Towards ambient pressure leaching of boehmite through mechanical activation

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ABSTRACT

This paper explores the possibility of manoeuvring the reactivity of boehmite through mechanical activation (MA) for enhancing the solid/liquid reaction between boehmite and NaOH. Synthetic boehmite, prepared by thermal dehydroxylation of gibbsite, used in this study has been characterised by a large specific surface area (~264 m^2/g). A planetary mill has been used for MA. Boehmite dissolution during caustic leaching (temperature: 70–90 °C, Na_2O concentration: 180 g/l) has been found to increase with the extent of MA. Energy accumulated in the solid (boehmite) structure makes its dissolution in aqueous phase easy. Significantly high dissolution (~23 g of boehmite in 210 ml of 180 g/l Na_2O solution) has been achieved at atmospheric pressure condition (90 °C) for 240 min milled sample. Kinetic analysis of the leaching data of boehmite milled for different durations (up to 240 min) has shown that the value of apparent activation energy for boehmite dissolution decreases with the extent of MA. Analysis of the results shows that MA has larger influence on dissolution than rise in leaching temperature. An attempt has been made to separate the effect MA from that of surface area.

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1. Introduction

Being less reactive, caustic dissolution of boehmite needs more aggressive condition (higher temperature, more caustic concentration, etc.) than that required for its trihydrate polymorph, gibbsite. Typically boehmitic bauxite is digested at temperatures above 200 °C while that for gibbsitic bauxite seldom exceeds 150 °C. Considering the difficulties and economics associated with the high temperature boehmite digestion process, conversion of monohydrate bauxite to a more easily digestible state has been identified as one of the priority areas of research and development in alumina industry (Amira International, 2001). Recently mechanical activation (MA), which enhances the reactivity of solids as a result of the ensuing structural degradation, has been explored in the leaching of these monohydrates to moderate the operating parameters (Pawlek et al., 1992; Taskin et al., 2009). Such a study by the authors has shown the influence of mechanical activation on the reactivity of a synthetic boehmite in terms of increased solubility and decrease in its thermal transformation temperature to various alumina polymorphs (Alex et al., 2011a, 2011b). This paper is a continuation of our earlier study on mechanical activation and reactivity of aluminium oxyhydroxides; a detailed analysis of the results of alkali leaching of MA boehmite is described in this paper. This study has been carried out with the same synthetic boehmite used in the previous

studies (Alex et al., 2011a, 2011b, 2013), since it is difficult to obtain natural boehmite in pure form.

2. Materials and methods

2.1. Boehmite

Details of the preparation and characterization of boehmite used in this study have been reported earlier (Alex et al., 2013). Detailed characterisation using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and thermal analysis studies has shown that the test sample is phase-pure boehmite. Large specific surface area (~264 m^2/g) and monomodal size distribution are the characteristics of the boehmite sample used. Detailed pore size analysis (Alex et al., 2011a) has shown that micropores having size <5 nm contribute towards 95% of the surface area; average pore diameter is found to be around 3 nm.

2.2. Mechanical activation

A batch type planetary mill (Pulverisette P6, Fritsch GmbH, Germany) has been used for mechanical activation (MA). Milling chamber and SS milling media (10 mm dia) used for MA are of stainless steel. The amount of sample (30 g) for each milling, ball to powder ratio (10:1), rotational speed (400 rpm) etc. have been kept constant in all the experiments. Every 5 min, the direction of rotation is reversed. Every 15 min, milling process is paused and milling is resumed after the contents are mixed thoroughly. This ensures uniform grinding and

prevents overheating of the grinding bowl and the charge material. The samples milled for different time durations, ranging from 0 to 240 min, are subsequently leached in caustic solution at atmospheric pressure.

2.3. Leaching

Leaching experiments have been carried out in a thermostatically controlled continuously stirred cylindrical glass vessel for a period up to 60 min keeping the initial solid:liquid ratio and the stirring speed fixed at 1:8 [mass (g):volume (ml)] and 400 rpm, respectively. Caustic soda solution (concentration of Na_2O, $C_{Na_2O} = 180$ g/l), prepared by dissolving analytical grade sodium hydroxide in double distilled water, has been used as the leaching medium. Boehmite sample (milled/unmilled) is transferred to the reactor after the temperature of the leaching medium stabilises at the desired value. At the end of each leaching experiment, the slurry is centrifuged immediately to separate out the undissolved boehmite. The residue thus separated is washed with hot water several times and then dried at 105 °C for 2 h. The dried residue is cooled in a desiccator and weighed subsequently. The extent of dissolution of synthetic boehmite is calculated from the weight of the residue. To cross-check the results obtained from residue analysis, leach solution has also been analysed randomly for dissolved alumina using standard EDTA method (Vogel, 1989); the error has been within ±5%. The leaching results have been expressed either in terms fraction dissolved, α or weight of the sample dissolved per litre of leachate. $\alpha_m - \alpha_{um}$ is used as a measure of reactivity (R) of milled sample where, α_m and α_{um} represent the fraction of boehmite dissolved from milled and unmilled boehmite, respectively under identical conditions.

