

A Comparative Study on the Precipitation of Hydrated Alumina from Different Sources

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Abstract Hydrated alumina from three different sources like sodium aluminate liquor, waste aluminium dross and synthetic salt like aluminium sulfate were studied to obtain various form of aluminium hydroxide. Boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), a form of hydrated alumina, has better performance in obtaining alumina, as the enthalpy of dehydration of boehmite is less as compared to gibbsite due to the less number of water molecules in the crystal lattice as compared to gibbsite. Precipitation of hydrated alumina was also studied by using synthetic aluminium sulfate solution with aqueous ammonia and alternating the sequence of reagent addition. Subsequently, the variation in the pH of precipitation and followed by variation of the ageing temperature produced a range of hydrated alumina with different phases and crystallinities. In another option hydrated alumina was precipitated from the sulfuric acid leach liquor of waste aluminium dross by varying the pH of the precipitation followed by temperature of ageing.

Keywords Hydrated Alumina, Sodium Aluminate, Waste Aluminium Dross, Aluminium Sulfate, Activated Alumina

1. Introduction

The research in the field of alumina is very interesting and encouraging as plenty of raw materials are available, which have to be exploited for newer applications as well as recovering the metal at a competitive cost. The process for the precipitation of boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) from sodium aluminate liquor instead of regular gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) precipitation is one such innovative option where reduction in the energy consumption can be investigated. The precipitation of crystalline boehmite from supersaturated sodium aluminate liquor was investigated [1-8] to ascertain its applicability. As the properties of the hydrated alumina can be steered by changing the method of preparation, more work can be done in this area. Variation in the condition of precipitation such as pH, temperature, ageing conditions etc. produces aluminium hydroxides of various compositions, structures, morphologies, etc [9-16]. Many investigators have also tried to modify the Bayer's process as well as to utilize raw materials other than the bauxite ore. Utilization of secondary sources of alumina is a search for alternate source to be used in future. Some of the attempts are already made in these directions [17-20].

The paper deals with the precipitation of boehmite. The preparation of activated alumina from waste aluminium dross, which can be considered as an alternate secondary

source, is a first step in advancing towards "from waste material to value-added products." Aluminium salts solutions are also having practical use of making different varieties of hydroxides and activated materials.

2. Experimental

2.1. Materials

Gibbsite was obtained from M/s National Aluminium Company, Bhubaneswar, India. Boehmite seed was prepared hydrothermally from the supplied gibbsite at 195°C for 4h. 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 in the precipitation process. Aluminium sulfate heptahydrate and 25% ammonia solution, used as the starting material, were supplied by Merck, India. Aluminium dross is a waste material obtained from aluminium melting plants. The $<850\ \mu\text{m}$ (Tyler 20) size particles were taken for the study.

2.2. Method

The supersaturated sodium aluminate liquor was prepared by dissolving required amounts of aluminium granules in sodium hydroxide solution. The liquor was prepared for different $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ (A/C) ratios. In general 150g/L Al_2O_3 solution with A/C ratios of 1.0 was prepared by taking 150g/L of Na_2O (added as NaOH). Precipitation experiments were carried out in a 300 mL capacity stainless steel reactor

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having a fitting lid. Stirring speed of 250 ± 25 rpm was maintained in each experiment. To the aluminate liquor (100 mL) with pre-adjusted A/C ratio 100g/L boehmite seed was added and stirred continuously at stipulated temperature. The time period mentioned 8hrs except where it was varied. The additives were added at the time of seed addition.

Aluminium sulfate solution (0.2M) was neutralized with 5% aqueous ammonia by alternate addition of the reagents like 1. Ammonia added to salt, 2. Salt added to ammonia. Three end point pH were selected for both the cases. Half of the samples were aged with a temperature of 150°C for 4h. The samples are named as A, B and C for pH 5, 7 and 10 of ammonia added to salt system and D, E and F for pH 5, 7 and 10 of salt added to ammonia system.

The experiments on the dissolution of dross in H_2SO_4 were carried out in a flat-bottomed glass reactor, which was placed on a magnetic stirrer with hot plate and temperature was maintained at $90 \pm 2^\circ\text{C}$. The leach liquor was analysed by conventional EDTA– ZnSO_4 method to determine the amount of alumina extracted. Precipitation and ageing were carried out exactly like the aforementioned procedure except the sequence adopted here is ammonia added to salt not the other one. After filtration each of the mentioned samples were washed with distilled water and dried in a hot air oven at 80°C for 48 h.

