Study on precipitation of microcrystalline boehmite from bayer process solutions

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This study was carried out to develop a process for synthesising ultra-fine boehmite powders by precipitation from the Bayer process liquor at a temperature within the range 85 ~ 95 °C. The study was conducted to investigate whether boehmite produced by this technique has the same physical properties as those prepared by hydrothermal synthesis at elevated temperature and commercially available for use as fire retardant in plastic making. As with gibbsite, the precipitation of boehmite requires seeding in which α-boehmite seeds were first produced by pyrolysis of a plant ultra-fine gibbsite at 420 °C for 60 min. The boehmite seeds of mean particle size (D_{50}) of 0.30 μm were obtained through subsequent hydrothermal synthesis. This process would yield a high purity well-crystalline boehmite of 1.30-1.47 μm mean particle size of low surface area (2 ~ 4 m^2/g) as required for commercial fire retardants.

Keywords: Boehmite, Bayer process, Hydrolysis, Pyrolysis, Precipitation.

Introduction

Boehmite (α-AlOOH or $Al_2O_3.H_2O$, alumina mono-hydrate, AMH) has found many applications in industry, including use as a precursor for making special alumina ceramics, as catalysts or fire retardants in plastic production. When boehmite used as a precursor is calcined for making specialty alumina such as α-Al_2O_3 catalysts its crystal morphology (of different shapes such as rhombic, hexagonal, etc.), purity and size determine the transformation temperature and other properties of the final product [3]. As a fire retardant boehmite decomposes to alumina (Al_2O_3), releasing water and absorbing heat at a higher temperature (> 350 °C) compared to alumina trihydrate/ATH ($Al(OH)_3$, gibbsite) or magnesium hydroxide ($Mg(OH)_2$). Boehmite fire retardants require specific particle properties (< 2 μm particles, specific crystal shape, low BET specific surface area, and high purity, etc.).

It is well known that under hydrothermal conditions gibbsite is converted to boehmite at a temperature in the range 100 ~ 350 °C, depending on pressure in the range 1 ~ 100 MPa [5, 15]. As an example, Panda et al. [9] could produce nano-crystalline boehmite (crystallite size 35 ~ 75 nm) by treating gibbsite (particle size range of P_{80} of 3 μm) hydrothermally at temperatures < 350 °C and 15 ~ 55 MPa pressure.

In the temperature range 350 ~ 450 °C, both boehmite and α-Al_2O_3 are formed. One of many techniques developed for the synthesis of boehmite as nanowire, nanotube or as nanoparticles (1 ~ 20 nm) of various crystallite shapes (hexagonal, rhombic, ellipsoidal, etc.) employs hydrothermal conditions at temperature in the range 150 ~ 250 °C under pressure for several days [7, 12-13, 16]. This was done by using different precursors as seeds, ranging from bayerite $Al(OH)_3$, gibbsite $Al(OH)_3$, to pseudo-boehmite sol gel, etc. As an example, flaky spherical boehmite could be produced from sodium aluminate (Bayer) liquor at 44.7 g/L Na_2O (caustic NaOH) and alumina set at A/C (alumina to caustic mass ratio, with A as g/L Al_2O_3 and C as g/L Na_2O) of 1.41, using 266 g/L gibbsite seed at 180 °C [6].

Several synthesis techniques were also proposed to produce boehmite directly from Bayer or sodium aluminate liquors at temperatures lower than 100 °C. Although the solubility of boehmite (30 ~ 40 g/L Al_2O_3 in the temperature range 80 ~ 100 °C) is generally lower than for gibbsite (60 ~ 120 g/L Al_2O_3) [6] the precipitation of boehmite is slow and controlled via a kinetic step [14] with an activation energy of 89 kJ/mol, compared to easier gibbsite formation over the same temperature range 70 ~ 90 °C. To produce pure boehmite without gibbsite contamination the precipitation has to be conducted at a very high total caustic concentration (equivalent to 210 g/L caustic as Na_2CO_3) equivalent to an A/C ratio of 0.67 [4]. Attempts to improve the reaction rate, particle size (via promoting applomeration) and strength (increasing via crystal growth) of boemite crystals have been made during the crystallisation step from aluminate liquors. While agglomeration of boemite is dependent on operating parameters and can be

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enhanced by longer aging time, higher seed ratio, higher liquor supersaturation (ie large difference of liquor Al_2O_3 concentration from equilibrium value), etc. crystal growth to control crystallite size to within a certain range is difficult.

