THE SYNTHESIS OF ALUMINIUM HYDROXIDE AND OXYHYDROXIDE

by

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Beta alumina is a ceramic with the ability to conduct certain ions. It is conventionally formed through the high temperature solid state reaction of α-alumina with soda and lithia, which results in a mixture of ß- and ß"-alumina phases. To maximise the amount of ß"-alumina formed, a second heat treatment step is required. Beta alumina may also be synthesised directly from the various aluminium hydroxide ($Al(OH)_3$) and aluminium oxyhydroxide (AlOOH) polymorphs. The particular oxygen sublattice of the starting material is critical in determining which phases of beta alumina are formed. Boehmite and bayerite are known to yield pure ß"-alumina.

In this investigation, the differences in structure and the identification of the polymorphs is discussed. A review of the methods of synthesis and concomitant mechanisms of reaction proposed in the literature are presented. Of these, the synthesis of boehmite and bayerite are investigated experimentally.

Attempts to synthesise boehmite at ambient conditions resulted in the formation of pseudoboehmite, and confirmed that boehmite can only be formed by the introduction of a hydrothermal step. However, it was possible to form bayerite at ambient conditions by simple chemical reaction. Control of the reaction pH and the removal of inhibiting ions were found to facilitate the formation of well crystallised bayerite. Although the factors governing the successful synthesis of bayerite need further investigation, the possibility of a direct synthesis route for ß"-alumina has been demonstrated.

Finally, the synthesis of ß"-alumina by the solid state reaction of the hydroxide and oxyhydroxide polymorphs was successfully completed.

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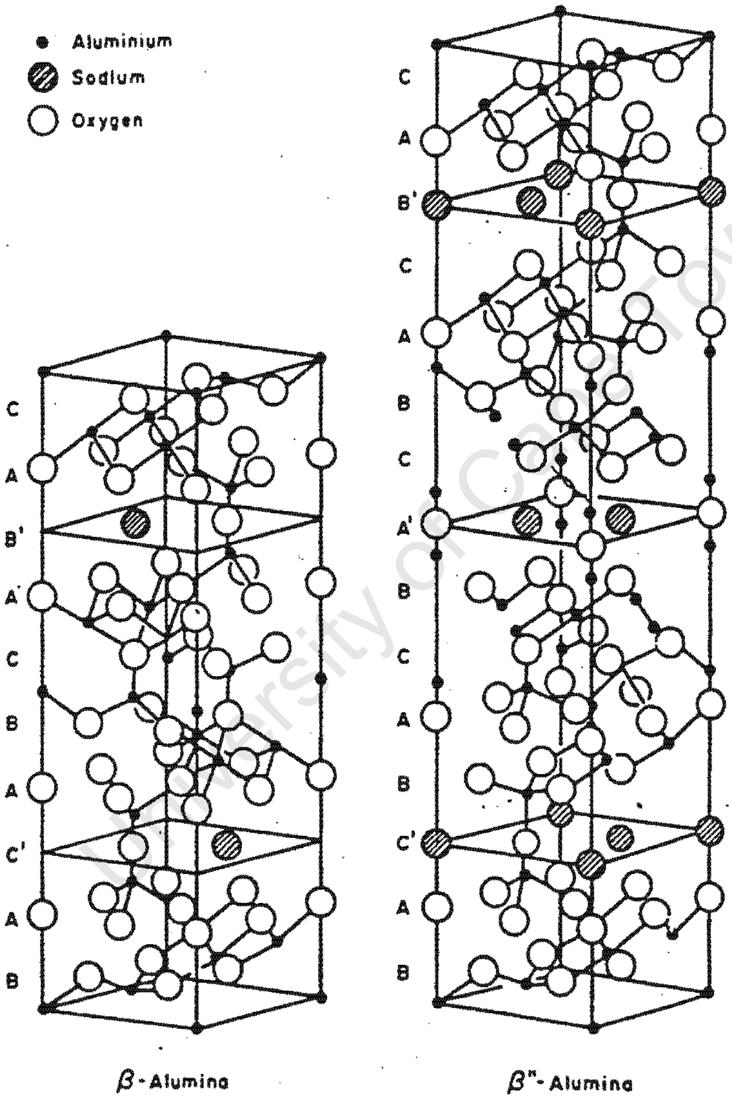


Fig. 1: Section through the idealised structure of ß-Al_2O_3 and ß"-Al_2O_3 showing the stacking sequence along the c-axis. (after Mosely 1985)

2. THE ALUMINIUM HYDROXIDE AND OXYHYDROXIDE PRECURSORS.

2.1 NOMENCLATURE.

Many crystalline compounds of aluminium and oxygen occur in nature. Apart from aluminium oxide (Al_2O_3), known as corundum, there exists a range of aluminium hydroxides and oxide-hydroxides. All occur naturally in soils or in bauxitic deposits, though not to the same extent.

The primary motivation for study of these compounds has come from geochemists and soil scientists attempting to formulate a theory of the formation of bauxite deposits and the action of such minerals in soil environments, though more recently the commercial potential of alumina catalysts has provided fresh impetus to research. This chapter will describe the range of polymorphs and the means by which they may be identified.

Two main groups of compounds exist: aluminium hydroxides ($Al(OH)_3$) and aluminium oxide hydroxides (AlOOH). These have in the past been referred to as hydrous oxides or hydrates, implying that the structure contains adsorbed water molecules. In fact, the water is bound as OH^- ions; consequently the International Committee on Aluminium Hydroxides Nomenclature (ICHAN) (Newsome et al, 1960) recommended that $Al(OH)_3$ be referred to as aluminium trihydroxide and AlOOH as aluminium oxide-hydroxide. The latter are also referred to as oxyhydroxides.

The various systems nomenclatures are summarised and compared in Table 2.1 below. Researchers familiar with crystallographic conventions have also used alpha (α)- and gamma (Γ)- to refer to those hydroxides whose structures are hexagonal close packed or cubic close packed related respectively. Krischner (1971), finding this convention inadequate for the number of transition aluminas identified, grouped the various hydroxides, oxide-hydroxides and their degradation products according to their oxygen stacking sequence: α for ABAB-ABAB; ß for ABAC-ABAC; Γ for ABC-ABC. This system has proved thorough in description and useful in predicting properties and behaviour.

Table 2.1: Comparison of Nomenclature Systems
(adapted from Van Zyl, 1987).

ICHAN	Previously called
Aluminium trihydroxide $Al(OH)_3$	Aluminium trihydrate $Al_2O_3.3H_2O$
gibbsite / hydragillite bayerite nordstrandite	Γ-aluminium trihydrate α-aluminium trihydrate ----
Aluminium oxide-hydroxide AlOOH	Aluminium monohydrate $Al_2O_3.H_2O$
boehmite diaspore	Γ-aluminium monohydrate α-aluminium monohydrate

2.2 STRUCTURE OF THE ALUMINIUM HYDROXIDES.

2.2.1 GIBBSITE.

The structure of Gibbsite was determined by Megaw in 1934. It is monoclinic, having a=8.659, b=5.077, c=9.703 Å and ß=94° 12' (ASTM 7-324).

The basic structural unit of gibbsite is simply two sheets of hydroxyl ions close-packed and bound together by the aluminium ions which occupy two thirds of the interstices, ie. a dioctahedral arrangement. As the double layers stack, they assume an open-packed structure, each hydroxyl layer lying directly above the one below. Schoen and Roberson (1970) report the following explanation for this:

Firstly the protons of the hydroxyl ions are displaced toward the neutral "holes" left by the dioctahedral filling of interstices. Secondly, the highly polarising effect of Al^{3+} leads to a tetrahedral hybridisation of the hydroxyl ion. Two aluminium ions bond with two negatively charged lobes, leaving one negative and one positive (with proton) lobe free. These can then bond with another hybridized hydroxyl group from another layer (Figure 2.1). This is called an hydroxyl bond and it leads to each superposed layer of gibbsite lying directly above the one below in an open-packed arrangement.(Figure 2.2). The hydroxyl ions are thus stacked according to the scheme

ABBA-ABBA. On heating, gibbsite dehydroxylates to yield an oxygen sublattice stacking ABAC-ABAC, classified as a ß-series material by Krishner (1971).

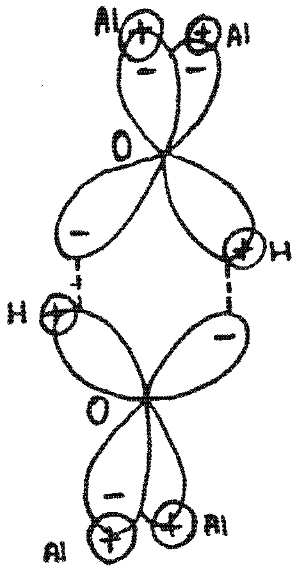


Fig. 2.1: Hydroxyl bonding between sp^3 hybridised orbitals

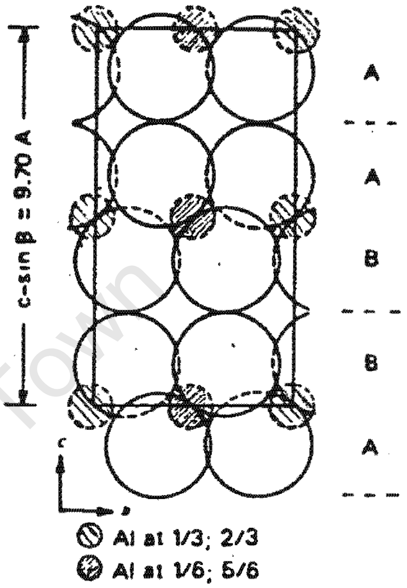


Fig. 2.2: ABBA-ABBA stacking in Gibbsite (from Schoen and Roberson, 1970)

These layers extend laterally by adding on more units, but because each unit is charge satisfied, no ionic forces exist to attach layers above and below. These add more slowly, giving rise to the characteristic plate-like shape of gibbsite crystals, described by Schoen and Roberson (1970) following their investigation by electron microscopy. Gibbsite forms as thin platelets whose surfaces are parallel to the basal planes {001} of its lattice, along which there is perfect cleavage (Figure 2.3.). Gibbsite is usually found as white or grey foliated masses.

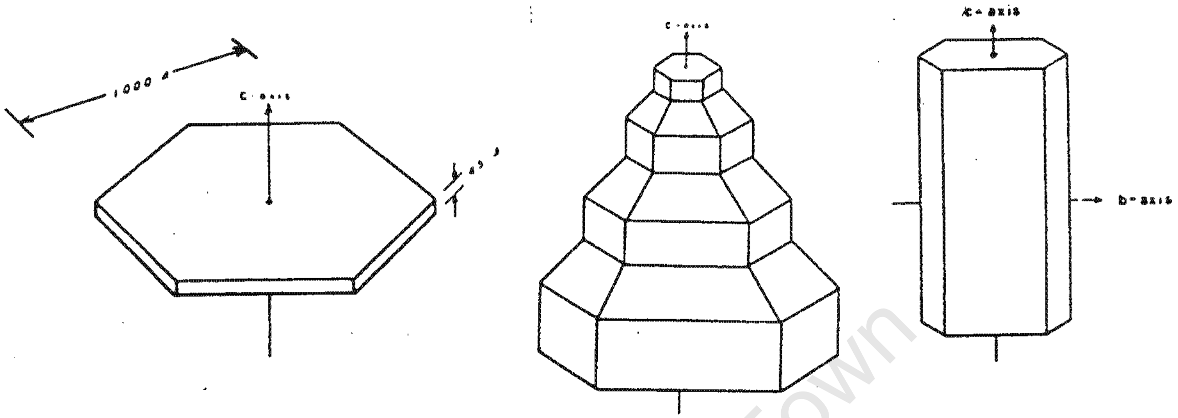


Fig. 2.3: Crystal Morphology (from Schoen and Roberson (1970)
(a) Gibbsite (b) Bayerite (c) Nordstrandite

Ginsberg et al (1962) and Saalfeld et al (1968) regarded the sodium they consistently found in gibbsite as being necessary to stabilise the structure and consequently regard gibbsite not as a pure aluminium hydroxide, but as a ternary compound.

2.2.2 BAYERITE.

Bayerite is monoclinic, having a=5.062, b=8.671, c=4.713 Å and ß=90.27° (ASTM 20-11).

The basic structural unit of bayerite is exactly the same as that of gibbsite, the only difference being in the manner in which the units are stacked. In bayerite, hydroxyl bonds do not form. There is still distortion owing to the neutral "holes", but overall the proton-oxygen bonds point upward from the sheet of ions. These protons repel each other, so that successive layers mesh together in a manner similar to close-packing. This gives the protons maximum separation. Although this structure resembles close-packing, the effective hydroxyl ion separation from the hydroxyl ions in the next layer is 1.57Å, whereas that of gibbsite was 1.39 Å, showing that the structure is really much more open than the so-called "open-packed" one. This "open" packing leads to the hydroxyl ions being stacked in the pattern ABAB-ABAB (Figure 2.4). When heated, bayerite dehydroxylates to yield an oxygen sublattice stacking of ABC-ABC, therefore belonging to the Γ-series according to Krishner (1971).

In bayerite, addition of new units is preferentially to the basal planes, with slower growing edges. This gives the characteristic shape of long, tapered rods, the long (c-axis) direction being perpendicular to the basal planes of the lattice. (Figure 2.3)

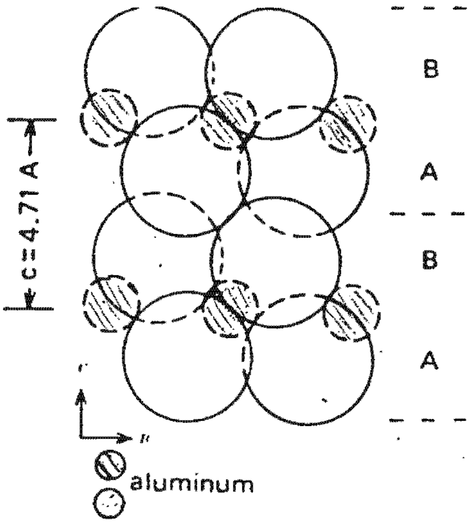


Fig. 2.4: ABAB-ABAB stacking in Bayerite

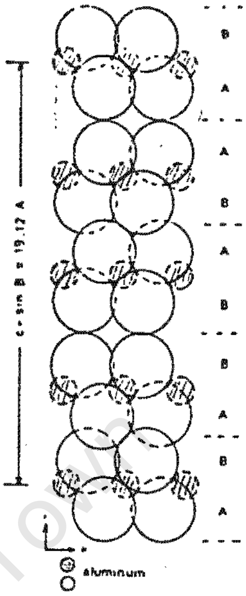


Fig. 2.5: ABBA-BABA stacking in Nordstrandite

(from Schoen and Roberson 1970)

2.2.3 NORDSTRANDITE.

Nordstrandite is triclinic, having a=8.893, b=5.004, c=10.237 Å and α=92°56' , ß=110°23' , Γ=90°32' (ASTM 18-31).

Nordstrandite can be regarded as having a structure midway between that of gibbsite and bayerite. It is proposed that the structure is made up of alternating gibbsite and bayerite layers, as depicted in Figure 2.5. This means the hydroxyl ions are packed according to the pattern ABAB-BABA. According to Schoen and Roberson (1970), this type of mirrored layer structure is not unusual, particularly among clay minerals. When heated, nordstrandite dehydroxylates to the oxygen sublattice stacking ABC-ABC, therefore belonging to the Γ-series according to Krishner (1971).

Nordstrandite takes the form of long rods with hexagonal cross-section (Figure 2.3). Crystal growth is slowest in the a-axis direction.

2.3 STRUCTURE OF THE OXIDE HYDROXIDES.

2.3.1 Diaspore.

Diaspore is orthorhombic, having a=4.396, b=9.426, c=2.844 Å (ASTM 5-355). It is isomorphous with Goethite (Γ-FeOOH). When heated, diaspore dehydroxylates to the oxygen sublattice stacking ABAB-ABAB, therefore it belongs to the α-series, according to Krischner (1971).

Diaspore crystals are thin, brittle {010} plates and the powder is white or grey.

2.3.2 Boehmite.

Boehmite has an orthorhombic structure. Milligan and McAtee (1965) determined the unit cell parameters to be a= 3.690 Å, b=12.227 Å and c=2.868 Å (ASTM 21-1307). Wilson (1979) and Lippens and Steggerda (1970) confirmed the structure of boehmite to be isomorphous with Lepidocrocite (FeOOH), in that each aluminium atom is surrounded by a distorted octahedron of oxygen atoms. These [$Al-O_6$] octahedra polymerise to form an interlocking double molecular layer, which the above researchers preferred to model as zigzag HO-Al-O chains. The successive double layers are held together by hydrogen bonds between the OH^- groups on the outside surfaces of the layers. This is evidenced by the O-H-O bond length of 2,70 Å, which is shorter than the length normal repulsion between oxygens would achieve. Extra interlamellar water disrupts the lattice and depending on the amount present, this may result in the formation of pseudoboehmite.

Diaspore and boehmite differ in their arrangement of the double chains, as is shown schematically in Figure 2.6.

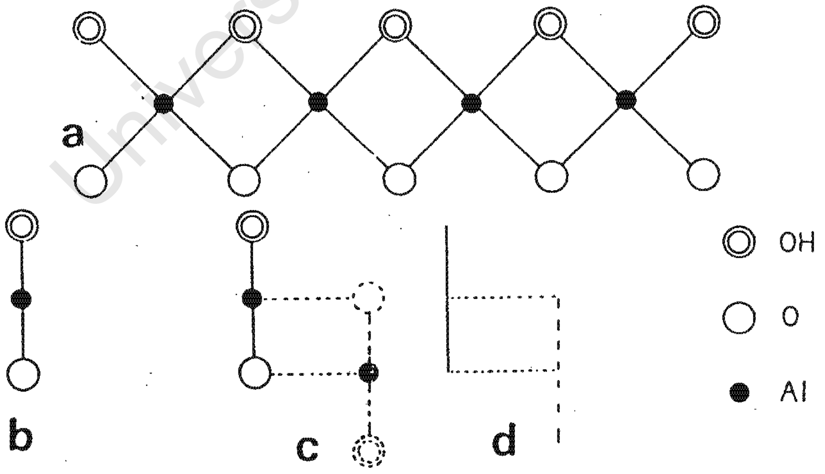


Fig. 2.6: Schematic representation of OH-Al-O chains.
(a) OH-Al-O chain parallel to plane of drawing
(b) 2 anti-parallel chains perpendicular to plane of drawing
(after Lippens et al, 1970)

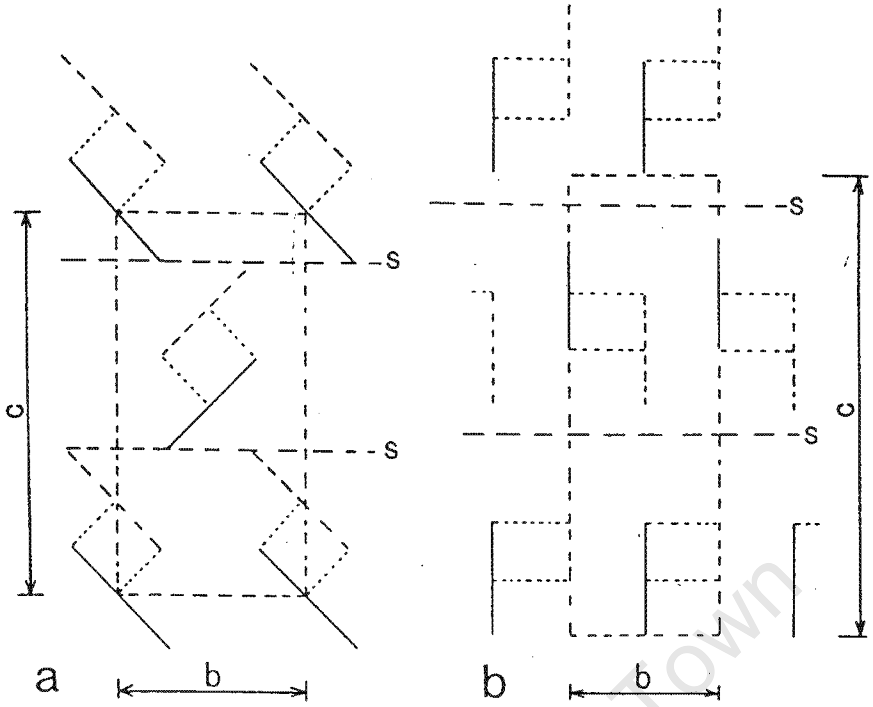


Fig. 2.7: Schematic representation of the crystal structure: (a) Diaspore ; (b) Boehmite
S represents cleavage planes (after Lippens et al, 1970)

The structure explains the crystal shape of orthorhombic plates, with easy cleavage on (010) corresponding to breaking of the weak hydrogen bonds. Boehmite forms a fine, white powder. When heated, boehmite dehydroxylates to the oxygen sublattice stacking ABC-ABC, therefore belonging to the Γ-series, according to Krishner (1971).

2.3.3 Pseudoboehmite.

There exists a poorly crystalline compound which has been called pseudoboehmite or gelatinous boehmite. It has basically the same structure as boehmite, but contains more water and has the overall appearance and behaviour of a gel or paste.

