BAYERITE: ELECTROCHEMICAL SYNTHESIS AND MECHANISM OF FORMATION

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ABSTRACT

A novel method of synthesis is reported for the preparation of pure and well crystallised bayerite, an aluminium hydroxide generally not obtained alone. The technique used is based on electrolysis with a cation exchange membrane between the anolyte and the catholyte. The obtained compound is then characterised using seven different techniques, namely XRD, SEM, ICP, laser diffraction, BET area, density and TGA. Our study of the kinetics of Al(OH)₃ precipitation in aqueous alkali solution and theoretical calculations allowed us to propose a reactional mechanism for the nucleation process of crystallised
Al(OH)$_3$ and also for formation of an alumino-gel. The existence of an intermediate alinate species in solution as a precursor of bayerite is shown in this work.

**INTRODUCTION**

This paper is devoted to a novel method of synthesis of pure and perfectly crystallised bayerite, Al(OH)$_3$. The synthesis of good quality bayerite was interesting on the one hand with a view of purely fundamental research on this hydroxide, on the other hand for its utilisation as a synthesis product because of its higher reactivity compared to other aluminium hydroxides.

Existing processes given by different authors do not lead to pure well-crystallised bayerite. Coprecipitation of gibbsite (hydrargillite), nordstrandite, pseudo-boehmite, boehmite and/or amorphous gels frequently occurs. The existing methods consist of (1) direct precipitation of aluminium hydroxide by acid addition into an aqueous solution of an alkali aluminate$^{1,4}$, (2) adjunction of a base on an aluminium salt solution$^{3,4}$, (3) carbonation of an alkali aluminate solution$^{3,5,6}$, (4) ripening of amorphous alumino-gel in water$^{5,7}$, (5) rehydration of transition aluminas$^{8,10}$, (6) decomposition by water on amalgamated aluminium$^{11}$. In each case, parameters such as pH, temperature, reagent concentration, stirring velocity, rate of mixing must be strictly controlled to obtain the desired form of aluminium hydroxide.

The novel synthesis process described in this paper requires a membrane-type electrolysis. During this electrolysis, the anolyte which is an aqueous solution of sodium aluminate is progressively acidified and the precipitation of bayerite will occur. The present work also concerns the investigation of the chemical reactions occurring in solution before and during the aluminium hydroxide precipitation.

**EXPERIMENTAL**

**Experimental Apparatus**

The apparatus (Fig. 1) for the synthesis of bayerite consists of a membrane-type electrolysis cell. The anolyte (aqueous solution of sodium aluminate) and the catholyte (slightly alkaline aqueous solution for ensuring conductivity in the catholyte chamber) were separated by a perm-selective membrane (a NAFION 901-type reinforced composite of perfluorinated carboxylic and sulfonic cation exchange copolymers) which allows Na$^+$ to flow from the anolyte to the catholyte chamber.

On both sides of the cation exchange membrane, 300 mL of solution were introduced. Two nickel flat-plates were used as electrodes with 45 cm$^2$
immersed area, whilst the useful membrane area was 30 cm². Current intensity was fixed at approximately 6 A with a voltage of about 12 V. The electrolysis apparatus was held in position by a plexiglas cell which is inert to basic solution.

Electrolysis Principle

Electrochemical reactions occurring during the electrolysis were merely the water dissociation: (1) H₂O oxidation takes place in the anodic side with the release of oxygen and the liberation of a proton in the anolyte;

$$\text{OH}^- \rightarrow \frac{1}{2} \text{O}_2 \uparrow + \text{H}^+ + 2 \text{e}^-$$

acidification of the solution in the anodic chamber leads to the aluminium hydroxide precipitation. The pH of the anolyte was maintained homogeneous by permanent and swift stirring with a magnetic stirrer. (2) H₂O reduction takes place on the other side of the membrane with the release of hydrogen and the production of hydroxide ions;

$$\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 \uparrow + \text{OH}^-$$

such in cathodic chamber the sodium hydroxide regeneration is allowed with Na⁺ migration through the cation exchange membrane.

According to the literature, experimental conditions in favour of bayerite precipitation during this electrolysis are the following: (1) slow and homogeneous acidification of an alkaline aluminate solution, (2) autogenous temperature of about 50°C at the hydroxide precipitation.

Sample Preparation

It is a well known fact that the method used to prepare these solutions has an influence on their subsequent behaviour. Hence, three initial sodium aluminate solutions prepared by different methods were used. The nature of the aluminium ionic species present in the solution depends on the way in which it was produced. It seems that parameters such as temperature, concentration, ageing, stirring, starting products and other ions present in the solution have a great influence on the aluminate species formed in solution and, hence, on the subsequent aluminium hydroxide precipitated with these solutions.