Wang and co-workers [18] found the crystal growth rate of boehmite is independent of seed sizes or seed ratio and is in the range 0.08 ~ 2.4 μm/h at 80 °C, 4 ~ 10 times less than that of gibbsite (2 ~ 7.2 μm/h). Panias and Krestou [11] first precipitated nano-crystalline boehmite (3 ~ 8 nm crystallites) by neutralising a supersaturated Bayer liquor to pH 5 ~ 7 at 30, 60 and 90 °C using nitric acid. Precipitates with higher crystallinity were formed at pH 7 and 90 °C, which after aging for one week would yield well crystalline boehmite of 22 ~ 37 μm mean particle size. At 90 °C, nano-crystalline boemite (30 ~ 80 nm) was produced using a concentrated sodium aluminate liquor (120 g/L Na_2O, 132 g/L Al_2O_3) within 24 h using 230 ~ 1200 g/L seeding with boehmite, without which seeds the reaction is extremely slow [14]. Dash et al. [1] found that to produce gibbsite within 8 h at a reasonable yield (~ 10 g/L boehmite) and at atmospheric conditions (85 ~ 95 °C, 1 atm). The Bayer liquors have to be supersaturated at high aluminate concentration > 150 g/L Al_2O_3, and the A/C ratio has to be in the range 1.0 ~ 1.2 with at least 100 g/L boehmite seeds of < 10 μm size added.

By adding an organic modifier, boehmite formation is enhanced, minimising the co-precipitation of gibbsite. Dash et al. [1] found that by adding 100 ~ 300 mg/L tartaric acid the nucleation of gibbsite is prohibited and boehmite is produced at a lower temperature of 80 °C. Wang et al. [18] also realised that by adding ethanol the activation energy of precipitation is reduced to 13.7 kJ/mol, shifting the reaction kinetics to a diffusion control mechanism, thus promoting boehmite formation.

The techniques studied and reported to date have been difficult in scaling up for plant production due to long residence time required for aging, either during hydrothermal processing or via precipitation at 85 ~ 95 °C. These methods could not produce microcrystalline boehmite with high crystallinity in the narrow size range 1 ~ 2 μm nor having a low surface area. Therefore, precipitation under Bayer process conditions was studied to determine optimum conditions of liquor composition, temperature and reaction time for producing micro-crystalline boehmite suitable to be used as a fire retardant. The materials synthesised from this study are also compared with existing commercial products currently on the market.

Experimental

Materials and reagents

The Bayer liquor used in this study was prepared from a bauxite ore sample from Weipa, Australia (Table 1), the same material has been used in the production of gibbsite/alumina trihydrate (ATH) at the Daejoo-KC alumina refinery at Mokpo, South Korea. As in plant operation the liquor used for the study was achieved by digesting bauxite to a caustic solution to achieve a caustic concentration of 210 ~ 220 g/L (as Na_2CO_3) and A/C ratio of 0.65 ~ 0.68.

All other reagents used in this study are of analytical grade.

Analytical techniques

Aluminum and caustic contents of the synthetic mother liquors and precipitation filtrate were analysed by acid-base neutralization/titration method. The precipitation (%) of boehmite/AMH based on the alumina analyses of the mother liquor and the filtrate was calculated from the following equation:

Precipitation (%) = [Alumina of mother liquor (g/L) – Alumina in filtrate (g/L)]/Alumina of mother liquor (g/L) × 100%

The prepared α-boehmite seeds used in this study were analysed using a Particle Size Analyzer (PSD, S3500, Microtrac), and the crystal phase was determined by an X-Ray Diffractometer (XRD, Ultima IV, Rigaku). A Surface Area Analyser (Quadrasorb-SI, Quantachrome) was used to confirm the specific surface area of the seeds. The thermal decomposition and composition of boemite (AMH) was evaluated using a thermal analyzer (DTG-60H, Shimadzu). A Scanning Electron Microscope (SEM, SSX-550, Shimadzu) was also used to evaluate the shapes of the particles produced. Chemical analysis was performed on digested samples using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, ICPS-7510, Shumadzu).

