AA11 - Boehmite Precipitation Kinetics and Calcination Study for Metallurgical Grade Alumina Production

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Abstract

Gibbsite precipitation is presently being employed in Bayer alumina refineries for alumina precipitation from sodium aluminate liquor. Precipitation of boehmite instead of gibbsite has been a topic of interest as boehmite reduces energy consumption significantly in the calcination step of the Bayer process. Boehmite has different precipitation parameters than gibbsite. Using boehmite as seed, its precipitation kinetics have been explored at optimized parameters in this study. A precipitation study using boehmite seed of different particle size, and its outcomes are explained. To estimate the suitability of the developed boehmite product for its use as smelter grade alumina, its calcination was studied, and the resulting product characteristics have been investigated. The alumina from the calcination of boehmite has properties like present smelter grade alumina and is suitable for use in the electrolysis process to produce aluminium. Flowcharts of conventional gibbsite and developed boehmite process are presented. The merits of the developed boehmite precipitation process and subsequent calcination are discussed.

Keywords: Boehmite, precipitation, kinetics, calcination, alumina.

1. Introduction

The Bayer process is the almost universal route for the extraction of alumina from bauxite. About 90 % of alumina is used to produce primary aluminium metal (referred to as “metallurgical grade alumina”), and the remaining 10 % is used in ceramics, refractories, chemicals, flame retardants, abrasives, fillers, and adsorbents [1]. Digestion of bauxite with caustic soda at elevated temperature and pressure, precipitation of sodium aluminate liquor to aluminium trihydrate, and its calcination to alumina are key production steps in the Bayer process. Gibbsite ($Al_2O_3.3H_2O$) precipitation takes place from a supersaturated sodium aluminate (or “Bayer”) liquor, typically in the temperature range of 55-80 ºC. Precipitation of boehmite instead of gibbsite has long been a topic of interest for researchers, as well as the alumina industry. Compared to boehmite calcination, 30-40 % more energy is required in gibbsite calcination, due to the considerable difference in enthalpy (about 1.1 GJ/t Al_2O_3) in the dehydration of the alumina hydrates [2]. Stoichiometrically, further energy can be saved as the material to be calcined will be reduced by 350 kg/t of alumina produced (boehmite contains 1 mole of water as compared to 3 moles of water molecules), which will increase calciner productivity [3].

Boehmite is also used to produce speciality-calcined aluminas and finds application in the chemical industry as catalysts [4]. Hydrothermal treatment of gibbsite, hydrothermal conversion of aluminium salts, and a by-product of alcohol production are the methods mentioned in the literature for boehmite production [5]. The idea of producing boehmite instead of gibbsite in the precipitation step was proposed by the National Technical University of Athens (NTUA), Universite Libre de Bruxelles (ULB), and Hellenic Alumina Industry (ELVA), South Africa in their patent [6]. Gibbsite can be transformed into boehmite hydrothermally [7, 8]. Using boehmite seed in precipitation, boehmite is precipitated at atmospheric pressure and below 100 °C [9]. But below 100 °C, the boehmite phase is accompanied by the gibbsite phase [3]. The role of organic additives (tartaric acid, xylose, and glucose) to inhibit gibbsite formation and promotion of boehmite nucleation has been studied [10]. A method has been proposed in which gibbsite acts as a preliminary seed and saturation modifier to precipitate spherical boehmite [11].

An innovative process developed by researchers at JNARDDC for the precipitation of boehmite in the Bayer circuit has been proposed and described [3]. In this study, various process parameters such as alumina supersaturation, caustic concentration, seed ratio have been optimized and boehmite has been successfully precipitated from the sodium aluminate liquor using boehmite seed.

This paper is an extension of the previous JNARDDC work [3], wherein precipitation kinetics have been explored. To see the effect of boehmite seed particle size on liquor productivity, a precipitation study with two different particle sizes of boehmite seed was investigated and its outcome is presented. Additionally, calcination studies have been carried out at different temperatures and times to evaluate the feasibility of produced boehmite as metallurgical grade alumina. Schematic process flowcharts for gibbsite and boehmite precipitation have been compared along with the merits of the developed process.

