

## Effect of urea on decomposition of sodium aluminate solution



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### ABSTRACT

Aluminium hydroxide particles were synthesized from sodium aluminate liquor by urea decomposition method at elevated temperatures in presence and absence of seed. Different parameters such as alumina to caustic (A:C) ratio, temperature, time period of precipitation, urea concentration, etc. were studied. Characterisations of the products were also carried out using X-ray diffraction, scanning electron microscopy, TG-DTA, etc. In general, higher precipitation ratios were observed with the addition of urea in sodium aluminate solution. Temperature was found to have a significant role in precipitating aluminium hydroxide with higher yield enhancement ratio compared to that obtained at lower temperatures. Higher precipitation ratios were also obtained with urea at elevated temperatures under available supersaturation. In the presence of urea, the precipitation ratios on yield enhancement front were observed to increase with decrease in A:C ratio. It has been observed that the liquor concentration reached below the equilibrium solubility limit after 30 h of precipitation when 460 mmol/L urea is added. The synthesized aluminium hydroxide particles showed gibbsitic nature and globular morphology, with agglomerates of mostly hexagonal platelets, as revealed through XRD and SEM studies, respectively. Calcination of the product at 1000 °C results in weight loss similar to that observed with gibbsite. Endothermic peaks at 325 °C and 550 °C revealed through DTA study indicated boehmite and chi-alumina transformations, respectively. The possible mechanism of urea decomposition method is also discussed.

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### 1. Introduction

Both the Bayer and the sintering [1,2] processes are used for the production of alumina via decomposition of metastable sodium aluminate solution. Bayer process mainly utilizes gibb bauxite ores through NaOH digestion for the production of sodium aluminate solution. Whereas in sintering process low grade diasporic/boehmitic bauxite or nepheline or other alumino silicates [1,3,4] are used by sintering it with sodium carbonate at high temperatures to form sodium aluminate solution after leaching the sintered mass. In the Bayer process sodium aluminate is decomposed through seeded precipitation method to obtain aluminium hydroxide whereas carbonization decomposition method is used for its recovery from leach solution. In Bayer method some of the sodium hydroxide transformed to sodium carbonate due to atmospheric CO<sub>2</sub>. This carbonate is in turn treated with lime to get back sodium hydroxide before being recycled for

further bauxite digestion. Generally in industries during precipitation of gibbsite in Bayer circuit, the alumina concentration could not be brought down to equilibrium solubility limit. However, in carbonization decomposition method more than 90% alumina is precipitated. As a result, the alumina concentration in the liquor goes well below equilibrium solubility limit. To enhance the precipitation ratio in Bayer aluminate decomposition process various efforts were made [5–18]. Activation [5–9] of seed hydrate is one of such methods but not yet commercialized due to additional steps and higher energy consumption. Addition of different polymers, surfactants, inorganic and organic additives [10–18] did not show encouraging results. Moreover, these additives would spoil the solution to a great extent as unwanted cations and anions are introduced which accumulate with time due to the cyclic nature of the Bayer process.

In this paper an attempt has been made to evaluate the effect of urea (NH<sub>2</sub>CO•NH<sub>2</sub>) in sodium aluminate liquor and the extent to which it can be utilized in decomposition of aluminate liquor under seeding condition. The decomposition of aluminate liquor is related to the supersaturation (Al<sub>2</sub>O<sub>3</sub>: Na<sub>2</sub>O, i.e. A:C ratio and temperature) level of the solution. However, the excessive supersaturation, particularly greater than 1.05 (A:C) or so, leads to the instability of the solution. This results in precipitation of hydroxide

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at various inappropriate locations during the operation leading to the loss of alumina and damage to the various equipment [12]. Therefore, excessive supersaturation should be avoided. Further, the release of hydroxyl ion ( $\text{OH}^-$ ) into the system during hydrolysis leads to the slowing down or finally stoppage of further hydrolysis. Consequently, NaOH concentration in the solution increases leading to low A:C ratio, i.e., supersaturation falls to a lower value. The following equation shows the decomposition of aluminate ion.



To enhance the hydrolysis of aluminate liquor,  $\text{OH}^-$  liberated should be consumed so as to continue the hydroxide precipitation process.

Urea is generally used for precipitating spherical hydrated basic aluminium salts, oxides etc. and high pure specialty alumina by utilizing it as hydrolysing precipitant for aluminium salt solutions at elevated temperatures [19,20]. As it slowly releases  $\text{NH}_4^+$ ,  $\text{CO}_2$  and hydroxyl ions at elevated temperatures, the pH of the solution increases and results in the precipitation of spherical basic aluminium salts. Use of urea as an additive for aluminium hydroxide precipitation would be advantageous in many respect; (i) the product would be free from any contamination; (ii) urea is cheap and available on plenty; (iii) urea is an ecofriendly chemical.

