v_0 C_C \tag{3.12}$$

Therefore,

$$\frac{dC_C}{dt} = -k'C_A^n - \frac{v_0}{V}C_C \tag{3.13}$$

And

$$\frac{dC_D}{dt} = -k'C_A^n - \frac{v_0}{V}C_D \tag{3.14}$$

The conversion of A is given as

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} \tag{3.15}$$

Thus

$$X_A = \frac{C_{A0}V_0 - C_A V}{C_{A0}V_0} \quad (3.16)$$

Equations 2.26, 3.9, 3.10, 3.13, 3.14, and 3.16 were then solved using the ODE solver in matlab to get the values for t, C_A, C_B, C_C, C_D, Vand X_A.

To determine the mixer power required for the stirred tank reactor,

From Harry Silla (2003), since we are dealing with a liquid-liquid mixture

$$P_n = pV_r \quad (3.17)$$

where p = power factor and V_r= volume of the reactor mix

To determine the stirrer specification, using standard stirred vessel configuration (Beek*et al*, 1999)where D is the Diameter of vessel:

Diameter of impeller (d) = 1/3 x D (3.18)

width of impeller blade (w) = d/5 (3.19)

Height of liquid in reactor(H) = D (3.20)

Height of bottom of vessel from the impeller (L) = 1/3 x H (3.21)

Width of Baffles = D/10 (3.22)

Length of impeller blade (l) = d/4 (3.23)

Number of Baffles = 6

Number of impeller blades = 4

$T(^{O}C)$	$Al_2(SO_4)_3$(ml)	NaOH(ml)	$Al(OH)_3$(g)

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Effect Of Temperature On Mass Of $Al(OH)_3$Produced From Alum From KankaraKaolin

The effect of temperature on the mass of $Al(OH)_3$ produced is shown in Table 4.1.

25	100	30	5.4
40	100	30	5.2
60	100	30	5.2
80	100	30	5.2
100	100	30	5.2

Table 4.1: Effect of temperature on the mass of $Al(OH)_3$ produced

The mass was observed to reduce from 5.4g to 5.2g as the temperature increased from $25^{O}C$ to $40^{O}C$ and remained constant from then on as the temperature was continually increased up to 100 ^{O}C.This showed that the amount of $Al(OH)_3$ produced only marginally differed with change in temperature.

4.2: Chemical Composition OfAluminium Hydroxide Obtained From Alum On A Laboratory Bench Scale

The chemical composition of aluminium hydroxide obtained from the alum was shown in Table 4.2.

Table 4.2: Chemical composition of Aluminiumhydroxide obtained from alum at pH of 6and pH of 7

Constituent	pH 6	pH 7
SiO_2	3.52	2.6
Al_2O_3	57.0	78.2

P_2O_5	0.4	0.76
SO_3	33.4	13.4
CaO	0.343	0.634
TiO_2	0.061	0.078
MgO	0.0	0.34
Cr_2O_3	0.034	0.072
MnO	0.006	0.094
Fe_2O_3	1.02	1.79
NiO	0.056	0.11
ZnO	0.15	0.30
CuO	0.0	0.085
Na_2O	3.70	1.53
Sc_2O_3	0.01	0.0
V_2O_5	0.027	0.0
ZrO_2	0.1	0.0

It indicated that from the sample,Al_2O_3 yielded the highest percentage of 57 while Sc_2O_3 yielded the least at 0.01 percent. The chemical composition of aluminium hydroxide obtained from the alum as shown in Table 4.2 at a pH of 7 showed a percentage for $Al_2O_3$of 78.2 as the highest and Cr_2O_3 as the lowest with a percentage of 0.072 showing a marked increase in the amount of Al_2O_3 present. This is consistent with the findings made by Misra (1990), the material produced at a pH of 7 showing a content of Al_2O_3 larger than that reported in literature, thus improving the expected yield after calcination.

4.3 Crystal PhasesOf Aluminum Hydroxide Produced From Alum From KankaraKaolin On A Laboratory Bench Scale

The crystal phases of aluminium hydroxide produced from Kankara kaolin at pH of 6 and 7 were given in Figures 4.1 and 4.2 respectively.

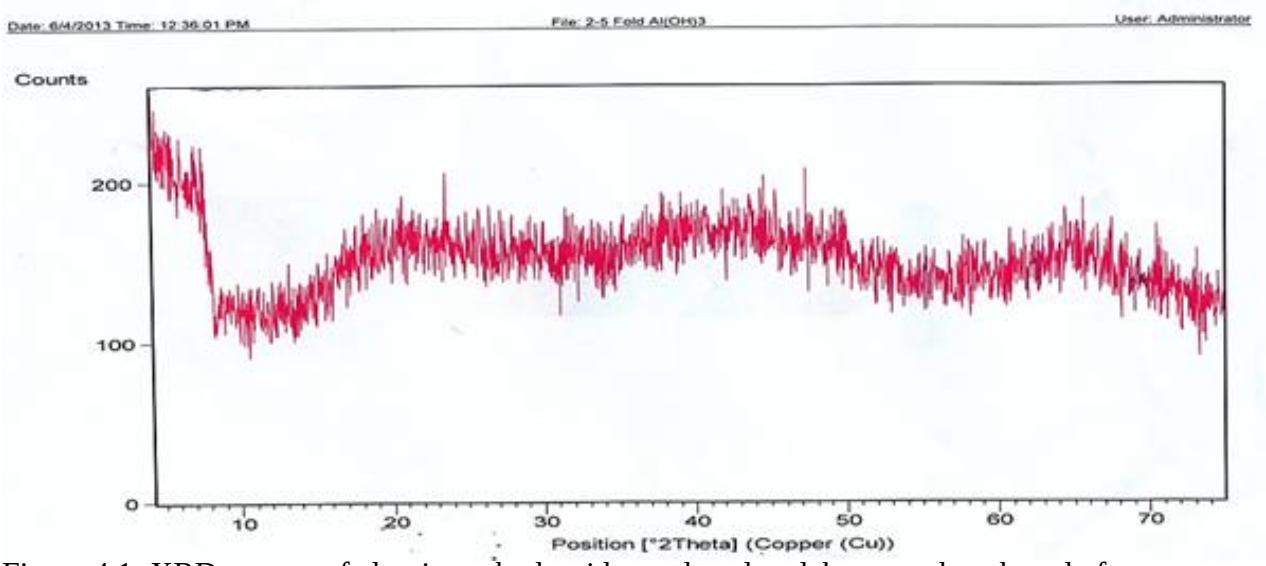


Figure 4.1: XRD pattern of aluminum hydroxide produced on laboratory bench scale from alum fromKankara kaolin at pH of 6

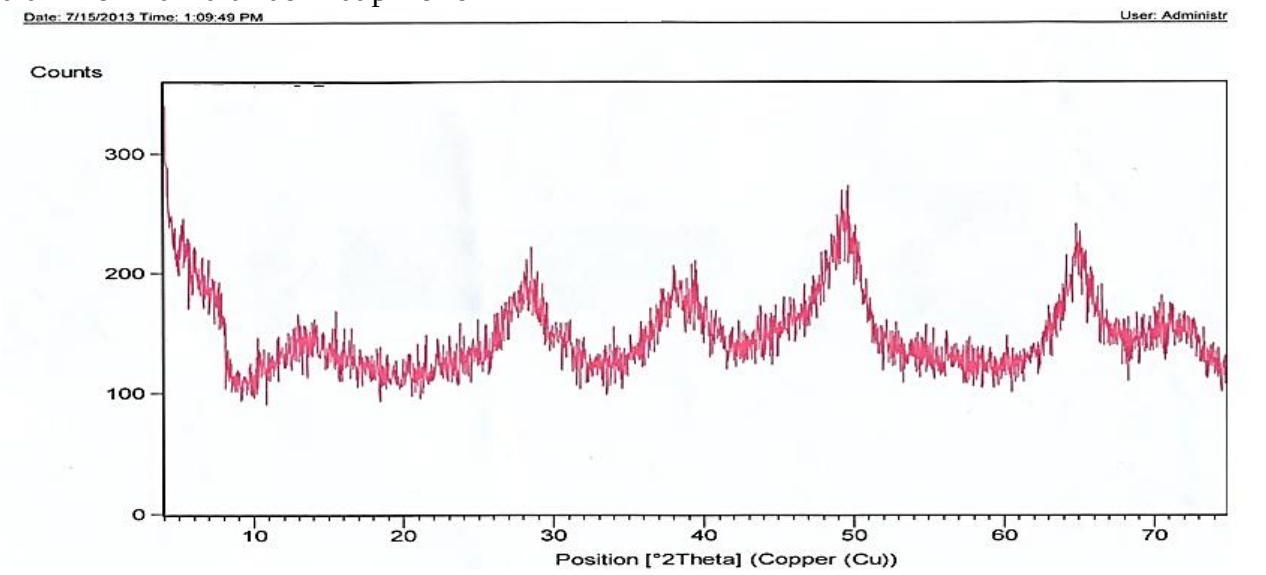


Figure 4.2: XRD pattern of aluminum hydroxide produced on laboratory bench scalefrom alum fromKankara kaolin at pH of 7

The pH value of the solution has been seen togreatly affect the structures of the aluminum hydroxides precipitated from the solution. This could be seen from the figuresof the XRD patterns of the aluminum hydroxides prepared at different pH values of 6 and 7, in which each phase was identified by its characteristic diffraction peaks. As observed in Figure 4.1, the diffuse peaks indicated the formation of the amorphous aluminium hydroxide phase at the pH value of 6. At pH of 7 as shown in Figure 4.2, the boemhite (γ-AlOOH) phase was

identified by the characteristic diffraction peaks of γ-AlOOH at 2θ=14.24°, 27.86°, 38.14°, 48.68°, and 64.88° in the aluminium hydroxides. Meanwhile, a small portion of the bayerite [α-$Al(OH)_3$] phase was recognized by its major diffraction peaks at 2θ=18.62°, 20.14°, and 40.34° respectively. It was interesting to note that different phases formed depending on the pH value of the solution during the precipitation step. From the XRD analysis results, it was seen that during the precipitation step an acidic condition and a neutral condition were favorable for the formation of amorphous aluminum hydroxide and boehmite phases, respectively(Xuelian*et al.*, 2009).

4.4 Surface Area And Pore Analysis Of Aluminium Hydroxide Produced From Alum From KankaraKaolin On A Laboratory Bench Scale

The surface area of the aluminium hydroxide is shown in Table 4.3.

Table 4.3: BET-surface area analysis of aluminum hydroxide produced from laboratory bench scale fromKankara kaolin at pH of 6 and 7

Sample ID	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
pH 6	78.275	0.0426	2.179
pH 7	209.799	0.104	1.989

BET surface area analysis by gas adsorption is the most widely used technique to characterize the surface area of solid materials. Adsorption of nitrogen at a temperature of 77K is mostly measured over porous materials. The principle is that at lower pressures gas adsorbs to solids in a monolayer. The analysis can then calculate the surface area covered by this layer based on the number of gas molecules in a monolayer and the dimensions of an individual molecule. Monolayer formation of gas molecules is thus applied to determine the specific surface area, while the principle of capillary condensation can be used to analyse porous

characteristics such as pore volume and pore size distribution. The BET-surface area analysis of aluminum hydroxide prepared on a laboratory bench scale from alum fromKankara kaolin at pH of 6 was 78.275m^2/g and at pH of 7, it was found to be 209.799m^2/g, as was shown in Table 4.3. These values for the surface area are in tandem with the work of Kosmulski (2009) as the 78m^2/g is what is obtained for an amorphous aluminium hydroxide while 210m^2/g is what is expected of a crystalline material.

4.5 KinteticData Determination Using Differential Method Of Analysis For The Production Of Aluminium Hydroxide From Alum From KankaraKaolin

The kinetic data were obtained after processing the data gotten from laboratory bench scale experiments. From Figures 4.3b, 4.4b and 4.5b, using Equation 3.6, the values for lnk' were found to be -1.6996, -2.002, and -3.5149 respectively. Also, the values for n were found to be 0.823, 0.6439, and 0.9169 respectively.