Often encountered by early researchers where a crystalline precipitate was expected, it was assumed to be an incompletely dehydrated form of boehmite. For example, Moeller (1952) reports that boehmite may simply be precipitated from boiling aluminium salt solutions by ammonia, or by ageing the amorphous gel precipitated by the same method at room temperature.

MacKenzie (1957), from his differential thermal investigation into synthesised alumina gels, reports that all fresh precipitates of aluminium chloride solutions consist of poorly-crystallised boehmite, which can be transformed to a crystalline form by ageing in the mother liquor at elevated temperatures.

Papee et al (1958) examined both fully crystalline and poorly crystalline boehmite by X-ray diffraction. They noted a considerable variation in the first reflection, from

6.11 Å for the former to 6.6-6.7 Å for the latter. The poorly crystalline material was then treated hydrothermally for up to 48 hours at 300^0C, during which process the first reflection shifted from 6.6-6.7 to 6.19 Å, accompanied by a drop in the percentage water content from 60% to 1%. From this they concluded that pseudoboehmite is not simply a poorly crystalline form of AlOOH, with the excess water adsorbed on the surface, but rather a different structure, with the water situated between the structural layers.

2.4 METHODS OF IDENTIFICATION.

Two main methods of identification are used: X-ray Diffraction and Differential Thermal Analysis:

2.4.1 X-ray Diffraction.

The method of X-ray diffraction analysis is discussed more fully in chapter 5.1.5.

Standard samples were supplied by the National Institute for Materials Research for comparative purposes. All samples were examined using Cu-Kα radiation. Random powder samples were used. All specimens were examined under the standard conditions:

Power:	45 kV ; 40 mA
Slits:	½ : ½ : 1
Scan Rate:	2^0 2θ/ min
Time Constant:	1
Range:	$1*10^3$

The results obtained are shown in figure 2.8 below.

X-ray powder diffraction was found to be able to differentiate between the polymorphs easily and quickly, as well as supplying quantitative data. Furthermore, it gives information on the relative crystallinity of the sample. The main limitation of the method is that it will not detect phases present in very low percentages.

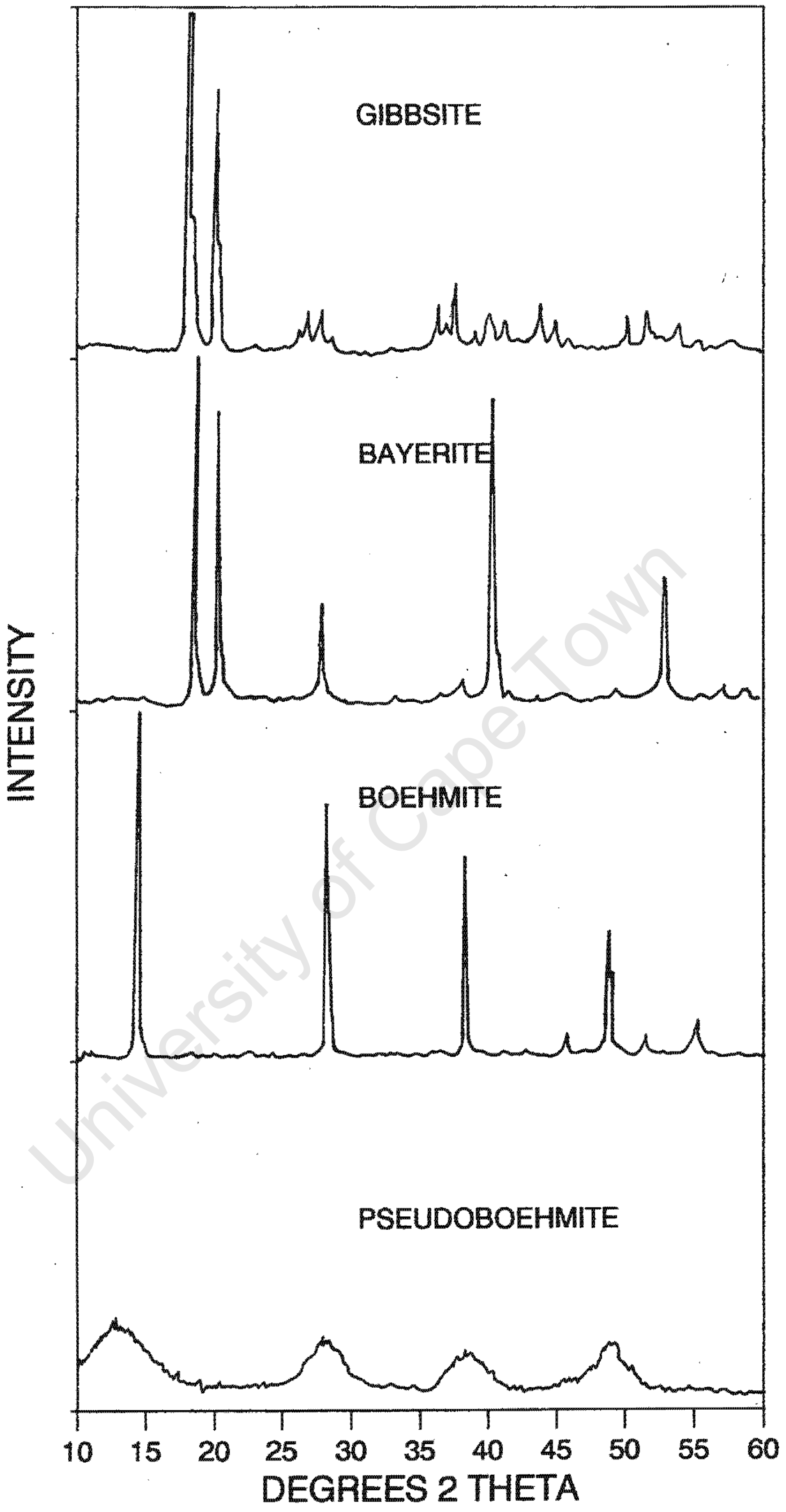


Fig. 2.8: Comparative XRD patterns for aluminium hydroxide and oxyhydroxide polymorphs

2.4.2 Thermal Analysis.

This technique is very sensitive, being able to detect very small percentages of phases present. In addition it can provide quantitative data, but it is usually used qualitatively to confirm or detect which polymorph is present. The fundamental investigation of this technique for clay minerals was done by MacKenzie (1957), who performed syntheses of the aluminium hydroxides and oxyhydroxides and examined the resulting powders by differential thermal analysis. He obtained the following results:

Mackensie found that the differential thermal curves for gibbsite all showed a strong endothermal peak between 320°C and 330°C, usually associated with two small endothermic peaks at 250-300°C and 525°C. The bayerite curves varied considerably, the main characterising feature being a strong endothermic peak at 310-315°C. He observed a single, strong endothermic peak in the region 450-580°C for boehmite, the position of which appeared to vary according to sample particle size. A smaller exothermic hump was sometimes observed between 850-950°C. Finally, Mackenzie prepared precipitates from $AlCl_3$ solution which he called poorly crystalline boehmite. These gave differential thermal curves characterised by broad endothermic peaks of intermediate strength, usually having maxima in the regions 100-150 °C and 400-500°C.

Van Zyl (1987) performed thermal analyses on his synthesised materials to characterise them. His results, reproduced in Figure 2.9 below, agree with those of Mackenzie, though the peak positions are consistently lower. This was probably as a result of the method of synthesis used by Van Zyl, which gives a product of smaller particle size. Mackenzie points out that smaller particles would tend to lower the peak temperature.

Differential thermal and thermogravimetric analyses were performed on the standard samples supplied by the National Institute for Materials Research. This was done in order to obtain comparative curves for work done at UCT and to gain experience with the technique, its limitations and potential.

All determinations were done under the same conditions:
Approximately 20g of sample was weighed out accurately. The temperature was raised from zero to 700°C at 10°C per minute in air flowing at 30 ml/min. Temperature differences and gravimetric changes were plotted against temperature. The results obtained are shown in Figure 2.10.

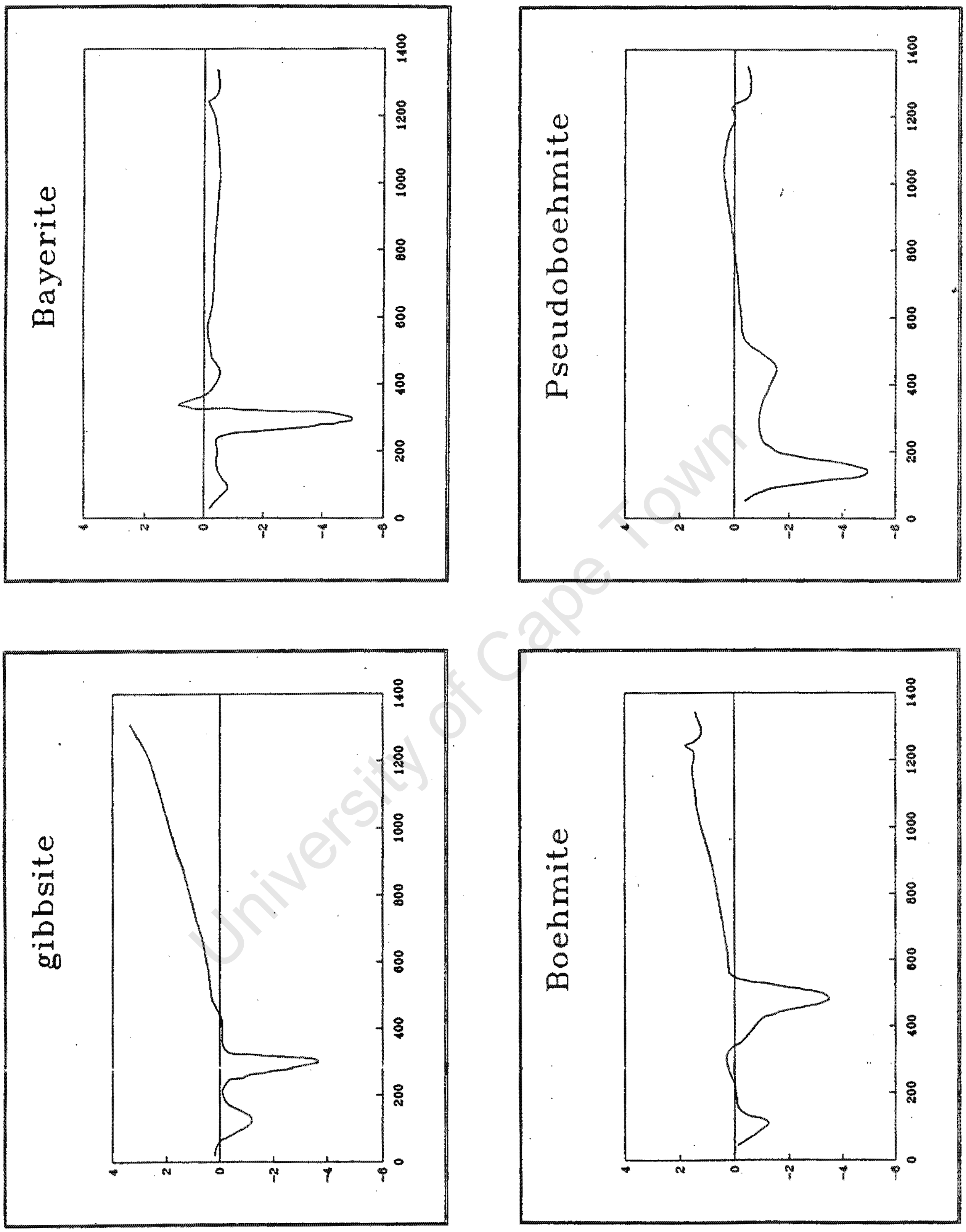


Fig. 2.9: DTA curves of aluminium hydroxides and oxyhydroxides. (Van Zyl, 1987)

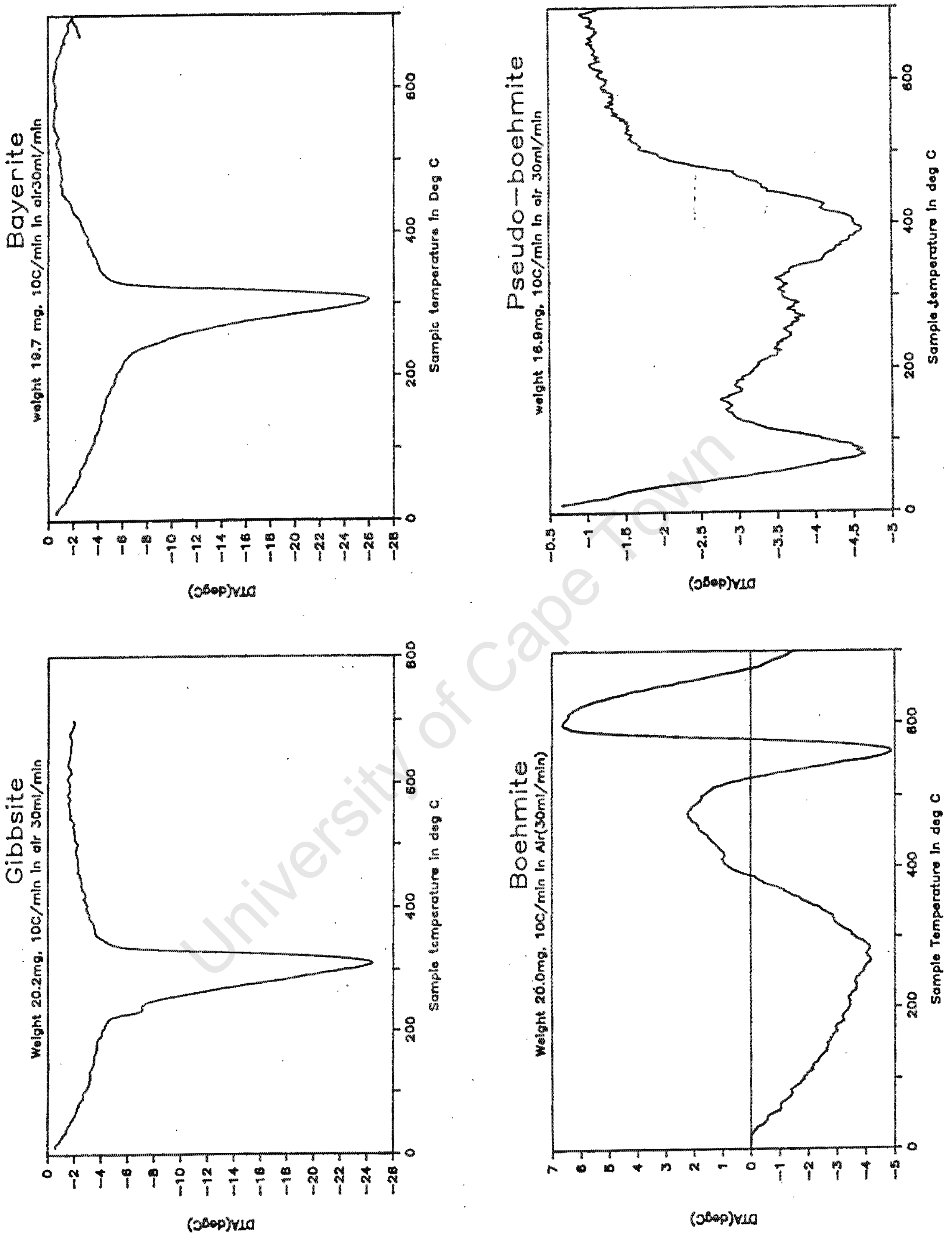


Fig. 2.10: DTA curves of NIMR standard samples:
(a) gibbsite (b) bayerite
(c) boehmite (d) pseudoboehmite

(i) Gibbsite:

There was no strong dehydration peak. Thermal and gravimetric changes began at 230°C. A small thermal event was recorded at 240°C followed by a larger peak at 310°C. The peaks were smooth, sharp and well defined. The thermal event was completed at 360°C. There was a sharp reduction in the rate of weight loss at 320°C. No subsidiary peaks were observed. This result agrees well with the results of both Mackenzie and Van Zyl.

(ii) Bayerite:

No initial dehydration took place. Thermal changes and weight loss began at approximately 240°C. One large endothermic peak was observed culminating just above 300°C. There was a slight change in slope of the curve at approximately 400°C, which may be evidence of a further thermal event. The peak was smooth, sharp and well defined. The main endothermic event was completed at approximately 340°C, and this corresponded to a sharp reduction in the rate of weight loss.

(c) Boehmite:

The boehmite differential thermal curve was more complex. Heat was immediately absorbed as shown by a broad, jagged peak reaching a maximum at 280°C. This was followed by a smooth, sharp peak at 560°C. This event was accompanied by a rapid weight loss up to 580°C whereafter the rate decreased. The peak maximum is higher than that found by Van Zyl, but within the range given by Mackenzie.

(d) Pseudoboehmite:

It can immediately be seen that this is an amorphous form from the broad and jagged shape of the peaks. There is an immediate absorption of energy reaching a maximum at 80°-100°C. This is accompanied by a rapid gravimetric loss. The first event can be ascribed to H_2O held in the gel being driven off. Van Zyl also found this peak to be strongest in pseudoboehmite. It is followed by a broad and very jagged peak, again with a maximum at about 270°-290°C, accompanied by a slow gravimetric loss. This may be ascribed to water held within the crystal structure being driven off. Finally there is a third peak which is less broad and less jagged. It begins at 330°C and reaches a maximum at 390°-400°C; there is a corresponding rapid gravimetric loss in this temperature range. This thermal event is completed at about 500°C. These results are consistent with those of Mackenzie and Van Zyl.

2.4.3 Other Methods of Identification.

All the compounds under discussion contain OH groups; consequently they may be identified by infrared absorption analysis as each shows characteristic OH bending and stretching bands. These characteristics are discussed by Ryskin (1974). This method was not used in this study, as the previously outlined methods proved sufficient for all purposes. Furthermore, infrared data must be interpreted with caution, requiring the prior acquisition of such skills.

Identification may also be made based on the different rates of dissolution of the polymorphs. This is an extremely difficult technique, as solubility can be affected by, among others, particle size, crystallinity and impurities. Hsu (1977) found this method particularly useful in analysing aluminium hydroxide components in soils.

3. MECHANISMS OF FORMATION OF ALUMINIUM HYDROXIDES AND OXYHYDROXIDES.

3.1 REVIEW OF SYNTHESIS PROCEDURES.

As researchers have attempted to understand the differences between the various polymorphs and the mechanism by which they form, many different methods of synthesis have been attempted. More recently, the commercial importance of these materials has spurred efforts to find methods of synthesis which are relatively simple and give good results. It is not possible to be comprehensive in this review of the methods of synthesis, but the examples selected should indicate the range and types of methods available.

3.1.1 Aluminium hydroxides.

Moeller (1952), in his "Textbook of Inorganic Chemistry", lists three methods by which aluminium hydroxides may be formed:

a) hydration of alumina,
b) hydrolysis of aluminate solution, and
c) reaction of aluminium salt solution with alkali.

Variations in the reaction conditions are said to yield the various crystal forms. For example, gibbsite may be formed by rapid hydrolysis of aluminate solutions, or by reaction with CO_2 at 100°C, or by ageing bayerite in dilute alkali at 60°C. Bayerite may be formed by rapid hydrolysis of aluminate solution.

Brauer (1963) describes two methods by which gibbsite may be obtained by dissolving existing aluminium hydroxide material and reprecipitating. Bayerite is precipitated by passing CO_2 gas through the solution.

The method of rapidly neutralizing sodium aluminate solution with Na_2CO_3 at room temperature was successfully used by Petz (1968) in preparing samples of amorphous alumina gel. Wade and Bannister (1973) in "Comprehensive Inorganic Chemistry" say that gibbsite can be precipitated from sodium aluminate by passing through CO_2 and recrystallising at 80°C, while bayerite results if the solution is held at 20°C.

More recently Sato (1981) precipitated hydroxides from aluminate solution with varying concentrations of HCl and HNO_3, so obtaining pseudoboehmite or bayerite, with the formation of bayerite enhanced by slow addition of the acid, higher temperatures and higher concentrations. When the pseudoboehmite was aged in the mother liquor, it transformed to gibbsite or bayerite, depending on the alkali concentration.

Many authors, in contributing to a definition of the mechanism of formation of these polymorphs, have adopted the method of synthesis involving the precipitation of the product from $AlCl_3$ solution by the addition of NaOH or other hydroxyl containing solutions. Among these researchers are Hsu and Bates (1964), Barnhisel and Rich (1965), Turner and Ross (1970), Stol et al (1976), Ng Kee Kwong and Huang (1979), and Violante and Violante (1980).

Hsu and Bates (1964) refer to the fact that, although earlier researchers formed the various polymorphs by controlling the pH of the reaction solution, a variety of products can be obtained at the same pH by varying other reaction conditions more widely, possibly as the result of changes in the reaction kinetics or the presence of extraneous anions. To study the mechanism of aluminium hydroxide formation, they prepared gibbsite, bayerite and nordstrandite, or mixtures of these, by reacting NaOH with $AlCl_3$ or $Al_2(SO_4)_3$ over a range of ratios.

Schoen and Roberson (1970) prepared the hydroxides by mixing three aqueous solutions in various ratios. The three solutions contained:
a) H^+ , $ClO_4^=$, Na^+ , Al^{3+}
b) Na^+, $ClO_4^=$,$OH^=$
c) Na^+, $ClO_4^=$, Al^{3+}.
They found that gibbsite precipitated slowly from solutions with $pH < 5,8$ and bayerite precipitated rapidly from those with $pH > 5,8$. Nordstrandite formed from bayerite when aged at high pH values, while at lower values both gibbsite and bayerite formed. On aging, the gibbsite converted to bayerite.