2. Materials and Method

Boehmite seed was synthesized through the hydrothermal conversion of gibbsite at 200-250 ºC for 20-30 minutes in presence of water in a bomb digestor /autoclave. Synthetic liquor having the desired alumina and caustic concentration was prepared at elevated temperatures of 150-180 ºC using alumina hydrate from an alumina refinery. The sodium hydroxide and alumina concentrations in the sodium aluminate liquor are as Al_2O_3 in g/L and Na_2Oc in g/L respectively, as analyzed by titrimetric methods.

The optimized parameters were established for boehmite precipitation as given in the previous paper [2]. A kinetic study was carried out at these optimised parameters (Na_2O = 120 g/L, RP = 1.1, seed charge of 700 g/L and temperature 110 ºC) using synthetic liquor. RP is Ratio Ponderal RP = $\frac{\text{Al2O3 g/L}}{\text{Na2Oc g/L}}$ and indicates the supersaturation of alumina in sodium aluminate liquor. The seed charge is defined as grams of hydrate added per liter of aluminate liquor, whereas seed ratio is defined as the ratio of the amount of seed hydrate added as Al_2O_3 to the aluminate liquor Al_2O_3 concentration. As the activity of refinery seed is higher, it is generally used for precipitation studies. The seed usually has some moisture which is to be accounted for in the seed charge calculation. Boehmite seed was charged to the synthetic liquor supersaturated with alumina, and the kinetic study was carried out by withdrawing each bomb after specific durations of 30 min, 1 h, 2 h, 4 h, 8 h, 16 h, 24 h, 32 h, 48 h and 60 h residence time.

The contents of each bomb were centrifuged at 2500 rpm. The supernatant liquor was analyzed for Al_2O_3 and Na_2O_c. After drying at 110 °C in an oven, the precipitated product was weighed. This data was used for the calculation of liquor productivity (LP), which was calculated for each of the experiments. Liquor productivity is expressed in g/L and is calculated as alumina precipitated per liter volume of aluminate liquor [3]. The precipitated hydrate was analyzed for

LOI (Loss on Ignition, the weight loss when heated) and phase analysis using TGA and XRD respectively.

The effect of boehmite seed particle size on liquor productivity was investigated by carrying out experiments with coarse (6.5% : -45 µm) and fine (17% : -45 µm) boehmite seed, with 60 hours residence time, at the same optimised parameters. The product was characterised for LOI, phase and chemical analysis. Product obtained using the coarse boehmite seed was characterized by SEM analysis. The aim was to achieve a significant liquor productivity and to produce a product coarse enough for smelter grade alumina after calcination.

The boehmite product (5.7%: -45 µm) was calcined at different temperatures in the range of 350-750 °C for 2 hours to optimize the calcination temperature to produce smelter grade alumina. TGA, specific surface area and XRD analysis were carried out at each calcination temperature.

To determine the specific calcination temperature and time to get an acceptable smelter grade alumina, calcination was further conducted in the temperature range of 650-700 °C, with time varied from 1-4 hr. LOI was measured in the temperature range of 300-1000 °C and specific surface area (SSA) was analysed.

Synthetic liquor preparation and the precipitation study was carried out in Bomb Digestor of 200 mL capacity (made by Noble Polymech Corporation, Mumbai, INDIA). Six bombs can be simultaneously operated at different temperatures and residence times. Solid (precipitated hydrate) and liquid (spent liquor after precipitation) were separated by centrifugation (REMI KPR-70). The phase of product hydrate and calcined alumina was determined using X-Ray diffraction (PANalytical, X-Pert Pro MPD, Netherland) using Cu Kα radiation (λ= 1.541 Å). Automated sorption system and micropore analysis equipment (Micromeritics ASAP 2020, USA) was used for specific surface area (BET) determination. The morphological analysis of the boehmite was studied using a Scanning Electron Microscope (JEOL – JSM IT300) at various magnifications. Size analysis of the boehmite seed was carried out using a 45 µm sieve (Jayant Scientific IND., Mumbai, ASTM 325). Loss on ignition (LOI) on heating thermally was analyzed by using TG analyzer (Netzsch, STA, 409, PC, Germany). Product hydrate was characterized using the chemical analysis method for Al_2O_3 %, Na_2O % and LOI.