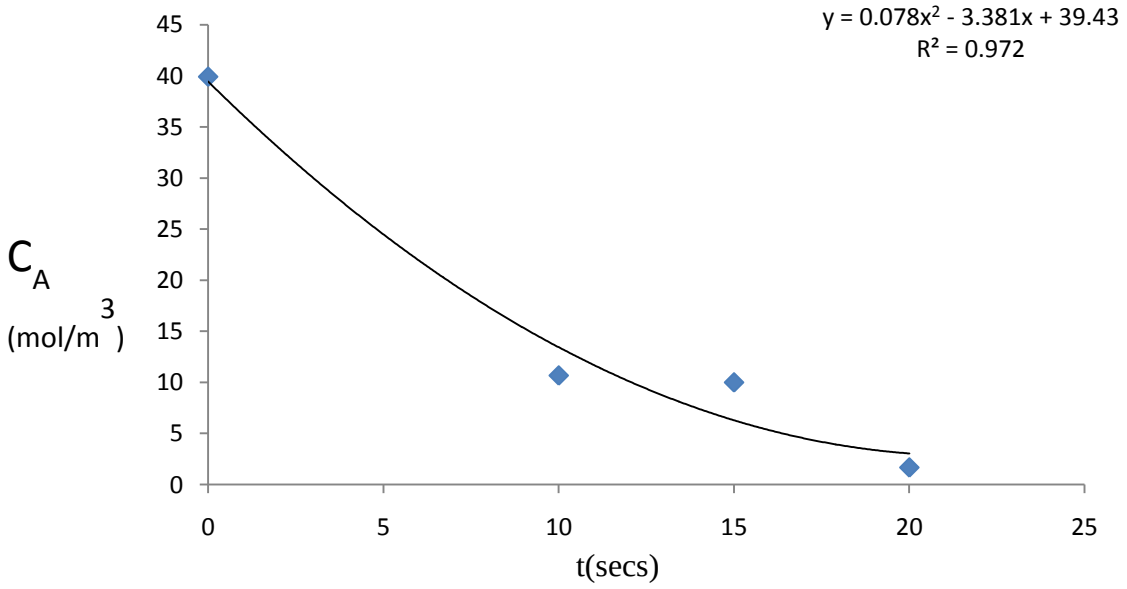


Figure 4.3a: Plot of concentration of $Al_2(SO_4)_3$ (C_A) with time (t) at 90^oC(in water bath at 100^oC)

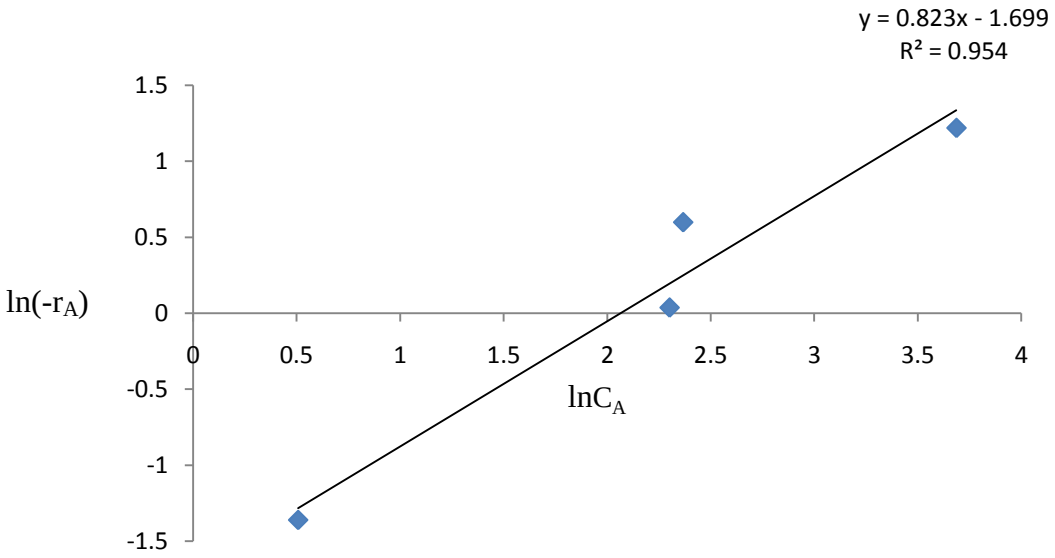


Figure 4.3b: Plot of rate with concentration on log-log scale at 90^{o}C(in water bath at 100^{o}C)

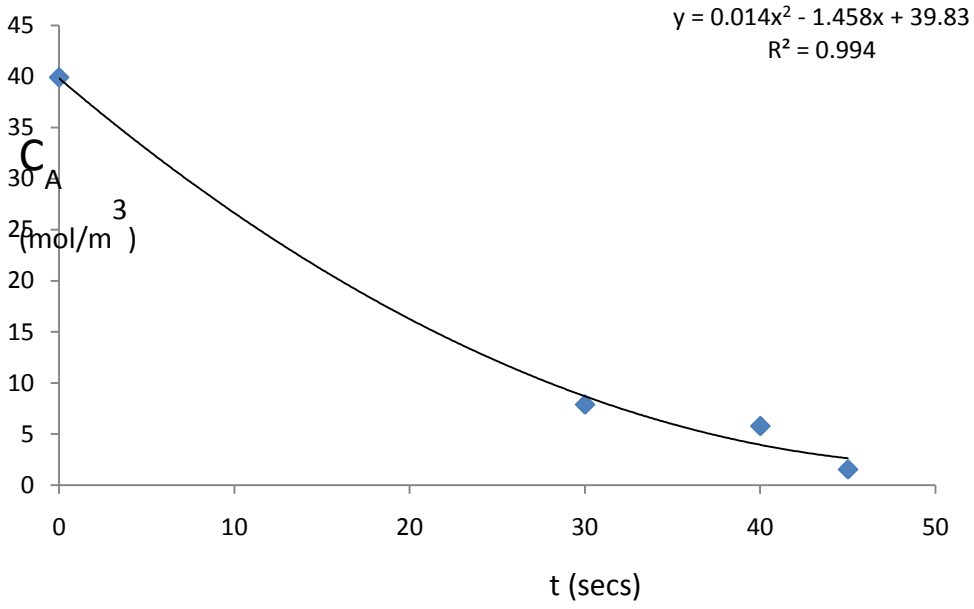


Figure 4.4a: Plot of concentration of $Al_2(SO_4)_3$ (C_A) with time (t) at 79^{o}C(ambient environment, 25^{o}C)

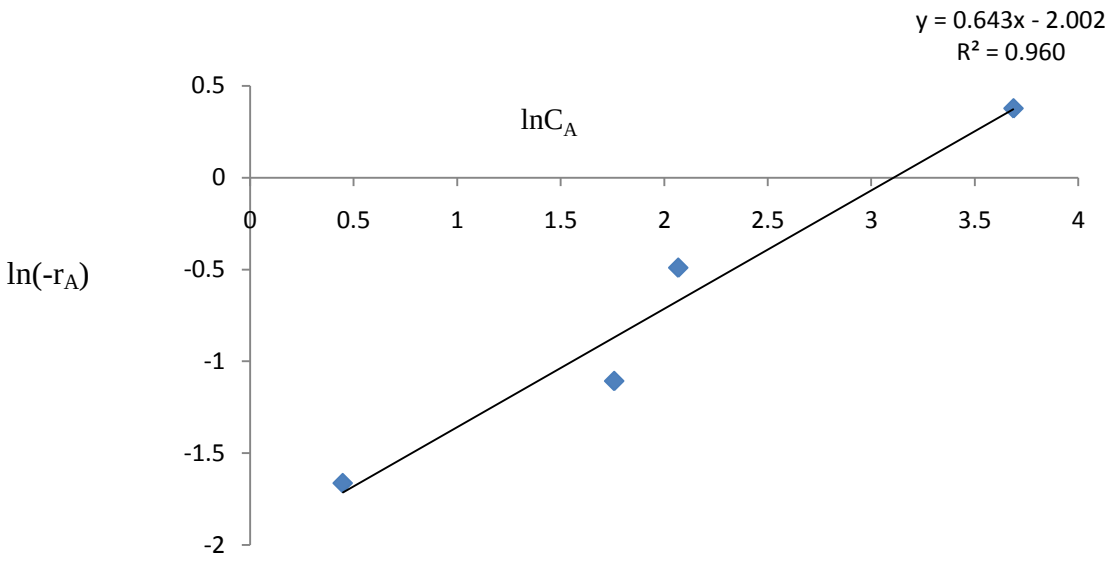


Figure 4.4b: Plot of rate with concentration on log-log scale at 79^{o}C(ambient environment, 25^{o}C)

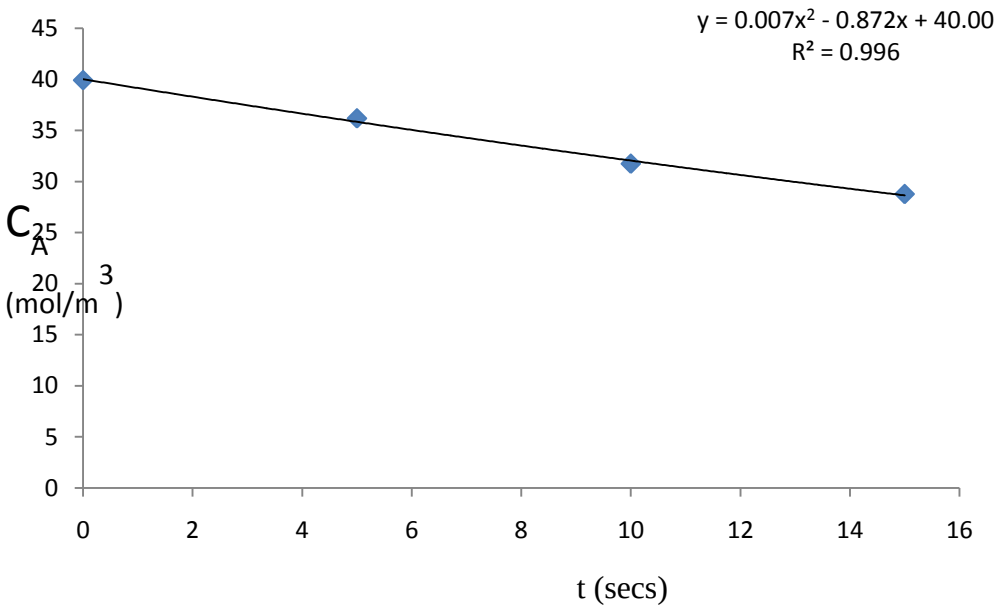


Figure 4.5a: Plot of concentration of $Al_2(SO_4)_3$ (C_A) with time (t) at 73^{o}C(in water bath, 20^{o}C)

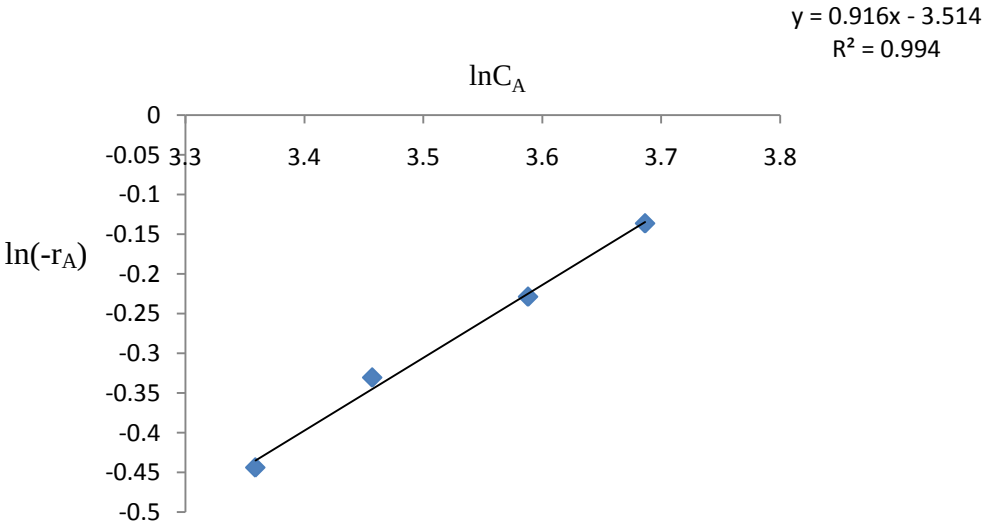


Figure 4.5b: Plot of rate with concentration on log-log scale at 73^{o}C(in water bath, 20^{o}C)