In 1971 Chesworth proposed a method for rapidly synthesizing $Al(OH)_3$ under conditions of low temperature and pressure and pointed out that the method had been available in the literature since 1870. Aluminium dissolved in mercury (ie. amalgamated) is highly reactive and displaces hydrogen from water to form gibbsite. Other polymorphs are easily formed by varying the reacting medium, thus 0,5M NaCl, 2M NaOH, 0,1M Na_2CO_3 and $NH_4OH_{conc.}$ yield bayerite, pseudoboehmite, nordstrandite and gibbsite respectively at different temperatures. In the same year McHardy and Thomson prepared $Al(OH)_3$ gels by the hydrolysis of amalgamated aluminium and by precipitation from aluminium salt solutions with an anion exchange resin. These gels then crystallized to give the polymorphs.

In order to examine the rate of crystallisation, Aldcroft et al (1968,1969) successfully produced hydroxide powders by hydrolysis of aluminium s-butoxide solutions in benzene or ethylbenzene, with equal volumes of water or aqueous organic solvent. Yoldas (1973) described a method of synthesizing bayerite and boehmite by hydrolysing aluminium alkoxides of formula $Al(OR)_3$ ($R = CHMe_2$ or $CHMeEt$) at 20°C and 75°C respectively. Bayerite is obtained by ageing the solution. Van Zyl (1987) extended this method successfully to produce a range of polymorphs from a stock alkoxide solution. He determined that this method produces pseudoboehmite, not boehmite as reported, with further processing necessary to obtain crystalline boehmite.

3.1.2 Aluminium oxide hydroxides.

Confusion exists and persists between the crystalline boehmite and the gel-like pseudoboehmite. Researchers routinely refer to "boehmite" when in fact the synthesis has produced pseudoboehmite. This makes outlining of methods of synthesis very complex. In producing boehmite, it is usually necessary first to produce a gel or another polymorph; in addition, most syntheses of $Al(OH)_3$ polymorphs can yield pseudoboehmite too, as will be discussed more fully below. In compiling this summary of methods of synthesis, the relevant data was examined wherever possible to determine which form was actually being produced. The earlier papers are more likely to be problematic, but have been included for completeness.

Moeller (1952) writes that boehmite may be precipitated from boiling solutions of aluminium salts by ammonia, or by ageing the gels formed when the reaction takes place at room temperature, or else by the reaction of amalgamated aluminium with water at 60°C and by ageing the gibbsite in an autoclave at 350°C.

Brauer (1963) also describes a method using amalgamated aluminium metal. He reports that boehmite is also formed when $Al(OH)_3$, which was precipitated with ammonia solution, is heated at 200°C for two hours in an autoclave.

In 1956 Milligan and McAtee determined the unit structure of boehmite using samples prepared firstly by precipitation from aluminium chloride or sulphate with dilute NH_4OH. Samples were then treated in an autoclave for seven days at 350°C and 340 atm. and for five days 400°C and 408 atm., after which a crystalline powder was recovered. Mukaibo et al (1969) report forming well crystallized boehmite by treating gibbsite in an autoclave at 300°C for 2 hours, while Juan and Lo (1975) found that boehmite formed easily between 302° and 374° C at pressures between 680 and 1700 atm. from gels which they made by mixing CaO, Al_2O_3, and silicic acid in suspension. They felt these values to be inflated owing to the retarding influence of the other components on the rate of nucleation and growth of the boehmite phase.

Cylindrical boehmite fibres 0,06 to 0,1 μm long were prepared by Packter (1976) by the hydrolysis of aluminium isopropoxide. This gave an amorphous gel which was then aged in water at 80°C for 30 minutes to form the crystals. In 1982 Krivoruchko et al studied the mechanism of boehmite formation in aged $Al(OH)_3$ precipitates. They found that when the hydroxide is aged at 200°C, boehmite is always formed, irrespective of the pH of solution, but that its morphology is determined by both the pH and the phase composition of the hydroxide, sometimes leading to the formation of needle-shaped crystals.

Fanelli and Burlew (1986) synthesised boehmite by the hydrolysis of sec-butoxide; however, water was not added to the system, but formed through the H_2SO_4 catalysed dehydration of the alcohol at the reaction temperature of 250°C. Basic aluminium sulphate was also formed.

In investigating the preparation of thin aluminium oxide films for use as catalyst supports by evaporation of aluminium in an oxidising atmosphere, Lamber (1986) observed that such films are easily hydrated by distilled water. Films of aluminium oxide were immersed in water at between 77°C and 87°C and held there for 1 to 2 minutes, after which electron micrographs revealed needle-shaped crystallites in an amorphous matrix.

The interest in boehmite as a material for use in catalysts has resulted in the filing of numerous patents covering various methods of synthesis. For example, in 1986 Misra and Sivakumar, of the Aluminium Company of America, published a patent for the preparation of boehmite by heating a solution containing caustic soda and Al_2O_3 to between 115°C and 145°C, then seeding the solution with boehmite or pseudoboehmite and ageing the seeded solution for six hours. There are references in the literature to many other patents of novel syntheses or manufacturing methods, from European countries, America, Canada, USSR, Japan and other wide-ranging sources. It was not possible to examine many of these, but they are plentiful enough to warrant care if patent infringements are to be avoided.

Apparently there has not been the same degree of interest in diaspore. Mukaibo et al (1969) report that diaspore can be prepared by treating boehmite in a NaOH solution, seeded with naturally occurring diaspore, in an autoclave at 380°C and 500 atm. for one week. Wade and Bannister, in the text "Comprehensive Inorganic Chemistry", quote Linsen ed.(1970) as saying that all aluminium hydroxides and oxides, when treated hydrothermally at pressures over 140 atm. and temperatures between 275° and 425°C, will be converted to diaspore if seeded with naturally occurring diaspore in this way.

Krause et al (1970) synthesized diaspore in a three stage process: firstly amorphous $Al(OH)_3$ was precipitated from $Al_2(SO_4)_3$ with excess ammonia; secondly, liquid air was poured over the gel, which transformed it to gibbsite; finally, the gibbsite was refluxed for 450 hours in 0,1M NaOH to form diaspore. They were also able to form boehmite by the same process, if the initial precipitation was performed with stoichiometric amounts of ammonia.

It can be seen that there are many similarities between all these procedures.

3.2 MECHANISMS OF FORMATION.

In this section an overview of the attempts by many researchers to formulate a consistent and useful mechanism of formation of aluminium hydroxide and oxyhydroxide polymorphs is presented.

3.2.1 Formation of the structural units.

Hsu and Bates (1964) proposed the following mechanism for the formation of aluminium hydroxides:

An Al^{3+} ion in solution is co-ordinated to six H_2O molecules, contributing half a positive charge to each water molecule. When NaOH is added to such a solution, one of these H_2O molecules is replaced by an OH^- ion. This ion, with its charge being only half satisfied, is able to co-ordinate to a second Al^{3+} ion, so acting as a bridge. In this way the hydroxy aluminium ions polymerise, until they form a six-member ring unit, $Al_6(OH)_{12}{}^{6+}$, which is the basic structural unit of the various crystalline and amorphous forms.

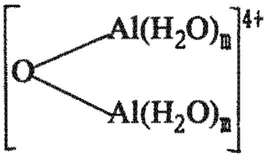
Hsu and Bates suggest that on adding NaOH to a solution containing aluminium ions, the reaction

$$Al^{3+} + OH^- = Al(OH)^{2+}$$

immediately occurs and, being unstable with respect to charge, polymerization would immediately follow, the complete scheme being

$$\begin{aligned} [\,Al(H_2O)_6\,]^{3+} \quad + \; OH^- &= [\,Al(H_2O)_5(OH)]^{2+} \quad + H_2O \\ [\,Al(H_2O)_5(OH)]^{2+} \quad + \; OH^- &= [\,Al(H_2O)_4(OH)_2]^{1+} \quad + H_2O \\ 6[\,Al(H_2O)_4(OH)_2]^{1+} \qquad &= Al_6(OH)_{12}{}^{6+}\,.12\,H_2O \end{aligned}$$

Although the principle of polymerization was accepted widely, the compounds suggested as products varied a great deal. For example, Matijevic and Tezak (1953) suggested that the monomers $[Al(H_2O)_5OH]^{2+}$ join to form



Brosset et al (1954) first proposed a ring-like structure $Al_6(H_2O)_{15}{}^{3+}$ as the main product. Hsu and Rich (1960), from studies of aluminium fixation in cation exchange resins, proposed that various polymers form, but that the most stable and consequently predominant structure would consist of a single six aluminium ion ring surrounded by twelve water molecules (Figure 3.1). They added that the single ring structure may be the result of the limited space available in the resin pores.

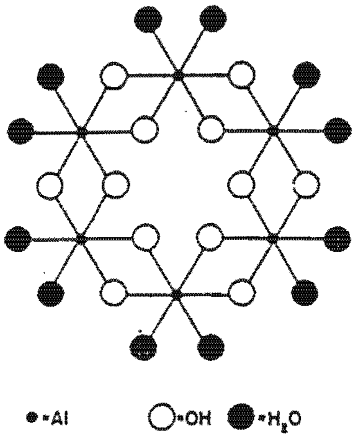


Fig. 3.1: Proposed structure of an hydroxy-aluminium polymer having an average positive charge of 1 per Al-atom (after Hsu and Rich, 1960)

Hsu and Bates proposed that the OH^- on the ring units would continue attaching other Al^{3+}, forming larger and increasingly basic double, triple and higher order rings in preference to neutral $Al(OH)_3$ molecules. However, because of the difference in charge density between these rings and Al^{3+}, very large polymers would not form until all the aluminium ions were formed into ring units. The charge per aluminium ion decreases from 3^+ to 1^+ as the OH/Al ratio increases, but the overall charge per unit increases, causing the units to repel, so slowing the rate of polymerization. Only when the ratio reaches 3 and sufficient hydroxyl ions are available to cancel the net positive charge, are they able to cluster together, forming crystalline $Al(OH)_3$.

Hem and Roberson (1967) proposed that the strong positive charge of the aluminium ion repels the two protons of co-ordinated water molecules. As the pH of the solution increases, a proton is eventually driven off, forming the complex ion $[Al(OH)(OH_2)_5]^{2+}$. Two of these may lose two water molecules and form a dimer:

$$2[Al(OH)(H_2O)_5]^{2+} \quad = \quad [Al_2(OH)_2(H_2O)_8]^{4+} + 2H_2O$$

Further dehydration and polymerization gives a ring structure of six octahedrally co-ordinated Al ions: $[Al_6(OH)_{12}(H_2O)_{12}]^{6+}$. The further growth and stacking of these units gives rise to the various polymorphs.

In more alkaline solutions, the dominant species is thought to be $[Al(OH)_4]^{1-}$. Precipitation occurs according to

$$[Al(OH)_4]^{1-} \; + \; H^+ \; = \; Al(OH)_3 \; + H_2O$$

accompanied by an increase in pH of the solution.

It is known from synthesis experiments that acid environments favour the precipitation of gibbsite, while alkaline environments favour bayerite. Also, it has been stated above that the only difference between the various crystalline forms is the stacking sequence of the basic structural units. The question is: how may these factors be linked?

Aluminium is amphoteric and can exist either as an anion or as a cation in solution, depending on pH. In acid solutions (pH 4 to 6) the cationic aluminium complex $[Al(OH)(H_2O)_5]^{2+}$ predominates. In this complex the full polarising power of the Al^{3+} is felt by one hydroxyl ion, making it energetically favourable for it to undergo tetrahedral hybridisation. As this ion polymerises, the polarising effect is reinforced by the influence of additional aluminium ions. Consequently, the compound formed from an acid solution should contain highly polarised hydroxyl ions, leading to the formation of hydrogen bonds and to the ABBA-ABBA stacking, which is characteristic of gibbsite.

In alkaline solutions the anionic complex $[Al(OH)_4]^{1-}$ predominates. Here the excess negative charge reduces the polarising effect of the Al^{3+} considerably. Hybridisation is energetically unfavourable; consequently the precipitate from an alkaline environment should contain weakly polarised hydroxyl ions leading to an open structure.

3.2.2 Formation of the hydroxides.

Bye and Robinson (1964), studying the crystallisation processes of hydroxide gels from systems as free as possible from foreign ions, summarized the relationships as:

freshly precipitated ---> pseudoboehmite--> bayerite*
amorphous gel
| (high pH)
↓
gibbsite*

* = nordstrandite may form

Each step is accelerated by increased pH and retarded by impurity ions. Progress of crystallisation was followed by determining changes of the specific surface area, which is affected by the following three factors:

a) Recrystallisation either without change in crystal form (Ostwald ripening), or with change to a more stable crystal form.
b) Aggregation of small particles.
c) Fracture of particles from strain arising from internal reordering.

Processes (a) and (b) decrease , but process (c) increases the surface area.

Two stages were noted: firstly, the surface area increased as pseudoboehmite appeared; secondly, it decreased as bayerite appeared. Increased surface area during initial ageing, ascribed to process (c), is said to confirm that pseudoboehmite is formed by condensation polymerization.

Aldcroft and Bye (1969) proposed that the condensation polymerization in the amorphous hydroxide suspension occurs by the formation of a boehmitic group, with net volume increase, as first suggested by Fricke and Meyring (1933) and Feitknecht (1954), for the formation of boehmite:

$$\left.\begin{matrix}(HO)_2\\(H_2O)_3\end{matrix}\right\}Al\text{-}OH + HO\text{-}Al\left\{\begin{matrix}(OH)_2\\(H_2O)_3\end{matrix}\right. \text{---->} \left.\begin{matrix}(HO)_2\\(H_2O)_3\end{matrix}\right\}Al\text{-}O\text{-}Al\left\{\begin{matrix}(OH)_2 + H_2O\\(H_2O)_3\end{matrix}\right.$$

furthermore, ligands may rearrange to form an hydroxide link

$$\left.\begin{matrix}(HO)_2\\(H_2O)_3\end{matrix}\right\}Al\text{-}OH + H_2O\text{-}Al\left\{\begin{matrix}(OH)_3\\(H_2O)_2\end{matrix}\right. \text{---->} \left.\begin{matrix}(HO)_2\\(H_2O)_3\end{matrix}\right\}Al\text{-}OH\text{-}Al\left\{\begin{matrix}(OH)_3 + H_2O\\(H_2O)_2\end{matrix}\right.$$

The rate of this process was determined by Aldcroft and Bye and found to fit the Avrami-Erofe'ev equation: $-\log(1-a) = (kt)n$ where a = fractional volume change and t = time.

Aldcroft et al (1969) continued the investigation into the second stage, namely the conversion of pseudoboehmite to trihydroxide by dissolution and recrystallisation. They proposed that the rate of formation of a trihydroxide would initially be determined by the rate of random nucleation and growth, which in turn are governed by the rate of dissolution of the pseudoboehmite. They found the kinetics of the reactions to be first order, while at a later stage the rate of the mass transfer processes becomes the governing factor.

The effect of the ageing medium, in particular organic solvents, on the process was examined in all three studies, and it was found that ethanol promoted aggregation relative to water, while glycerol inhibited it. This variation was ascribed to their differing ability to form a solvation sheath on the aggregate surfaces. In addition, ethanol reduces the dielectric constant at the particle surfaces, promoting aggregation, which in turn appeared to promote the condensation process by which pseudoboehmite is formed. It should, at the same time, inhibit the dissolution process by reducing the exposed surface area. This would have the net effect of stabilising pseudoboehmite relative to bayerite, which was in fact observed by Aldcroft et al (1969). However, a second type of gel is mentioned, pseudoboehmite-c, which has a more strained lattice. This strain appears to increase solubility to such an extent that crystallisation of bayerite is rapid and linear with time.

McHardy and Thomson (1971) found that when aluminium hydroxide is precipitated in aqueous suspension, two different types of gel may be formed: In the absence of acids, an uncharged gel, which they called pseudoboehmite, forms and rapidly crystallises to bayerite. However, in acid solutions, a positively charged gel, which they called pre-gibbsite gel, may crystallise slowly to gibbsite if extraneous anions are removed. The pseudoboehmite was characterised by reflections at 6,5; 3,2; 2,35; 1,85; and 1,42 Å, while the pre-gibbsite gel gave reflections at 1,85 and 1,439 Å only. The variation of pH with time is given in Figure 3.2. In stage A to B a positively charged colloid with basic counterion forms; the gel acts as a base and a reversible neutralizing reaction occurs. During stage B to C pre-gibbsite gel slowly transforms to gibbsite, the gel acting as an acid toward the solution.

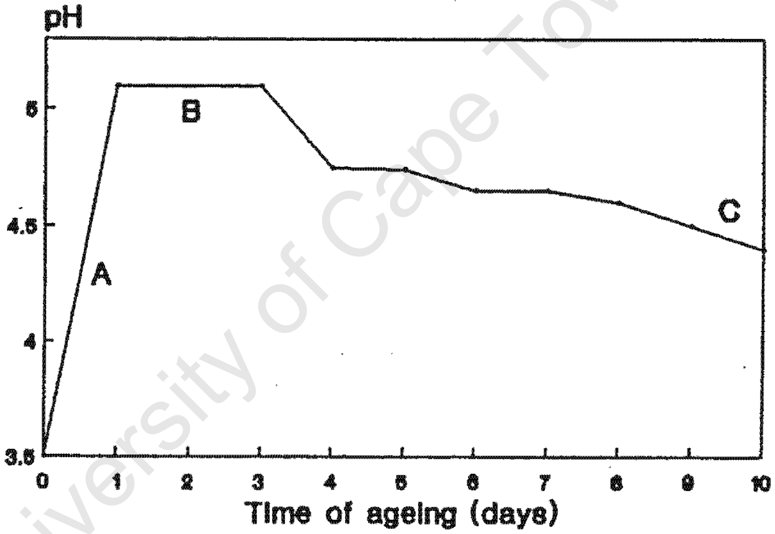


Fig. 3.2: Variation in pH with time.

Ng Kee Kwong and Huang (1977, 1979) and Violante and Violante (1980) investigated the influence of organic acids, such as may be found in natural systems, on the crystallisation of aluminium hydroxides. They found that the acids hindered the crystallisation of the hydroxides, because of their tendency to block the co-ordination sites on the charged edges of the hydroxyaluminium polymers through forming complexes, thus obstructing the hydrolysis mechanism by which the polymerization proceeds (see Figure 3.3).

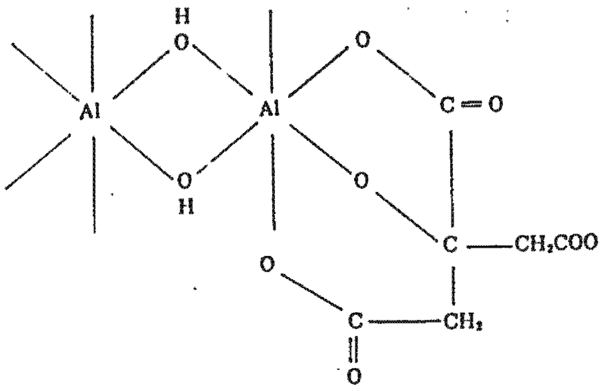


Fig. 3.3: Hydroxyl bridging mechanism of edge-Al is hampered by the citrate.

This mechanism, together with pH, and the steric hindrance of the often large organic groups, promoted the formation of amorphous structures. The promotion of amorphous forms increases with increasing organic acid concentration, but also with increasing affinity of the chelating group for aluminium. The order of effectiveness was found to be:
tartaric > citric > malic ≥ salicylic > oxalic > aspartic > p-hydroxybenzoic acid.

Barnhisel and Rich (1965), working from the theories derived from the study of pure systems, investigated the effect of other factors encountered in natural systems, such as the presence of salts. They produced the phase diagram reproduced in Figure 3.4, showing the influence of salts on the phases which may form. The broad lines indicate a large degree of overlap, and the authors note that experimental conditions may change the shape of the diagram considerably.