Experimental procedures

The following stages were conducted for the experiments:

(a) Liquor used: The Bayer mother liquor from which boehmite was precipitated from was prepared by varying the A/C ratio, seed mass ratio (mass of boehmite seeds/mass of Al_2O_3 in the liquor),

(b) Precipitation of seeds: α-boehmite seeds were prepared for the precipitation of boehmite by calcination of a KC superfine (< 2 μm) gibbsite/ATH product (alumina trihydrate, $Al(OH)_3$) at 420

Table 1. Chemical composition (%) of the raw material (bauxite from Weipa, Australia).

Elements	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	LOI (%)	Moisture (%)
Contents	52.27	8.73	11.56	2.5	24.48	15.4
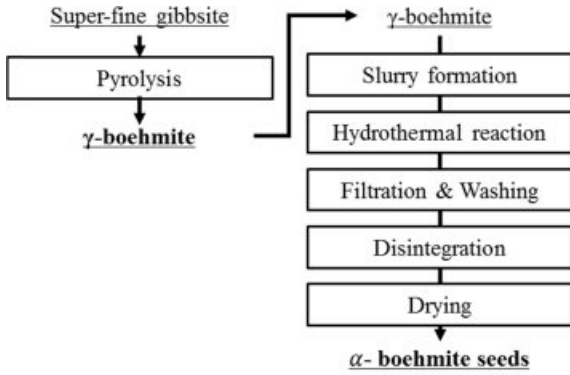
Fig. 1. Flowsheet of manufacturing α-boehmite seeds.

°C. The calcined material was then subjected to a hydrothermal reaction, filtered and ground to produce nano-AMH (boemite) material as shown in Fig. 1.

(c) Boehmite precipitation – The boehmite precipitation experiments were carried out by adding the above freshly prepared seeds into the Bayer sodium aluminate liquor at different temperatures, caustic soda concentrations, and amounts of seeds used.

Results and Discussion

Thermodynamic Study

A thermodynamic simulation of the precipitation conditions was conducted using HSC program [8]. Data obtained (Fig. 2) confirm that boehmite could be thermodynamically precipitated from 95 °C, in preference to gibbsite. The formation of gibbsite peaks at 110 °C and decreases slowly as the temperature rises to 200 °C. More boehmite is formed in this temperature range (95 ~ 200 °C).

Seed preparation

Seed preparation is a critical step for this process.

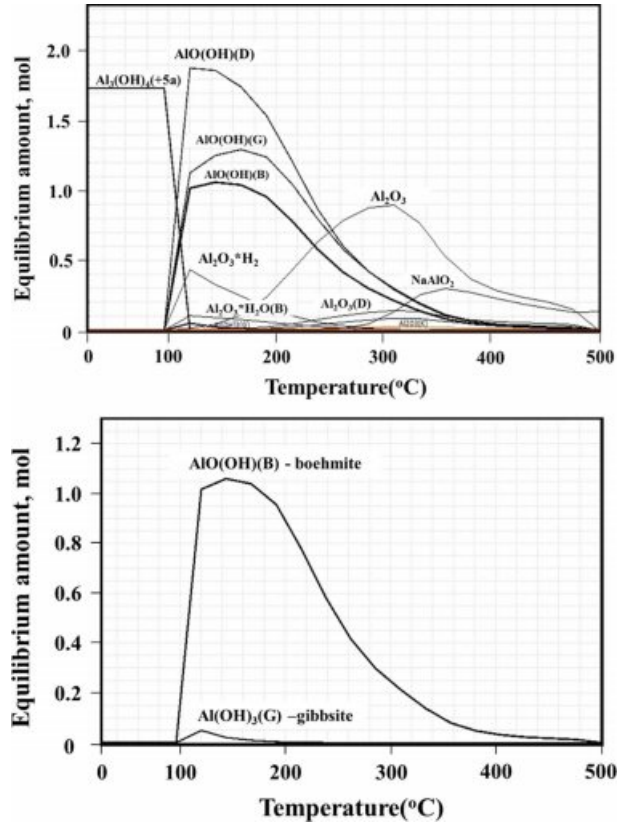**Fig. 2.** HSC simulation of boehmite precipitation at different temperatures.