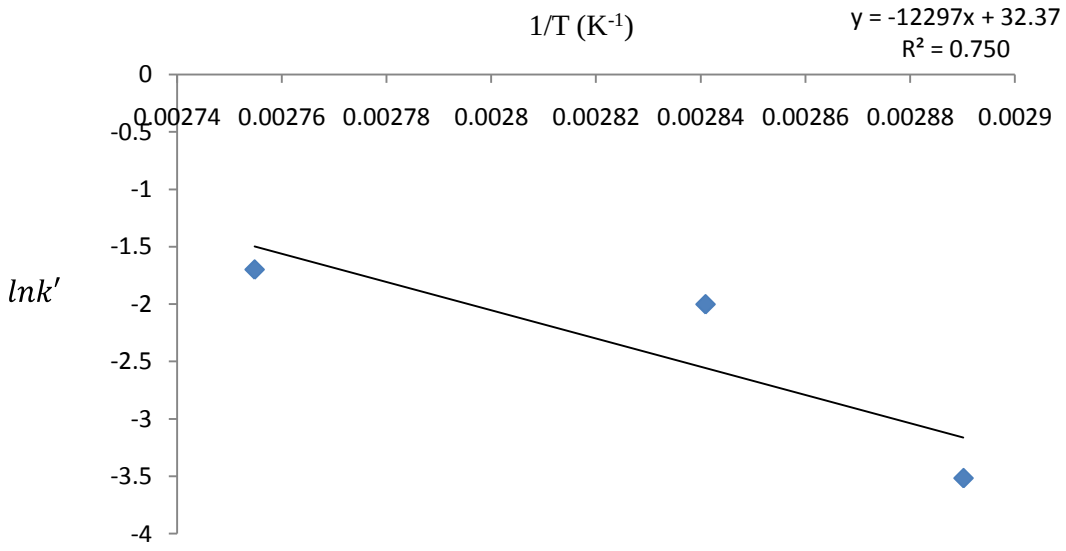


Figure 4.6: Plot of lnk' with temperature (1/T)

From the plot of lnk' against 1/T, from Equation 3.8, and using R= 8.314J/molK, it was found out that

$$E_A = 102.237\ kJ/mol$$

$$A = 1.153509E14\ sec^{-1}$$

$$n \cong 1$$

E_A= Activation energy

A = Pre exponential factor

n = Order of the reaction

4.6 Design of Pilot Scale Reactor

For a reaction temperature of 79^0C, substituting in Arrhenius equation, it was found that

k' = 1.153509*10^14 * exp [- 102,237.258 / 8.314 (352)] = 0.07764 sec^{-1} = 4.6584min^{-1}

From Appendix VII, V_0=32.2469L;C_{A0}=39.9006mol/m^3; C_{B0}=37,875mol/m^3;v_o=0.3224L/min

After solving Equations 2.26, 3.9, 3.10, 3.13, 3.14, and 3.16 using the ODE solver in MATLAB to get the values for t, C_A, C_B, C_C and C_D, V and X_A:

At a volume of 42.5litres in the reactor, the conversion was found to be 99.98%.

The time for the reaction was found to be 31.9 minutes.

The total volume of the reactor is 50 litres, allowing for 15% head space as recommended by Blaasel (1990).

To determine the mixer power required for the stirred tank reactor from Equation 3.17:

Since the reaction is between two liquids,

Therefore p = 5hp/1000gal and V_r= volume of the reactor mixture

But 1 gallon = 3.784 litres

Therefore for 42.5 litres reaction volume, we have

P_n = 5 x 42.5/(3.784 x 1000) = 0.05616hp

To determine the stirrer and baffle specificationfrom Equations 3.18 through 3.23:

Where D is diameter of reactor = 38cm,

Height of reactor (H_r) = 55cm

Diameter of impeller (d) = 12.67cm,

Width of impeller blade (w) = 2.534cm

Height of liquid in reactor(H) = 38cm

Height of bottom of vessel from the impeller (L) = 12.67cm

Width of baffles (w) = 3.8cm

Length of the impeller (l) = 3.17cm

4.7 FabricationOf Pilot Scale Reactor

The pilot scale reactor was drawn using AUTOCAD (2013 version). Figure 4.7 is an x-ray projection of the drawn pilot scale reactor. The pilot scale reactor was constructed at HANIGHA in Kaduna, Kaduna State using the specifications obtained from the reactor design. Plate IV.I is a pictorial view of the fabricated reactor.

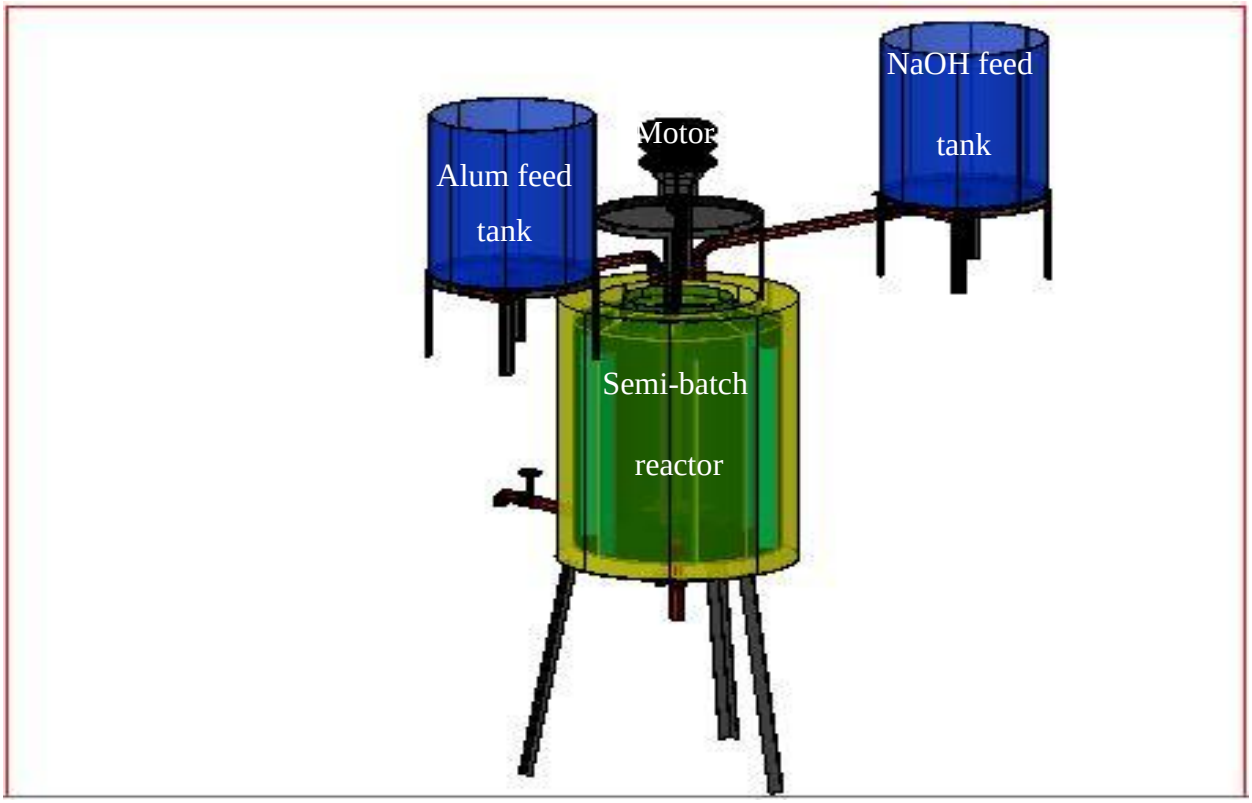


Figure 4.7: X-ray projection of aluminium hydroxide pilot scale reactor using AUTOCAD, 2013 version.



Plate IV.I: Fabricated pilot scale reactorfor the production of aluminium hydroxide from alum from Kankara kaolin.

4.8 Crystal Phases Of Aluminium Hydroxide Produced From Alum From KankaraKaolin From The Pilot Scale Reactor

The XRD patterns of aluminium hydroxide produced from the pilot scale reactor were determined.

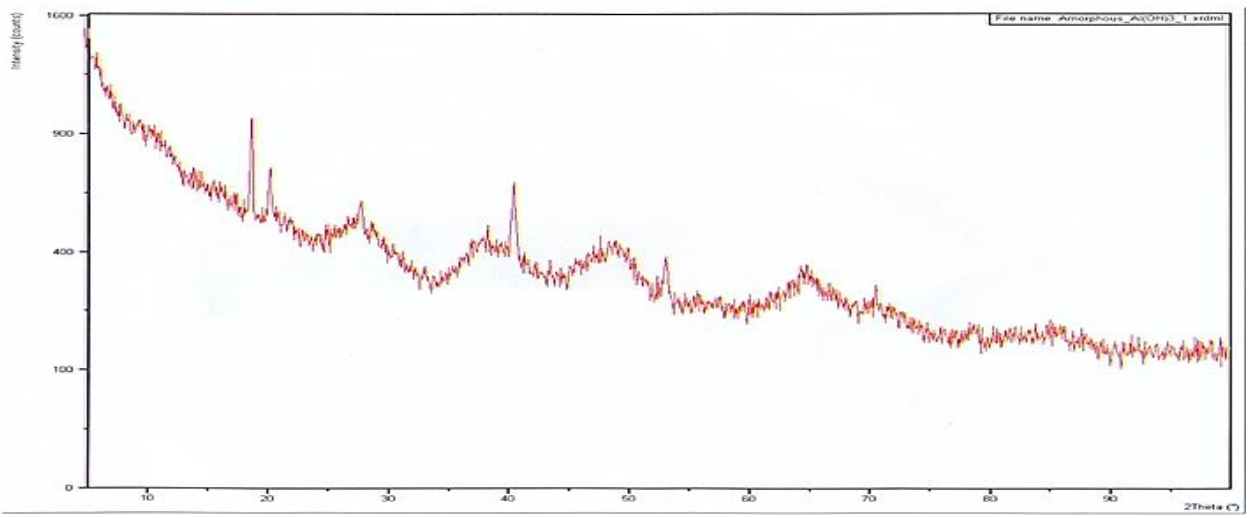


Figure 4.8: XRD pattern of aluminum hydroxide produced from pilot scale reactor from alum from Kankara kaolin for run 1

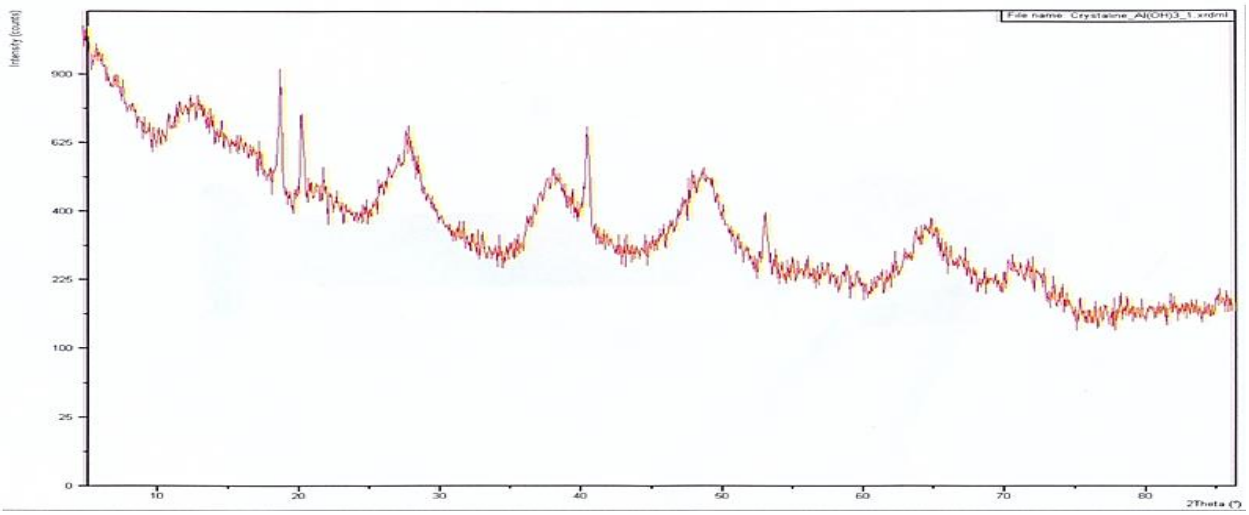


Figure 4.9: XRD pattern of aluminum hydroxide produced from pilot scale reactor from alum from Kankara kaolinfor run 2

From Figure 4.8, it can be seen that the characteristic diffraction peaks for boehmite at 2θ= 27.86°, 38.14°, 48.68°, and 64.88° appear albeit dwarfed. The major diffraction peaks for bayerite could be seen at 2θ=18.62°, 20.14°, 40.34° and 53.64^{o}. From Figure 4.9, the characteristic diffraction peaks of boehmite at 2θ=14.24°, 27.86°, 38.14°, 48.68°, and 64.88°were well identified. Also the major diffraction peaks for bayerite at at 2θ=18.62°, 20.14°, 40.34° and 53.64^{o}. This showed that the product from the pilot scale reactor was formed between the pH of 7 and 8 as seen in Appendix II. For run 1, the transition from pH 7 to 8 is less advanced as that seen in run 2.