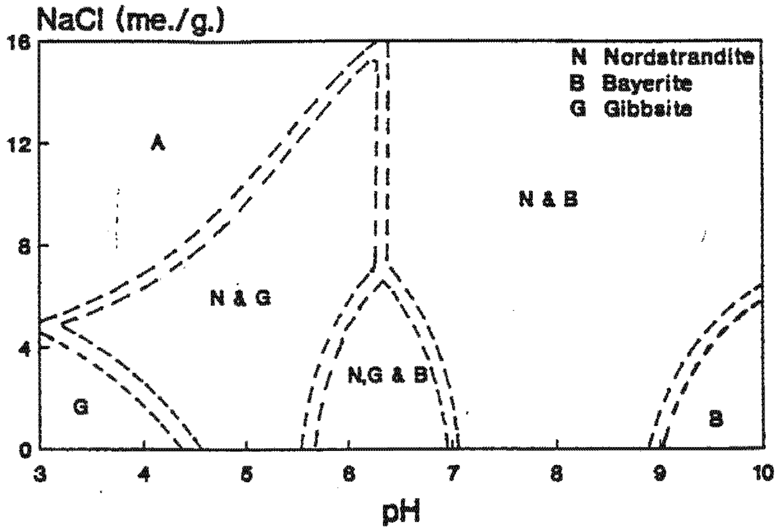
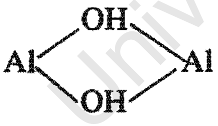


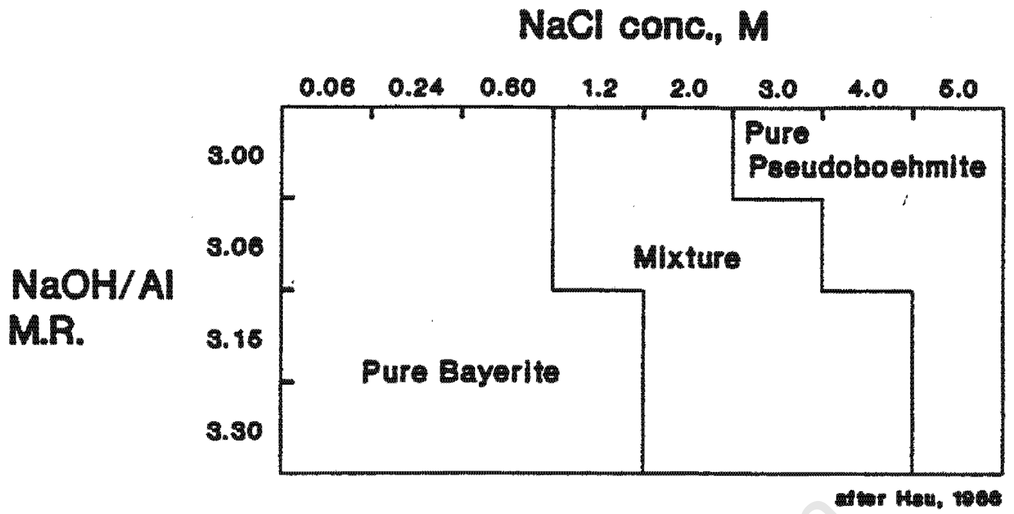
Fig. 3.4: Effect of final pH and salt concentration on polymorph formation.

Hsu (1966) examined the effect of salts on the preferential formation of bayerite or pseudoboehmite, constructing the phase diagram reproduced in Figure 3.5. At low NaCl concentrations stable, well-crystallized bayerite formed quickly, while at high concentrations stable pseudoboehmite was formed. In the intermediate range both were formed, with the pseudoboehmite gradually transforming to bayerite with ageing. From this Hsu concluded there was an irreversible or slowly reversible step in the process of formation. He proposed that, if the salt concentration is very high in the early stages of formation, the salt, in forming its own hydration sheath, may dehydrate the



links in the gel to Al--O--Al;

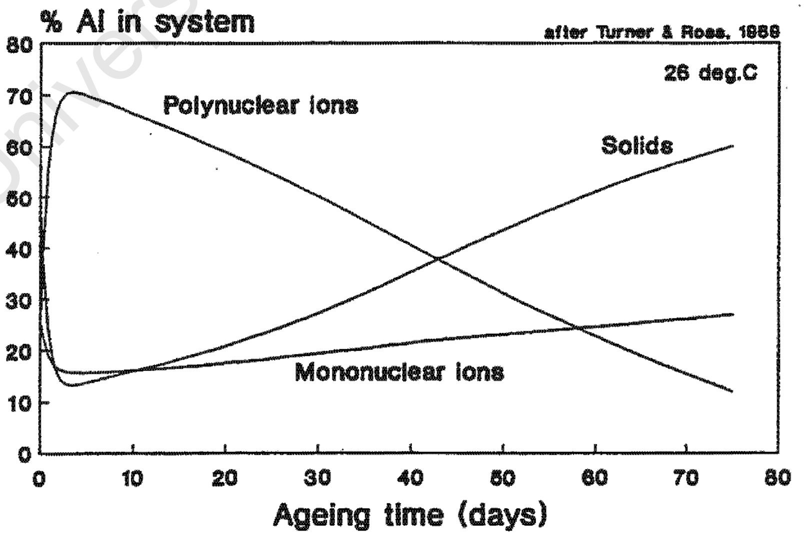
the latter would rehydrate only very slowly. He reported the relative effectiveness of anions in stabilising pseudoboehmite as:
$Cl^- > ClO_4^- > NO_3^- > Br^- > I^-$.



after Hsu, 1966

Fig.3.5: Effect of OH/Al ratio and salt concentration on polymorph formation.

Interesting experimental evidence is presented by Turner and Ross (1970) to support their somewhat contradictory proposed mechanism. Analysing the amount of polynuclear hydroxyaluminium ions present in solution by the 8-quinolinolate extraction method, they found that the concentration of such ions was initially relatively low, increasing rapidly to a maximum, and then decreasing, while for the solids the inverse occurred, as shown by Figure 3.6.



after Turner & Ross, 1969

Fig.3.6: Effect of temperature and ageing time on the concentration of solid material, mononuclear ions and polynuclear ions.

The length of time to reach these maxima and minima, as well as for the polynuclear ion concentration to reach zero, increased with decreasing temperature and with increasing $AlCl_3$ concentration. Above 0,6 M $AlCl_3$ aluminium hydroxychloride and not gibbsite crystallized. These findings agree with the proposal of Fripiat and Pennequin (1965) that the first solid to form on addition of a base to $AlCl_3$ solution contains Cl^- ions substituting for OH^- ions, which prevent trihydroxide forming. If these Cl^- ions are washed out soon after addition, gibbsite crystallises rapidly.

Turner and Ross (1970) found that the first order rate constant for the reaction between the polynuclear ions and the 8-quinolinol mixture was constant at constant temperature and independent of ageing time or extent of neutralisation. This evidence is said to contradict the mechanism proposed by Hsu and Bates (1964), whereby the aluminium hydroxide is formed by polymerization, the polynuclear ions increasing in size and changing the OH/Al ratio, which would cause the rate constant to vary with the ageing time or neutralisation. They suggest that only one polynuclear cationic species may exist, though it may be any of those proposed by other researchers.

Turner and Ross (1970) propose the following mechanism:

When base is added to an $AlCl_3$ solution, the most rapid reaction is:

I: $Al.6H_2O^{3+}Cl_3^- + nNaOH = Al(OH)_nCl_{3-n}.3H_2O + nNaCl + 3H_2O$

An initial solid high in Cl^- and H_2O is formed, which is soluble. Simultaneously, but more slowly, the polynuclear cations form:

II: $6Al.6H_2O^{3+}Cl_3^- + 15NaOH = Al_6(OH)_{15}^{3+}Cl_3^- + 15\ NaCl + 36H_2O$

The initial solid product is metastable with respect to the cations; consequently equilibrium shifts to the left in reaction I and the solid dissolves. In addition, Turner and Ross propose a third reaction consecutive to reaction I, which is a gradual solid phase reaction involving the elimination of Cl^- and H_2O and rearrangement to gibbsite, which is insoluble and stable with respect to the cations:

III: $Al(OH)_nCl_{3-n}\ 3H_2O = Al(OH)_3 + (3-n)HCl + nH_2O$

The equilibrium of reaction II then goes to the left and solid trihydroxide particles begin to grow as the cation concentration decreases.

There is considerable experimental evidence presented to support this mechanism, and the authors are also able to interpret the findings of other researchers in the light of their mechanism.

In 1976 Stol, Van Helden and De Bruyn published an investigation of the kinetics of the hydrolysis process. Improved techniques facilitated the investigation of the individual stages leading to precipitation. Continuous titrations, relaxation and dilution tests were used to investigate the effect of aluminium concentration, ionic strength and temperature.

In conjunction with these titrations, light scattering experiments were conducted to ascertain the size of particles involved in the various stages of reaction. The turbidities determined where OH/Al < 2,5, were low and stable over an eight month period. In samples where OH/Al > 2,5, a sharp increase in turbidity was noted. Measured turbidity was translated into degree of polymerization by the method outlined by Tobias and Tyree (1959). The resulting curve is reproduced in Figure 3.7.

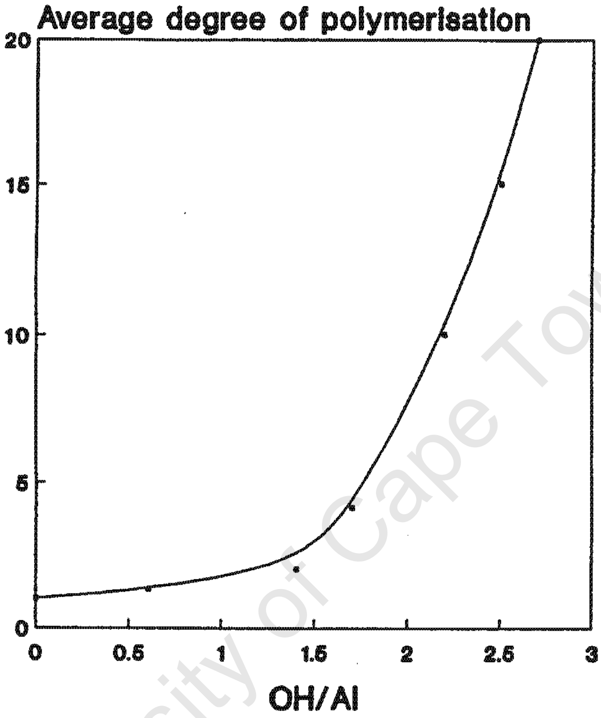


Fig.3.7: Average degree of polymerization versus OH/Al ratio.

Interpreting the titration results, Stol et al propose that at low Al^{3+} concentrations ($5x10^{-5}$ M), only monomeric species exist [$Al(OH)^{2+}$; $Al(OH)_2{}^+$; $Al(OH)_3$]. At higher concentrations, but within the range 0 > OH/Al < 0.5, only monomeric and dimeric species exist [$Al_2(OH)_2]^{4+}$].

Increasing the ionic strength will promote the dimerisation reaction:

$$2Al^{3+} + 4H_2O = Al_2(OH)_2{}^{4+} + 2H_3O^+$$

For higher concentrations and 0,5 < OH/Al < 2,2, the composition of the solutions cannot be explained without introducing the concept of polymerization. Relaxation experiments and light scattering measurements both showed the polymerization which occurs on this first plateau to be rapid and to increase in degree. The further increase in polymerization on the addition of salts is ascribed to the screening of the high positive charge on the polynuclear compounds by the added negative ions.

Further kinetic studies using the "go-stop-reverse-go" relaxation method showed that while the formation of polymers was fast relative to the rate of addition, their breakdown was slow, indicating that the two processes are not simply the inverse of each other. The breakdown of the polymers by acid was found to be a second order reaction and the proposed mechanism is shown in Figure 3.8.

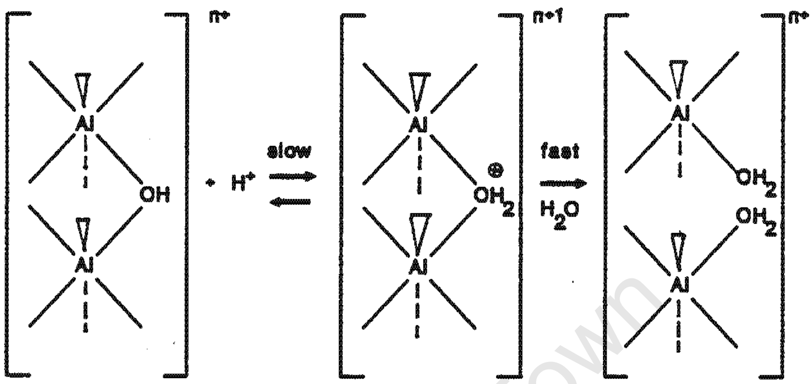


Fig.3.8: Mechanism of breakdown of polymers by acid.

The slow loosening of the Al-OH-Al bridge is followed by the fast breaking of the bond and addition of H_2O.

A structural model was proposed consistent with the experimental finding that within the range $0,5 < OH/Al < 2,5$ the majority of OH^- ions are bridging. Possible compounds not resembling the crystalline structure were eliminated as options. The resulting structures are consistent with the proposals of Hsu (1964) and with the light scattering data.

In summary, Stol et al (1976) found that in the range $0 < OH/Al < 0,5$ or for very low Al^{3+} concentrations, monomeric species dominate. Thereafter relatively small polymeric compounds are formed, with a rapid increase in the degree of polymerization. At $OH/Al = 2,5$, hexameric polymers dominate, and although these may grow, a different process begins by which non-bridging OH^- ions are attached to the edges of the polynuclear complex, reducing the high charge at the edges and thus permitting aggregation and the formation of the solid precipitate. This process consumes the excess OH^- ions, causing the appearance of the second plateau, as seen in Figure 3.7. This may be regarded as the nucleation stage preceding precipitation. The prevalence of amorphous forms is understood in the light of the steric constraints on crystallisation imposed by the orientation of the hexameric plates relative to one another.

3.2.3 Formation of the Oxyhydroxides.

The oxyhydroxides form by solid state reaction when hydroxides are subjected to conditions of high temperature and pressure. The formation of the structural units is the same for oxyhydroxides as for hydroxides, the differences again arising in the relative stacking of these cell units as discussed fully in section 3.2.1.

In all the investigations where the presence of true boehmite and diaspore have been confirmed, a hydrothermal treatment step has been reported. However, there is some controversy in the literature as to whether these forms are stable polymorphs or metastable states induced by the hydrothermal conditioning. As with the amorphous gels, there is ambiguity about the phase boundaries defining the polymorphs.

Juan and Lo (1975) investigated the formation of boehmite and other natural deposits of aluminous material. They proposed that a bauxite deposit consisting primarily of boehmite would form by burial metamorphism of weathered argillaceous limestone. To simulate this, they prepared mixtures of CaO. Al_2O_3 and silicic acid and subjected these to a range of temperatures and pressures in a hydrothermal reactor for 120 to 168 hours. Temperatures ranged from 302°C to 374°C and the corresponding pressures from 68910 kPa (10000 psi) to 172 275 kPa (25000 psi), under which conditions boehmite was easily formed.

Laubengayer and Weisz (1943) reported that gibbsite converted to boehmite at 150°C, which in turn converted to diaspore at 275°C, and finally to corundum at temperatures above 400°C and pressure of 40 000 kPa (400 bars). They suggested that boehmite was not a stable phase, but that the rate of change to diaspore was very slow. On the other hand, Ervin and Osborn (1951) considered boehmite to be a stable phase which could be converted to corundum at temperatures above 300°C and pressures below 13782 kPa (2000 psi), but which would convert to diaspore at higher pressures (see figure 3.9).

Kennedy (1959) found that gibbsite converted to boehmite below 260°C, while gibbsite converted to a mixture of diaspore and boehmite at temperatures above 260°C and pressures of 2,6 MPa (26 kbar) (see figure 3.10). He concluded that while boehmite was metastable, diaspore was the stable phase.

While Juan and Lo's work could not resolve this disagreement, they did find that boehmite was never converted directly to corundum, implying that a stable phase having a slow nucleation rate could exist between the phase fields of the two forms, and that this phase could be diaspore.

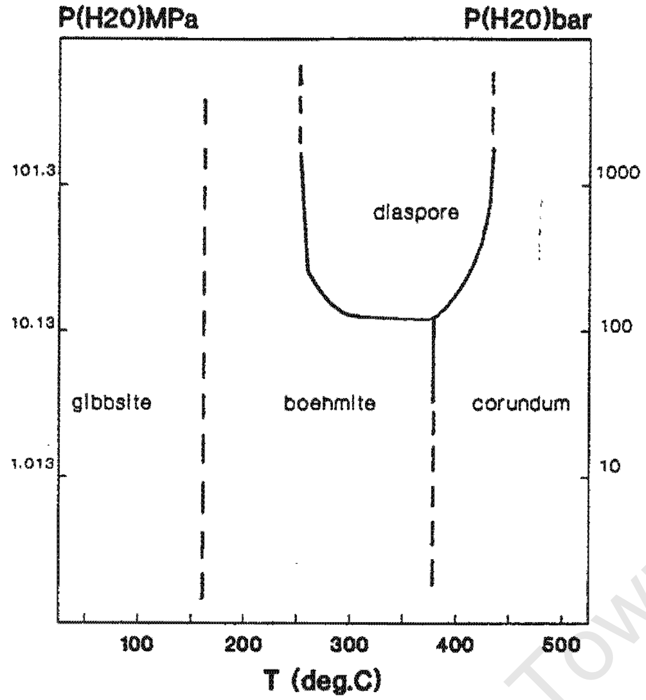


Fig.3.9: Equilibrium diagram for the system Al_2O_3-H_2O (after Ervin and Osborn, 1951)

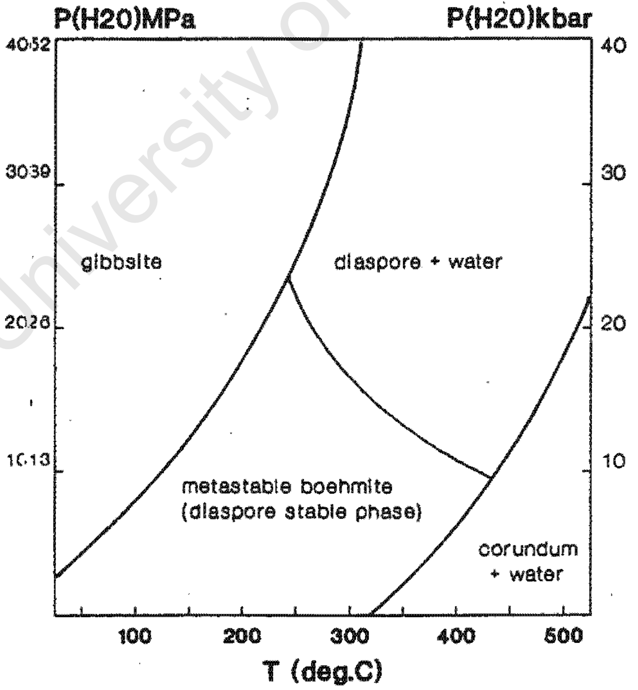
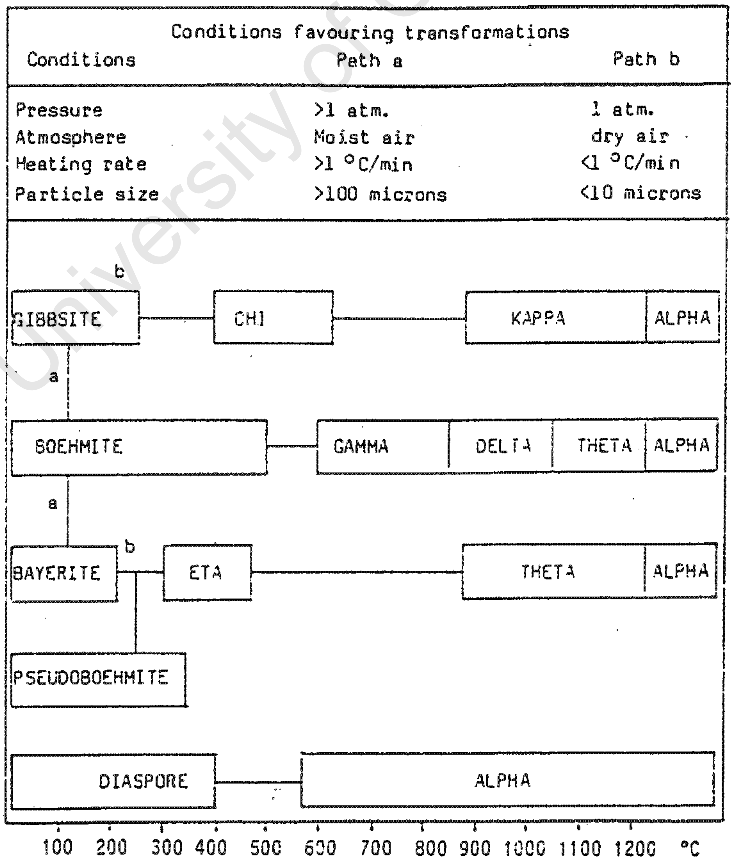


Fig.3.10: Equilibrium diagram for the system Al_2O_3-H_2O (after Kennedy, 1959)

Van Zyl (1987) reported quantitative conversion of gibbsite to boehmite at 100°C under the pressure of saturated water vapour. This shows the importance of water vapour pressure as a condition of formation along with temperature and pressure, although all these are linked, as highlighted by Voigt et al (1977).

The variations in the condition of formation of the oxyhydroxides, as reported by various researchers, could also be linked to grain size. Within larger grains of hydroxide material, high water vapour pressures may be generated at relatively low temperatures. This may create the correct conditions for the solid state reaction to oxyhydroxide on a micro-scale well before the bulk conditions are appropriate.

Less work has been published on the precise mechanisms of transformation of aluminium oxyhydroxides than on the mechanisms of formation of hydroxides. Van Zyl (1987) outlined a general mechanism for the hydrothermal decomposition of aluminium hydroxide, developed from the work of Feitknecht et al (1961) and Freund (1967). Initially on heating, protons diffuse between the layers and react with the bridging OH groups to form water. This removes the binding forces between the layers, facilitating structural and chemical changes within the layers. The inherent lattice structure, the interlayer spacing, and the presence of impurities all affect the mobility of the protons. The solid state reaction is further influenced by the pressure, atmosphere, heating rate and particle size of the hydroxide. The dehydroxylation and structural transformations of the aluminium hydroxides and oxyhydroxides have been summarised by Gitzen (1970) in Figure 3.11.