Seeds were produced by roasting gibbsite (superfine < 2 μm gibbsite/ATH from KC plant) at different temperatures to determine the condition for making boemite. XRD analysis (Fig. 3) shows that gibbsite remains stable at less than 350 °C during roasting. Above 400 °C γ-boehmite/AMH is formed. The pyrolysis of superfine gibbsite to form g-boehmite seeds was therefore conducted at 420 °C subsequently for the study. After hydrolysis to 190 ~ 200 °C this material is
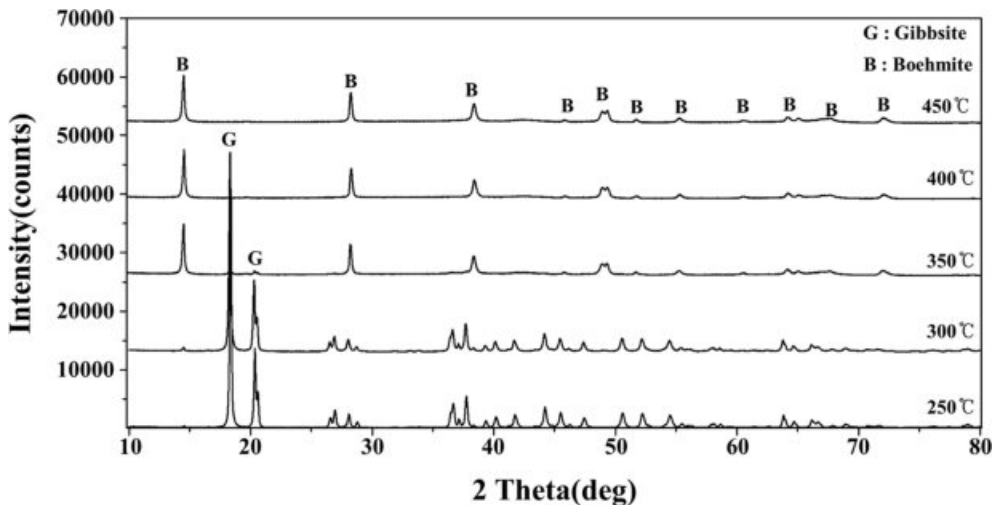

Fig. 3. XRD patterns of KC superfine plant gibbsite/ATH after calcining at different temperatures in the range 250 ~ 450 °C.
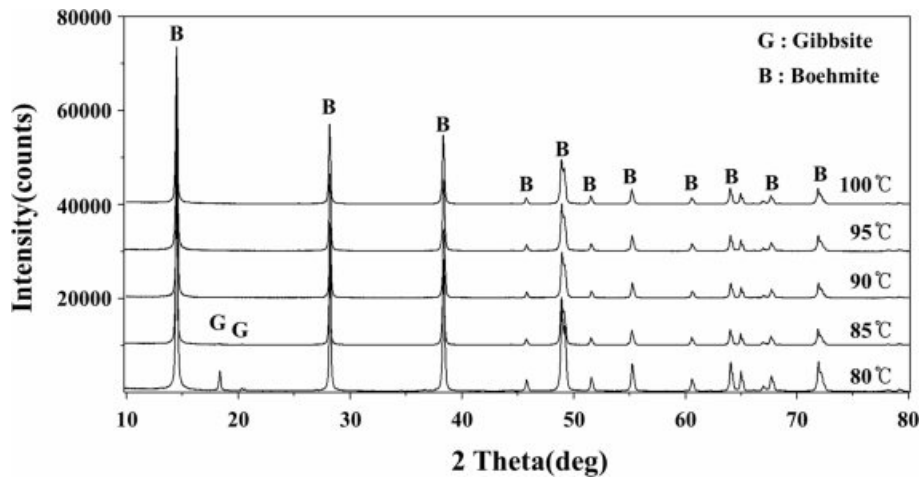
Fig. 4. XRD patterns of boehmite products according to different precipitation (isothermal) temperatures, showing contamination of gibbsite when precipitation was at 80 °C.

converted to α-boemite/AMH.

Optimum boehmite precipitation temperature

To determine the optimum precipitation temperature, tests were conducted at the caustic NaOH concentration of 220 g/L (as Na_2CO_3), pregnant liquor A/C ratio 0.68, mass seed ratio (boemite AlOOH seed/Al_2O_3 in the liquor, both in g) of 2.0 with the isothermal (fixed) temperature varying from 80 to 100 °C. It was found that gibbsite was formed when the precipitation temperature

was 85 °C or less and boemite could only be produced when the temperature was set at higher than 90 °C. These results were confirmed by XRD analysis of the boehmite products as shown in Fig. 4. It was also observed that the precipitation rate was very slow, up to 48 h at which time the A/C ratio still has not reached a steady state (ie. equilibrium has not been reached) as shown in Fig. 5.