3. Results and Discussion

3.1 Boehmite Precipitation

Boehmite is precipitated from the supersaturated sodium aluminate liquor using boehmite seed prepared by hydrothermal conversion of gibbsite. It was observed from our previous study that at caustic (Na_2Oc) concentration of 120 g/L, 110 °C and at RP 1.1, a low seed charge of 300 g/L produces a mixed product of gibbsite and boehmite. The supersaturated sodium aluminate liquor needs a large seed surface area (m^2/L liquor) for an extended period to precipitate alumina from the liquor. Hence, it is essential to have a high seed charge to get boehmite product and high liquor productivity at the same time. Though the parameters were optimized at 120 g/L Na_2Oc, it was found that the process was stable at 145 g/L Na_2O_c, the caustic concentration of pregnant aluminate liquor found in some alumina refineries [3].

The boehmite product has a coarse particle size which is a prerequisite for its application in smelters [3]. Similar results are obtained with boehmite precipitation using plant liquor with approximately the same liquor productivity and product characteristics. The quantity of boehmite to be calcined would be less as compared to gibbsite. The boehmite required would be 1.18 t/t while gibbsite required would be 1.53 t/ t of alumina production. Hence the process can be applied in an alumina refinery by preparing the boehmite seed initially, and the product boehmite can then be classified into coarse and fine fractions. The fine fraction can be recirculated into the precipitation circuit as seed, while the coarse fraction can be calcined to get product alumina.

3.2 Kinetic Study of Boehmite Precipitation

The decomposition reaction taking place during precipitation can be written as follows:

$$2NaAlO_2 + 2H_2O = Al_2O_3.H_2O + 2NaOH \tag{1}$$

The factors affecting the boehmite precipitation process are alumina supersaturation, caustic concentration, boehmite seed charge, and temperature, with boehmite seed being a necessary component. It has been established that temperature and boehmite seed charges are the primary factors to get the boehmite phase in product hydrate, along with significant liquor productivity. The results of the subsequent kinetic study with liquor productivity vs time is shown in Figure 1, carried out at Na_2O_c 120 g/L, 110 °C, and seed charge of 700 g/L. Figures 2 and 3 show the respective plots of liquor productivity and alumina concentration vs time plotted on a logarithmic scale.

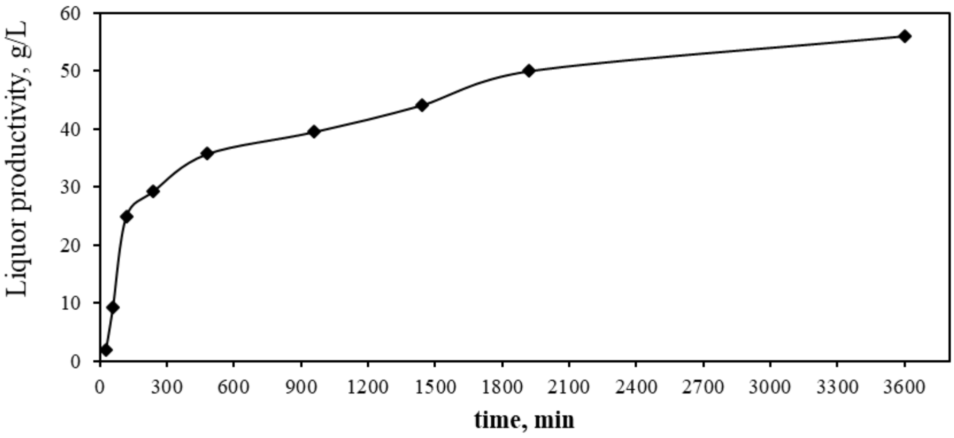


Figure 1. Kinetic study of boehmite precipitation.

Figure 1 shows the increase in liquor productivity with time. The precipitation yield gradually increases up to 24 h (45 g/L liquor productivity), after which the rate slows, and the liquor productivity increases by only 10 g/L in the next 36 h. After 60 h, liquor productivity is 55 g/L. The rate of boehmite precipitation is quite slow compared to gibbsite, due to the higher activation energy required by boehmite. This can also be ascertained from the higher temperature (90-110 °C) is needed, compared to a gibbsite precipitation temperature of 60 °C.