For the three sodium aluminate solutions used, concentrations were adjusted so as to achieve a final solution with 1 mol/L of free NaOH and a ratio $\frac{Na}{Al} = 6$:

**Solution 1:** Prepared by oxidation of aluminium metal chips in sodium hydroxide solution (14 g of Solvay caustic soda NaOH dissolved in 300 mL distilled water in which 1.353 g of Pechiney aluminium chips, 99.9% pure, were introduced). The reaction occurred in a polyethylene bottle at room temperature using a cooling bath in order to control the kinetics of this highly exothermic reaction.

**Solution 2:** Preparation identical to that of Solution 1 with an ageing period of one month at room temperature in a polyethylene bottle in a CO₂-free atmosphere. The solution was filtered before the electrolysis to eliminate the light precipitate formed at the surface of the solution during ageing.

**Solution 3:** Prepared by dissolving sodium aluminate powder in sodium hydroxide solution (12 g of Solvay caustic soda NaOH and 4.918 g of Prolabo sodium aluminate coarse powder were dissolved in 300 mL distilled water).

A fourth solution without aluminate (merely a sodium hydroxide solution with 1 mol/L NaOH) was used as a reference solution in order to understand the phenomena observed in the three aluminate solutions before, during and after the Al(OH)₃ precipitation.
Methods of Analysis

XRD analysis: the XRD apparatus is a Guinier type chamber ($\varnothing = 114.6$ mm) using filtered Co radiation ($K_a = 1.78897$ Å). Guinier films were read with an LS20 optical densitometer and the data treated successively by the ScanPil and Diffrac-AT programs. The cell parameters were refined by using silicon as an internal standard using the Ufit program. The pH was measured with a Tacussel Isis 20 000 type pH meter and a Tacussel XG200 type glass electrode. SEM (scanning electron microscopy) observations were made to determine the morphology of the obtained bayerite particles. ICP-emission and ICP-MS (inductive coupling plasma with, respectively, atomic emission spectroscopy and mass spectroscopy) analysis were used to determine the purity of the obtained bayerite powder. Granulometric analysis was done by laser diffraction with a Malvern Mastersizer granulometer. The specific surface area was calculated by the BET method with a volumetric method to determine the krypton adsorption isotherm (desorption of sample at room temperature until a residual pressure of $10^{-3}$ torr followed by a Kr adsorption at 77 K). The density was determined by a pycnometric method using decalin at 30°C as a reference. Thermogravimetric analysis using a self-regulating Chenouard-Joumier type oven (room temperature to 800°C with a heating rate of $3^\circ$C/min. in a nitrogen inert atmosphere) connected to an electronic Ugea Eyraud system B70 type beam scale.

RESULTS AND DISCUSSION

Electrolysis Study

As planned, the following reactions were observed: catholyte basification showing the NaOH regeneration and anolyte acidification where a white precipitate can be observed after about two hours of electrolysis. The precipitate

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<th>30</th>
<th>60</th>
<th>90</th>
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obtained from Solution 1 is strongly encrusted on the walls of the plexiglas reactor. This aluminium hydroxide forms a very fine powder. The X-ray diffraction pattern is shown on Fig. 2. It indicates a pure and perfectly crystallised bayerite (the yields of this reaction product are indicated in Table I).
precipitates obtained from Solutions 2 and 3 are more sticky and very poorly
crystallised products.

The values of temperature and hydroxyl concentration in the anodic
chamber during electrolysis are represented as a function of time in Fig. 3 and 4a,
respectively. These measurements are made for the four solution. The curves
obtained with the fourth NaOH solution are used as ‘blank’ curves. Such
measurements permit us to follow the kinetics of the reactions.

The autogenous temperature variation during experimentation is
approximately the same in the four basic solutions. Hence, the temperature
parameter cannot be exploited to explain the different final products obtained.

On the other hand, a comparison of the hydroxyl concentration curves for
the three aluminate solutions during the electrolysis are rather interesting. These

Fig. 3. Variation of the Anolyte Temperature During Electrolysis

Fig. 4. Hydroxide Anion Concentration in the Anolyte During Electrolysis
a: Variation of [OH⁻] for the different anolytes.
b: Three different steps observed in Solution 1.
are reported in Fig. 4a. The three curves start at an identical value of the [OH⁻] concentration, that is approximately 1 mol/L, identical to that of the reference solution. However, after a few minutes of reaction, the aluminate solutions show a more pronounced decrease on the [OH⁻] concentration curve in comparison with the fourth simple NaOH anolyte. In Solution 1, this decrease is also more pronounced but occurs at a later stage, after 80 minutes. Beyond 110 minutes, when the hydroxide precipitate becomes visible, we note a distinct increase on the [OH⁻] curve for Solution 1 only (where the solid formed is a perfectly crystallised bayerite), which progressively rejoins the reference curve. This interesting and reproducible hook observed on the [OH⁻] curve for Solution 1 could lead to the key to understanding the crystallisation process, as it corresponds to the precipitation of a well crystallised bayerite. In Solutions 2 and 3, where the precipitate is an amorphous gel which occurs earlier, the [OH⁻] concentration decreases continuously until 120 minutes and then maintains a constant value.