3. Results and Discussion

3.1. Precipitation of boehmite

Precipitation of hydrated aluminas from sodium aluminate liquor is strongly dependent on A/C ratio which refers to the degree of supersaturation as the main driving force for precipitation. Seed provides surface on which newer crystals grow. Therefore, more seed amount and lesser seed size, more is the yield as illustrated in Figure 1&2. When the A/C ratios varied from 0.75 to 1.2 it was found that at A/C ratio ≥ 1 and when temperature was $\leq 80^\circ\text{C}$ the precipitated boehmite was mixed with gibbsite phase because at that condition supersaturation was more and gibbsite precipitation is kinetically more favoured (Figure 3).

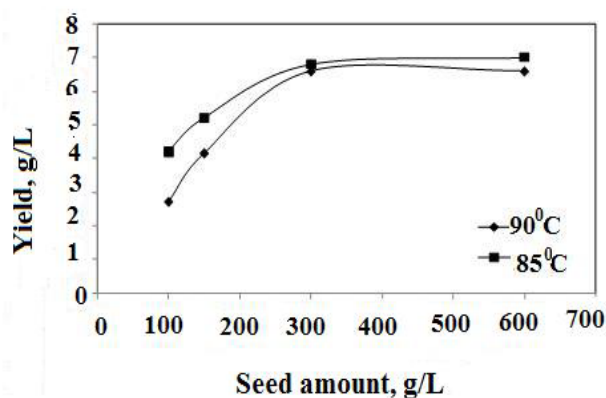


Figure 1. Effect of seed quantity on boehmite yield, A/C = 1.0, 8h, $62.2\mu\text{m}$ (Dash et al., Hydrometallurgy, 2009)

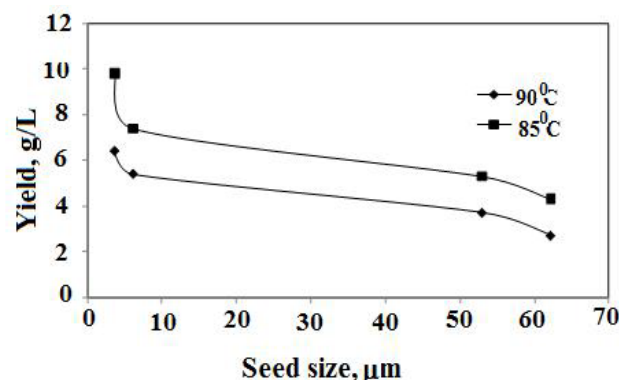


Figure 2. Effect of seed size on boehmite yield, A/C= 1.0, 100 g/L, 8h (Dash et al., Hydrometallurgy, 2009)

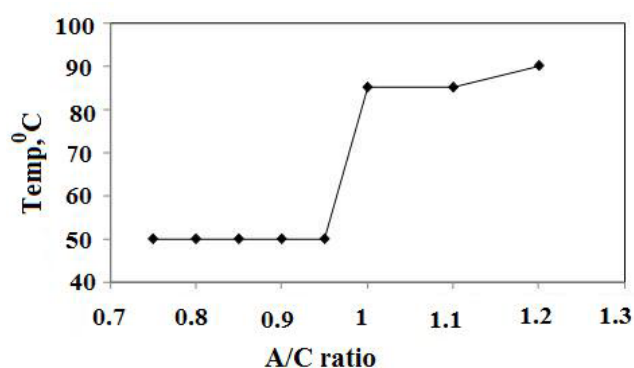


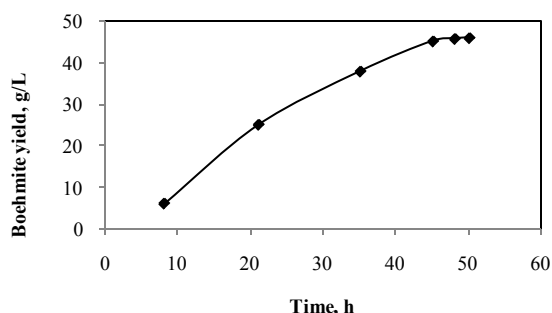
Figure 3. Lowest temperature of boehmite (only) precipitation vs A/C ratio, 8 h, 100 g/L, $62.2\mu\text{m}$ (Dash et al., Hydrometallurgy, 2009) View Within Article