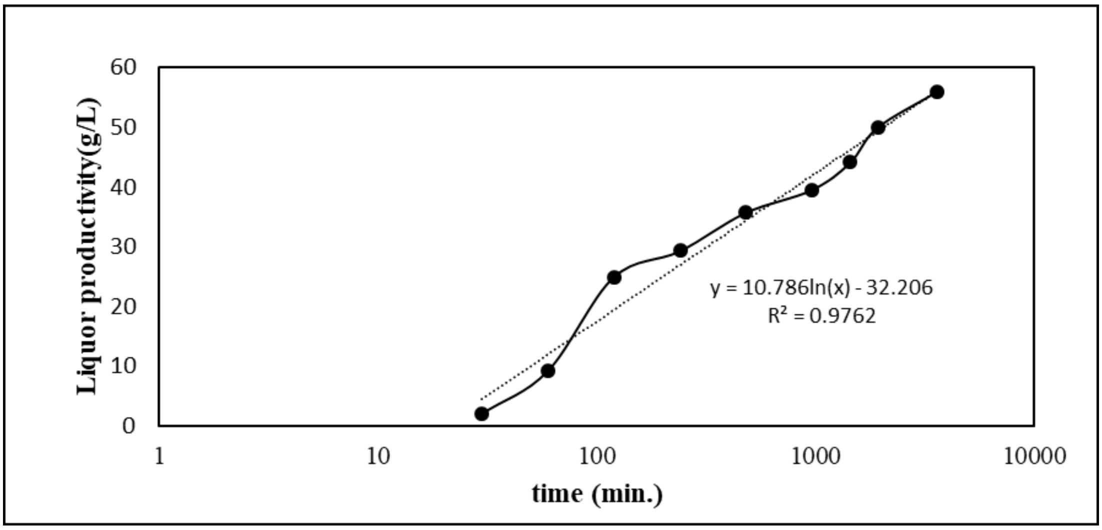


Figure 2. Liquor productivity vs time for boehmite precipitation.

Figure 2 shows the graph of liquor productivity (predictor variable) plotted against the response variable, time t. The rate of precipitation is inversely proportional to time. Liquor productivity can be stated as

$$\mathrm{LP} = 10.786 \times \text{logarithmic time of precipitation} - 32.206\ (\text{constant}) \qquad (2)$$

The R^2 (regression coefficient) value is 0.9762 indicates a good correlation between liquor productivity and the logarithm of precipitation time. The above graph shows that the liquor productivity rate in boehmite precipitation decreases with an increase in time of precipitation due to a reduction in the aluminate liquor supersaturation.

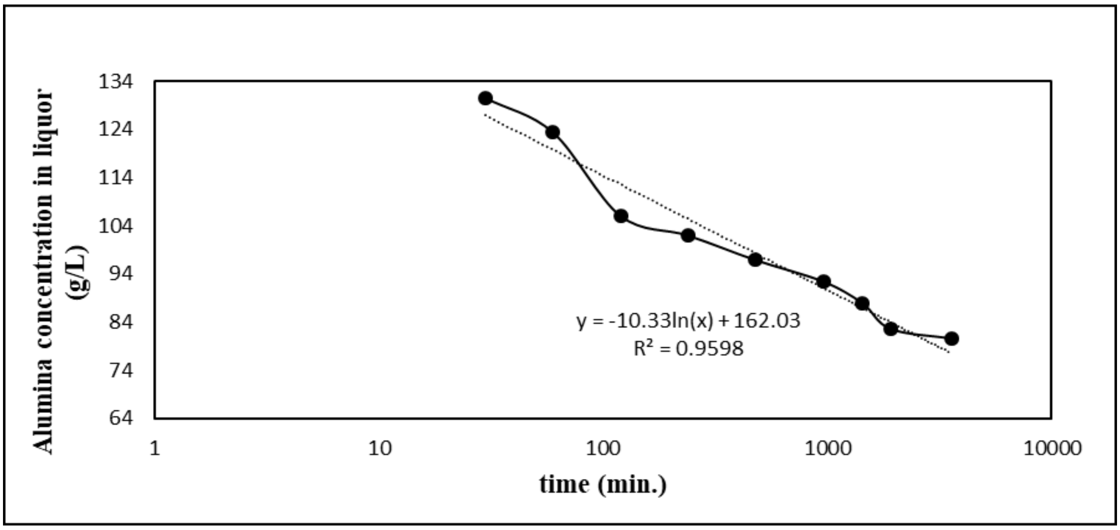


Figure 3. Alumina concentration vs time during precipitation.