4.9 Chemical Composition OfAluminium Hydroxide Produced From Alum From KanakaraKaolin From The Pilot Scale Reactor

Table 4.4 showed the chemical composition of $Al(OH)_3$ produced from the pilot-scale reactor.

Table 4.4: Chemical composition of aluminiumhydroxide obtained from alum from Kankara kaolin from the pilot scale reactor

Constituents	Run1	Run2
SiO_2	4.97	3.32
Al_2O_3	70.54	74.34
MoO_3	3.00	1.86
SO_3	13.3	15.78
CaO	0.500	0.335
TiO_2	0.053	0.036
MgO	1.63	1.20
Cr_2O_3	0.289	0.236
MnO	0.039	0.040
Fe_2O_3	3.10	2.55
NiO	0.079	0.055
ZnO	0.19	0.18
CuO	0.039	0.041
Na_2O	2.18	1.96
K_2O	0.059	0.025
V_2O_5	0.028	0.038

The probable percentage increase in yield noticed at pH of 7 due to a larger Al_2O_3content than commercial value was also observed in the oxide content of the sample for Al_2O_3 at 70.54 for run 1 and 74.34 percent for run 2. V_2O_5 showed the lowest (0.028) percentage for run1 and (0.025) for $K_2O$for run 2 as was seen in Table 4.4. This findings are consistent with

the report of Misra (1990) and are a pointer to highly crystalline nature of the samples obtained from the pilot-scale reactor.

4.10 Surface Area And Pore Analysis Of Aluminium Hydroxide Produced From Alum From KankaraKaolin From The Pilot Scale Reactor

The surface area of the aluminium hydroxide produced from the pilot scale reactor was shown in Table 4.5

Table 4.5: BET-surface area analysis of aluminum hydroxide produced from pilot scale reactor setup

Sample ID	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Run 1	97.736	0.051	2.074
Run 2	227.779	0.113	1.980

The product of the pilot scale reactor setup yielded a much higher surface area of 97.73m^2/g for Run 1and 227.77m^2/g for Run 2, as was seen from Table 4.5. Also, the values of the surface areas of the two runs in the pilot scale setup compared favourably with the reported values in the literature (Patrick *et al.*, 2002). However, the value of 97.73m^2/g for the run1 in the pilot scale reactor setupfurther confirmed that the sample was partly amorphous and is consistent with the findings ofKosmulski (2009).

4.11 Crystal Phase OfZeolite Y Produced From Aluminium Hydroxide

The XRD pattern of Zeolite Y produced using Kankara kaolin based aluminium hydroxide was presented in Figure 4.10.

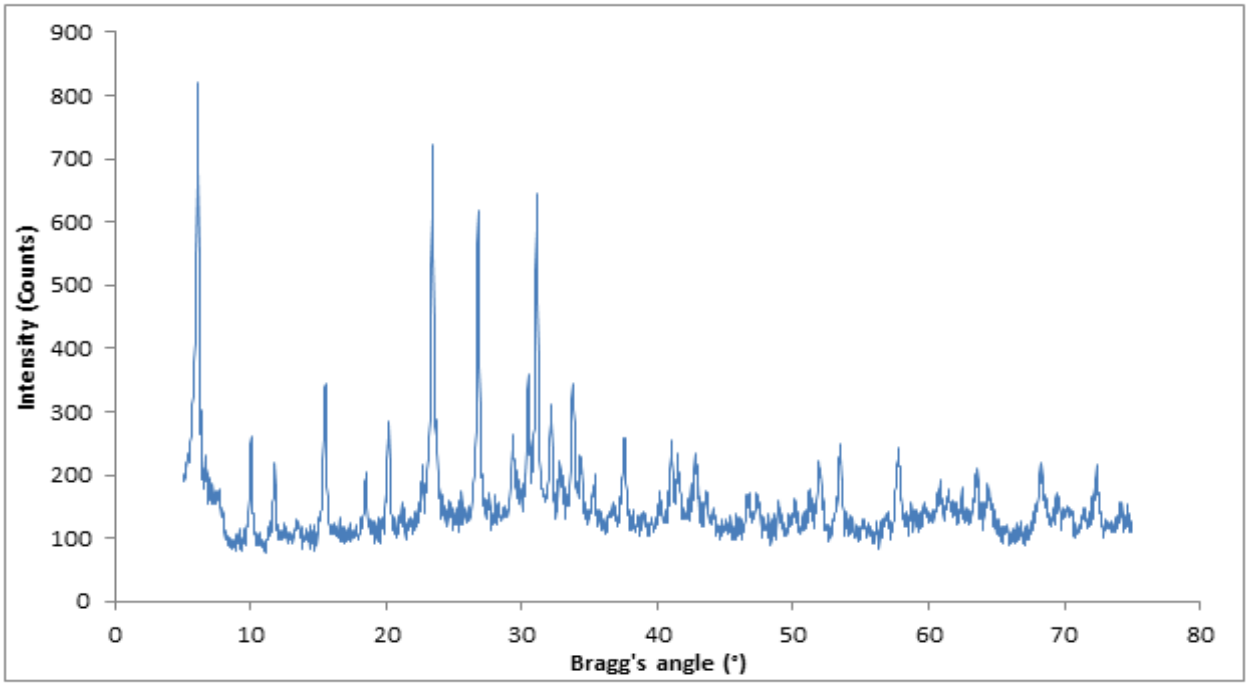


Figure 4.10: XRD pattern of Zeolite Y produced from aluminum hydroxide from Kankara kaolin (Salahudeen, 2014).

. The XRD spectrum of the zeolite Y produced from the aluminium hydroxide which was locally sourced by Salahudeen (2014) was consistent with that of Zeolite Y produced by the verified synthesis method (Appendix III) as shown by the overlapping of their major characteristic diffraction peaks at2θ = 6.12°, 10.05°, 11.96°, 15.55°, 20.2°, 23.3°, 23.63°, and 31.05° (Pei-Yuan, 1977).

CHAPTER FIVE

5.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

i. Aluminium hydroxide has been synthesized from Kankara kaolin based alum.

ii. Aluminium hydroxide pilot scale reactor was designed and fabricated with a capacityof 10.448kg of $Al(OH)_3$ production per day.

iii. The $Al(OH)_3$preparedwas successfully used for the synthesis of Zeolite Y.

5.2 Conclusions

i. With increasing pH value from 6 to 7, the aluminum hydroxide precipitated from Kankara kaolin by the reaction between Kankara kaolin based alum and sodium hydroxide varies from amorphous aluminium hydroxide through γ-AlOOH to α-$Al(OH)_3$.

ii. Aluminium hydroxide precipitated fromKankara kaolin by the reaction betweenaluminiumsulphate and sodium hydroxide was found to obey *psuedo*first order kinetics.

iii. Aluminium hydroxide precipitated from Kankara kaolin and activated by thermal decomposition can well be used in the production of high quality Zeolite Y.

5.3 Recommendations

The following further actions are recommended:

i. Optimization of the pilot scale reactor using design of experiments.

ii. Incorporation of new equipment like an online pH meter to the pilot scale reactor to improve selectivity of product.

iii. The usage of the product from the pilot scale reactor to produce zeolite Y should further be explored.

iv. Further characterization of the aluminium hydroxide precipitated should be carried out using TEM, SEM, TG-DTA, and FTIR techniques.

REFERENCES

Aderemi, B.O., Edomwonyi-Otu L.and Adefila S.S. (2009). A New Approach ToMetakaolinDealumination, *Australian Journal of Basic and Applied Sciences*, 3(3): 2243-2248.

Alkan, M.,Hopa, C.,Yimaz, Z. andGuler, H. (2005). The effect of alkali concentrationand solid/liquid ratio on the hydrothermal synthesis of zeolite NaA from natural kaolinite,*Microporous and Mesoporous Materials*, 86 :176−184.

Andersson, E. and Hansson, H. (2000).*Precipitation of Reactive Aluminium Hydroxide from an AcididcAluminiumSulphate Solution by Addition of Sodium Hydroxide*,(academic study), Department of Chemical Engineering, University of Lund, Sweden.

Arulmurugu, A.,Karthick, B.M.,Vasanthakumar, P. andChendrayaperumal, J. (2014) Emission Control In IC Engine - Selective CatalyticReduction Method, *International Journal of Engineering Research & Technology*, Vol. 3, Issue 2.

AZoM.com (2002).Alumina (Aluminium Oxide) – The Different Types of Commercially Available Grades,*The A to Z of Materials*,Archived from the original on 10 October 2007.Retrieved from http://www.azom.com/article.aspx?ArticleID=1389

Bailey, S.W.(1980). Summary of recommendations of AIPEA nomenclature committee on clay minerals, *American Mineralogist*, Vol. 65, pp. 1-7.

Baker, B.R. and Pearson, R.M.,(1974). Water Content of Pseudoboehmite: A New Model for its Structure, *Journal of Catalysis*, 33, 265-278.

Barrer, R.M. (1982). *Hydrothermal Chemistry of Zeolites*, Academic Press, London, UK.pp. 360.

Bawa, S.G. (2012).*Development of Gamma Alumina from Kankara Kaolin for Potential Application as Catalyst Support*, (Unpublished Msc Thesis). Chemical Engineering Department,Ahmadu Bello University, Zaria.

Beek, W.J., Muttzall, K.M.K. and Van Heuten, J.W. (1999).*Transport Phemomena*, (2nd Ed.) John Wiley and Sons, England.pp. 131, 228.

Bekkum, V. H., Flanigen, E.M., Jacobs, P.A and Jansen, J.C. (1991).*Introduction to Zeolite Science and Practice*(2nd. Revised Ed.) Elsevier, Amsterdam.pp. 13-34.

Bellotto, M., Gualtieri, A., Artioli, G. and Clark, S.M. (1995).Kinetic study of the kaolinite-mullite reaction sequence. Part I: kaolinite dehydroxylation,*Physical Chemical. Minerals*, 22 (4): 207–214.

Brandon, L. and Brandon, D. (1998).Metastable Alumina Polymorphs: Crystal Structures and Transition Sequences,*Journal of the American Ceramic Society*, 81 (8): 1995–2012

Bray, E.L. (2012) *US Geological Survey Mineral Commodity Summaries*. Retrieved from http://www.minerals.usgs.gov/minerals/pubs/commodity/bauxite/mcs-2015-bauxi.pdf

Busacca,C.A., Fandrick, D.R., Song, J.J.and Senanayake,C.H. (2012).*Transition Metal Catalysis in the Pharmaceutical Industry*, John Wiley & Sons, Inc.

Campbell, T., Kalia, R, Nakano, A., Vashishta, P., Ogata, S.and Rodgers, S. (1999).Dynamics of Oxidation of AluminiumNanoclusters using Variable Charge Molecular-Dynamics Simulations on Parallel Computers,*Physical Review Letters*, 82 (24): 4866.