Conditions for the tests to determine the optimum precipitation temperature are tabulated in Table 2.
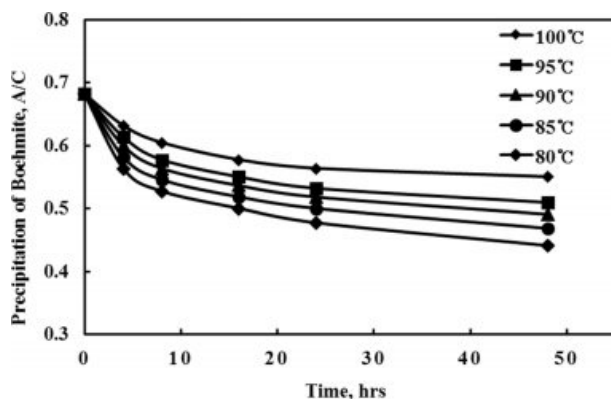
Precipitation with slow cooling

In the Bayer process, the precipitation rate of gibbsite/ATH increases depending on the difference between the initial precipitation temperature and its final value afterwards after cooling. Based on this, it was also applied to boehmite precipitation and the cooling rate was 0.4 °C/hr from the starting temperature. Conditions for this test series are tabulated in Table 3.

The experimental results (Fig. 6) show that the lower the initial temperature is, the higher precipitation rate and yield, as expected with lower final A/C ratio. It was also confirmed by XRD analysis (Fig. 7) that gibbsite will be formed if the final temperature is less

Fig 5. Change of boehmite precipitation A/C ratio with set temperature

Table 2. Conditions for determining optimum temperatures for making boemite product

	Item	Unit	Condition
Synthetic liquor	Caustic as Na_2CO_3	g/L	220
	Alumina as Al_2O_3	g/L	150
	A/C ratio	-	0.682
Seed (α-boehmite)	SSA	m^2/g	5.8
	D_{50}	μm	0.9
	Mass seed ratio	-	2:1
Temperature	Isothermal	°C	80, 85, 90, 95, 100
Time (Sampling point)		hr	4, 8, 16, 24, 48

Table 3. Condition for boehmite precipitation at different final temperatures.

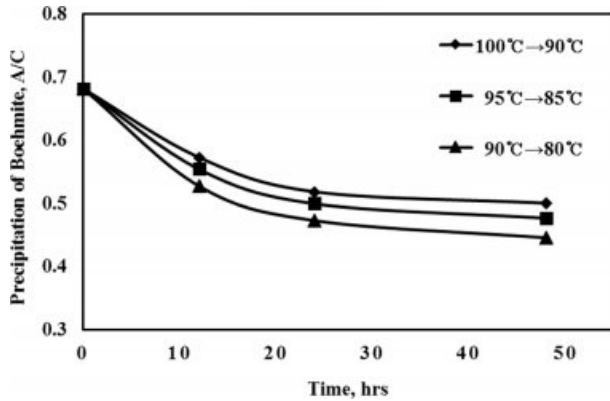|	Item	Unit	Conditions
Synthetic P/L	Na_2CO_3	g/L	220
	Al_2O_3	g/L	150
	A/C	-	0.682
Seed (α-boehmite)	SSA	m^2/g	5.8
	D_{50}	μm	0.9
	Seed mass ratio	-	2:1
Temperature	Cooling	°C	90 → 80
			95 → 85
			100 → 90
Time (Sampling point)		h	12, 24, 48

Fig 6. Change of boehmite precipitation A/C at different cooling regimes

than 85 °C.

The effect of other parameters such as A/C ratios, seed ratio, etc was also studied and results are as follows.

Precipitation at different A/C ratios

Tests were conducted to evaluate the effect of varying A/C ratios during boehmite precipitation according to conditions shown in Table 4.

As expected at a higher A/C ratio the precipitation rate and yield are higher. At all conditions the steady state would be reached slowly merging to an A/C ratio of ~ 0.45 after 48 h (Fig. 8).

It is best therefore to use a liquor having an initial A/C ratio of 0.68 to achieve maximum product yield. This value therefore was chosen for all tests.