As given in the equation,

$$\text{Alumina concentration} = 10.33 \times \text{logarithmic time of precipitation} + 162.03\ (\text{constant})$$

The equation shows the relationship between the response variable (time) on X-axis and the predictor variable (liquor alumina concentration) on Y-axis. The R^2 value is 0.9598 indicating a close correlation between the decrease in alumina concentration and the log of precipitation time.

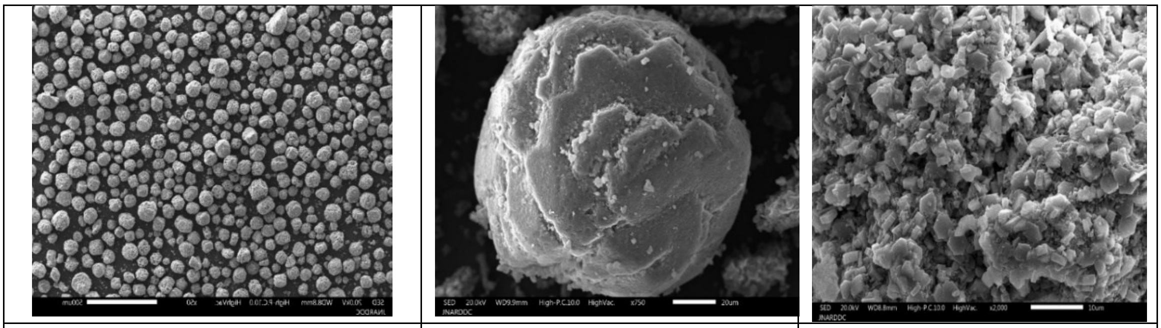
The regression coefficients are nearly the same in both graphs. However, further studies on different variables are required to make accurate kinetics predictions for boehmite precipitation and to formulate a kinetic model.

3.3 Effect of Boehmite Seed Particle Size on Liquor Productivity

Table 1 shows the results of the precipitation study carried out with coarse (6.5 %: -45 µm) and fine (17 %: -45 µm) boehmite seed with 60 hours precipitation time. The Table shows liquor productivity and product characteristics, with the two different particle size boehmite seed. SEM micrograph of precipitated hydrate using coarse size boehmite seed at 50, 750, and 2000 magnification is shown in Figure 4.

Table1. Liquor productivity with different particle size of boehmite seed.

Parameters	Particle size of boehmite seed	
	6.5 % -45 µm	17 % -45 µm
Liquor productivity (from liquor analysis in g/L)	55-56	68-69
Product analysis		
LOI (%) from TG analysis	16.12	14.92
LOI at 420 °C	1.50	1.31
LOI at 550 °C	14.64	13.87
Phase (from XRD analysis)	Boehmite	Boehmite
Specific surface area (m^2/g)	2.6099	2.8604
Chemical Analysis		
Al_2O_3 %	82.36	82.62
Na_2O %	0.13-0.2	0.15-0.2
LOI (%)	16.88	16.93



50 Magnification | 750 Magnification | 2000 Magnification

Figure 4. SEM images of boehmite at 50X, 750X, and 2000X magnifications.

The outcome of the study shows that liquor productivity increases with the finer size of the boehmite seed, with other characteristics of the product being nearly the same. A significant liquor productivity change (10-12 g/L) is observed with a change in particle size of boehmite seed, with finer seed providing more surface area. This effect can be utilized to get high liquor productivity during boehmite precipitation. The product can be classified into coarser and finer fractions as one of the important properties of alumina to be used in smelters is its particle size. The primary requirement is that alumina should consists of minus 45-micron size particles below 10 %. The coarser product can be forwarded to calcination to get product alumina, while the finer fraction can be recycled to the precipitation circuit as seed.