	Conditions favouring transformations	
Conditions	Path a	Path b
Pressure	>1 atm.	1 atm.
Atmosphere	Moist air	dry air
Heating rate	>1 °C/min	<1 °C/min
Particle size	>100 microns	<10 microns

Note: Enclosed area indicates range of occurrence. Open area indicates range of transition.

Fig.3.11: Composition sequence of aluminium hydroxide and oxyhydroxide polymorphs (after Gitzen, 1987)

3.2.4. Discussion of the proposed mechanisms.

What emerges from this review of mechanisms proposed for the formation of the hydroxides of aluminium is that one is dealing with a complex system which is understood only in broad outline, and about which there is still much disagreement among researchers. This complexity arises from the occurrence of amorphous forms and gels as much as from the occurrence of polymorphs. While it is beyond the scope of this project to propose a mechanism of formation, certain observations can be made.

The basic mechanisms proposed by early researchers appear to be widely supported in the literature. They provide a satisfactory explanation for the origin of the polymorphs, although the exact chemical mechanisms by which they form are not elucidated, particularly the polymerization of the $[Al(OH)_4]^{-1}$ anion. The formation of gels is not dealt with, but this is understandable, remembering that these were still regarded as immature forms of the crystalline precipitate.

The proposal that the polymorph type is determined at the polymerization stage by the chemical environment appears well founded and explains the observed reactions better than the consecutive mechanism proposed by Bye and Robinson (1964). However, the experimental work of Bye and Robinson contributes other useful information, particularly on the role of pseudoboehmite and the assertion that it does not rearrange to a crystalline product, but dissolves and recrystallises. The influence of solvents, salts and impurities can be understood in the light of this. Whether or not the salts dehydrate the linkages, block polymerization, promote aggregation, or prevent dissolution of pseudoboehmite, the net effect is to stabilise amorphous or gel forms relative to crystalline trihydroxide. To promote the latter, it is obviously necessary to remove all excess salts and impurities from the system as soon as possible.

The assertion of Turner and Ross (1970) that the first product contains Cl^- ions substituted for OH^- ions appears well founded and explains why the precipitates are occasionally observed to dissolve in the mother liquor. However, the mechanism they propose is somewhat problematic for a number of reasons:

> Firstly, the formation of the polynuclear ions is seen as merely an energetically favourable blind alley along which the reaction proceeds temporarily. This appears inconsistent with the degree of order achieved.
>
> Secondly, the final trihydroxide structure is said to be formed by solid phase reaction and rearrangement. The energy required for rearrangement of this structure would seem intuitively to be more than that available under the given reaction conditions.
>
> Thirdly, the mechanism does not acknowledge the occurrence of polymorphs or consider factors which may determine preferential formation of one above

the other. More evidence than that provided by the authors is required to support this mechanism.

The finding of Turner and Ross that only one polynuclear cation exists and that the trihydroxide is not formed by polymerization does not find support in the literature and contradicts the findings of Stol et al (1967), who measured the degree of polymerisation directly. The concentrations and OH/Al ratios used by Turner and Ross are outside the ranges given by Stol et al wherein only monomers and small polymers exist. However, Stol et al do suggest that above OH/Al = 2,5 polymerization is not the dominant mechanism, but rather the attachment of non-bridging OH^-, leading to aggregation.

Although the mechanism Stol et al propose does not discuss the formation of polymorphs, it does allow to a large extent for the conditions and mechanisms put forward in Hsu's various publications. Its principal weakness is that the formation and prevalence of gels are not discussed, though this is perhaps outside the scope of Stol et al's investigations.

The major problem in understanding this system remains the occurrence of gels and how they fit into the overall mechanism. Many researchers have attempted to elucidate these issues, yet many grey areas remain. McHardy and Thomson (1971) and Aldcroft et al (1969) each identified two different gel forms, one which crystallized rapidly to bayerite, and one which crystallized slowly to gibbsite. In the former paper, an uncharged gel is reported to crystallise quickly to bayerite, while in the latter a more strained lattice is given as reason for the same behaviour. However, it is not known whether these two sets are in fact the same phenomenon with differing interpretation, or merely the edge of a minefield of varying gel types. No systematic and comprehensive study of the aluminium hydroxide gels appears to be available, although attempts have been made to identify the phase limits.

An additional complication is that the term "gel" can be applied to anything from a disrupted water matrix, through to the well developed structure of pseudoboehmite. Furthermore, although gels are referred to as being amorphous, it would be incorrect to assume that they are uniformly amorphous throughout; within each there exist areas of greater and lesser long range order.

Another unresolved issue is whether the gel forms and redissolves before crystallising, or whether nucleation takes place within the areas of greater local order, or whether polymers aggregate directly into a crystalline structure, with gels being simply a frequent aberration owing to unfavourable conditions (or all of the above). The experimental evidence presented by all the various authors indicates a two stage process.

3.2.5 Summary.

If all the proposed mechanisms of the discussed authors are integrated, the following sequence emerges:

On addition of base to $AlCl_3$ the most rapid reaction is

$$AlCl_3 + n\ OH^- <-> Al(OH)_nCl_{3-n} + n\ Cl^-$$

Simultaneously, the first bridging reactions occur, giving rise to a variety of monomers, dimers and polymers. As the first product is metastable with respect to the polynuclear ions, equilibrium in the above reaction shifts to the left and the initial solid dissolves:

$$[Al(H_2O)_6]^{3+} + OH^- <-> [Al(OH)(H_2O)_5]^{2+} + H_2O$$

$$2\ [Al(OH)(H_2O)_5]^{2+} <-> [Al_2(OH)_2(H_2O)_8]^{4+} + H_2O$$

or:

$$[Al(OH)(H_2O)_5]^{2+} + OH^- <-> [Al(OH)_2(H_2O)_4]^{1+} + H_2O$$

$$6\ [Al(OH_2)(H_2O)_4]^{1+} <-> Al_6(OH)_{12}{}^{6+}.12H_2O + 12H_2O$$

The environment determines which ions are stable and the relative equilibria. Under certain conditions of ion concentration, impurities, ligand or solvent interference, gelation may possibly occur at this stage. This gel would be positively charged. If, on the other hand, conditions are favourable, non-bridging OH^- can attach to the edges of the polymers, reducing the charge and allowing aggregation and rapid crystallisation to bayerite:

-------------> aggregation ------------->
Polymers Crystals
--> gel --> dissolution --> nucleation -->

It may be necessary for the fixed gel to redissolve and nucleate. If in this process the hydrated structure $[Al(OH)(H_2O)_5]^{2+}$ is maintained, the recrystallising solid may be gibbsite. If excess salt has stabilised the gel, removing it by washing may enable the trihydroxide to crystallise out. Another possibility is that the initial solid may form a gel. This would then need to redissolve before polymerising and aggregating to crystalline trihydroxide, in which case washing would also be beneficial. Many gaps remain in this scheme, but it seems consistent with the experimental evidence. Obviously, specific mechanistic investigations would be necessary to confirm the sequence of formation, as proposed above.

There appears to be consensus among researchers that true boehmite and diaspore are formed by solid state reaction under conditions of elevated temperature and pressure. This conclusion has been substantiated by attempts to synthesise these polymorphs.

Differences of opinion persist as to whether the two oxyhydroxide polymorphs are completely stable phases. However those authors who argue that boehmite is metastable acknowledge that its rate of transition is extremely slow, so that for practical purposes it may be regarded as stable. The variations in the optimal conditions specified by the various authors may be attributed to the inherent differences in lattice structure and grain size, and to differences in reaction parameters which always exist. The control of water vapour pressure as a critical reaction parameter has been highlighted more recently, and lack of consideration of this parameter may explain some of the differences in findings.

The general mechanism outlined for the formation of oxyhydroxide polymorphs, based of the diffusion of protons through the structural layers, appears straightforward and consistant with the experimental findings of most researchers. The structural transformations of the hydroxide and oxyhydroxide polymorphs have been well documented by Krischner (1971) and Van Zyl (1987). The interest in these transition aluminas, particularly for their catalytic properties, should generate increasingly detailed research and discussion into the conditions and mechanisms of their formation. This will greatly benefit the understanding of the general mechanisms of formation of these polymorphs.

4. SYNTHESIS OF BOEHMITE AND BAYERITE.

The initial brief for this study was to synthesise pure ß"-alumina from the appropriate polymorphs, and furthermore to synthesise those polymorphs from readily available starting reactants. Previous investigators, most notably Van Zyl (1987), had established that the oxygen sublattice of the hydroxide or oxyhydroxide starting material was critical for the successful and optimal synthesis of pure ß"-alumina. Based on the analysis of the polymorph structures presented in Chapter 2, the two polymorphs whose oxygen sublattice render them most likely to yield pure ß"-alumina on reaction are boehmite and bayerite, both of whom have the required ABC-ABC stacking sequence in the oxygen sub-lattice.

4.1 THE SYNTHESIS OF BOEHMITE.

In accordance with the brief, synthesis methods reported in the literature which claimed to form boehmite by simple reactions were examined and tested. In particular, the influence of the reaction parameters on the efficiency of the process was investigated.

As a starting point, the precipitation of boehmite from an $AlCl_3.6H_2O$ solution with NH_4OH was selected. The equation for this reaction is:

$$AlCl_3.6H_2O + NH_4OH \dashrightarrow Al(OH)_3 + NH_4Cl$$

An attractive feature of this method is that while the insoluble $Al(OH)_3$ precipitates, the soluble NH_4Cl can be separated by washing, or under certain conditions of temperature and pressure may dissociate to NH_3 (gas) and Cl_2 (gas) and escape thus.

4.1.1 Effect of reaction temperature.

Moeller (1952) reported that the reaction temperature determined which hydroxide polymorph was precipitated. Accordingly, known amounts of $AlCl_3.6H_2O$ were dissolved in known volumes of distilled water. The solutions were stirred vigorously and continuously with magnetic stirrers, while the reaction temperature of one solution was controlled at boiling point by means of a hot plate. To these vigorously stirred solutions stoichiometric quantities of NH_4OH were added dropwise from a burette.

In both cases, a thick, white precipitate was immediately formed, which initially took the form of discrete globules in the solution. As more NH_4OH was added, the mixture became thick and pasty and the stirring sluggish. Stirring was continued for ten minutes after all the alkali had been added. The precipitate was very fine and did not settle to the bottom completely, but rather formed a diffuse, almost colloidal, cloud with ill-defined boundaries. This made separation very difficult. The final pH of the solutions was tested by indicator paper and found to be in the range pH 9 to 10, as reported in the literature.

Once precipitation was complete, a further volume of distilled water was added to both the reaction vessels and the solutions vigorously stirred. The precipitates were allowed to settle and the clear liquid decanted. Owing to the diffuse boundaries, this proved very difficult. A second volume of distilled water was added, the solutions stirred, and the precipitates separated by filtration on a Buchner funnel. Because the precipitate was so fine and had so much water associated with it, it formed a translucent white gel at the point of drainage, which then considerably slowed the filtration process. The filtrates were then washed three times on the filter, after which the odour of ammonia could no longer be detected in the precipitate.

The filter cakes were dried overnight in a laboratory drying oven at 90^{0}C. The appearance of the filtrates changed, from that of a translucent gel to large, solid white chips. The change is associated with a great reduction in volume, indicating the loss of associated water held within the precipitate. These large pieces were then ground down to a powder by hand in a pestle and mortar for X-ray diffraction examination.

The X-ray diffraction spectra were compared with those obtained for standard materials. Both samples showed the flat, broad peaks typical of an amorphous material, as shown in Figure 4.1. The positions of the peaks corresponded to the known reflections of pseudoboehmite. These results indicated that, contrary to Moeller, reaction temperature did not appear to influence the form of aluminium hydroxide which would precipitate. Furthermore, it suggests that where early researchers refer to "boehmite", they are actually referring to pseudoboehmite.

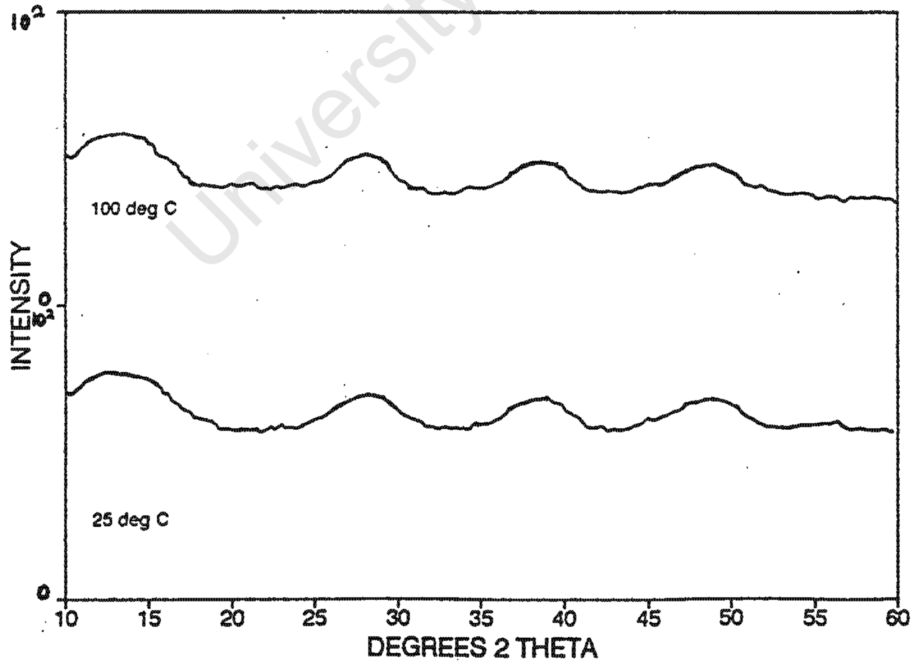


Fig.4.1: XRD spectrum of pseudoboehmite obtained by reaction at 25^{0}C and 100^{0}C

4.1.2 Effect of ageing.

Following the reported findings of Mackenzie (1957), it was decided to investigate the effect of ageing the precipitate in the mother liquor. It was also felt that an aged precipitate may separate more easily, the average particle size being greater. Consequently, NH_4OH was added to boiling solutions of $AlCl_3.6H_2O$ to pH 10, as described above. The resultant precipitates were aged in the mother liquor under reflux, under the conditions listed in Table 4.1, whereafter the precipitates were washed, filtered, dried and prepared for X-ray diffraction analysis as described above.

Table 4.1: Ageing conditions of precipitates

TEMP (°C)	TIME (hr)		
20	2	24	50
70	2	24	50

The resulting X-ray diffraction spectra for the 20°C and 70°C batches are shown in Figure 4.2. All the samples aged at 20°C showed the flat, broad peaks in the regions 10-18° 2Θ, 27°-29° 2Θ and 37°-40° 2Θ which are associated with pseudoboehmite.

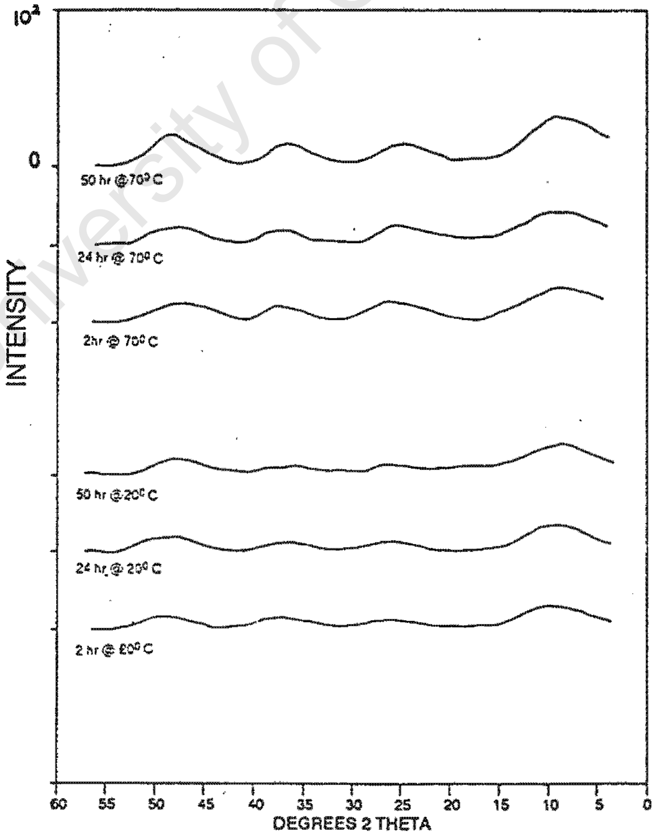


Fig.4.2: XRD spectra of batches aged at 20°C and 70°C

There was no discernable increase in crystallinity with increased ageing time. The samples aged at 70^{0}C showed slightly stronger reflections, however the peaks were still broad and flat, once again indicating a pseudoboehmite structure. There was a slight, but insignificant, increase in crystallinity between the unaged sample and those aged for long periods, that is 24 - 50 hours.

Ageing under these conditions does not appear to enhance the transformation of amorphous pseudoboehmite to either bayerite or boehmite, as was reported by Mackenzie. It is possible that some small differences between the conditions or geometry of these investigations and those of Mackenzie are the source of the discrepancy, however, every effort was made to follow the same procedure as that given in the literature.

4.1.3 Discussion.

It would appear that those researchers who reported the formation of boehmite by the simple reaction given above were, in fact, forming pseudoboehmite. Neither reaction temperatures in the range suggested by Moeller, nor solution ageing as reported by Mackenzie were found to effect the synthesis of true boehmite. The failure to reproduce the findings of these researchers might be owing to the difficulty of repeating the exact conditions employed by them. However, the overwhelming evidence presented by later researchers, as discussed in Chapter 3, is that boehmite is a hydrothermally formed phase which can only be synthesised under conditions of simultaneous high temperature and high pressure. The above results support this conclusion.

It is more likely that these authors, writing before Papee et al (1958) established that pseudoboehmite was not simply an immature form of boehmite but a different structure, were using the two terms interchangeably. This is one example of how confusion over nomenclature has complicated the study of these compounds. To produce true boehmite following this method of synthesis, it would be necessary to subject the pseudoboehmite described above to the required conditions of temperature, pressure and water-vapour pressure as discussed in Chapter 3.

The motivation for investigating methods of direct synthesis of the appropriate precursors was to avoid the double-peak firing schedule employed in the synthesis of β"-alumina in order to avoid the costs incurred by the extra energy input. If boehmite is to be the chosen starting material, the anticipated cost savings will not be realised owing to the reintroduction of a costly hydrothermal treatment step during the synthesis of the precursor.

4.2. THE SYNTHESIS OF BAYERITE.

As bayerite has the same favorable oxygen sub-lattice for optimal synthesis of ß"-alumina, that is: ABC-ABC stacking, emphasis shifted to the investigation of the synthesis of this hydroxide polymorph. A study of the literature revealed two main guidelines for the formation of bayerite:

a) the system should be as free as possible from interfering anions, ligands or solvents which might promote the amorphous state, and
b) the formation of bayerite is favoured if the reaction takes place in an alkaline environment.

The same basic experimental method as that used above was employed. Known quantities of $AlCl_3.6H_2O$ were dissolved in known volumes of distilled water as before. This solution was transferred to a burette. Stoichiometric quantities of NH_4OH were placed in a glass beaker on a magnetic stirrer. Thus the aluminium chloride solution was added dropwise to the stirred alkali, that is, the geometry of the reaction was the inverse of that used before. This was done to satisfy condition (b) above. The rate of addition was controlled at approximately 5ml per minute. The pH of the solution was monitored throughout, with the final pH being four. Immediately on contact of the two solutions, a thick, white precipitate was formed, initially taking the form of discrete globules. As more aluminium chloride was added, the mixture became progressively thicker and the stirring sluggish. Stirring was continued for ten minutes after all the aluminium chloride solution had been added. Once stirring was stopped, no settling of the precipitate was observed.

4.2.1 Effect of final pH.

The precipitated mixture was split into two equal portions. One portion was filtered immediately on a Buchner filter . A very small amount of precipitate was recovered (Sample A). The liquid which passed straight through the filter, being cloudy, was allowed to stand overnight in the hope that more solid might be recovered. After twelve hours the liquid was completely clear, the unrecovered precipitate apparently having dissolved in the highly acidic medium. It was then decided to adjust the pH of this solution to the range previously successful (pH 8 to 10) with excess NH_4OH, which resulted in the formation of a more manageable paste, which was white and not translucent. This paste was washed on a Buchner filter, oven dried at 100^0C, crushed and prepared for XRD analysis (Sample B).

4.2.2 Effect of washing.

The other portion of the original reaction mixture was also corrected to pH 8 with excess NH_4OH. This was again split into two equal parts to examine the effect of washing, that is the removal of NH_4^+ and Cl^-, on crystallinity. The one part (Sample C) was filtered unwashed, oven dried at 100^0C, crushed and prepared for XRD analysis. The other part (Sample D) was treated as follows:

In order to wash as much of the NH_4Cl as possible from the paste, it was necessary to use a centrifuge to separate the liquid from the gel-like precipitate. Each centrifuge tube was half filled with gel, topped up with distilled water, and then stirred until the contents were well mixed. The homogenised mixture was then spun for thirty minutes at 3000 rpm, after which the gel and washing liquid were well separated. This process was repeated five times, after which the odour of ammonia could no longer be detected. The washed gel was dried first on a Buchner funnel and finally in an oven at 110^{0}C, whereafter the hard, white filtercake, much decreased in volume, was crushed for XRD analysis.