Clark, J. (2010) *Energy profiles for Simple Reactions.* Retrieved from http://www.chemguide.co.uk/physical/basicrates/catprofile.gif

Edonwonyi-Otu, L. and Aderemi, B.O. (2009). Alums from Kankara Kaolin, *Journal of Research in Engineering*, Vol. 6, Number 1.

Elschenbroich, C. (2006).*Organometallics*, Wiley-VCH: Weinheim.

Fogler, H. S. (2006).*Elements ofChemical Reaction Engineering*, (4th Ed.), Prentice Hall. pp. 215-230, 256-271.

Frost R.L. and Vassallo A.M. (1996). The Dehydroxylation Of The Kaolinite Clay Minerals Using Infrared Emission Spectroscopy,*Clays And Clay Minerals*, Vol. 44, No. 5, 635-651.

Georgiev, D., Bogdanov, B., Markovska, I., and Hristov,Y. (2011).*Synthesis of NaA Zeolite from Natural Kaolinite, Oxidation Communications*, 34, No 4, 812−819.

Georgiev, D., Bogdanov, B., Markovska, I., Hristov,Y. and Stanev,D. (2011). *Investigation on the crystal structure of zeolite NaA and modeling the sorbtion kinetics of Cu(II) ions from aqueous solution*, Book of ISIC18 international symposium on industrial Crystallization, Zurich, 260-262.

Ghobarkar, H. and Schaf, O. (1998). *Microporous and Mesoporous Materials*, 23:55−60.

Grabow, L.C. (2010) *Molecular Structure of ZeoliteZSM5*. Retrieved from http://www.chee.uh.edu/sites/chbe.egr.uh.edu/files/images/ZSM5.png

Greenwood, N.N. andEarnshaw, A. (1997).*Chemistry of Elements*(2nd Ed.) Butterworth and Heinemann.

Harper, D. (2012). *Kaolin*. Online Etymology Dictionary.

Hind, A.R., Bhargava, S.K. andGrocott, S.C. (1999).The Surface Chemistry of Bayer Process Solids: A Review,*Colloids Surface Physiochemical Engineering Aspects*, 146: pp. 359–74.

Hosseini, S.A., Niaei, A. andSalari, D. (2011). Production of Gamma-Alumina from Kaolin,*Open Journal of Physical Chemistry*, 1, 23-27.

Hudson, L. K., Misra, C., Perrotta, A.J., Wefers, K. Williams,F. S.(2012).Aluminium Oxide, *Ullmann's Encyclopedia of Industrial Chemistry* Wiley VCH, Weinheim, Germany.

International Zeolite Association (2002).*Database of Zeolite Structures*. Retrieved fromhttp://www.iza-structure.org/

Jovanovic, N., Novakovic, T., Janackovic, J. andTerlecki-Baricevic, A. (1992). Properties of Activated Alumina Obtained By Flash Calcination Of Gibbsite, *Journal of Colloid and Interface Science*,Vol. 150, No. 1.

Karamalidis, A.K. andDzombak, D.A. (2010).*Surface Complexation Modeling: Gibbsite*,John Wiley & Sons.pp. 15–17.

Kanazirev, V.I. and Rumfola, P. (2011).*Hydrothermally Stable Alumina*, United States Patent Application Publication Us2011/0111955 A1.

Kim, W., Zhang, Q. and Saito, F.(2000).*Journal of Chemical Engineering ofJapan*, 33: 217−222.

Kloprogge, J.T., Ruan, H.D. and Frost, R.L. (2002). Thermal Decomposition Of Bauxite Minerals: Infrared Emission Spectroscopy Of Gibbsite, Boehmite And Diaspore, *Journal Of Materials Science*, 37(6), 1121-1129.

Knözinger, H. andKochloeflK.(2002).Heterogeneous Catalysis and Solid Catalysts,*Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim.

Kosmulski,M. (2009).*Surface Charging and Points of Zero Charge*, CRC press, USA. pp. 186

Lerner, L. (2011).*7 things you may not know about catalysis*, Argonne National Laboratory

Luyken, H. (2012) *Chemical structure of pseudoboehmite*. Retrieved from http://www.familie-luyken.de/07Genealogie/13Gen/13064a.htm

Masel, R.I. (2001).*Chemical Kinetics and Catalysis*, Wiley-Interscience, New York.

McCusker,L.B.,Liebau, F. andEngelhardt, D.G. (2001). Nomenclature of structuraland compositional characteristics of ordered microporous and mesoporous materials withinorganic hosts, *Pure and Applied Chemistry*, Vol. 73, No. 2, pp. 381−394.

Meier, W. M and Olson, D. H (1987).*Atlas of Zeolites Structure Types*,(2ndEd.), Butterworth and Co.

Mindat.org(2009).*Kaolinite mineral Information and Data*. Retrieved from http://www.mindat.org/min-2156.html

Mohapatra M., Anand S., Mishra B.K., Giles D.E.and Singh, P. (2009).Review of Fluoride Removal from Drinking Water,*Elsevier Journal of Environmental Management*, 91 67–77.

Moore, D. andReynolds Jr., R.C. (1997).*X-Ray Diffraction and the Identification and Analysis of Clay Minerals*, (2nd Ed.) Oxford University Press, New York.

Naito, M., Shinohara, N. and Uematsu, K. (2003). Raw Materials, Chapter 2, *Handbook of Advanced Ceramics*, Elsevier Inc.,89-129.

Nelson, D. L. andCox Lehninger, M.M. (2000).*Principles of Biochemistry*(3rd Ed.) Worth Publishing: New York.

Nogi, K., Naito, M.and Yokoyama, T. (2003)*Nanoparticle Technology Handbook*, S. 204.

Ostbo N.P. (2002).*Evolution Of Alpha Phase Alumina In Agglomerates Upon Addition To Cryolitic Melts*, Thesis Submitted In Partial Fulfillment Of The Requirements For The Degree DoktoringeniorNorwegian University Of Science And Technology Department Of Materials Technology And Electrochemistry.

Paglia, G. (2004).*Determination of the Structure of γ-Alumina using Empirical and First Principles Calculations Combined with Supporting Experiments*, Curtin University of Technology, Perth. Retrieved 2009-05-05.

Pearson, A. (2000). *Kirk Othmer Encyclopedia of Chemical Technology*(4th Ed.)Vol 2. John Wiley and Sons, Inc. 391-401.

Pohl, W.L. (2011). *Economic geology: principles and practice: metals, minerals, coal and hydrocarbons – introduction to formation and sustainable exploitation of mineral deposits*,Chichester, West Sussex: Wiley-Blackwell. pp. 331

Rios, C.A., Williams, C.D and Fullen, M.A.(2009). Nucleation and growthhistory of zeolite LTA synthesized from kaolinite by two different methods, *Applied Clay Science*, 42. pp.446-454

Rowe, A. (2008).*Nanoparticles help gauze stop gushing wounds*, Wired.com.

Roy, R. (1994). Accelerating the Kinetics of Low-Temperature InorganicSyntheses, *Journal of Solid State Chemistry*, 111:11−17

Rozic, L., Novakovic, T., Jovanovic, N., Terlecki-Baricevic, A. and Grbavcic,Z. (2001). The Kinetics of the Partial Dehydration of Gibbsite to Activated Alumina in a Reactor for Pneumatic Transport, *Journal of Serbian Chemical Society*, 66(4)273–280.

Rozic, L., Novakovic, T., Petrovic, S., Cupic, Z., Grbavcic, Z. and Rosic, A. (2006).The Sorption and Crystallographic Characteristics of Alumina Activated in a Reactor for Pneumatic Transport, *Journal of Serbian Chemical Society*, 71 (11) 1237–1246.

Rozic, L.S.,Petrovic, S.P., Novakovic, T.B., Cupic, Z.D., Grbavcic, Z.B. and Jovanovic, D.M. (2006). Textural and Fractal Properties of CuO/Al_2O_3 Catalyst Supports, *Elsevier Chemical Engineering Journal*, 120 55–61.

Santos, D.S.,Viera Coelho, A.C., Kunihiko, H.and Kiyohara, P.,(2009). Hydrothermal Synthesis of Well-CrysatllizedBohemite Crystals of Various Shapes, *Materials Research*, Vol. 12, No. 4, 437-445.

Saukkoriipi, J. (2010).*Theoretical Study of the Hydrolysis of Aluminium Complexes*, (academic dissertation). Chemistry Department, University of Oulu, Finland.

Schoen, R. and Roberson, C.E. (1970). Structures of Aluminum Hydroxide and Geochemical Implications, *The American Mineralogist,* Vol. 55, 43-77.

Shaheen, F., Shah, W.A., Mirza, M.L. and Iqbal, M.P. (2005). Effect Of Concentration Of $Al_2(SO_4)_3.18H_2O$ On The Synthesis Of Nanosized Alumina, *Journal of Chemical Society of Pakistan*, Vol. 27. No. 6.

Silla, H.(2013).*Chemical Process Engineering Design and Economics*,Marcel Dekker, USA, 375-401.

Slangen,P.M., Jansen,J.C. and Bekkum, H.V.(1997).*Microporous Materials*, 9:259−265.

Sohlberg K., Pennycook S.J., and Pantelides S.T. (1999).Hydrogen And The Structure Of The Transition Aluminas,*Journal of American Chemical. Society*, 121, 7493-7499.

Speight,J.G. (2006). *The Chemistry and Technology of Petroleum* (4th Ed.) CRC Press.

Suresh, B.,Kishi,A., andSchlage, S. (2001).*Chemical Economics Handbook*, SRI, Menio Park, Nov.

Temuujin, J., Okada,K.and MacKenzie,K.J.D.(2002).*Materials Letters*, 52: 91−95.

Tettenhorst, R. and Hofmann, D.A. (1980).Crystal Chemistry of Boehmite, *Clays and Clay Minerals*, Vol. 28, No. 5, 373-380.

The Essential Chemical Industry Online (2013) Retrieved from http://www.essentialchemicalindustry.org/images/stories/030_reactors/01chem_reactorsA.jpg

The Mineral Gibbsite(2014).. Retrieved from http://www.galleries.com/Gibbsite.

Vieira Coelho, A.C. (2008).Specific Surface Area and Structures of Aluminas from FibrillarPseudoboehmite, *RevistaMatéria*, 13, 2. pp. 329-341.

Virta, R.L. (2014) *US Geological Survey Mineral Commodity Summaries*. Retrieved from http://minerals.usgs.gov/minerals/pubs/commodity/clay/mcs-2014-clay.pdf

Wells, A.F. (1975)*Structural Inorganic Chemistry* (4th Ed.) Oxford: Clarendon Press

Williams, F.S. andMisra, C.(2011).Pressure Calcination Revisited, *Light Metals TMS* (The Minerals, Metals & Materials Society).