The SEM images in Figure 4 show densely packed, well cemented rhomboidal shaped boehmite particles. The compactness of the particles suggests that the precipitated boehmite will have good strength, and particle breakage during calcination will not be excessive.

3.4 Calcination Study for the Conversion of Boehmite into Smelter Grade Alumina

Product characteristics when boehmite is calcined in the temperature range of 350-750 °C, for 2 hours' duration to achieve the properties of smelter grade alumina is shown in Table 2. Figure 5 shows the variation in the specific surface area of product obtained from boehmite calcination at different temperatures.

Table 2. Characteristics of product obtained from boehmite calcination at different temperatures.

Calcination Temperature (°C)	Product characteristics		
	TG Analysis (% LOI at 0-1000 °C)	Specific Surface Area (m^2/g)	Phase
350	16.80	3.61	Boehmite
450	16.73	5.63	Gamma Alumina
550	10.01	80.79	Gamma Alumina
650	4.03	65.91	Gamma Alumina
675	3.90	65.58	Gamma Alumina
700	3.70	58.03	Gamma Alumina
750	1.49	50.98	Gamma Alumina

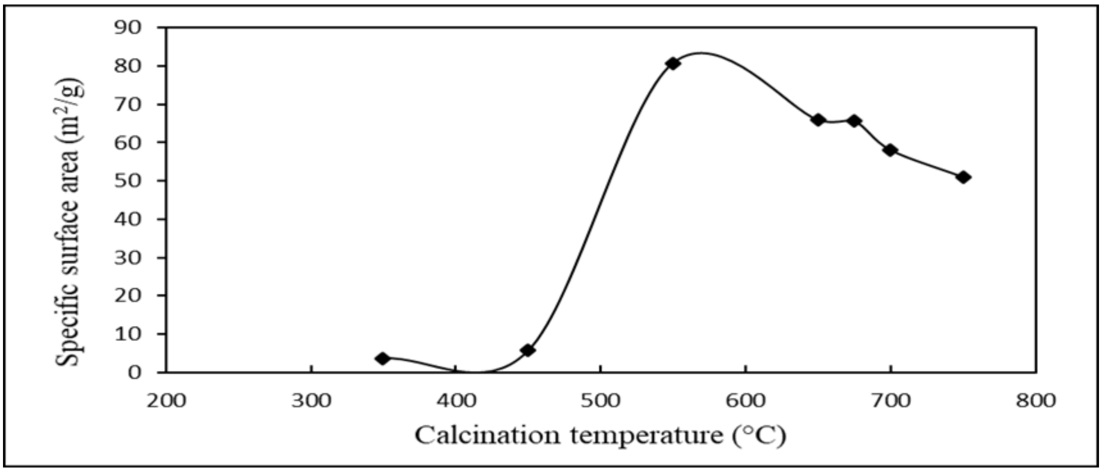
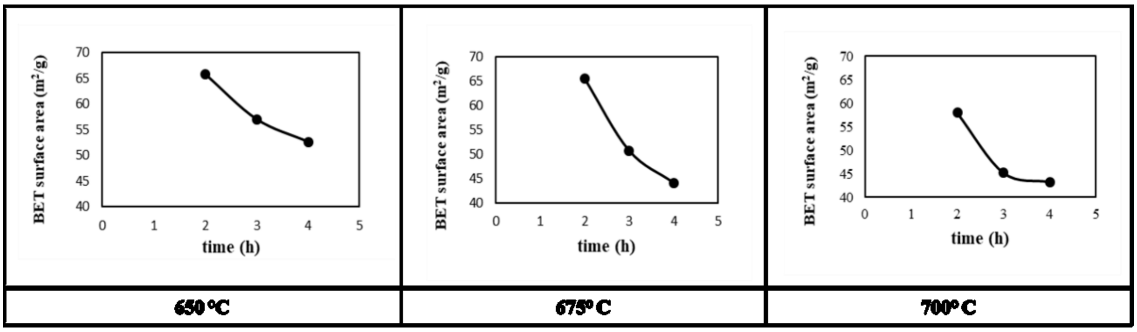


Figure 5. Specific surface area of product obtained from boehmite calcination at different temperatures.