2.4. Characterization

Particle size distributions (PSD) of activated boehmite and residues obtained after leaching for different time intervals have been determined using a laser diffraction particle size analyzer (Model: Mastersizer, Malvern, UK). Prior to the analysis, the particles are dispersed using a dispersant, sodium hexametaphosphate and ultrasonic vibration. PSD is obtained in terms of volume distribution. BET specific surface area and pore size distributions have been estimated from the amount of high purity N_2 (XL Grade, BOC, India) adsorbed per gramme of the material at various relative pressures (from 0 to 1) using a surface area analyser (ASAP2020, Micromeritics, USA). Morphological features are studied using a scanning electron microscope (SEM) (Model: 840A, Hitachi, Japan) while phase identification and structural analysis have been done by powder X-ray diffraction (XRD) method using a Bruker diffractometer (Model: Discover D8) [2θ range: 10–80°, scan rate: 1°/min, radiation: CuK$_\alpha$].

2.5. Leaching data analysis approach

Leaching data, fraction of boehmite dissolved (α) at various time intervals, are used for analysing the process. Physicochemical characteristics of boehmite, viz. d_{50}, specific surface area, pore size ..., undergo changes during leaching. Since the nature of the solid phase changes continuously with the progress of leaching, an empirical approach based on integral kinetic equation as given below is used for data analysis:

$$G(\alpha) = kt \tag{1}$$

where, k is the rate constant. The analytical integral form of $G(\alpha)$ depends on the prevailing reaction mechanism. Various reaction mechanisms and analytical forms of their $G(\alpha)$ are available in literature (Levenspiel, 1978; Ray, 1992).

Analysis of the data using Eq. (1) is carried out to find the empirical equation which describes the leaching kinetics. $G(\alpha)$ for each model is plotted against leaching time, t and then fitted linearly. The equation for which $G(\alpha)$ vs. t plot matches best, having the highest R^2 value, is

selected. The value of rate constant, k is obtained from the slope of the least square linear fit of the identified model, i.e. having the highest R^2 value. Using the k values at various temperatures, Arrhenius plot, $ln\ k$ vs. $1/T$ [Eq. (2)] is constructed. The activation energy, E_a and pre-exponential factor, A are extracted from the slope and intercept of this plot, respectively.

$$ln\ k = \ ln A - (E_a/R). \frac{1}{T} \tag{2}$$

3. Results

Detailed characterisation of the boehmite used in this study is described earlier (Alex et al., 2013). Its particulate characteristics are summarised in Table 1. SEM micrograph presented in Fig. 1(a) reveals that these particles are essentially agglomerates of platelet shaped particles. Porous nature of the particles, arising from numerous slit shaped pores as illustrated in Fig. 1(b), is responsible for its large surface area.

3.1. Leaching of milled boehmite

Leaching of as synthesized (unmilled) boehmite is described earlier (Alex et al., 2013). However, some of these results are also presented here for comparison of the leaching behaviour of boehmite milled in a planetary mill for different durations of time.

3.1.1. α-t plots
The α-t plots pertaining to leaching of boehmite milled for 15, 30, 60, 120, and 240 min at different temperatures in NaOH solution ($C_{Na_2O} = 180$ g/l) are presented along with that of unmilled boehmite in Fig. 2; Fig. 2(a), (b), and (c) describes the changes in α values (fraction dissolved during leaching) at 70, 80, and 90 °C, respectively. In all the cases, there is an increase in boehmite leaching with milling time at any of the considered temperatures. In general, faster leaching is observed during the initial stages and no appreciable change in the α value is observed beyond 60 min of leaching.

3.1.2. Selection of appropriate kinetic equation
In our earlier publication (Alex et al., 2013), it is reported that shrinking core model with surface reaction (R3) adequately represents the leaching behaviour of unmilled boehmite. Reduced time plots (not shown here) for leaching of milled boehmite (up to 240 min), however, have been found to deviate from that of the shrinking core model with surface reaction (R3). Such deviations are probable since the physico-chemical changes brought about during high energy milling are expected to influence the leaching behaviour. However, reduced time plots are found to be closer to the order based reaction models. Further, to ascertain the model, $G(\alpha)$ vs. t plots for order based models, first order (F1) and second order (F2) are made for leaching time up to 15 min and are presented as scatter plots in Fig. 3 and Fig. 4, respectively. Least square linear fitting of the data (lines in Fig. 3 and 4) has shown that the R^2 values for F2 model are higher than that for F1 model. Since F2 model is found to represent the leaching data more appropriately, it has been chosen for studying the leaching process.

Table 1
Particulate characteristics of boehmite used.

Characteristic diameters, μm			Nature of size distribution	Specific surface area, m^2/g		Average pore diameter, nm
d_{10}	d_{50}	d_{90}		Geometric	BET	
77.0	110.2	153.4	Monomodal	0.1	264	3.2

$d_x - x\%$ of the particles below this size.