

Additive action on boehmite precipitation in sodium aluminate solution

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Precipitation of boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) instead of gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) from sodium aluminate liquor can be an energy saving option for alumina production. Gibbsite is stable at precipitation temperature lower than 90 °C. Thus when boehmite is precipitated below 90 °C it is always accompanied with a gibbsite phase. However, the addition of certain organic additives favours precipitation of a monophasic product *i.e.* boehmite at a temperature lower than 90 °C. At a temperature as low as 60 °C additives like tartaric acid, xylose and glucose could favour the precipitation of single phase boehmite precipitation. The role of the additive is proposed to be complete inhibition of gibbsite formation and facilitation of boehmite nucleation through different extent of complex formation by multidentate ligands.

1. Introduction

The Bayer process is mainly adopted for precipitation of gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). Several attempts have been made to precipitate boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) from sodium aluminate liquor. Boehmite precipitation is an energy saving option because it needs to remove only one water molecule as compared to three water molecules in the case of gibbsite. Though this technique is not yet commercialised, laboratory scale experiments were carried out at above 100 °C,¹ 90 °C,² and as low as 60 °C.³ Various other low temperature boehmite precipitations from emulsion and aqueous system of aluminium salts^{4,5} and alkoxides^{6–9} have been found in the literature. For the synthesis of materials with nano-structures, for mostly non-metallurgical applications, a strategy of “synthesis with construction” is being adopted by these research schools.¹⁰

In the case of boehmite precipitation from sodium aluminate liquor, when the temperature is below 90 °C and alumina/caustic ratio is ≥ 1 , the precipitate is always accompanied by gibbsite. Trials had been taken to avoid the precipitation of gibbsite along with boehmite by using some organic additives, for example, tartaric acid and oxalic acid *etc.* were used in boehmite precipitation.¹¹ A monophasic product containing only boehmite was obtained at a range of temperatures of 60–80 °C. The additives, otherwise known as nucleation inhibitors, also help in stabilization of sodium aluminate in solution resulting in decrease of the supersaturation, reducing the driving force for precipitation of aluminium hydrate.¹² These additives do not allow the gibbsite nucleation, which generally gets accompanied with boehmite formation at temperatures lower than 90 °C. Gibbsite inhibition could be carried out by a number of organic additives like polyols such as ethylene glycol, glycerol, erythritol, arabinitol and mannitol,¹³ acyclic polyols,¹⁴ sodium gluconate,¹⁵ alditols and hydroxycarboxylic acids¹⁶ and oleic acid.¹⁷ Original Bayer liquor contains various humic acids which, inhibit the gibbsite precipitation and yield which is finally reflected through its crystal morphology.¹⁸ Crystal morphology is sensitive for the binding of the additives through oxy-functional groups with the surface hydroxyl groups of gibbsite,¹⁹ steric

effects²⁰ and the number of carboxylic acids and the distance between them for polyacids.²¹

During the process, some common additives, mostly some low-molecular-weight organic carboxylates degrade in a synthetic Bayer liquor at 90–180 °C.²² Aliphatic carboxylates without hydroxyl substituents were stable at 90 °C but decomposed at 180 °C, except for formate, acetate, oxalate and succinate, which were stable even at 180 °C. Both aliphatic and aromatic carboxylates with hydroxyl substituents were unstable at 90 °C except for lactate and 4-hydroxy-benzoate. The present investigation is an attempt to reduce the temperature of boehmite precipitation by adding various organic additives with carboxylic and/or hydroxylic groups. The present study also investigates the probable mechanism of boehmite precipitation.

2. Experimental

2.1. Materials

Boehmite seed was prepared hydrothermally from gibbsite supplied from M/s NALCO, Bhubaneswar, India. Aluminium granules and sodium hydroxide (AR) obtained from Merck, India. The additives like tartaric acid, oxalic acid and EDTA (Rankem, India); succinic acid, salicylic acid, glutaric acid and citric acid (Acros Chemical, India); aspartic acid, xylose, glucose and glycerol (Merck, India) were used during precipitation study.

2.2. Preparation of sodium aluminate liquor

Sodium aluminate liquor was prepared by dissolving metallic aluminium granules (67.5 g L^{−1} to have 150 g L^{−1} of alumina) in sodium hydroxide (193.54 g L^{−1} to have 150 g L^{−1} of caustic) solution to achieve desired A/C ratio of 1.0. For varied A/C ratio, the amount of aluminium and sodium hydroxides were changed accordingly.

2.3. Preparation of boehmite seed

The boehmite seed was prepared hydrothermally by stirring gibbsite (300 g) in water (1.0 L) for 3 h in a PARR autoclave (Model no. 4542) at 195 °C as reported earlier.³ After the experiment was over the pulp was cooled down and removed from the autoclave.