Effect of seed mass ratio (AlOOH mass/Al_2O_3 mass in liquor)

Since the boehmite precipitation process requires a higher precipitation temperature compared top gibbsite, a relatively high seed mass ratio is required to increase the initial precipitation rate. The effect of seed mass ratio is shown in Fig. 9, showing a higher precipitation rate at a higher seed mass ratio in the range 0.5 ~ 2:1. Above this 2:1 ratio, there is not much of a change of A/C ratio with respect to the seed mass ratio. The 2:1 seed mass ratio was therefore chosen as optimum conditions as shown in previous results.

Under SEM typical materials through different stages of the process are shown in Fig. 10. It is clear that the raw material (gibbsite) was transformed to g-boehmite after heating to 420 °C, when the calcined crystallites tended to sinter to hexagonal agglomerates > 2 μm in sizes. After hydrothermal treatment at 190 ~ 200 °C
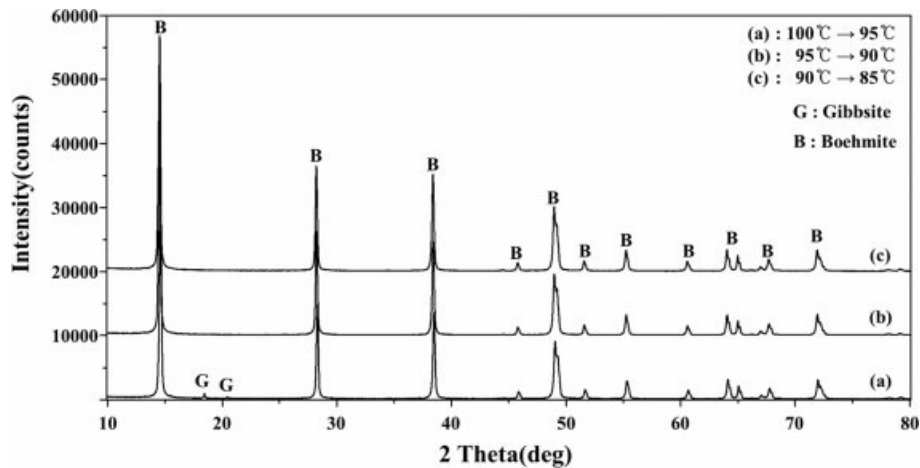

Fig. 7. XRD patterns of boehmite product according to different cooling regimes showing boemite can only be formed at a final temperature > 85 °C.

Table 4. Conditions for boehmite precipitation at different A/C ratios.

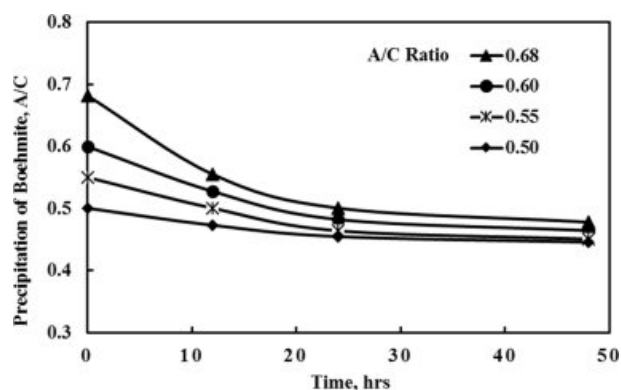| Item		Unit	Condition			
Synthetic P/L	Na_2CO_3	g/L	220			
	Al_2O_3	g/L	110	121	132	150
	A/C	-	0.500	0.550	0.600	0.680
Seed (α-boehmite)	SSA	m²/g	5.8			
	D_{50}	μm	0.9			
	Seed mass ratio	-	2:1			
Temperature	Cooling	°C	95 → 85			
Time (Sampling point)		h	12, 24, 48			

Fig 8. Change of boehmite precipitation A/C ratio at different initial conditions.
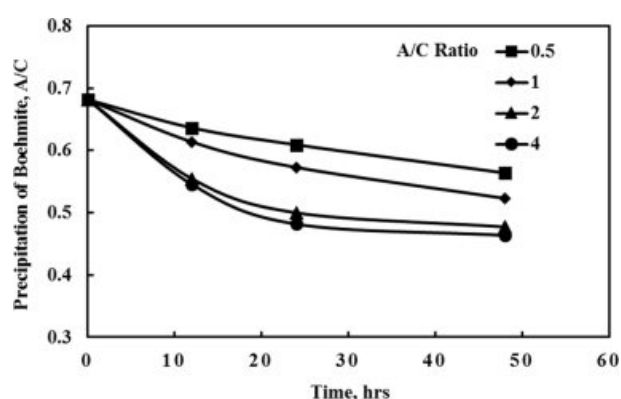
Fig. 9. Change of boehmite precipitation A/C ratio according to different seed ratio.