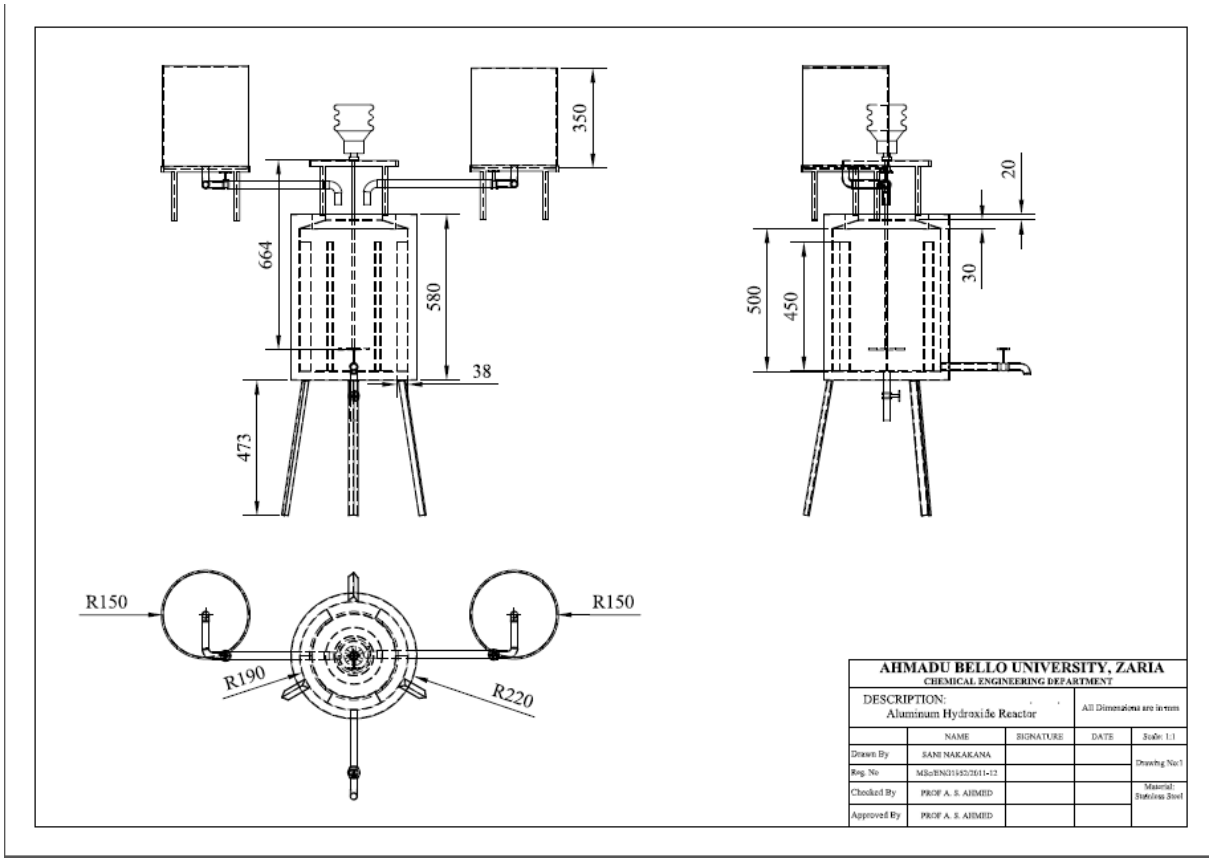
Wilson, M.J. (1999). The origin and formation of clay minerals in soils: past, present and future perspectives,*Clay Minerals*, 34, 7-25.

Xuelian, D., Yanqin, W., Xinghua, S.and Jiangong, L. (2009). Influences of pH value on the microstructure and phase transformation of aluminum hydroxide, *Powder Technology*, 192:40–46

Yang, W.C. (2003).*Handbook of Fluidization and Fluid Particle Systems*, CRC Press, pp. 381.

APPENDIX I

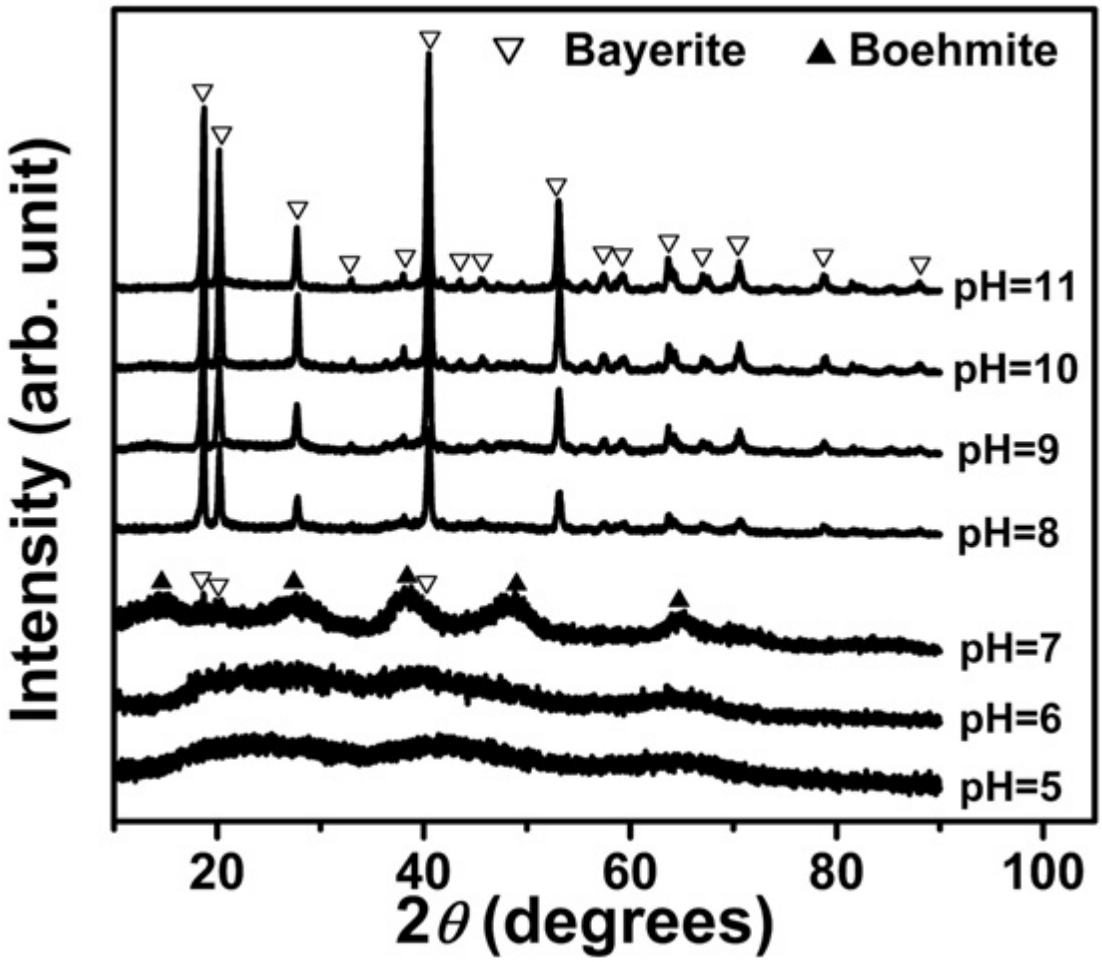
ORTHOGRAPHIC PROJECTION OF THE PILOT SCALE REACTOR USING AUTOCAD (2013 VERSION)



Autocad drawing of the pilot-scale reactor for the production of aluminium hydroxide from Kankara kaolin

APPENDIX II

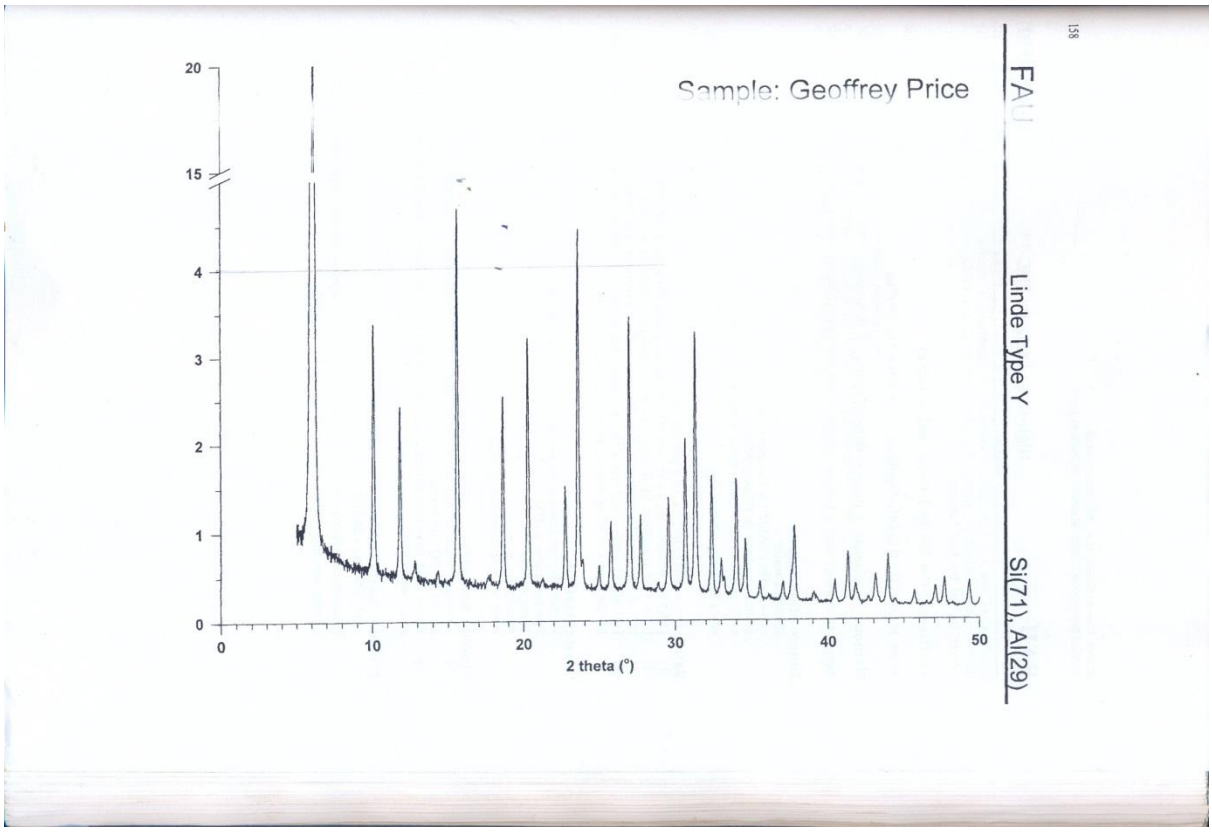
REFERENCE XRD PATTERNS FOR ALUMINIUM HYDROXIDE (XUELIAN, 2008)



XRD patterns of the aluminum hydroxides precipitated at different pH values.

APPENDIX III

XRD PATTERN OF ZEOLITE Y FROM THE VERIFIED SYNTHESIS METHOD.



XRD pattern of zeolite Y produced by the verified synthesis method

APPENDIX IV

BET SURFACE AREA AND PORE ANALYSIS FOR ALUMINIUM HYDROXIDE FROM KANKARA KAOLIN BASED ALUM

Sample ID:Al(OH)3 run 1

Model:V- Sorb 2800P Surface Area and Porosimetry Analyzer

Company:NARICT

Report Time:15th July 2014

Analysis Information
Mass:0.08550 (g)

Method:Multi-Point BET

Room Temp.:Ambient
Pretreatment:16 Hrs

Multi-BET:97.735685 (m2/g)

BET Tabular Report

P/P0	Quantity Adsorbed(ml/g)	(P/P0)/(V*(1- P/P0))	Single point BET
0.207238	25.217039	0.010366	87.001345
0.182341	23.527734	0.009478	83.722304
0.158442	22.029217	0.008546	80.681153
0.131006	20.255302	0.007443	76.602729
0.109581	18.888226	0.006516	73.193817
0.081887	17.219671	0.005180	68.803430
0.055500	15.284097	0.003845	62.824713

Slope	Intercept	Vm(ml)	C Value
0.042864	0.001669	22.455191	26.685582

R	Multi-BET Area	Langmuir Area
0.998004	97.735685	134.638149

Sample ID:Al(OH)3 2-5 Fold pH 6

Model:V- Sorb 2800P Surface Area and Porosimetry Analyzer

Company:NARICT

Report Time:17th July 2014

Analysis Information
Mass:0.09150 (g))

Method:Multi-Point BET

Room Temp.:Ambient
Pretreatment:16 Hrs

Multi-BET:78.275294 (m2/g)

BET Tabular Report

P/P0	Quantity Adsorbed(ml/g)	(P/P0)/(V*(1- P/P0))	Single point BET
0.205938	19.869774	0.013052	68.665112
0.180710	18.584424	0.011868	66.263734
0.155224	17.378827	0.010573	63.892615
0.131214	16.079788	0.009393	60.797003
0.106024	14.710363	0.008062	57.231926
0.081692	13.387920	0.006645	53.504492
0.054451	11.766404	0.004894	48.419102

Slope	Intercept	Vm(ml)	C Value
0.053370	0.002234	17.984083	24.886839
R	Multi-BET Area	Langmuir Area	
0.998517	78.275294	107.910233	