4.2.3 Effect of ageing.

The entire synthesis procedure was repeated in order to verify the previous findings and examine the effect of ageing on crystallinity. The above synthesis method was repeated exactly, and the final pH adjusted to pH 8 as before. The reaction mixture was again devided into two parts. The one part was washed as described for sample D above, filtered, oven dried at 100^{0}C, and prepared for XRD analysis (Sample E). The second part was aged for three days in the pH adjusted mother liquor, thereafter it was washed, filtered and dried (Sample F).

4.3 RESULTS.

4.3.1 Changes in pH.

The pH of the reaction mixtures were monitored throughout and were found to undergo a sudden transition in the region pH 9 to 4. This transition corresponded to a marked thickening of the mixture, whereafter the mixture returned to its previous viscosity. The final pH before adjustment was in the region pH 3 to 5. Where excess NH_4OH was added the final pH was in the region of pH 8 to 10.

4.3.2 Effect of final pH.

All samples were examined by XRD as described fully in 5.1.5. The resulting spectra are presented in Figure 4.3 below.

Sample A was found to consist entirely of pseudoboehmite, showing the broad reflections typical of this poorly crystalline form. Sample B, for which the final pH of the reaction mixture had been adjusted back into the alkaline range, also showed the broad reflections in its XRD spectrum, but in addition revealed the existence of sharp, well-defined peaks, which confirmed that crystalline bayerite had also been formed.

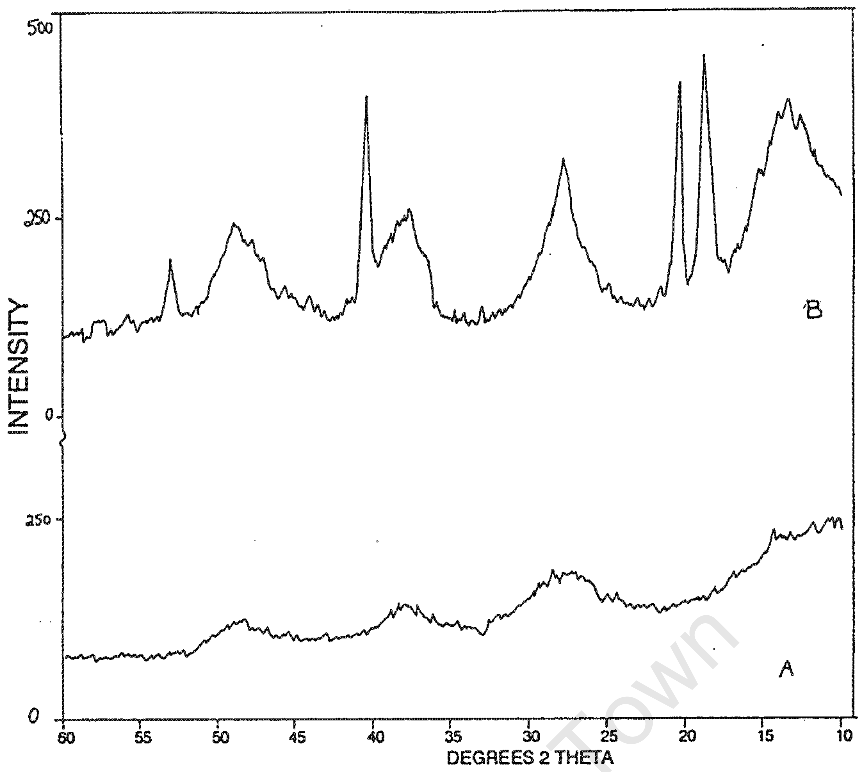


Fig.4 3: XRD spectra:
Sample A - Reaction precipitate.
Sample B - Reaction precipitate, pH adjusted

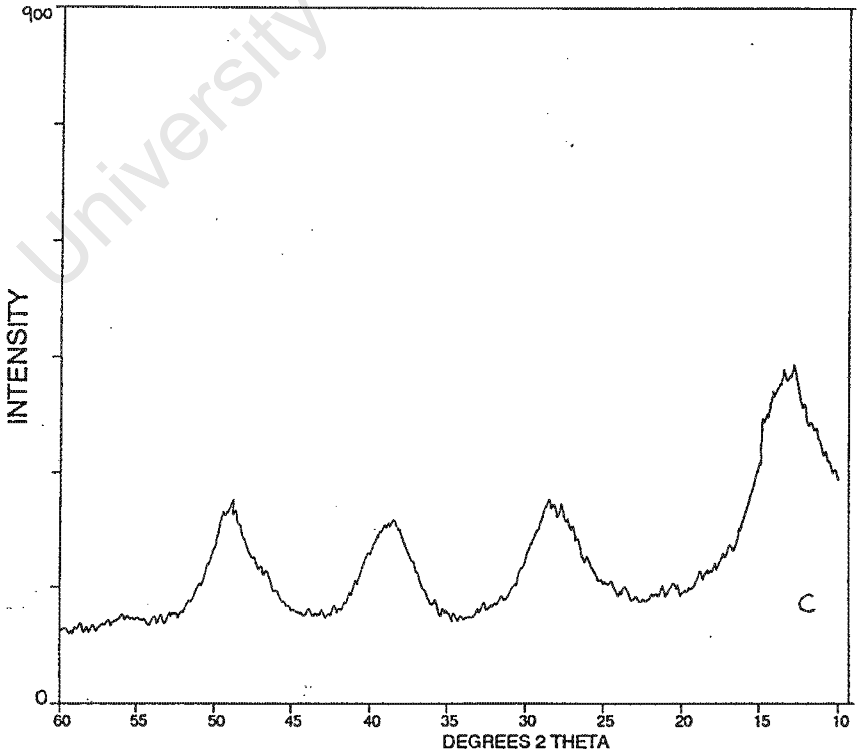


Fig.4 4: XRD spectrum of Sample C:
Reaction precipitate; pH adjusted.

4.3.3 Effect of washing.

Analysis of Sample C by XRD once again revealed the broad reflections typical of pseudoboehmite as shown in Figure 4.4. In contrast to Sample B, no sharp bayerite peaks were observed, although the sharper peaks indicate that the removal of salts by washing has assisted the formation of more ordered pseudoboehmite.

Sample D, however, showed mainly the strong, sharp peaks typical of well-crystallised bayerite, but a slightly raised baseline in places indicates the possible presence of a very small amount of pseudoboehmite (Figure 4.5).

4.3.4 Effect of ageing.

XRD analysis of both Sample E and Sample F revealed the well-defined spectrum of bayerite, with very little difference between the two materials, as shown in figures 4.6 and 4.7 respectively. However, in both spectra evidence can be seen of the superposition of the typical pseudoboehmite spectrum shown in figure 4.5. This is particularly noticeable in the raised backgrounds in the regions 46^0-50^0 2Θ, 35^0-42^0 2Θ and 26^0-32^0 2Θ. This indicates the formation or retention of more pseudoboehmite than was observed in Sample D.

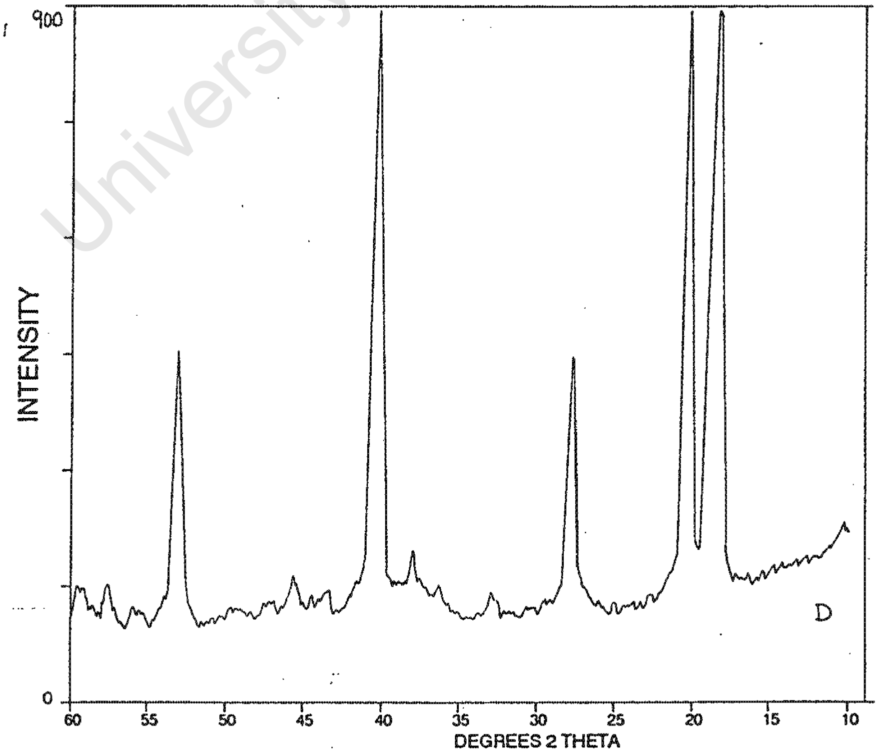


Fig.4.5: XRD spectrum of Sample D:
Reaction precipitate; pH adjusted; washed.

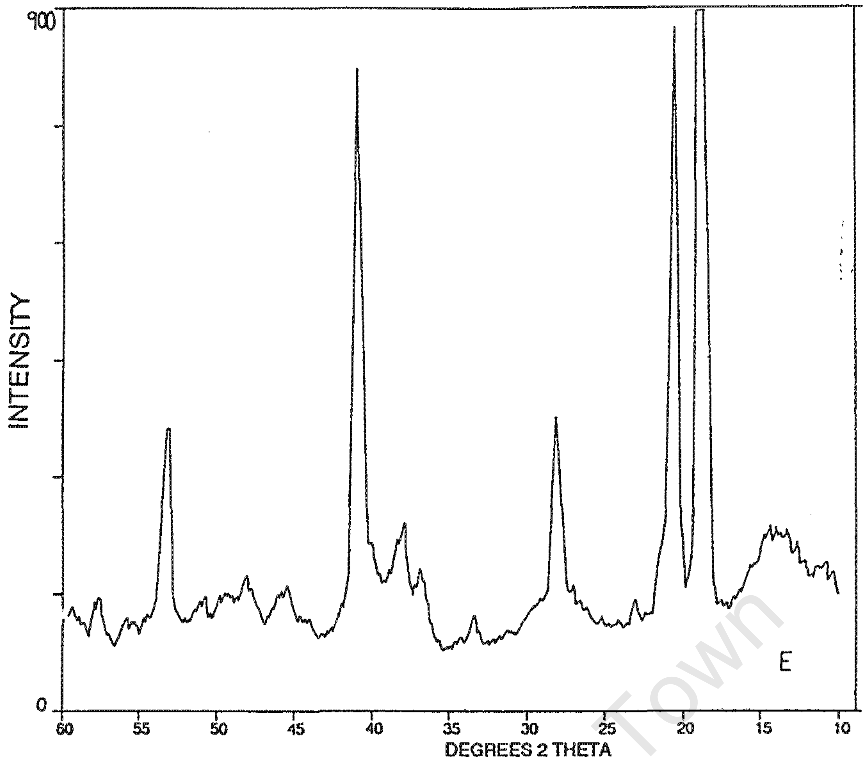


Fig.4 6: XRD spectrum of Sample E:
Reaction precipitate, pH adjusted, washed.

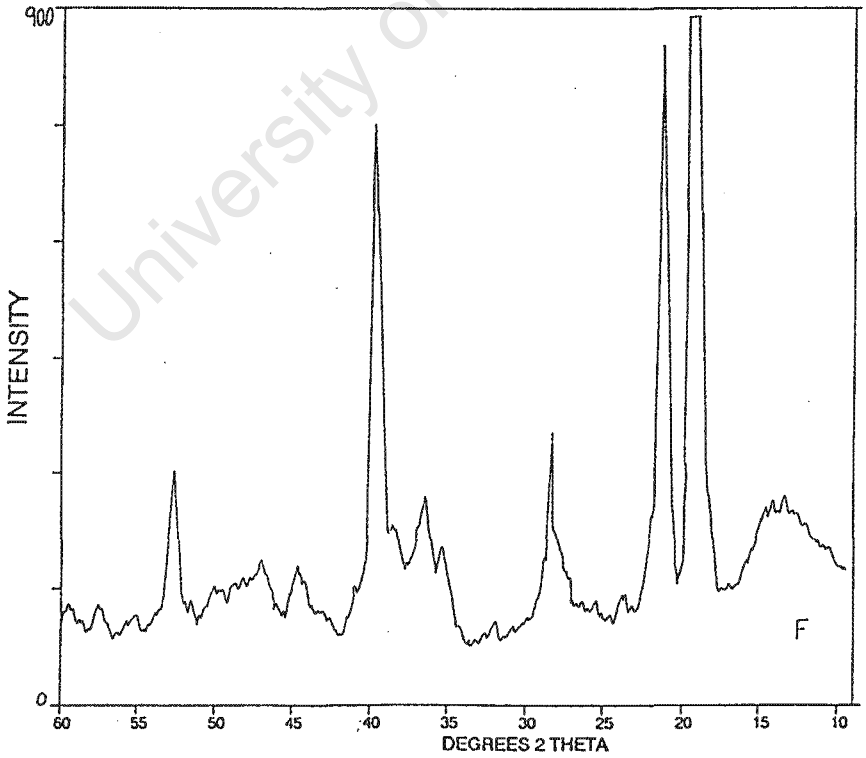


Fig.4.7: XRD spectrum of Sample F:
Aged 3 days, then as for Sample E.

4.4 DISCUSSION AND CONCLUSIONS.

While neither the pH of the reaction mixture, the specific surface area of the precipitates, nor the turbidity of the solutions were studied in detail as by previously discussed researchers, the course and outcome of the reaction discussed were observed to be consistent in all respects with their observations.

The inversion of the reaction, that is the addition of the $AlCl_3$ to the NaOH solution, such that the reaction takes place in an alkaline environment, is successful in promoting the formation of bayerite. This is consistant with the literature reviewed. The stoichiometrically required volumes of NH_4OH do not appear to be adequate to maintain the alkaline environment required for the formation of bayerite under the conditions of batch processing, although it is possible that the correct ratio might be achieved more easily in a continuous processing configuration. Adjusting the final pH to pH 8 to 10 is effective in promoting the formation of bayerite over pseudoboehmite. Samples B and C, having been formed under similar conditions, were quite different. This can be ascribed to small differences in the reaction environment, in particular the concentration of Cl^- ions.

Washing to remove NH_4^+ and Cl^- significantly promotes the formation of, or transformation to, bayerite from pseudoboehmite. This is consistant with the findings of Barnhisel and Rich (1965) and Hsu (1967) that the presence of Cl^- ions stabilises pseudoboehmite relative to bayerite.

Ageing of the mixture in the pH adjusted mother liquor before washing did not appear to enhance the formation of bayerite, nor significantly affect the amount of pseudoboehmite retained. This seems to confirm that pseudoboehmite will not transform to bayerite under these conditions of ageing. However, it may do so after the conditions have been altered by washing as discussed by Barnhisel and Rich and Hsu. The regions of stability of the various phases as defined by these researchers were not explored in this exercise.

The two main guidelines derived from the literature study for the formation of bayerite appear to have been substantiated by this experimental investigation. It is possible to form fully-crystalline bayerite by the simple reaction of $AlCl_3.6H_2O$ with NH_4OH at room temperature. The reaction must take place in an alkaline environment, which must be maintained, in a batch processing configuration, by the addition of excess NH_4OH to bring the final pH to pH 8 to 10. Ageing at this stage produces no significant advantage. Washing to remove as much as possible of the Cl^- ions greatly aids and/or facilitates the formation of well-crystallised bayerite.

However, the system is complex and the governing factors interact in such a way so as to produce varying results under seemingly identical conditions. As a consequence, results are not always perfectly reproducible. This is problematic if one is attempting to generate large amounts of the same material. Furthermore, until the governing factors are better understood, and a consistant and credible mechanism of reaction is derived, attempts to scale up the synthesis to any significant extent are likely to be

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5. SYNTHESIS OF ß"-ALUMINA.

The ultimate aim of these investigations remained the synthesis of ß"- Alumina; therefore it was important to subject the precursors examined in chapters 4 and 5 to the solid state reaction forming beta alumina and to examine the results. The procedures used were in accordance with the standard method described by Van Zyl (1987).

5.1 SYNTHESIS.

Two samples of commercially available, hydrothermally formed boehmite were obtained for examination and comparison: Cera Hydrate from America, and Timcerm from Holland. The average particle size of the two powders were 28,9 microns and 2,6 microns respectively. Owing to the small volume of bayerite produced experimentally in this study, a sample of bayerite was obtained from Germany for comparison with boehmite as a precursor for beta alumina. The average particle size of this powder was 27,4 microns. XRD analysis confirmed the composition of these powder samples.

5.1.1 Composition.

Sodium and lithium were added to the aluminium hydroxide so as to obtain a composition of 84,0 mole percent Al_2O_3, 13,5 mole percent Na_2O and 2,5 mole percent Li_2O. The sodium and lithium were added in the form of Na_2CO_3 and Li_2CO_3 respectively. Because the latter is hydroscopic, it was dried at 320^0 C for 5 hours to ensure consistent composition of the batches.

5.1.2 Powder preparation.

The powder batches were prepared as follows: The boehmite or bayerite powder was weighed into a teflon beaker, and the sodium and lithium carbonates added in the correct stoichiometric ratio. To this 100 ml of distilled water and 300 g of 2 mm ZrO_2 grinding beads were added. The beaker was then attached to an attritor mill and the slurry milled at 850 rpm for two hours. After milling the slurry was separated from the ZrO_2 beads by seiving. The resultant slurry was well dispersed and no settling was observed after five hours.

Because the slurry contained a soluble component (Na_2CO_3), a partly soluble component (Li_2CO_3), and an insoluble component (aluminium hydroxide), it was necessary to freeze-dry the mixture in order to preserve it's homogeneity. The slurry was transferred to round-bottomed freeze drying flasks which were immersed in a refrigerant solution and rotated until a uniform, solid shell of frozen slurry coated the vessel.

The flasks were then transferred to the freeze dryer where they were evacuated until all the water had sublimated. This method produced homogeneous, free-flowing powders which were then stored in sealed containers in an oven at 110° C to prevent the re-adsorption of water.

The yield for this entire procedure always exceeded 95 percent.

5.1.3 Solid state reaction.

The prepared powders were formed into standard discs 10mm in diameter and 3 to 5 mm thick in a uniaxial press at 300 kPa. All test discs was accompanied by two discs above and two below to limit sodium ion loss during firing. Each disc was numbered so that any differences which might emerge could be correlated with its position. The five discs were stacked neatly inside a magnesia crucible which was sealed with a lid.

The crucible was then placed inside a furnace and heated at 20° C per minute to the required reaction temperatures ranging from 1100° C to 1600°C, where it was held for periods ranging from 1 to 5 hours and thereafter cooled at 20° C per minute to room temperature. After reaction, the cooled discs were removed from the crucible and stored in sealed containers in a desiccator.

5.1.4 Density determination.

The density of each of the fired discs was determined according to the Archimedes principle by immersion in xylene.