Table 2 shows that the Gamma alumina phase is achieved above 350 °C. According to the literature available, boehmite is transformed into the gamma phase during calcination at about 500 °C [5], more or less consistent with the data shown in the table. The LOI decreases with an increase in temperature and approaches the required value. The decomposition by dehydration of boehmite starts between 350-400 °C. From Figure 5, the specific surface area increases up to 550 °C and decreases thereafter. This is mainly attributed to micropore volume, which decreases with the increase in temperature above 550 °C. This is purely due to loss of water molecules, which causes shrinkage of particles, while no new pores are formed [5]. Figure 6 shows the variation in specific surface area with holding time at calcination temperatures.

Table 3. Calcined product characteristics with variation in temperature and time.

Parameters		Product characteristics		
Calcination temperature (°C)	**Time (h)**	**% LOI (from 0 °C to 1000 °C)**	**% LOI (from 300 °C to 1000 °C)**	**Specific surface area (m^2/g)**
650	1	6.28	3.06	101.88
	2	4.03	1.16	65.91
	3	5.23	2.02	57.05
	4	3.51	1.03	52.60
675	2	3.90	1.05	65.58
	3	3.00	0.90	50.75
	4	3.30	0.58	44.12
700	2	3.70	0.85	58.02
	3	3.37	0.79	45.24
	4	1.98	0.13	43.36



650 °C

675° C

700° C

Figure 6. Variation of specific surface area with time and temperature.

Table 3 shows that the two most important and vital properties of smelter grade alumina i.e. LOI below 1% (300-1000 °C) and specific surface area of 60-70 m^2/g is achieved in the temperature range of 650-675 °C. Time has a significant impact on the BET surface area of calcined alumina as can also be seen from Figure 6. At 650 °C, and at a duration of 1 h, the specific surface area obtained is 101.88 m^2/g. It decreases with increased time and is nearly halved with an increase in time to 2 h. Comparison of 650 °C and 675 °C temperatures, shows that although the specific surface area is the same at both temperatures at 2 h residence time, LOI is higher at 650 °C which is unacceptable. At 700 °C, LOI and specific surface area are both comparatively low. Figure 6 also shows a sharp decrease in specific surface area with an increase in time and temperature. Hence a temperature of 675 °C seems to achieve both the LOI and specific surface area specification for smelter grade alumina.

This method could also be used for generating gamma-alumina from boehmite (SGA or special grade alumina) with varying specific surface areas for various special applications such as catalysts.

3.5 Comparison of Boehmite Precipitation and Calcination with Conventional Gibbsite Process

Figures 7 and 8 show schematic flowcharts of the respective processes.

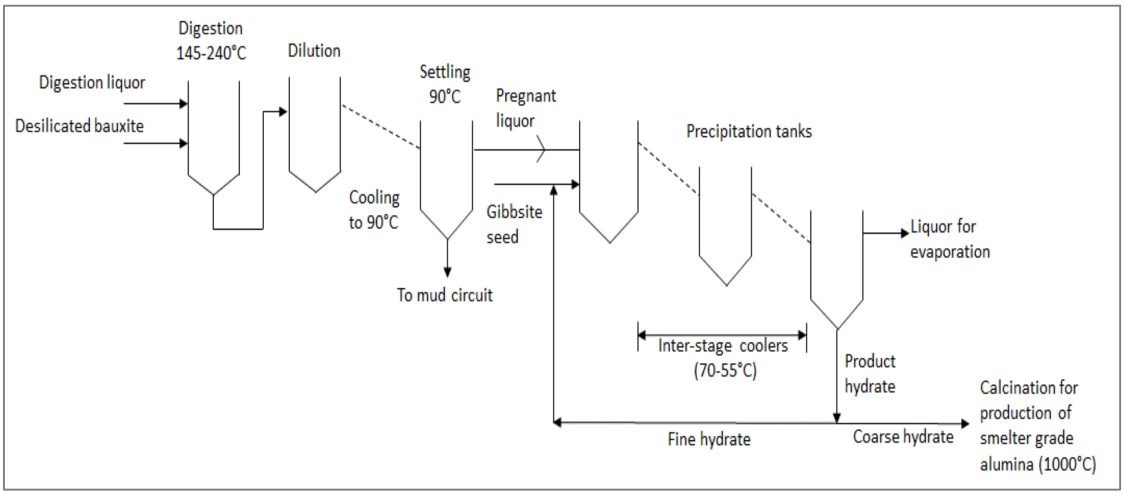


Figure 7. Simple flow chart of gibbsite precipitation and calcination.