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The residue obtained after filtration was dried in a hot air oven at 110 °C for 24 h to obtain the boehmite seed. Formation of boehmite was also supported by X-ray diffraction study. This seed was used for boehmite precipitation studies.

2.4. Precipitation

The aluminate liquor (1.0 L) with A/C of 1.0 was poured into the precipitation reactor and kept in the temperature bath. Once the stipulated temperature of 80 °C was achieved, boehmite seed (100 g) was added with the additives and stirred continuously. The experiment was carried out under isothermal conditions for the precipitation time period of 8 h. After the reaction was over, the slurry was taken out and filtered. The residue was re-pulped with 250–300 mL of water and filtered. This process was repeated until the pH of the filtrate reached 7. Finally the precipitate was dried at 110 °C for 24 h. The yield was measured as the amount of boehmite obtained after deduction of the amount of the seed added. Subsequent precipitation of boehmite was obtained by varying A/C ratio, the amount of additives and the temperature.

2.5. Characterization

For structural investigations of the boehmite samples (seed and precipitate), X-ray diffraction (XRD) was used. Cu-K α radiation was used for the intensity vs. 2θ scans, with the generator set to 30 kV and 30 mA run on a Philips powder diffractometer model PW 1830 x'pert system in the 2θ range of 10 to 70° using a Cu target. The d -values of the peaks obtained in XRD were matched with the standard peaks of boehmite (JCPDS-21-1307 with 6.11 Å at 2θ value of 14.5° for 100% peak intensity) and gibbsite (JCPDS-7-324 with 4.84 Å at 2θ value of 18.27° for 100% peak intensity), and accordingly the phases were determined.

Raman spectra of the precipitated boehmite were run on a Renishaw Invia Raman microscope using laser source of wavelength 514 Å and stokes scattering to study the vibrational, rotational, and other low-frequency modes.

3. Results and discussion

Sodium aluminate exists in polymeric clusters in precrystalline species.²³ The dimers of aluminate species, gibbsite and boehmite are presented in Fig. 1.^{24,25} There exists a structural similarity between boehmite, gibbsite and sodium aluminate liquor. It is in accordance with the genesis of gibbsite and boehmite from the aluminate species. Therefore, the structure of the liquor is also part of the precipitation system. During precipitation, crystal grows spirally on the primary nucleus just continuing the original crystal habit. The species of the aluminate liquor adsorb on the surface of the seed, where the surface energy promotes the arrangements of the crystal and grows to form precipitates.²⁶

3.1. Effect of additive

Precipitation of boehmite below 90 °C is always accompanied by gibbsite precipitation when the A/C \geq 1.¹¹ This is because gibbsite is a stable phase at a temperature below 90 °C and boehmite above 90 °C. It is necessary to suppress the nucleation of gibbsite when boehmite precipitation has to be carried out below 90 °C. When addition of organic additives is a solution

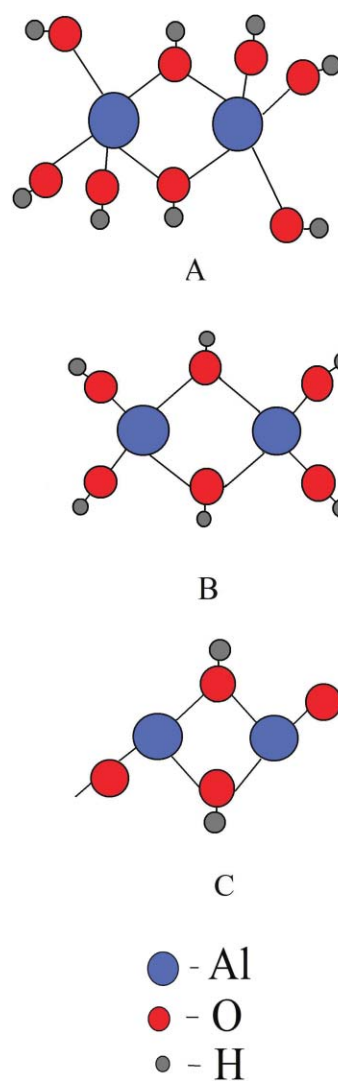


Fig. 1 Dimer of A: sodium aluminate, B: gibbsite, C: boehmite.

to the above problem, a few factors come around regarding the structure and stereochemistry of the additives. The additives block the sites of adsorption, thus, there is a decrease in the number of available active adsorption sites for the crystal growth. The additives form molecular complexes with aluminium species in basic aluminate solution. The aluminium atom gets attached to the functional hydroxyl groups through Al–O–C bonds. An increase in the number of hydroxyls cause increase organic adsorption on the gibbsite surface.²⁷ Monohydroxy compounds have not been found to inhibit crystallization and so it must be assumed that at least two adjacent hydroxyl groups are a minimum requirement.²⁸ The likely mechanism of inhibition is through adsorption of these compounds onto the active sites of the surface of the seed.