Fig. 10. SEM analysis showing morphology of the different materials throughout the synthesis of α-boehmite.

APYRAL AOH-30 and SR-100 MES produced by TOR MINERALS – USA (Table 5). The boemite produced from this study meets the specifications for particle size with D_{50} in between $1 \sim 2$ μm, surface area $3 \sim 6$ m^2/g. The purity of boehmite from this study is better than these commercial products.

Conclusions

This study was conducted to investigate the production of $1 \sim 2$ μm particle sizes required commercially as a fire retardant. Boehmite seeds (mean particle size 0.30 μm) were first produced by pyrolysis of a plant superfine gibbsite (< 2 μm) at 420 ºC, which was then subsequently treated by a hydrothermal process at $190 \sim 200$ ºC. These seeds were then used in a precipitation step at optimum conditions determined from this study.

Optimum conditions for precipitation are : caustic

these agglomerates were broken and the a-boemite seeds became cubic in form with reduced sizes to mostly < 2 μm. This mainly cubic shape is maintained after precipitation into the final boemite product.

Adopting the optimum conditions for precipitating boemite, the products obtained are very compatible to typical commercial products such as Nabaltec
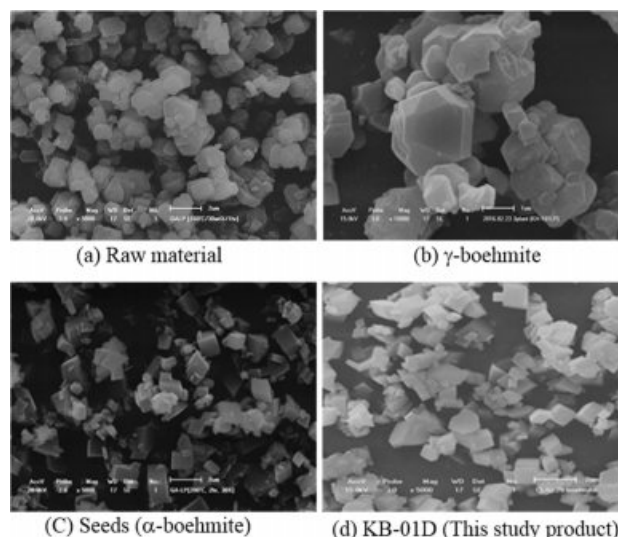
Table 5. Comparison of the boehmite product produced from this study to other commercial products.

	Specifications	NABALTEC (*) (Germany) APYRAL AOH-30	TOR MINERALS (**) (USA) SR-100 MES	Product KB-01D - This study
	D_{50} (μm)	2.04	2-4	1.63
	Specific surface area (m^2/g)	2.76	-	3.2
XRF	Na$_2$O	0.17	< 0.08	0.05
	Fe$_2$O$_3$	0.06	< 0.03	0.011
	SiO$_2$	0.04	< 0.02	0.004
	CaO	0.06	-	0.008
	LOI (%)	17.21	17	17
XRD	AlOOH	Main	Main	Main
	γ-Al(OH)$_3$ Gibbsite	Trace	-	N.D.

*Note : (*) APYRAL AOH-30 product data sheet shows D_{50} 1.8 μm, Specific surface area 3 m^2/g
       https://nabaltec.de/en/products/boehmite/
       (**) SR-100 MES product data sheet from TOR MINERALS company.
       https://www.torminerals.com/aluprem/

(NaOH) concentration of 220 g/L measured as Na_2CO_3, alumina/caustic (A/C) ratio of 0.68, seed mass ratio (boemite/Al_2O_3 in the liquor) of 2:1 and precipitation temperature of 85 to 95 ℃ and in 48 h. Following these conditions the process would yield a high quality crystalline boehmite of 1 ~ 2 μm in sizes, 2 ~ 4 m^2/g surface area. The boemite produced from this process are compatible to other high quality commercial products.

Acknowledgement

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