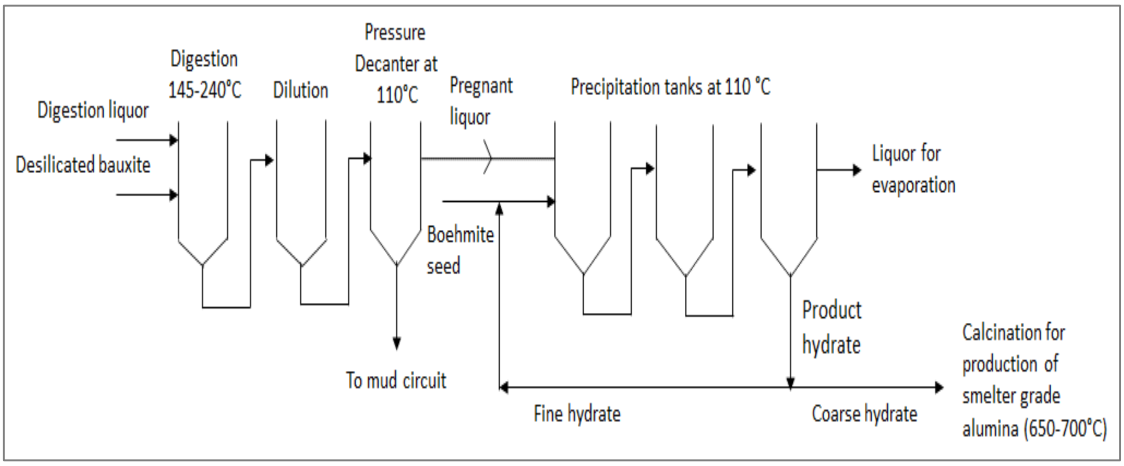


Figure 8. Simple flow chart of boehmite precipitation and calcination.

Although there is a difference between the precipitation temperatures of gibbsite and boehmite, there are several merits of boehmite precipitation and calcination compared to gibbsite. These can be listed as:

- No cooling of pregnant liquor required as in gibbsite precipitation.
- No inter-stage coolers required during precipitation.
- Installation of pressure decanter instead of settlers. Consequently, reduction in alumina hydrolysis losses with faster and better separation of supersaturated sodium aluminate liquor and mud.
- The required heat will be reduced in the evaporation stage, as the liquor will be at 110 °C, compared to the ~60 °C of spent liquor generated in gibbsite precipitation.
- About 30-40 % of energy will be saved in calcination, which is carried out at 650-700 °C, compared to 1000 °C in the conventional process.
- Less mass of boehmite needs to be calcined (about 350 kg) as compared to gibbsite. Hence calcination throughput can be increased.
- Complete formation of the gamma phase during calcination will favor HF adsorption during feeding in smelters.

4. Conclusions

Boehmite production can be adopted in any Bayer alumina refinery and can be produced in an economical way with a significant production capacity under specific precipitation conditions and equipment. Production of boehmite in the Bayer process would result in significant energy savings in several process steps. The process for the precipitation of boehmite ($Al_2O_3.H_2O$) from a sodium aluminate liquor instead of regular gibbsite precipitation is an innovative option, where an energy consumption reduction can be achieved in calcination. High surface area gamma alumina is in high demand and can be used for catalytic purposes. Hence the process also generates special grade alumina which can be used for special/specific applications. Further study would be required to fully understand the kinetics of the boehmite precipitation process, and to formulate a kinetic model. The full Bayer flowsheet, including boehmite precipitation and calcination, needs to be simulated to determine its overall impact on refinery performances.

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Conflict of interest statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.