The effect of additives on the precipitation of boehmite from sodium aluminate liquor at temperatures below 90 °C is presented in Table 1.

From Table 1 it is observed that oxalic acid, succinic acid, citric acid, EDTA, aspartic acid and glycerol, were not able to inhibit the formation of gibbsite, while glutaric acid and salicylic acid could do this up to 70 °C and not below that. Tartaric acid, xylose and glucose could produce boehmite as the single phase

Table 1 Effect of additives on boehmite precipitation, B: boehmite, G: gibbsite conditions; A/C: 1, seed: 100 g L⁻¹, additives: 5 g L⁻¹ each

Additives	Temp./°C	Yield/g L ⁻¹	Phase
Tartaric acid	70	5.6	B
	60	4	B
Oxalic acid	70	120	B + G
	60	125	B + G
Succinic acid	70	17	B + G
	60	24	B + G
Salicylic acid	70	2.3	B
	60	10	B + G
Glutaric acid	70	0.35	B
	60	3.15	B + G
Citric acid	70	1.9	B + G
	60	3.5	B + G
EDTA	70	50.75	B + G
	60	60	B + G
Glucose	70	2.5	B
	60	22.4	B
Xylose	70	1.8	B
	60	3.35	B
Aspartic acid	70	5.15	B + G
	60	6.3	B + G
Glycerol	70	1.7	B + G
	60	70	B + G

at a temperature as low as 60 °C. In order to prove that the XRD of the obtained phase is the precipitated boehmite and not the seed, the yield of each precipitation is mentioned against the additive. It was observed that when the mixed phases of boehmite and gibbsite were formed the yield was higher as compared to the precipitation of only boehmite.

The XRD patterns of the mixed phases of boehmite and gibbsite, and the monophasic boehmite are presented in Fig. 2a and b. The *d*-spacings of the 100% peak in both a and b are 6.11 angstrom which matches perfectly with boehmite peak. Two extra peaks in the XRD of mixed phases are having the *d*-spacings of 4.84 and 4.35 angstrom matching perfectly with gibbsite.

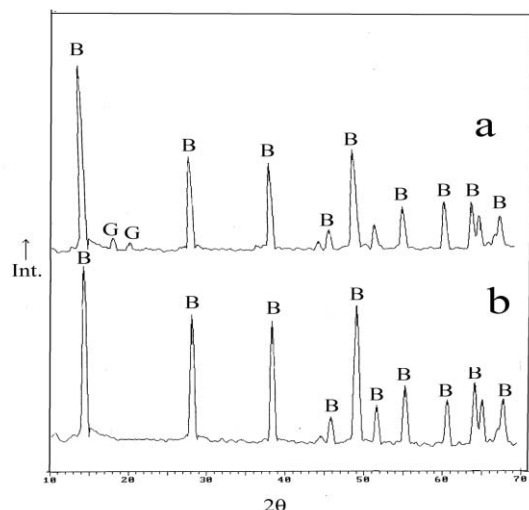


Fig. 2 XRD of (a) mixed gibbsite on boehmite seed, (b) pure boehmite.

The Raman spectra of the precipitated boehmite is shown below in Fig. 3. The band at 360 cm⁻¹ is the most intense peak. Its strength marks it as a fully symmetric mode (*A_g*) where all aluminium and oxygen move parallel to *b*-axis.²⁹ The small band at 491 cm⁻¹ and

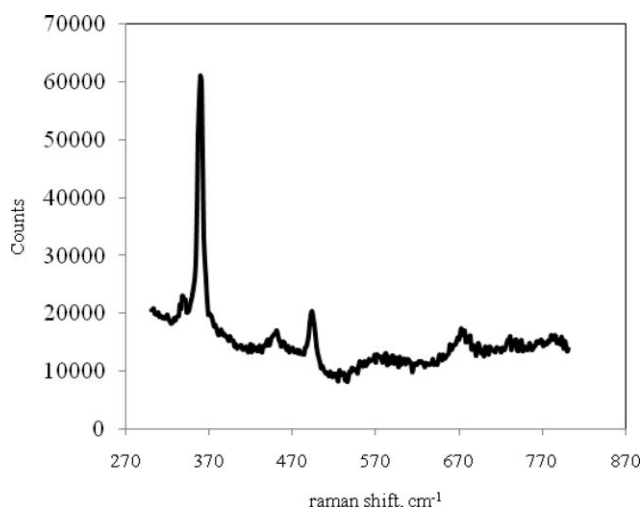
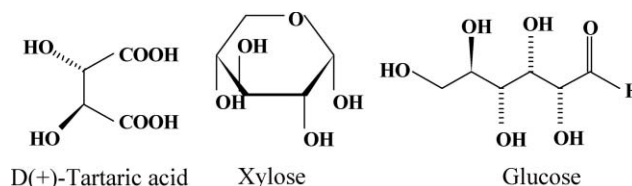


Fig. 3 Raman spectra of boehmite without additive.

a shoulder at 438.6 cm⁻¹ represent Al–O bond bending.³⁰ These bands are same for boehmite with and without additive.