Sample ID:Al(OH)3 run 2

Model:V- Sorb 2800P Surface Area and Porosimetry Analyzer

Company:NARICT

Report Time:17th July 2014

Analysis Information
Mass:0.07750 (g)

Method:Multi-Point BET

Room Temp.:Ambient
Pretreatment:16 Hrs

Multi-BET:227.778639 (m2/g)

BET Tabular Report

P/P0	Quantity Adsorbed(ml/g)	(P/P0)/(V*(1- P/P0))	Single point BET
0.215223	62.448772	0.004392	213.284278
0.183669	58.937994	0.003817	209.387299
0.158685	56.216079	0.003355	205.829724
0.131701	51.834935	0.002926	195.875822
0.106600	49.071762	0.002432	190.794698
0.081936	46.233646	0.001930	184.722622
0.054451	42.582817	0.001352	175.229552

Slope	Intercept	Vm(ml)	C Value
0.018714	0.000394	52.333116	48.500893
R	Multi-BET Area	Langmuir Area	
0.999177	227.778639	311.144916	

Sample IDAl(OH)3 2-5 Fold pH7

Model:V- Sorb 2800P Surface Area and Porosimetry Analyzer

Company:NARICT

Report Time:15th July 2014

Analysis Information
Mass:0.07380 (g)

Method:Multi-Point BET

Room Temp.:Ambient

Pretreatment:16 Hrs

Multi-BET:209.799276 (m2/g)

BET Tabular Report

P/P0	Quantity Adsorbed(ml/g)	(P/P0)/(V*(1- P/P0))	Single point BET
0.215284	55.465901	0.004946	189.420698
0.187017	51.828541	0.004438	183.374616
0.157430	48.221710	0.003875	176.822492
0.130579	43.881147	0.003423	166.034015
0.105876	40.909593	0.002895	159.188457
0.079749	37.635963	0.002303	150.729450
0.056096	34.592286	0.001718	142.100602

Slope	Intercept	Vm(ml)	C Value
0.020044	0.000702	48.202281	29.541434

R	Multi-BET Area	Langmuir Area
0.997939	209.799276	290.757247

APPENDIX V

KINETIC DATA OBTAINED FROM LABORATORY SYNTHESIS OF ALUMINIUM HYDROXIDE FROM KANKARA KAOLIN BASED ALUM

Table I: Kinetic data obtained from the laboratory batch process at $90^{O}C$

t (Sec)	CA	rA	lnCA	lnrA
0	39.9006	3.381	3.686391	1.218172
10	10.6633	1.819	2.366808	0.598287
15	9.9862	1.038	2.301204	0.037296
20	1.6615	0.257	0.507721	-1.35868

Table II: Kinetic data obtained from the laboratory batch process at $79^{O}C$

T (Sec)	CA	rA	lnCA	lnrA
0	39.9006	1.4586	3.686391	0.377477
30	7.9065	0.6126	2.067685	-0.49004
40	5.803	0.3306	1.758375	-1.10685
45	1.5646	0.1896	0.44763	-1.66284

Table III: Kinetic data obtained from the laboratory batch process at $73^{O}C$

T (Sec)	CA	rA	lnCA	lnrA
0	39.9006	0.8725	3.686391	-0.13639
5	36.1648	0.7955	3.588086	-0.22878
10	31.7265	0.7185	3.457152	-0.33059
15	28.7586	0.6415	3.358937	-0.44395

Table IV: Kinetic data obtained from the laboratory batch process for lnk and 1/T

1/T	lnk
0.002755	-1.6996
0.002841	-2.002
0.00289	-3.5149

APPENDIX VI

MATLAB PROGRAM FOR SOLVING THE ODES' FOR THE SEMI-BATCH REACTOR DESIGN

Main file

```
functiondCdt= batch(t,C)
%parameters

k=4.6584;
V0=32.2469;
v0=0.3225;

CA0=39.9006;
CB0=37875;
CC0=0;
CD0=0;

CA=C(1)
CB=C(2);
CC=C(3);
CD=C(4);
V = V0+v0*t;
dCdt(1) = -k*CA-v0*CA/V;
dCdt(2) = -k*CA+v0*(CB0-CB)/V;
dCdt(3) = k*CA-v0*CC/V;
dCdt(4) = k*CA-v0*CD/V;

X = (CA0*V0-CA*V)/(CA0*V0);
X = X(:)
V = V(:)
t = t(:)
dCdt=dCdt(:);
```

Call file

```
clc
clf
clearall

tspan=[0 50];

C0=[39.9006 37875 0 0];
[t C]=ode45(@batch, tspan, C0);

figure(1)
plot(t,C(:,1),'--')
xlabel('Time (sec)')
ylabel('CONCENTRATION CA')

figure(2)
plot(t,C(:,2),'--')
xlabel('Time (sec)')
ylabel('Concentration CB')
```

```
figure(3)
plot(t,C(:,3),'--')
xlabel('Time (sec)')
ylabel('CONCENTRATION CC')

figure(4)
plot(t,C(:,4),'--')
xlabel('Time (sec)')
ylabel('Concentration CD')

[t C]
```

t C_A C_B C_C C_D

0	0.0040	3.7875	0	0
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
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0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000

0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0040	3.7875	0.0000	0.0000
0.0000	0.0039	3.7875	0.0000	0.0000
0.0000	0.0039	3.7874	0.0001	0.0001
0.0000	0.0039	3.7874	0.0001	0.0001
0.0000	0.0038	3.7873	0.0002	0.0002
0.0000	0.0038	3.7873	0.0002	0.0002
0.0000	0.0037	3.7872	0.0003	0.0003
0.0000	0.0036	3.7871	0.0004	0.0004
0.0000	0.0033	3.7868	0.0007	0.0007
0.0000	0.0030	3.7865	0.0010	0.0010
0.0000	0.0027	3.7862	0.0013	0.0013
0.0000	0.0024	3.7860	0.0015	0.0015
0.0000	0.0021	3.7856	0.0019	0.0019
0.0000	0.0017	3.7852	0.0023	0.0023
0.0000	0.0015	3.7850	0.0025	0.0025
0.0000	0.0012	3.7848	0.0027	0.0027
0.0000	0.0010	3.7845	0.0030	0.0030
0.0000	0.0008	3.7844	0.0031	0.0031
0.0000	0.0007	3.7842	0.0033	0.0033
0.0000	0.0006	3.7841	0.0034	0.0034
0.0000	0.0005	3.7840	0.0035	0.0035
0.0001	0.0004	3.7839	0.0036	0.0036

0.0001	0.0003	3.7838	0.0037	0.0037
0.0001	0.0003	3.7838	0.0037	0.0037
0.0001	0.0002	3.7837	0.0038	0.0038
0.0001	0.0002	3.7837	0.0038	0.0038
0.0001	0.0001	3.7837	0.0038	0.0038
0.0001	0.0001	3.7837	0.0038	0.0038
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0.0001	0.0001	3.7836	0.0039	0.0039
0.0001	0.0001	3.7836	0.0039	0.0039
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0.0002	0.0000	3.7836	0.0039	0.0039
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0.0005	-0.0000	3.7837	0.0038	0.0038

0.0005	-0.0000	3.7837	0.0038	0.0038
0.0005	0.0000	3.7837	0.0038	0.0038
0.0005	0.0000	3.7837	0.0038	0.0038
0.0006	-0.0000	3.7837	0.0038	0.0038
0.0006	-0.0000	3.7837	0.0038	0.0038
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0.0006	0.0000	3.7837	0.0038	0.0038
0.0006	0.0000	3.7838	0.0037	0.0037
0.0007	-0.0000	3.7838	0.0037	0.0037
0.0007	0.0000	3.7838	0.0037	0.0037
0.0007	0.0000	3.7838	0.0037	0.0037
0.0007	0.0000	3.7838	0.0037	0.0037
0.0007	-0.0000	3.7838	0.0037	0.0037
0.0007	0.0000	3.7838	0.0037	0.0037
0.0008	0.0000	3.7838	0.0037	0.0037
0.0008	-0.0000	3.7838	0.0037	0.0037
0.0008	-0.0000	3.7838	0.0037	0.0037
0.0008	0.0000	3.7838	0.0037	0.0037
0.0008	0.0000	3.7838	0.0037	0.0037
0.0008	-0.0000	3.7838	0.0037	0.0037
0.0009	-0.0000	3.7838	0.0037	0.0037
0.0009	0.0000	3.7838	0.0037	0.0037
0.0009	0.0000	3.7838	0.0037	0.0037
0.0009	0.0000	3.7839	0.0036	0.0036
0.0009	-0.0000	3.7839	0.0036	0.0036

0.0010	0.0000	3.7839	0.0036	0.0036
0.0010	0.0000	3.7839	0.0036	0.0036
0.0010	0.0000	3.7839	0.0036	0.0036
0.0010	-0.0000	3.7839	0.0036	0.0036
0.0010	0.0000	3.7839	0.0036	0.0036
0.0010	0.0000	3.7839	0.0036	0.0036
0.0011	-0.0000	3.7839	0.0036	0.0036
0.0011	-0.0000	3.7839	0.0036	0.0036
0.0011	0.0000	3.7839	0.0036	0.0036
0.0011	0.0000	3.7839	0.0036	0.0036
0.0011	-0.0000	3.7839	0.0036	0.0036
0.0012	-0.0000	3.7839	0.0036	0.0036
0.0012	0.0000	3.7839	0.0036	0.0036
0.0012	0.0000	3.7839	0.0036	0.0036
0.0012	0.0000	3.7839	0.0036	0.0036
0.0012	-0.0000	3.7839	0.0036	0.0036
0.0012	0.0000	3.7840	0.0035	0.0035
0.0013	0.0000	3.7840	0.0035	0.0035
0.0013	0.0000	3.7840	0.0035	0.0035
0.0013	-0.0000	3.7840	0.0035	0.0035
0.0013	0.0000	3.7840	0.0035	0.0035
0.0013	0.0000	3.7840	0.0035	0.0035
0.0013	-0.0000	3.7840	0.0035	0.0035
0.0014	-0.0000	3.7840	0.0035	0.0035
0.0014	0.0000	3.7840	0.0035	0.0035

0.0014	0.0000	3.7840	0.0035	0.0035
0.0014	-0.0000	3.7840	0.0035	0.0035
0.0014	-0.0000	3.7840	0.0035	0.0035
0.0015	0.0000	3.7840	0.0035	0.0035
0.0015	0.0000	3.7840	0.0035	0.0035
0.0015	-0.0000	3.7840	0.0035	0.0035
0.0015	-0.0000	3.7840	0.0035	0.0035
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0.0016	0.0000	3.7840	0.0035	0.0035
0.0016	0.0000	3.7841	0.0034	0.0034
0.0016	-0.0000	3.7841	0.0034	0.0034
0.0016	0.0000	3.7841	0.0034	0.0034
0.0016	0.0000	3.7841	0.0034	0.0034
0.0016	0.0000	3.7841	0.0034	0.0034
0.0017	-0.0000	3.7841	0.0034	0.0034
0.0017	0.0000	3.7841	0.0034	0.0034
0.0017	0.0000	3.7841	0.0034	0.0034
0.0017	-0.0000	3.7841	0.0034	0.0034
0.0017	-0.0000	3.7841	0.0034	0.0034
0.0017	0.0000	3.7841	0.0034	0.0034
0.0018	0.0000	3.7841	0.0034	0.0034
0.0018	-0.0000	3.7841	0.0034	0.0034
0.0018	-0.0000	3.7841	0.0034	0.0034
0.0018	0.0000	3.7841	0.0034	0.0034
0.0018	0.0000	3.7841	0.0034	0.0034