Having accurately obtained the weight in air of the discs, they were immersed in boiling xylene for 10 minutes to eliminate air from surface pores. The discs were then weighed while suspended in xylene, and the bulk density calculated from

$$\text{Bulk Density} = \frac{(\text{Mass}_{\text{air}} \times \text{Xylene density})}{(\text{Mass}_{\text{air}} - \text{Mass}_{\text{xylene}})}$$

5.1.5 X-ray determination.

Many researchers have characterised the beta-aluminas by X-ray diffraction and there is good agreement between their results. For example, Schmid (1986) reported a full and detailed characterisation of the diffraction patterns of ß"- and ß-alumina. These are illustrated in Figure 5.1 (a) and (b) respectively:

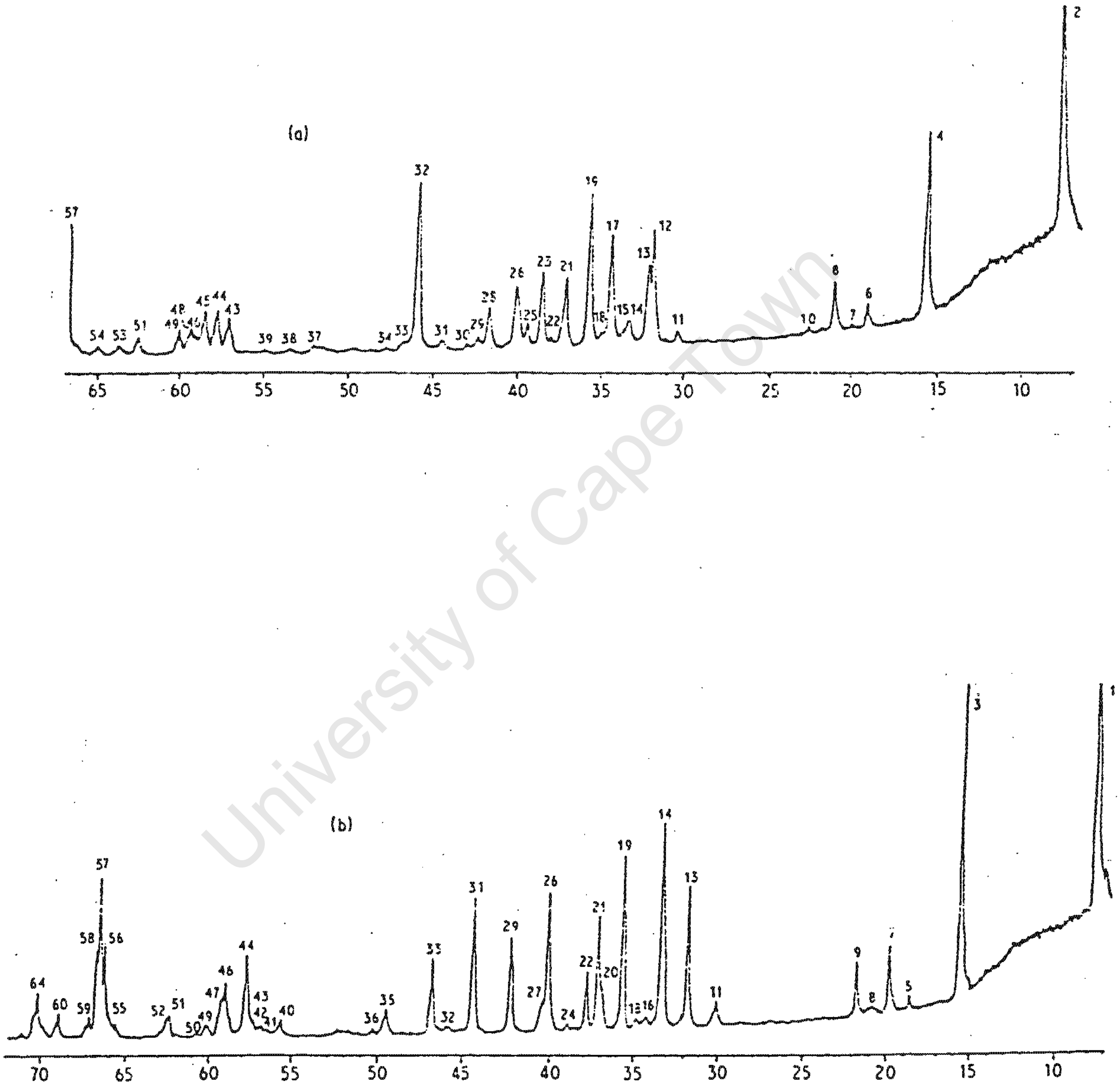


Fig 5.1 XRD pattern of (a) ß"-Alumina and (b) ß-Alumina
(Schmid, 1986)

Various researchers report using different peaks to characterise the beta phases. Some of these are presented in Table 5.1.

Table 5.1: Characteristic peaks identified by researchers. (notation as quoted)

RESEARCHER	ß hkl	d (Å)	ß" hkl	d(Å)
Schmid (1986)	026 027 017 012	2.03 1.94 2.68 4.46	0111 0210 014	2.60 1.97 4.20
Hodge (1983)	017 026	2.68 2.03	0111 0210	2.60 1.97
Kvachkov et al (1982)	2026 2027	2.03 1.94	022.10	1.97
Pekarsky and Nicholson (1980)	017 026	2.69 2.04	0111 0210	2.60 1.97
Johnson et al (1979)	012	4.46	104	4.20
May (1978)	013 0226 0227	4.08 2.03 1.94	1014 02210	4.20 1.97

The peaks in these ranges are well defined and provide a convenient contrast between the patterns of the two phases, which is easily identifiable. Furthermore there is good separation of the peaks, reducing the need for complex mathematical manipulation of results. Another important factor is the clear background region on either side of both sets of peaks, which would facilitate the determination of absolute intensities.

Johnson et al (1979) determined, by examining the relevant JCPDS powder diffraction file cards for ß- and ß"-alumina (19-1173 and 25-775 respectively), that the fraction of ß"-Alumina present in a mixture of the two phases may be calculated from the expression

$$f(\beta'') = \frac{1.5\,\beta''I_{104}}{1.5\beta''I_{104} + \beta I_{012}}$$

Pekarsky and Nicholson (1980) modified this relationship to work with the normalised intensity values for the characteristic peaks of their choice. Morgan (1982), in discussing a paper by Kvachkov et al (1981), disputed this method because the intensity of X-ray lines can be greatly affected by syntactic intergrowth effects. The latter refuted this, saying that the peaks selected were well separated and could be accurately measured. They also pointed out that the powder diffraction method ensured the averaging of intensities so that it was unlikely that syntactic intergrowths would affect the intensity ratios.

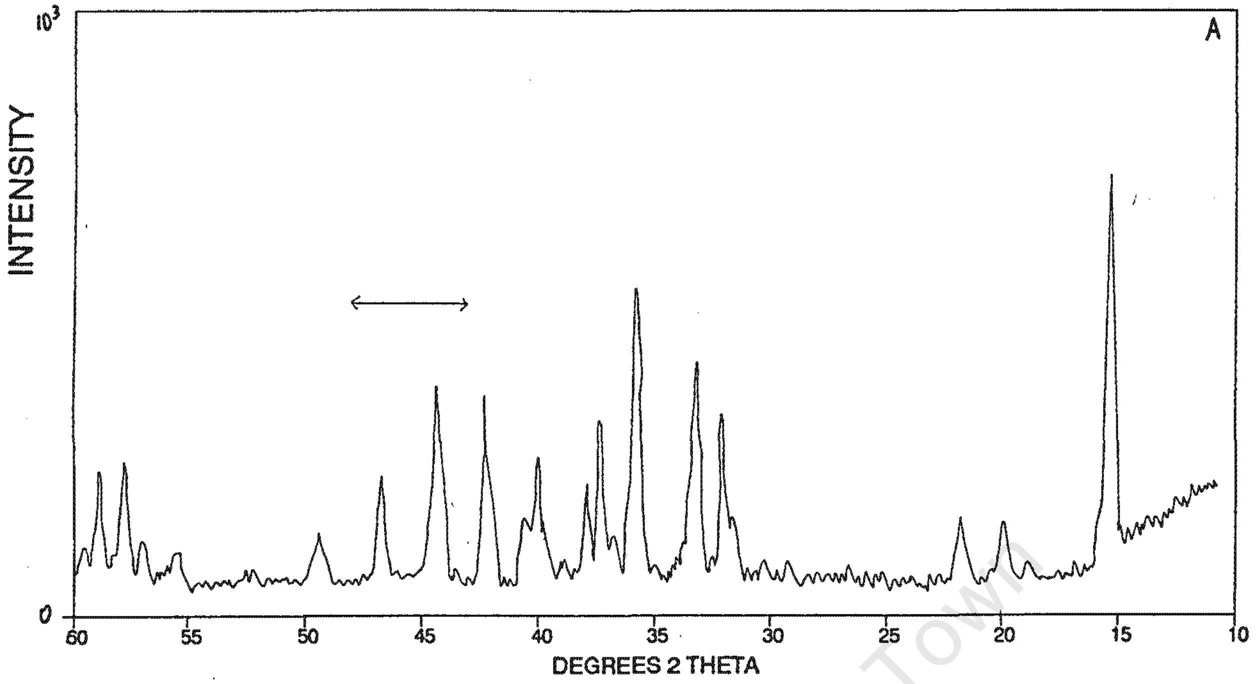
Hodge (1983) observed that diffraction lines corresponding to planes which are similar in the ß- and ß"-alumina appeared to be sharp, whereas those unique to one phase were more diffuse. This type of X-ray pattern was earlier described by Morgan (1982), who attributed the pattern to intermixed layers of the two phases along the c-axis, and also by Poulieff et al (1978), who attributed it to faulty stacking inherited from the starting structure.

X-ray diffraction investigations were performed on a Philips diffractometer using Cu Kα radiation and the following standard conditions:

45 kV; 40 mA;
Range = $1\text{x}10^3$; Time constant = 1
Scan rate = 2^0 2Θ/min

All samples were milled in a mechanical ball mill for a standard period of ten minutes and were mounted in standard aluminium side-loading sample holders. Preliminary trials of different milling times and mounting techniques showed no preferred orientation effects or other significant variations. Milled samples were stored in an oven at 110^0C to prevent the adsorption of water.

After exploratory scans to determine the best experimental conditions, diffraction patterns were obtained on standard ß"- and ß-aluminas obtained from the CSIR. The patterns corresponded well with those reported in the literature. They are presented in Figure 5.2 (a) and (b) respectively.



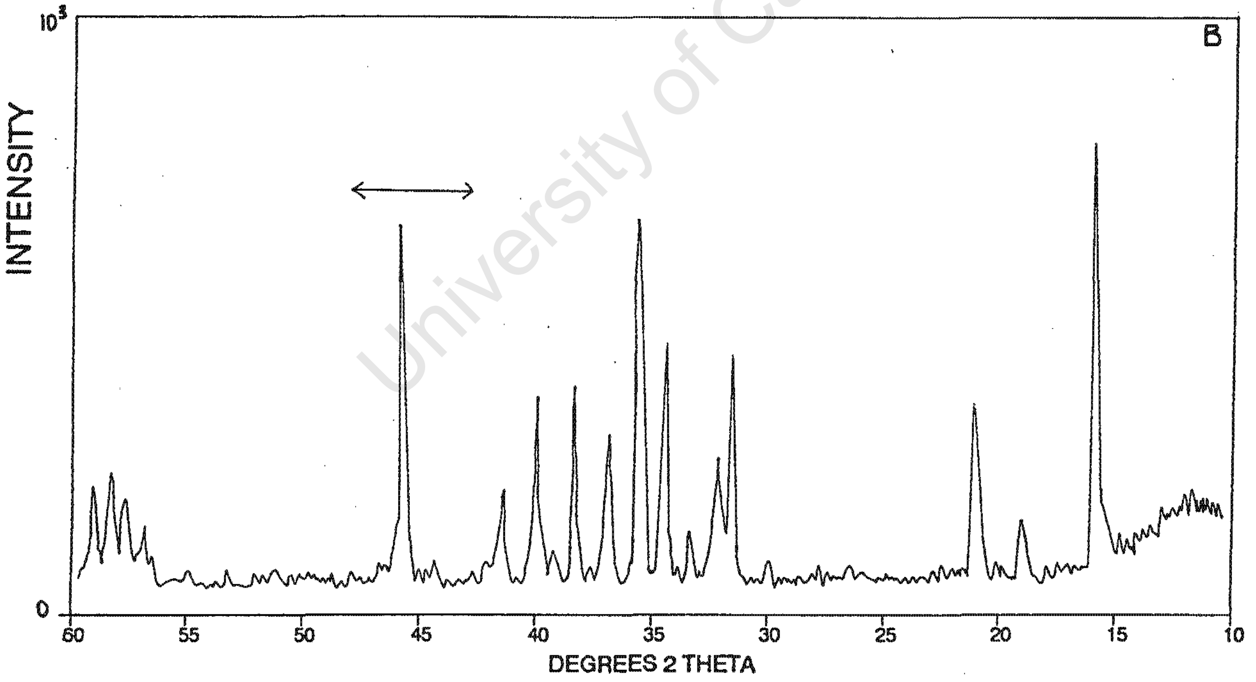


Fig 5.2 (a) XRD pattern of standard ß-alumina
Fig 5.2 (b) XRD pattern of standard ß"-alumina

From examination of the patterns and of the literature the following identification peaks were selected for the reasons given previously:

Phase	Position	Identification
ß-alumina	$44{,}36^{0}\ 2\Theta$	026
ß"-alumina	$46{,}03^{0}\ 2\Theta$	0210

Initially all patterns were recorded graphically; later the patterns were collected digitally, which allowed the data to be manipulated using standard software packages.

The ß-alumina fraction was calculated from the normalised intensity values for the characteristic peaks according to the method of Pekarsky and Nicholson, that is

$$f(\beta) = \frac{2{,}29\ I_{\beta(2{,}04\ \text{A})}}{2{,}29\ I_{\beta(2{,}04\ \text{A})} + I_{\beta''(1{,}97\ \text{A})}}$$

Using the standard conditions specified, the f(ß) results calculated after repeated scans of the same material agreed within 0,5% of the mean f(ß).

The same standard conditions were used in identifying and characterising the various aluminium hydroxide precursor materials.

5.2 RESULTS.

5.2.1 Observations.

As might be expected, the discs shrank during firing, the amount of shrinkage being proportional to the firing temperature. The maximum decrease in diameter was approximately twenty percent. The crucible in which the discs were fired developed a light pink discoloration on the inside, indicating that some sodium had escaped from the discs during firing.

5.2.2 Density.

As shown by Figures 5.3 and 5.4 both Timcerm and Cera Hydrate achieved a maximum density of approximately 3,15 g/ml at a firing temperature 1350°C and 5 hours. Lowering the soak time to 2,5 hours decreased the density achieved at 1200°C, but did not have a significant influence at 1600°C.

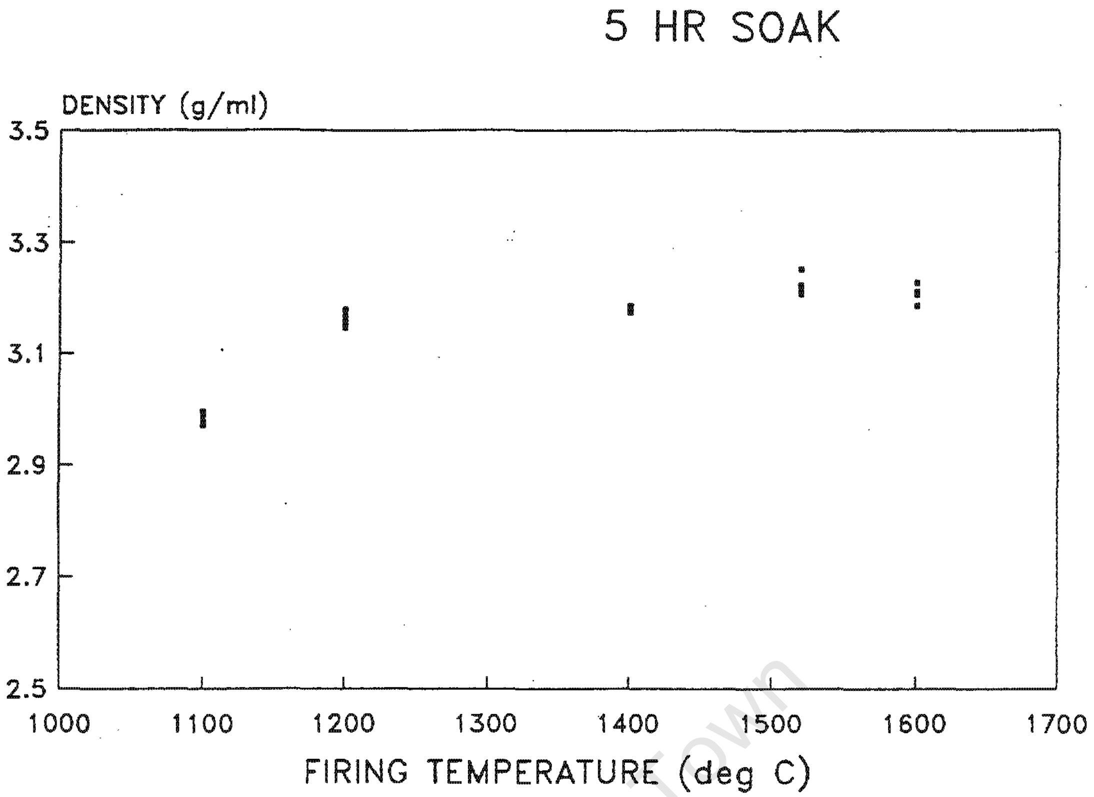


Fig. 5.3: Density vs Firing Temperature - Timcerm

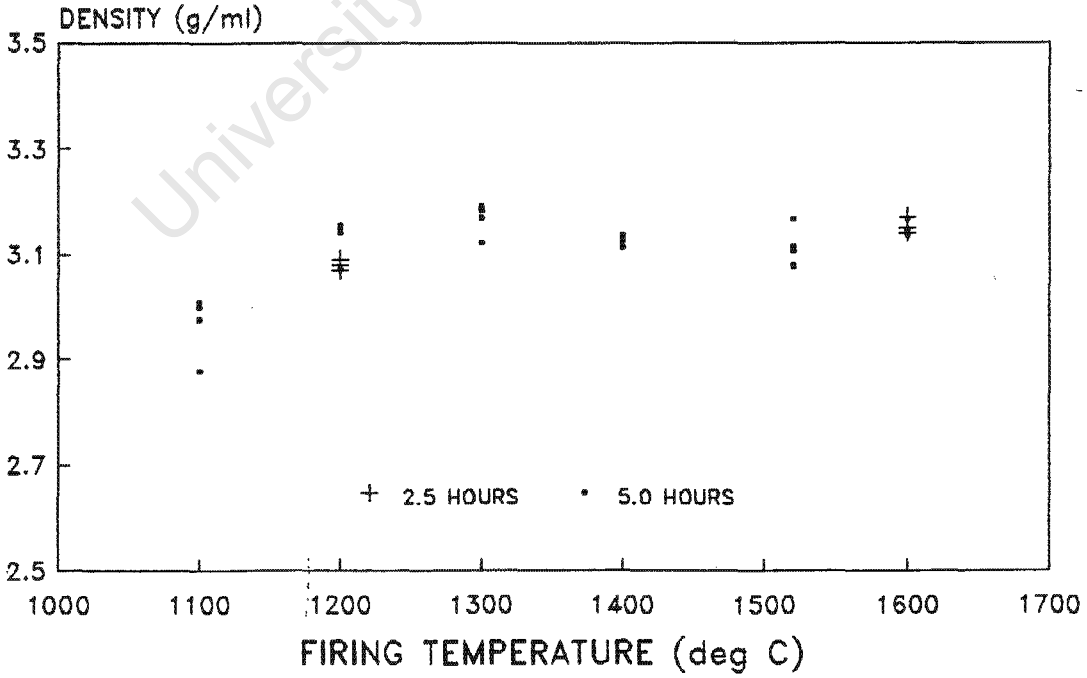


Fig. 5.4: Density vs Firing Temperature - Cera Hydrate

The trends for the bayerite material were not as well defined as may be seen from Figure 5.5. The overall densities achieved were also lower, the average density at 1500°C and 4 hours being 2,9 g/ml.

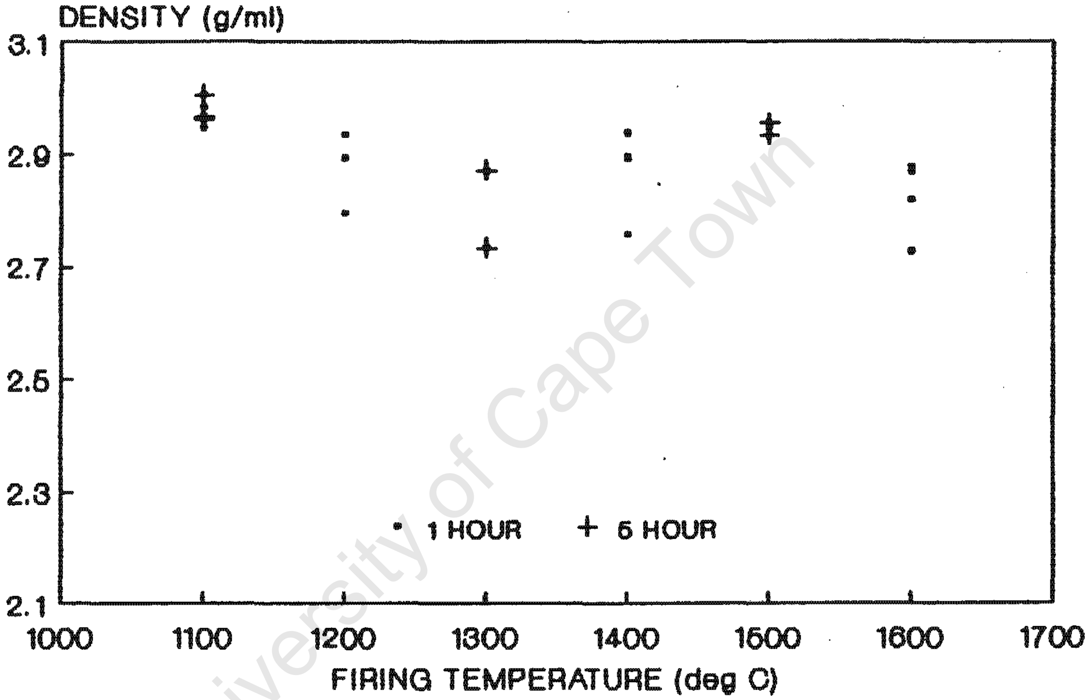


Fig. 5.5: Density vs Firing Temperature - Bayerite

5.2.3 X-ray Diffraction Analysis.

The results of the X-ray diffraction analysis of the material obtained after firing were as follows:

i) Boehmite precursor:

An examination of Figures 5.6 and 5.7 showed that in the beta alumina synthesised from both Timcerm and Cera Hydrate by the method described above, only ß"- alumina was present. There was no evidence at all of a peak at 47° 2Θ which would have indicated the presence of ß-alumina.