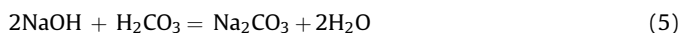
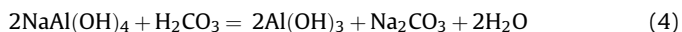
In the present study at elevated temperature urea decomposes to give  $\text{NH}_3$  and  $\text{CO}_2$  and in this case  $\text{CO}_2$  is mainly responsible for hydrolysis of aluminate solution. This process may be analogous to carbonization decomposition process. But the later carbonization decomposition is utilized for total decomposition of the solution whereas the idea in this study is to find an extent to which urea can be utilized in addition to seed effect because in all the Bayer plants conversion of sodium carbonate to sodium hydroxide is carried out routinely.

### 1.1. Conceptual mechanism of urea assisted aluminium hydroxide precipitation

The carbonization decomposition process [21,22] is one of the major steps in sintering process for producing aluminium hydroxide. In carbonization decomposition process  $\text{CO}_2$  gas is introduced into sodium aluminate solution to precipitate aluminium hydroxide. There are various mechanisms of precipitation of aluminium hydroxide in carbonization process discussed by Li [2]. The carbon dioxide when added to aluminate liquor either neutralizes (Eq. (2)) sodium hydroxide present in the solution thereby increasing the A:C ratio which leads to continuous precipitation or direct decomposition of sodium aluminate to aluminium hydroxide (Eq. (3)).



In another opinion [2]  $\text{CO}_2$  first forms carbonic acid which then decomposes sodium aluminate to form aluminium hydroxide and sodium carbonate.



According to Besuzin as mentioned by Li [2] carbon dioxide first reacts with  $\text{OH}^-$  ion and reduces the activity of  $\text{OH}^-$  ion as follows,



As the concentration of  $\text{OH}^-$  decreases, the polymerization of aluminate species increases and forms aluminium hydroxide precipitates.

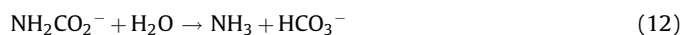
As regards seeded precipitation method, sodium aluminate solution decomposes under seeded condition where seed provides the surface onto which new particles nucleates and grows. The hydrolysis reaction taking place as follows, producing  $\text{Al(OH)}_3$  and NaOH.



Generation of NaOH as per the above reaction (9) reduces the A:C ratio continuously, thus decreasing the super saturation level to such an extent where further precipitation is stopped. In case  $\text{OH}^-$  is consumed by some other means, the supersaturation level stabilizes producing continuous precipitation.

The use of urea to precipitate aluminium hydroxide from sodium aluminate liquor was not reported earlier. It has been discussed in literature [23–25] that urea dissociation in aqueous system produces ultimately  $\text{NH}_3$  and  $\text{CO}_2$  but various mechanisms occur before the formation of  $\text{NH}_3$  and  $\text{CO}_2$ . As our system is consisting of sodium aluminate, sodium hydroxide and  $\text{H}_2\text{O}$ , the reaction pathway may not follow a simpler rule like in pure aqueous system. At neutral pH, activation energy for urea decomposition varies from 28.4 to 32.4 kcal/mol [26] and in alkaline medium the activation energy calculated was 22 kcal/mol [27]. Therefore under alkaline condition decomposition of urea is easier than in neutral pH.

In aqueous system urea decomposes at an elevated temperature to cyanate and ammonium ions [28–30]. This cyanate ion then hydrolyses to carbamate anion which subsequently hydrolyses to bicarbonate ion [31] as per the following equations.



$\text{HCO}_3^-$  then reacts with  $\text{OH}^-$  ion to produce  $\text{CO}_3^{=}$  as follows



Thus  $\text{OH}^-$  concentration in the solution decreases with enhanced aluminium hydroxide precipitation ratio along with the formation of sodium carbonate.

## 2. Experimental

### 2.1. Chemicals and apparatus

The chemicals used in this study are of analytical grade and obtained from Merck, India. Supersaturated sodium aluminate solution was prepared by dissolving measured quantity of aluminium granules in sodium hydroxide solution. In the present study the mass ratio of  $\text{Al}_2\text{O}_3$  to  $\text{Na}_2\text{O}$  (A:C) was varied from 0.9 to 1.0. During the precipitation study, temperature was maintained between  $60^\circ$  to  $80 \pm 0.1^\circ \text{C}$ . The gibbsite seed ( $d_{50} = 62.2 \mu\text{m}$ ) used for this study was obtained from NALCO, Bhubaneswar, India.

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