It appears from these results that the kinetics of formation of an aluminogel and of crystallised bayerite are different, and hence must be explained by different mechanisms.

**Physico-chemical Characteristics of the Bayerite Obtained in Solution 1**

As can be seen in Fig. 2, the X-ray diffraction pattern of the precipitate obtained in Solution 1 reveals a perfectly crystallised bayerite where no other phases are detected. The refined monoclinic parameters (space group P2₁/c) are: \(a = 6.901(2) \text{ Å}, b = 8.668(3) \text{ Å}, c = 5.061(2) \text{ Å} \) and \(\beta = 136.92(2)°\). These values are in good agreement with those reported in the literature\(^9\).

The igniting loss (see Fig. 5) indicates a value of 35.0%, slightly greater than the theoretical value of 34.6% obtained in the case of complete dehydration of Al₂O₃·3H₂O.

![TGA graph](image)

**Fig. 5. Thermogravimetric Analysis on Bayerite Obtained in Solution 1**

The specific surface area has a value of 1.4 m²/g and granulometric measurements indicate the following distribution: \(d_r(0.1) = 9.4 \text{ μm, } d_r(0.9) = 32.8 \text{ μm and } d_r(0.9) = 68.5 \text{ μm. These results are illustrated in Table II. The sizes of particles obtained by the laser diffraction technique compared to those measured directly by the SEM technique (see Fig. 6a) indicate that grains form aggregates. The grains have an oval shape clearly visible in Fig. 6a. They are formed by crystallites with triangular faces (Fig. 6b) characteristic of the pseudo-trigonal symmetry encountered in this compound.\(^9\)

The density has a value of 2.513 g/cm³, compared to the theoretical value of 2.51 g/cm³.

The chemical purity of this powder was evaluated by ICP-emission and ICP-MS analysis. It contains only very small amounts of impurities due to the preparation method: 0.08 weight per cent of Na from the solution and 0.01 weight per cent of Ni from the anode. No other impurity was detected in the final product.
The fact that the pH decreases faster in sodium aluminate solutions than in the reference NaOH solution suggests that the starting aluminate species in solution was subject to a chemical reaction which involves hydroxyl anion consumption. This reaction could be at the origin of the formation of new aluminate species in solution which are precursors of the subsequent hydroxide precipitate.

In the initial basic solution, the predominant aluminate species consists of tetrahedral monomeric \([\text{Al(OH)}_4]^-\) ions. In the final \(\text{Al(OH)}_3\) compound, the aluminium atoms are six-fold coordinated. The change from a four-fold to a six-fold coordination could be done in the solution by the way of intermediate species, considered as precursors of the solid form of \(\text{Al(OH)}_3\). The octahedral species \([\text{Al(OH)}_6]^{2-}\) was envisaged earlier as such a precursor. Recent calculations based on a semi-empirical quantum mechanical molecular model have shown that this monomeric species doesn’t exist, but we have shown the existence of the tetramer \(\left[\text{Al}_4\text{(OH)}_{12}\right]^{16-}\) and \(\left[\text{Al}_4\text{(OH)}_{16}\right]^{16-}\) species. These aluminate are stable enough to be considered as potential precursors. Moreover, the polymerisation gives rise either to a T-shaped or a linear tetramer. Their chemical formulas are reported in Fig. 7. The assumption of a T-shaped tetramer as a bayerite or gibbsite precursor made in reference 1 is justified by the fact that its geometrical shape corresponds well to that of the bayerite structure as can be seen by comparison of Fig. 7 and Fig. 8.
Fig. 7. Chemical Formula of the Tetramer
a: Linear and neutral \[\text{Al}_4(\text{OH})_{12}\] tetramer with [4-5-5-4] co-ordination.
b: Linear and charged \[\text{Al}_4(\text{OH})_{18}\] tetramer with [6-6-6-6] co-ordination.
c: T-shaped and neutral \[\text{Al}_4(\text{OH})_{12}\] tetramer with [4-6(4)-4] co-ordination.
d: T-shaped and charged \[\text{Al}_4(\text{OH})_{18}\] tetramer with [6-6(6)-6] co-ordination.