At a firing temperature of 1100°C, the ß"-alumina structure had not yet fully developed, as evidenced by the lower peak heights and increased peak width. However, at 1200°C the ß"-alumina was fully crystalline, showing no further sharpening or increase in peak height at increasingly higher firing temperatures.

ii) Bayerite precursor:

An examination of Figures 5.8 and 5.9 showed that the beta alumina synthesised from commercial bayerite by the method described above consisted entirely of ß"-alumina. There was no evidence of a peak at 47 °2Θ which would have indicated the presence of ß-alumina. At a firing temperature of 1100 °C, the ß"-alumina structure had not yet fully developed as evidenced by a slightly broadened peak at 46,0 °2Θ. However, above 1200°C the ß"-alumina was fully crystalline, and showed little further sharpening or increase in peak height as the soak time and temperature increased. Some of the minor peaks, such as that at 41,65°2Θ showed an increase in sharpness with increasing firing temperature, while others such as at 44,5°2Θ remained unchanged throughout.

An examination of the XRD pattern obtained for the beta alumina synthesised from a sample of experimentally precipitated bayerite type material showed that it contained both ß- and ß"-alumina (Figure 5.10).

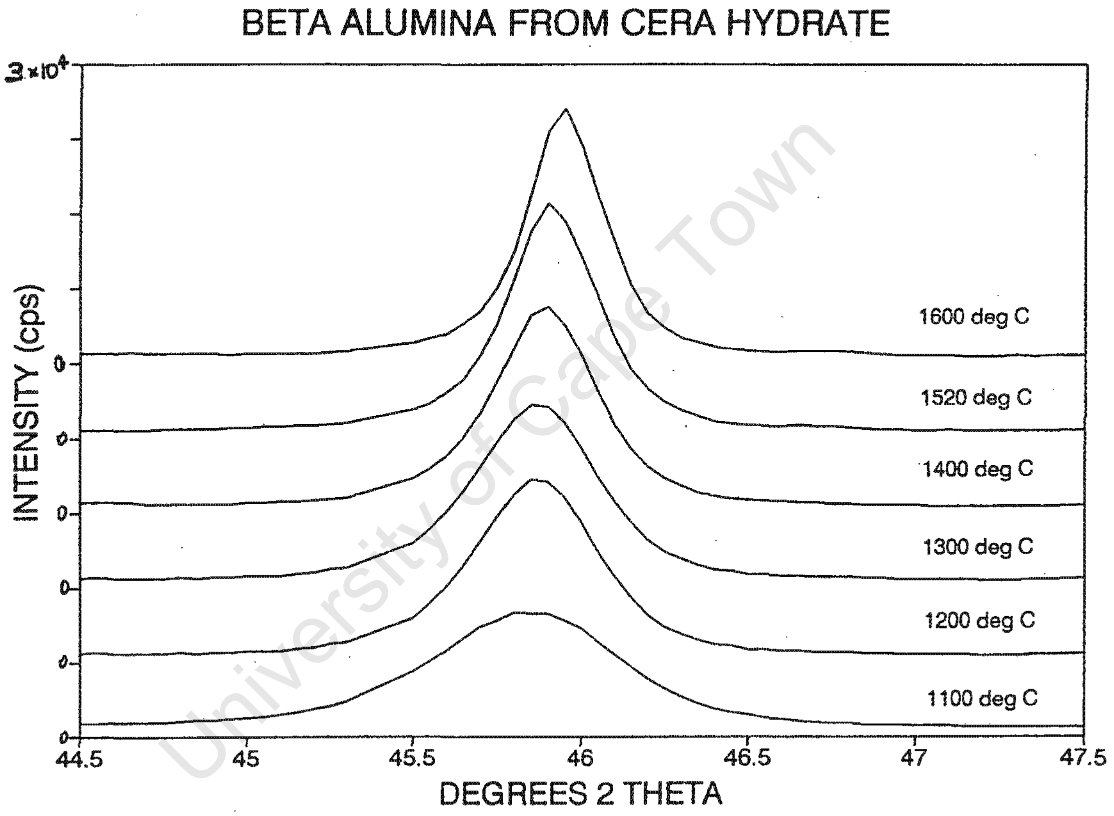


Fig. 5.6: ß"-alumina from boehmite - Cera Hydrate

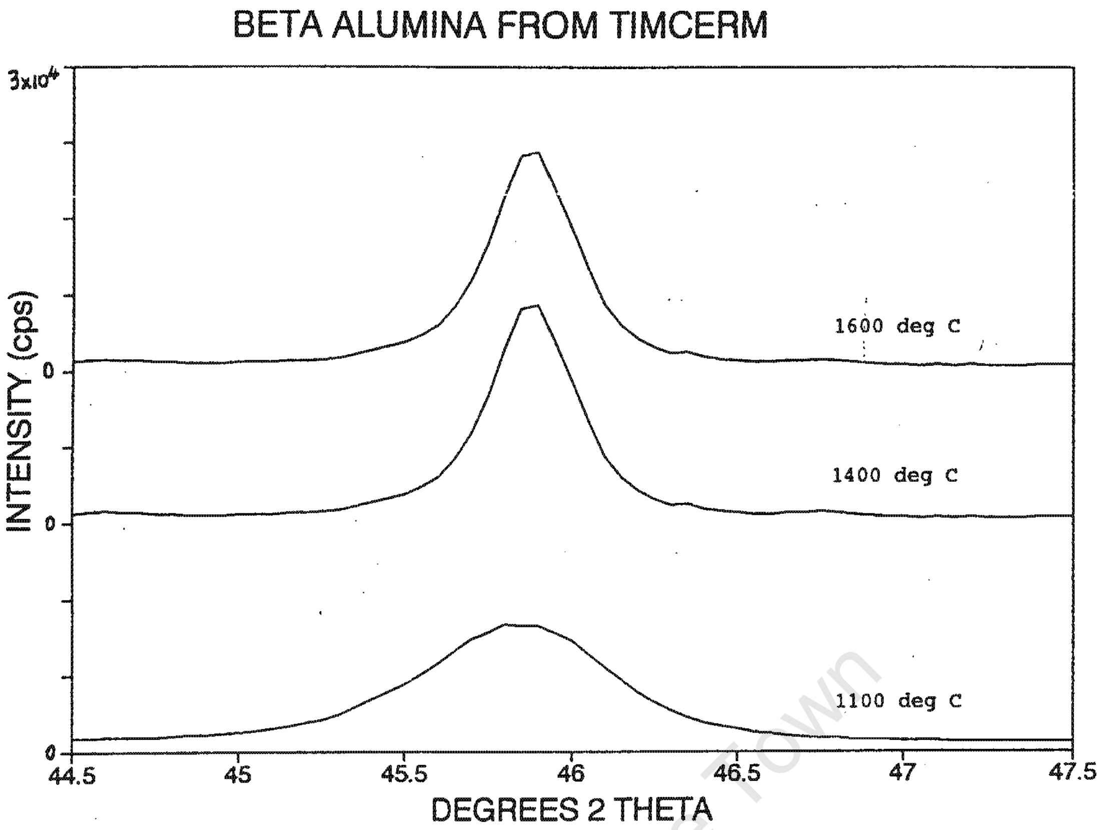


Fig. 5.7: ß"-Alumina from boehmite - Timcerm

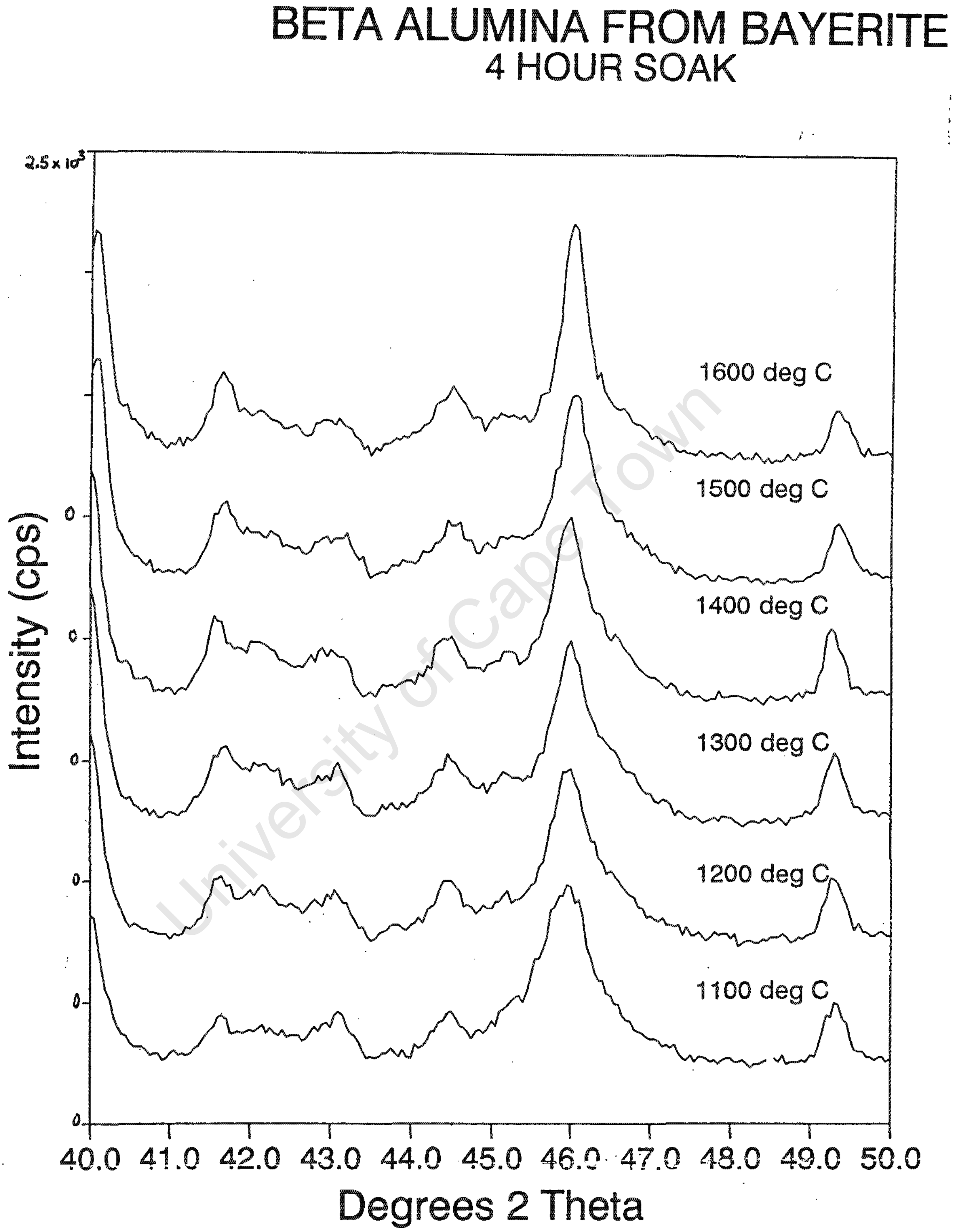


Fig. 5.8: ß"-Alumina from Bayerite - 4 hour soak

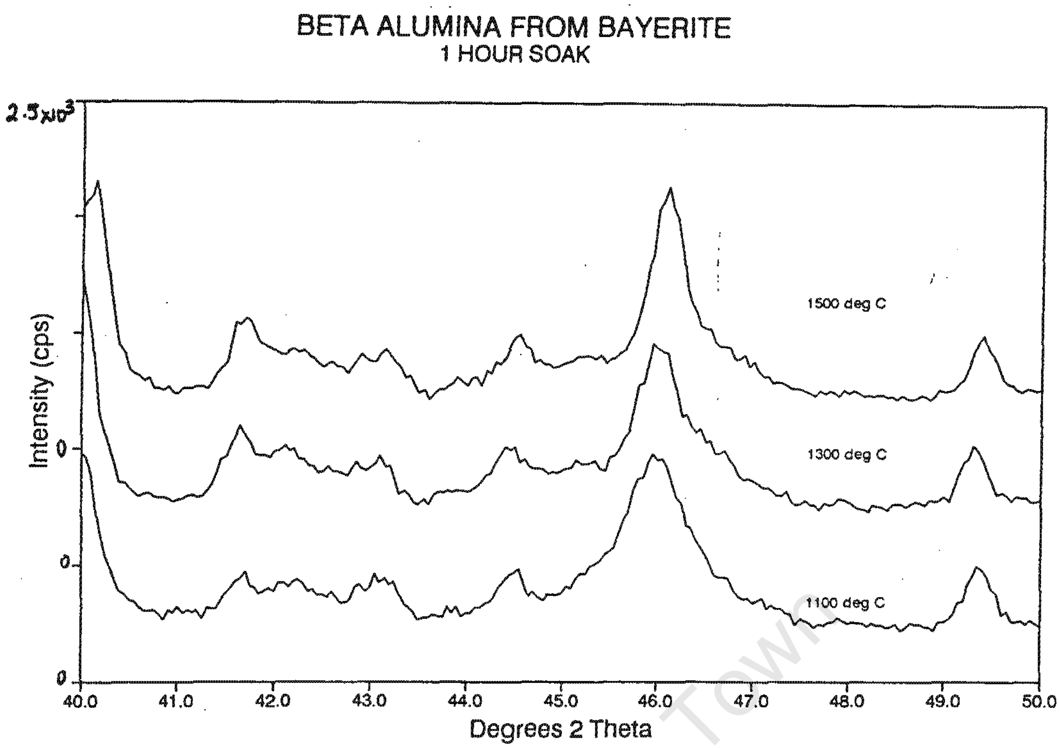


Fig. 5.9: ß"-alumina from Bayerite - 1 hour soak

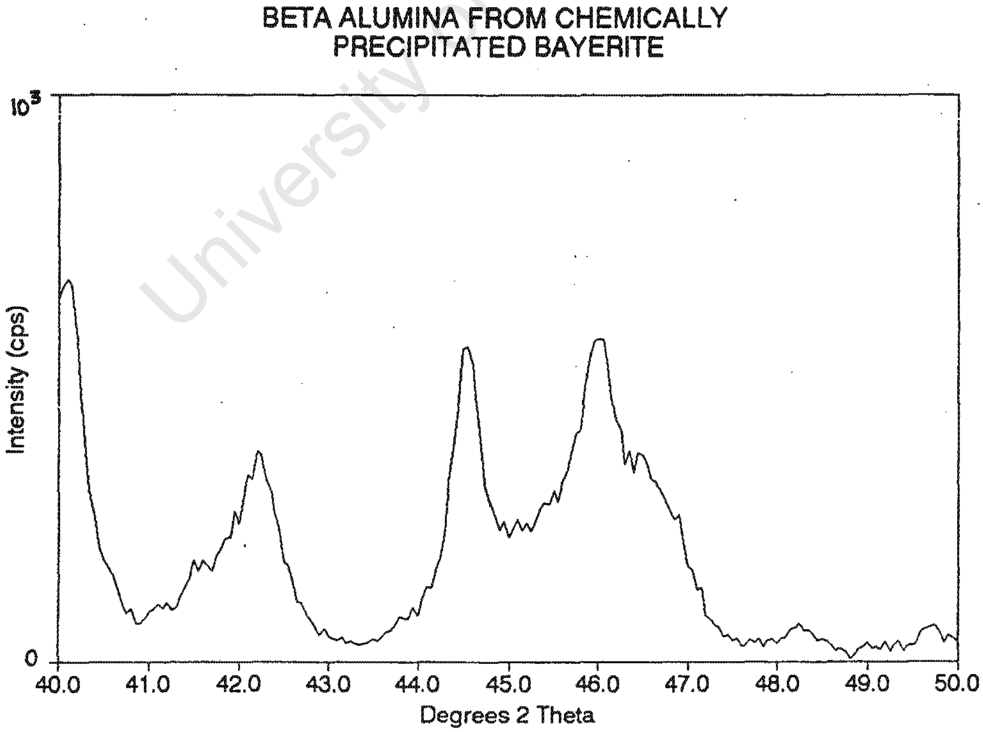


Fig. 5.10: Mixed ß"- and ß-alumina from chemically precipitated bayerite

Using the equation

$$\%\beta = 2{,}29\ I_{(026)} / (2{,}29\ I_{(026)} + I_{(0210)})$$

derived from the work of Pekarsky and Nicholson (1980) as discussed above, the amount of ß-alumina present was estimated to be 68.5 percent.

5.3 DISCUSSION.

The amount of sodium lost during firing appears to have been limited sufficiently by the method of stacking five discs together such that the stoichiometric composition of the central disc was maintained.

The densities achieved by the boehmite derived ß"-alumina are approximately the theoretical density of the material. There appears to be no need to employ a firing temperature higher than 1250 to 1300°C in order to ensure full densification of the powder compact.

The lower densities achieved by the bayerite derived ß"-alumina may be attributed to the slightly coarser powder used as starting material. Kalsi et al (1984) found that the sintered density of ß"-alumina was independent of uniaxial compacting pressure, but decreased with an increase in particle size of the powder.

X-ray diffraction was found to be a simple yet precise way of determining the ß/ß"-alumina ratio. The beta alumina derived from both pure boehmite and pure bayerite was found to consist entirely of ß"-alumina, as predicted by Van Zyl(1987). A fully crystalline ß"-alumina structure could be achieved by firing at temperatures as low as 1200°C in both cases. Where a mixture of aluminium hydroxide precursors was reacted to form beta alumina, a mixture of ß- and ß"-alumina was obtained, as expected from the investigations of Van Zyl (1987).

6. CONCLUSION.

The conventional route for the formation of beta alumina has involved the high temperature solid state reaction of α-alumina with soda and lithia or magnesia, and resulted in a mixture of β- and β''-alumina. A second heat-treatment was then necessary to maximise the amount of β''-alumina in the mixture in order to ensure the optimal conductivity of the solid electrolyte material. Van Zyl (1987) demonstrated that by replacing the α-alumina component with an aluminium hydroxide precursor that has a compatible oxygen sub-lattice, it was possible to form virtually single phase β''-alumina directly. The two precursors which best fulfilled this condition were found to be boehmite and bayerite.

This study has investigated the possibility of synthesising the necessary aluminium hydroxide precursors directly from readily available chemicals in order to further simplify the production process of beta alumina. The differences in structure of the aluminium trihydroxides and oxyhydroxides have been highlighted and effective methods of identification discussed. In particular, historical problems of the incorrect identification of the polymorphs have been addressed.

A study of the methods of synthesis reported in the literature for these trihydroxide and oxyhydroxide polymorphs was conducted and several methods were examined experimentally. Efforts to synthesise boehmite by simple reaction at room temperature were unsuccessful, consistently yielding pseudoboehmite, and confirming that boehmite is a hydrothermally formed phase which can only be synthesised under conditions of simultaneous high temperature and pressure. The introduction of such a reaction step would re-incur the energy cost which this investigation sought to avoid, although this may still be lower than the cost of the α-alumina route depending on the economies of scale.

The synthesis of bayerite proved more successful, although not without difficulty. By manipulating the reaction conditions, particularly pH and washing to remove extraneous ions, well-crystallised bayerite was formed by simple reaction at ambient conditions. This offers a route for the direct synthesis of bayerite from readily available chemicals with no cost penalties from extra heat-treatment steps. It may also promise a route for the direct synthesis of β''-alumina from such starting materials without the intermediate precursor drying stage, if the efficient removal of undesirable ions can be achieved. This may be an area for future investigation.

Unfortunately, a mixture of bayerite and pseudoboehmite was frequently formed under seemingly identical conditions. This is problematic as it will lead to the formation of a mixture of β- and β''-alumina. A greater understanding of factors controlling the reaction is necessary in order to overcome this obstacle.

A study of the mechanisms of formation presented in the literature was conducted, and certain common factors identified. There appeared to be agreement that the polymorph type is determined at the polymerisation stage by the general chemical environment. The assertion that an alkaline environment favours the formation of bayerite was supported by experimental evidence. Furthermore, the fact that any ions, solvent or impurities act to stabilise amorphous structures relative to crystalline forms was widely identified and confirmed in experiment.

However, the formation of gels and the role they play in the reaction mechanism remains poorly defined. This is an obstacle to effective control of the reaction to give the reproducible results necessary for larger scale production, and is an area in which more detailed study is required. A comprehensive and coherent mechanism of formation needs to be derived as the basis for further experimental investigation and optimisation of the process.

Finally, the synthesis of ß"-alumina by the solid state reaction of the hydroxide precursors with sodium- and lithium carbonate, was successfully completed. The beta alumina derived from both pure boehmite and pure bayerite was found to consist entirely of ß"-alumina.

Where a mixture of mixture of crystalline bayerite and amorphous pseudoboehmite was reacted to form beta alumina, a mixture of ß- and ß"-alumina was formed. No investigation of varying ratios of intimately mixed polymorphs on the ratio of ß- to ß"-alumina was conducted. Future examination of this relationship may yield information concerning the effects of seeding on the solid state reaction and on the kinetics of the reaction. An understanding of this will be necessary if it proves impractical to obtain consistently pure bayerite by the method described.

In conclusion, it is possible by reaction of $AlCl_3.6H_2O$ with Na_4OH at ambient temperature to form bayerite, an aluminium trihydroxide polymorph having the ideal oxygen sublattice structure for the direct formation of pure ß"-alumina by solid state reaction. This offers the opportunity for significant cost savings in the production of beta alumina products by eliminating the need for a second heat-treatment stage to optimise the ratio of ß- to ß"-alumina. The possibility of further simplifying the synthesis route by eliminating the drying stage, that is adding the ingredients for the solid state reaction directly to the polymorph slurry, may exist. However, further work on understanding and controlling the reaction conditions will be necessary before this could be achieved.

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