To get only boehmite precipitation at temperature $\leq 80^\circ\text{C}$ without any gibbsite precipitation A/C ratios less than 1.0 is mostly favoured. But under this condition the yield of precipitation is less. So, for industrial practice yield has to be increased and to increase the yield the A/C ratio has to be increased. Here comes the real problem when A/C is higher and temperature is lower, gibbsite precipitation occurs along with boehmite. So, to restrict gibbsite precipitation some additives were selected which when used only boehmite is precipitated without the gibbsite precipitation even at higher A/C ratio and low temperature as mentioned. The details of the additives are mentioned in Table-1. (Dash et al., Dalton Trans, 2010)

Only four additives such as tartaric acid, xylose, glucose and starch are successful in resisting the precipitation of gibbsite with boehmite at 60°C . The reason behind the fact may be attributed to their stereochemical structures. All these four additives have minimum four vicinal –OH group and all the –OH groups are in threo position. This arrangement makes a stable complex where it may form a boehmite template so that preferably boehmite is precipitated. Alternative reason may be attributed to the formation of hydration shell around the precipitation site at the seed surface with the additives as all the shortlisted additives are hydrotopes. The ultimate result of the use of additive in a precipitation and the yield is shown in Figure 4.

Table 1. Effect Of Additives On Boehmite Precipitation, Conditions: A/C:1, Seed: 100g/L⁻¹, Additives: 5g/L⁻¹ Each. B: Boehmite, G: Gibbsite

Additives	Temp./°C	Yield/gL ⁻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

**Figure 4.** Effect of precipitation time on boehmite yield, A/C = 1.1, temp.=80°C, tartaric acid=6g/L

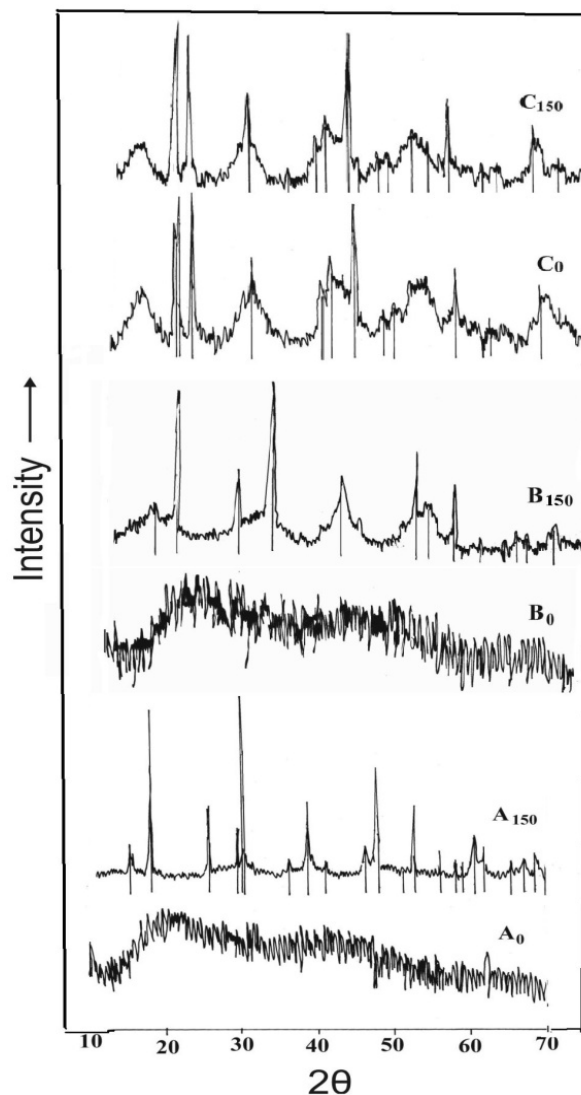
3.2. Precipitation of Hydrated Alumina from Sulfate Salt of Aluminium

X-ray diffraction patterns of A₀ and B₀ (without ageing) were found to be broad indicating an amorphous structure and having gel like characteristics. Thus no crystallinity was observed in these cases. However, with higher ageing temperature like 150°C, the XRD-patterns of A₁₅₀ and B₁₅₀ showed sharp peaks indicating a crystalline structure as shown in Figure 5. Thus crystallinity was found to develop on ageing at higher temperature. The diffraction patterns of the materials obtained at pH 10 (C₀ and C₁₅₀) were found to be distinctly crystalline bayerite for both aged and unaged samples.