0.0019	-0.0000	3.7841	0.0034	0.0034
0.0019	-0.0000	3.7841	0.0034	0.0034
0.0019	0.0000	3.7841	0.0034	0.0034
0.0019	0.0000	3.7842	0.0033	0.0033
0.0019	-0.0000	3.7842	0.0033	0.0033
0.0020	-0.0000	3.7842	0.0033	0.0033
0.0020	0.0000	3.7842	0.0033	0.0033
0.0020	0.0000	3.7842	0.0033	0.0033
0.0020	0.0000	3.7842	0.0033	0.0033
0.0020	-0.0000	3.7842	0.0033	0.0033
0.0020	0.0000	3.7842	0.0033	0.0033
0.0020	0.0000	3.7842	0.0033	0.0033
0.0021	0.0000	3.7842	0.0033	0.0033
0.0021	-0.0000	3.7842	0.0033	0.0033
0.0021	0.0000	3.7842	0.0033	0.0033
0.0021	0.0000	3.7842	0.0033	0.0033
0.0021	-0.0000	3.7842	0.0033	0.0033
0.0021	-0.0000	3.7842	0.0033	0.0033
0.0022	0.0000	3.7842	0.0033	0.0033
0.0022	0.0000	3.7842	0.0033	0.0033
0.0022	-0.0000	3.7842	0.0033	0.0033
0.0022	-0.0000	3.7842	0.0033	0.0033
0.0022	0.0000	3.7842	0.0033	0.0033
0.0023	0.0000	3.7842	0.0033	0.0033
0.0023	0.0000	3.7843	0.0032	0.0032

0.0023	-0.0000	3.7843	0.0032	0.0032
0.0023	0.0000	3.7843	0.0032	0.0032
0.0023	0.0000	3.7843	0.0032	0.0032
0.0023	0.0000	3.7843	0.0032	0.0032
0.0024	-0.0000	3.7843	0.0032	0.0032
0.0024	0.0000	3.7843	0.0032	0.0032
0.0024	0.0000	3.7843	0.0032	0.0032
0.0024	-0.0000	3.7843	0.0032	0.0032
0.0024	-0.0000	3.7843	0.0032	0.0032
0.0024	0.0000	3.7843	0.0032	0.0032
0.0025	0.0000	3.7843	0.0032	0.0032
0.0025	-0.0000	3.7843	0.0032	0.0032
0.0025	-0.0000	3.7843	0.0032	0.0032
0.0025	0.0000	3.7843	0.0032	0.0032
0.0026	0.0000	3.7843	0.0032	0.0032
0.0026	-0.0000	3.7843	0.0032	0.0032
0.0026	-0.0000	3.7843	0.0032	0.0032
0.0026	0.0000	3.7843	0.0032	0.0032
0.0026	0.0000	3.7843	0.0032	0.0032
0.0026	0.0000	3.7843	0.0032	0.0032
0.0027	-0.0000	3.7843	0.0032	0.0032
0.0027	0.0000	3.7844	0.0031	0.0031
0.0027	0.0000	3.7844	0.0031	0.0031
0.0027	0.0000	3.7844	0.0031	0.0031
0.0027	-0.0000	3.7844	0.0031	0.0031

0.0027	0.0000	3.7844	0.0031	0.0031
0.0027	0.0000	3.7844	0.0031	0.0031
0.0028	-0.0000	3.7844	0.0031	0.0031
0.0028	-0.0000	3.7844	0.0031	0.0031
0.0028	0.0000	3.7844	0.0031	0.0031
0.0028	0.0000	3.7844	0.0031	0.0031
0.0028	-0.0000	3.7844	0.0031	0.0031
0.0029	-0.0000	3.7844	0.0031	0.0031
0.0029	0.0000	3.7844	0.0031	0.0031
0.0029	0.0000	3.7844	0.0031	0.0031
0.0029	-0.0000	3.7844	0.0031	0.0031
0.0029	-0.0000	3.7844	0.0031	0.0031
0.0030	0.0000	3.7844	0.0031	0.0031
0.0030	0.0000	3.7844	0.0031	0.0031
0.0030	-0.0000	3.7844	0.0031	0.0031
0.0030	-0.0000	3.7844	0.0031	0.0031
0.0030	0.0000	3.7844	0.0031	0.0031
0.0031	0.0000	3.7844	0.0031	0.0031
0.0031	0.0000	3.7844	0.0031	0.0031
0.0031	-0.0000	3.7845	0.0030	0.0030
0.0031	0.0000	3.7845	0.0030	0.0030
0.0031	0.0000	3.7845	0.0030	0.0030
0.0031	0.0000	3.7845	0.0030	0.0030
0.0031	-0.0000	3.7845	0.0030	0.0030
0.0032	0.0000	3.7845	0.0030	0.0030

0.0032	0.0000	3.7845	0.0030	0.0030
0.0032	-0.0000	3.7845	0.0030	0.0030
0.0032	-0.0000	3.7845	0.0030	0.0030
0.0032	0.0000	3.7845	0.0030	0.0030
0.0032	0.0000	3.7845	0.0030	0.0030
0.0033	-0.0000	3.7845	0.0030	0.0030
0.0033	-0.0000	3.7845	0.0030	0.0030
0.0033	0.0000	3.7845	0.0030	0.0030
0.0033	0.0000	3.7845	0.0030	0.0030
0.0034	0.0000	3.7845	0.0030	0.0030
0.0034	-0.0000	3.7845	0.0030	0.0030
0.0034	0.0000	3.7845	0.0030	0.0030
0.0034	0.0000	3.7845	0.0030	0.0030
0.0034	0.0000	3.7845	0.0030	0.0030
0.0034	-0.0000	3.7845	0.0030	0.0030
0.0034	0.0000	3.7845	0.0030	0.0030
0.0035	0.0000	3.7845	0.0030	0.0030
0.0035	-0.0000	3.7845	0.0030	0.0030
0.0035	-0.0000	3.7845	0.0030	0.0030
0.0035	0.0000	3.7845	0.0030	0.0030
0.0035	0.0000	3.7846	0.0029	0.0029
0.0036	-0.0000	3.7846	0.0029	0.0029
0.0036	-0.0000	3.7846	0.0029	0.0029
0.0036	0.0000	3.7846	0.0029	0.0029
0.0036	0.0000	3.7846	0.0029	0.0029

0.0036	-0.0000	3.7846	0.0029	0.0029
0.0037	-0.0000	3.7846	0.0029	0.0029
0.0037	0.0000	3.7846	0.0029	0.0029
0.0037	0.0000	3.7846	0.0029	0.0029
0.0037	0.0000	3.7846	0.0029	0.0029
0.0037	-0.0000	3.7846	0.0029	0.0029
0.0037	0.0000	3.7846	0.0029	0.0029
0.0038	0.0000	3.7846	0.0029	0.0029
0.0038	0.0000	3.7846	0.0029	0.0029
0.0038	-0.0000	3.7846	0.0029	0.0029
0.0038	0.0000	3.7846	0.0029	0.0029
0.0038	0.0000	3.7846	0.0029	0.0029
0.0038	-0.0000	3.7846	0.0029	0.0029
0.0039	-0.0000	3.7846	0.0029	0.0029
0.0039	0.0000	3.7846	0.0029	0.0029
0.0039	0.0000	3.7846	0.0029	0.0029
0.0039	-0.0000	3.7846	0.0029	0.0029
0.0039	-0.0000	3.7846	0.0029	0.0029
0.0039	0.0000	3.7846	0.0029	0.0029
0.0040	0.0000	3.7846	0.0029	0.0029
0.0040	-0.0000	3.7846	0.0029	0.0029
0.0040	-0.0000	3.7847	0.0028	0.0028
0.0040	0.0000	3.7847	0.0028	0.0028
0.0041	0.0000	3.7847	0.0028	0.0028
0.0041	-0.0000	3.7847	0.0028	0.0028

0.0041	-0.0000	3.7847	0.0028	0.0028
0.0041	0.0000	3.7847	0.0028	0.0028
0.0041	0.0000	3.7847	0.0028	0.0028
0.0041	0.0000	3.7847	0.0028	0.0028
0.0041	-0.0000	3.7847	0.0028	0.0028
0.0042	0.0000	3.7847	0.0028	0.0028
0.0042	0.0000	3.7847	0.0028	0.0028
0.0042	0.0000	3.7847	0.0028	0.0028
0.0042	-0.0000	3.7847	0.0028	0.0028
0.0042	0.0000	3.7847	0.0028	0.0028
0.0042	0.0000	3.7847	0.0028	0.0028
0.0043	-0.0000	3.7847	0.0028	0.0028
0.0043	-0.0000	3.7847	0.0028	0.0028
0.0043	0.0000	3.7847	0.0028	0.0028
0.0043	0.0000	3.7847	0.0028	0.0028
0.0043	-0.0000	3.7847	0.0028	0.0028
0.0044	-0.0000	3.7847	0.0028	0.0028
0.0044	0.0000	3.7847	0.0028	0.0028
0.0044	0.0000	3.7847	0.0028	0.0028
0.0044	0.0000	3.7847	0.0028	0.0028
0.0044	-0.0000	3.7847	0.0028	0.0028
0.0044	0.0000	3.7847	0.0028	0.0028
0.0045	0.0000	3.7847	0.0028	0.0028
0.0045	0.0000	3.7847	0.0028	0.0028
0.0045	-0.0000	3.7847	0.0028	0.0028

0.0045	0.0000	3.7848	0.0027	0.0027
0.0045	0.0000	3.7848	0.0027	0.0027
0.0045	-0.0000	3.7848	0.0027	0.0027
0.0046	-0.0000	3.7848	0.0027	0.0027
0.0046	0.0000	3.7848	0.0027	0.0027
0.0046	0.0000	3.7848	0.0027	0.0027
0.0046	-0.0000	3.7848	0.0027	0.0027
0.0046	-0.0000	3.7848	0.0027	0.0027
0.0047	0.0000	3.7848	0.0027	0.0027
0.0047	0.0000	3.7848	0.0027	0.0027
0.0047	-0.0000	3.7848	0.0027	0.0027
0.0047	-0.0000	3.7848	0.0027	0.0027
0.0047	0.0000	3.7848	0.0027	0.0027
0.0048	0.0000	3.7848	0.0027	0.0027
0.0048	0.0000	3.7848	0.0027	0.0027
0.0048	-0.0000	3.7848	0.0027	0.0027
0.0048	0.0000	3.7848	0.0027	0.0027
0.0048	0.0000	3.7848	0.0027	0.0027
0.0048	0.0000	3.7848	0.0027	0.0027
0.0049	-0.0000	3.7848	0.0027	0.0027
0.0049	0.0000	3.7848	0.0027	0.0027
0.0049	0.0000	3.7848	0.0027	0.0027
0.0049	-0.0000	3.7848	0.0027	0.0027
0.0049	-0.0000	3.7848	0.0027	0.0027
0.0049	0.0000	3.7848	0.0027	0.0027

0.0050	0.0000	3.7848	0.0027	0.0027
0.0050	0.0000	3.7848	0.0027	0.0027
0.0050	0.0000	3.7848	0.0027	0.0027
0.0050	0.0000	3.7848	0.0027	0.0027
0.0050	0.0000	3.7848	0.0027	0.0027

APPENDIX VII

DETERMINATION OF VOLUME OF FEED AND CONCENTRATIONS OF REACTANTS

To determine the value of V_0, from the amount of $Al(OH)_3$ in Table 4.1, we have at ambient temperature (25^OC),

5.4g of $Al(OH)_3$ was produced by 100ml of $Al_2(SO_4)_3$,

1g of $Al(OH)_3$ would be produced by 100/5.4 ml of $Al_2(SO_4)_3$,

1.7413kg of $Al(OH)_3$ would be produced by 100/5.4 x 1.7413 litres of $Al_2(SO_4)_3$,

Total volume of used would be

100 x 1.7413/5.4 = 32.2469 litres of $Al_2(SO_4)_3$= V_0

To calculate v_0, it is known that

5.4g of $Al(OH)_3$ was produced by 30ml of NaOH,

1g of $Al(OH)_3$would be produced by 30/5.4ml of NaOH,

1.7413kg of $Al(OH)_3$ would be produced by 30/5.4 x 1.7413 litres of NaOH

Total volume of NaOH used would be

30 x 1.7413/5.4 = 9.6739 litres of NaOH

Assuming the batch time is 30 minutes,

Therefore, v_0 = 9.6739/30 L/min = 0.3225L/min

From AAS analysis, C_{A0} = 39.9006mol/m^3

For 50wt% NaOH at $25^{O}C$, C_{B0} = 1.515kg/L

In mol/m^3,

Therefore 50wt% NaOH = 1515 x 1000/40 = $37,875 mol/m^3$