The analysis of the structure and stereochemistry of these three additives, which could produce boehmite at or below 60 °C reveals some common features in the structure of these additives.



All these three compounds have two things in common:

1. These compounds have minimum four vicinal –OH groups either as alcohol or acid.
2. The –OH groups are of *threo* configuration.

Accordingly the following propositions can be made for the action of additives on boehmite precipitation as a single phase.

At least one hydroxyl group of the additives having four ligating hydroxyl groups may sit over the seed surface and the rest may provide a conducive environment for the nucleation of boehmite only. The relative adsorption affinities of polyols are determined by the number of vicinal hydroxyl groups present, the number and sequencing of the *erythro* and *threo* configurations of the used additive.¹⁵ The *threo* configuration was found to adsorb more strongly than the *erythro* configuration. Thus, herein, for the precipitation of the boehmite with additive it may be suggested that during the adsorption of the additive on the seed surface, two hydroxyl group with *threo* configuration binds to the boehmite seed and the other two hydroxyl groups with similar configuration helps in nucleation of alumina with a single water molecule thus inhibiting the nucleation of gibbsite and favouring boehmite formation as shown in Fig. 4. After the nucleation, the ligand may be free for recycling the nucleation process. With increasing amount of tartaric acid the yield of boehmite precipitation almost remains unchanged indicating a catalytic role of the additive.

This proposition gets support from the earlier studies by different research schools. Additives are mostly ligands and can form weak complexes with aluminate in solution. These additives may act as carriers of the alumina to the seed for nucleation

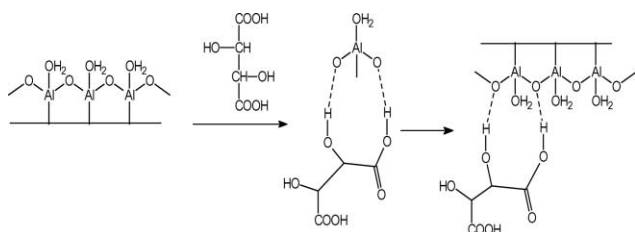


Fig. 4 Proposed scheme for the additive action.

Table 2 Effect of the amount of additives on boehmite precipitation, conditions; A/C: 1.0, seed: 100 g L⁻¹, temp. = 60 °C

Additive type	Additive amount/g L ⁻¹	Phase obtained
Tartaric acid	0.9	B + G
	1.5	B + G
	2.25	B
Xylose	2.25	B + G
	3	B
	5	B
Glucose	2.25	B + G
	3	B
	5	B

process. While proposing a tartarate mediated morphological transformation of boehmite, Cai *et al.*³¹ have also proposed the formation of a tartarate-aluminium complex, where the carboxylate anion of tartarate ligates to the Al³⁺ and the hydroxyl groups help in adsorbing on aluminium surface through hydrogen bonding with surface OH groups of aluminium oxyhydroxide. In polyacrylate-mediated boehmite preparation, formation of nanostructure has been favoured due to inhibition of coalescence of negatively charged carboxylate-aluminium complexes.³² The hydroxyl groups of additives like xylitol can form weak hydrogen bonding with the oxygen or hydroxyl group of boehmite, for facilitating nucleation process in growth of boehmite particles.³³

3.2. Effect of amount of additive

The effect of additive amounts on the formation of different phases during the precipitation from aluminate solution is given in Table 2. The amount 2.25 g L⁻¹ was found to be adequate for tartaric acid, 3 g L⁻¹ for xylose and glucose to inhibit the gibbsite nucleation effectively when the alumina/caustic ratio was 1.0. The additives became effective in inhibiting gibbsite nucleation and the products obtained were all boehmite.

4. Conclusion

Several additives were added to precipitate boehmite from synthetic sodium aluminate liquor. Stearic, citric, glutaric, salicylic, succinic, oxalic and aspartic acids, and EDTA showed no improvement as far as yield and lowering of boehmite precipitation temperature were concerned. The effect of tartaric acid, xylose and glucose as additive could reduce the boehmite precipitation temperature to 60 °C at A/C ratios investigated such as 1.0, 1.1. The mechanism of effect of additives on the formation of boehmite on boehmite seed has been proposed by considering complexation of the additives with aluminate.

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