The conditions are different in the case when salt added to ammonia. The XRD pattern of all the samples (D, E and F) was found to be crystalline as shown in Fig.6. Even the freshly precipitated samples (D₀, E₀ and F₀) i.e. the unaged ones were also crystalline. The peaks are however broad enough showing low maturity in the crystal growth. When

the materials were aged at 150°C proper crystallinity was marked in the X-ray diffraction pattern.

It was observed that in the system where ammonia is added to salt the crystallinity is either a function of pH or ageing. But if the addition is reversed precipitate crystallinity was obtained.

**Figure 5.** XRD pattern of samples of ammonia added to salt without ageing (subscript 0) and with ageing at 150°C (subscript 150)

The reason behind the difference in crystallinity with respect to sequence of reagent addition is attributed to the fact that when drops of alkali falls on the salt solution there exist competition between Al³⁺ ions to take the OH⁻ ions. That's why if more and more OH⁻ ions are added more crystalline precipitate is formed. And reverse is the case when drops of salts fall into the large excess of ammonia for each Al³⁺ ion there are number of OH⁻ ions. There is no competition for OH⁻ ions. The aluminium ions transforms into fully crystalline aluminium hydroxide. That's why all the samples are crystalline in salt added to ammonia system.

All the six aged samples from both the systems are calcined at different temperatures ranging from 300 to

1300°C and it was found that at 900°C η -alumina was formed and at 1300°C α -alumina was formed. All the samples follow same trend of calcined phases.

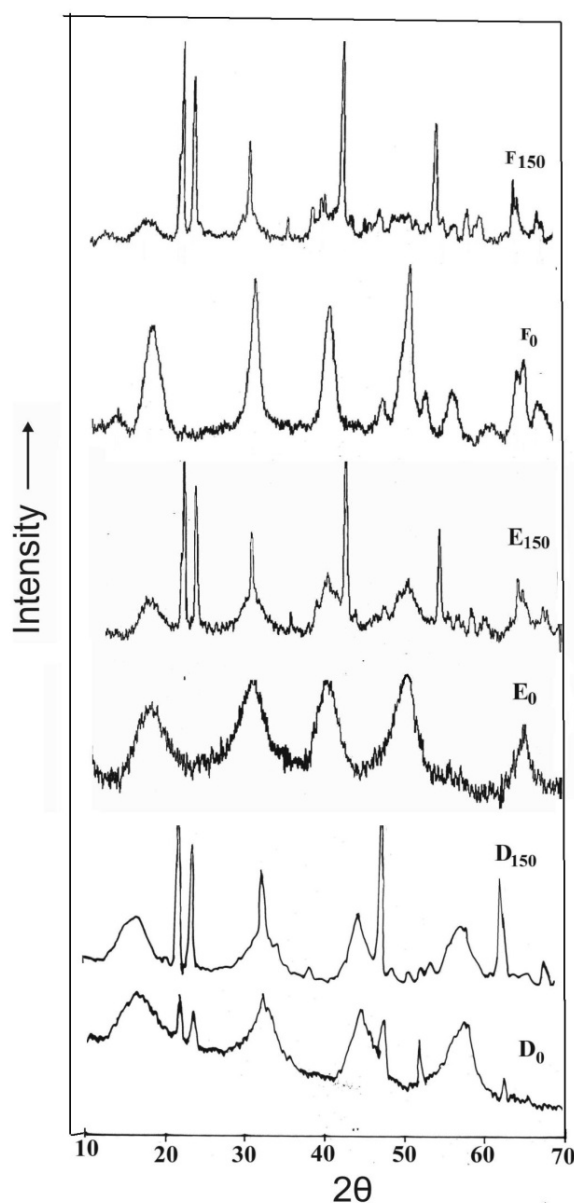


Figure 6. XRD pattern of samples of salt added to ammonia without ageing (Subscript 0) and with ageing at 150°C (subscript 150)

3.3. Precipitation of Hydrated Alumina from Waste Aluminium Dross

The typical dross sample taken was found to be containing 64.8% of alumina. It was found to be containing both alumina and Al metallic phases. The leaching with sulfuric acid brings the aluminium values in any form to ionic form in the leach liquor. The following reactions are supposed to be taking place-