Fig. 8. Bayerite Layer Structure (in the monoclinic P2_1/c space group)
a: projection on the (100) plane.
b: projection on the (010) plane.

Taking into account the potential precursors of the \text{Al(OH)}_3 formation and the experimental results, two possible mechanisms have been developed, one for the formation of crystallised bayerite, the other for the formation of alumino-gel.

Proposed Mechanism of the Crystallised Bayerite Formation

As it is shown in Fig. 4b, the mechanism leading to bayerite formation can be broken down into three steps.

**Step 1:** formation of the T-shaped and neutral tetramer

\[4 \text{Al(OH)}_3(\text{H}_2\text{O}) \rightarrow \text{Al}_4(\text{OH})_{12} + 4 \text{H}_2\text{O}\]

The concentration of the neutral tetramer species increases with time and probably reaches a maxima at \(t = 80\) minutes.
At a relatively high concentration, neutral \([\text{Al}_4(\text{OH})_{12}]\) is transformed into \([\text{Al}_4(\text{OH})_{18}]^{6-}\) according to the reaction:

\[
[\text{Al}_4(\text{OH})_{12}] + 6 \text{OH}^- \rightarrow [\text{Al}_4(\text{OH})_{18}]^{6-}
\]

The concentration of \([\text{Al}_4(\text{OH})_{12}]\) at \(t = 80\) minutes is high enough in the basic solution to give rise to this reaction in which six hydroxyl ions are consumed, hence the fast decrease of the \([\text{OH}^-]\) concentration during this second step. Here, all conditions are fulfilled to start the nucleation process.

**Step 5: nucleation process**

Two successive equilibrium reactions can describe this process:

\[
[\text{Al}_4(\text{OH})_{12}] + [\text{Al}_4(\text{OH})_{18}]^{6-} \rightarrow [\text{Al}_8(\text{OH})_{30}]^{6-}
\]

\[
[\text{Al}_8(\text{OH})_{30}]^{6-} \rightarrow [\text{Al}_6(\text{OH})_{24}] + 6 \text{OH}^-
\]

which can be further structurally and schematically as follows:

\[\text{ring formation}\]

**Proposed Mechanism of the Amorphous Alumino-gel Formation**

A gel is characterised by a non-organised framework, meaning that the polymerisation process leading to its formation is not as restricted by the geometry as in the case of the formation of an ordered framework. Hence, the gel formation can be described as a continuation of the polymerisation starting with the simplest form of tetramer, the linear and neutral tetramer symbolised as \([4-5-5-4]\) (see Fig. 7). An example of the continuation of the polymerisation reaction could be expressed as follow:

\[\text{[4-5-5-4]} + [4] \rightarrow \text{[4-5-5-5-4]}\text{ or } [[4],6-5-4-4]\]

where a linear tetramer reacts with a four-fold coordinated monomer, symbolised as \([4]\), leading to two possible species. Indeed, the connection between the different species leading to more complicated polymerised forms is controlled by less drastic geometrical conditions than for the bayerite formation. The connections can occur elsewhere along the linear polymer. Thus, the polymerised chains are not periodically ordered leading to an alumino-gel formation.

The continuous variation seen on the \([\text{OH}^-]\) curve is in agreement with this model. Indeed, contrary to the bayerite nucleation process previously
discussed, this model does not show any discontinuity for the hydroxyl free ion consumption.

Notice that in this model, the aluminium atoms in the fresh amorphous gel are not necessarily only six-fold coordinated, but can also be four or five-fold coordinated, in agreement with the literature.\textsuperscript{24,25}

CONCLUSIONS

Our results show how to obtain pure and well crystallised bayerite by electolysis synthesis. Moreover, it is shown that the precipitation of $\text{Al(OH)}_3$ from an alkali aluminate solution occurs with possible intermediate species, which are precursors of the subsequent aluminium hydroxide formed. The form of the $\text{Al(OH)}_3$ obtained, either crystallised or amorphous, is dependant on the geometrical shape of the precursors. Two types of polymerisation from the precursors are possible: ring polymerisation from a T-shaped tetramer, and linear polymerisation from a linear tetramer, which, respectively, involve a crystallised bayerite and an amorphous alumino-gel. In the case of bayerite precipitation, the existence of an aluminate precursor species in solution with aluminium in octahedral coordination was linked to the hook observed on the $[\text{OH}^-]$ kinetic curve.

Factors which favour the formation of a T-shaped precursor compared to that of the linear precursor are yet to be discovered. The analysis of the starting solutions which differ merely by the method of preparation may lead to some answers. The physico-chemical properties in such more or less colloidal aluminate solutions could thus be dependant on the preparation. An $^{27}$Al NMR study of the different starting solutions could clarify this point.

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