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

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.

5. References

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