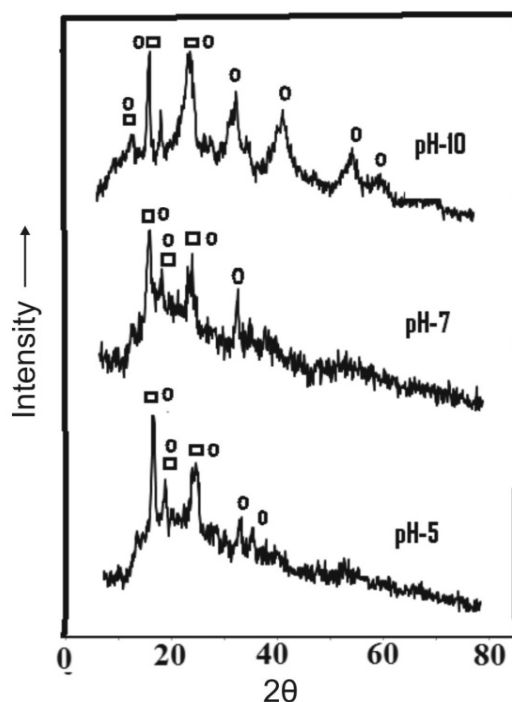
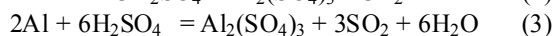
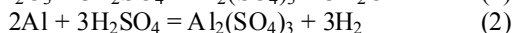
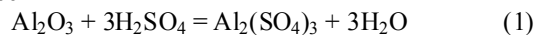


Figure 7. XRD pattern of the precipitated aluminium hydroxide without ageing; \circ : aluminium hydroxide, \square : iron hydroxide

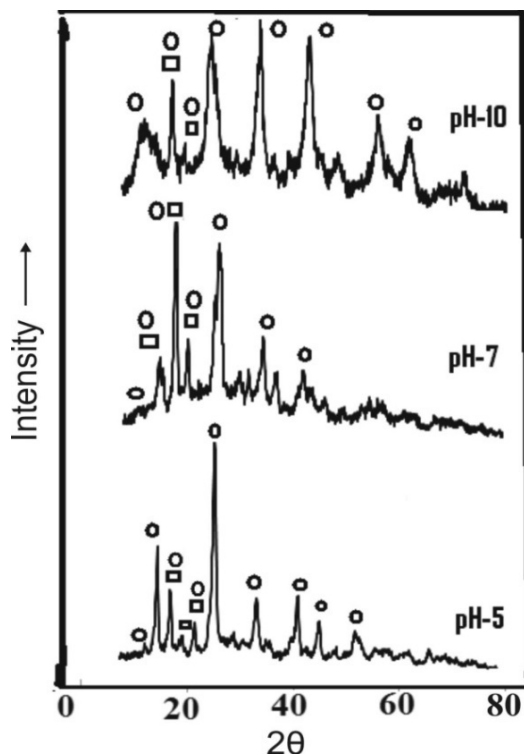


Figure 8. XRD pattern of the precipitated and aged aluminium hydroxide \circ : aluminium hydroxide, \square : iron hydroxide

The optimized leaching conditions are 10% pulp density, 30% acid at room temperature for 1hr. The obtained leach liquor was then neutralized with 10% aqueous ammonia upto pH 5, 7 and 10 without ageing and aged at 150°C. Similar to the earlier case the unaged samples were less crystalline as compared to the aged one. As the solution was a leach liquor

the aluminium was accompanied with iron also. So, peaks of iron hydroxides are also appeared with aluminium hydroxide (Figure 7&8). To remove iron from the solution the early formed precipitate at pH 4.5 was discarded where iron was removed from the system. The percentage of alumina present in precipitate of each pH is given in Table-2.

Table 2. Composition Of The Precipitates

Sample	Al ₂ O ₃ (%)	SO ₄ ²⁻ +H ₂ O (%)
pH-5 (aged)	29.84	67.92
pH-7 (aged)	33.76	63.04
pH-10 (aged)	47.22	45.68

The precipitated hydroxide at pH 10 was subjected to calcinations in the range of 300–1300°C. The transformation to η -alumina at 1100°C and finally to α -alumina at 1300°C was observed.

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