Surface and bulk activation of a siliceous bauxite during attrition milling

T.C. Alex *, Rakesh Kumar

CSIR-National Metallurgical Laboratory, Jamshedpur, India

ABSTRACT

Physicochemical changes in a siliceous bauxite ore during attrition milling, and corresponding changes in reactivity are described in this paper. Atrition milling of bauxite has been found to have high milling efficiency. BET Specific surface area has sharply increased in the initial stages, but flattened eventually. Decrease in the enthalpy and temperature of transformation (gibbsite to boehmite) with increase in milling time is a consequence of mechanically induced reactivity. The surface charge, as measured by zeta potential, altered as the milling time is increased; such changes in the surface, surface activation, are also a manifestation of reactivity enhancement with milling. The increase in surface reactivity has been explained in terms of generation of more proton active species ($\equiv$AlOH) at the surface. Analysis of X-ray diffraction patterns of bauxite milled for different duration shows progressive breakdown of gibbsite structure to an amorphous state – high energy state - with milling. Reactivity enhancement ensuing attrition milling leads to near complete digestion of bauxite (alumina) in Bayer (caustic soda) solution even at ambient pressure. Alumina recovery correlates well with specific surface area and degree of amorphisation; however, amorphisation (mechanical activation) is more relevant than specific surface area for multiphase systems like that of bauxite used in this study.

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1. Introduction

Bauxite is the chief raw material for the production of alumina -an industrially relevant material for different applications; majority of the alumina produced in the world is by Bayer process, wherein bauxite is digested with hot caustic soda at elevated temperature and pressure. Temperature of operation (and hence pressure as well) is dependent on the mineralogical composition; bauxite with gibbsite [γ-Al(OH)$_3$] as the Al bearing phase is digested at moderate conditions (100–150 °C) whereas bauxites containing monohydrates of Al (γ-AlOOH or α-AlOOH) need more stringent conditions (>200 °C) (Xu et al., 2013). Requirement of higher temperature for the process is a consequence of low reactivity of the aluminium bearing phases in bauxite towards caustic soda. Mechanical activation or high energy milling has been used to enhance the reactivity of solids. Physicochemical changes induced in the solid structure during high energy milling are responsible for the increase in reactivity; Fernandez-Bertran (1999) lists various such physicochemical changes.

Literature available on mechanical activation of naturally occurring bauxite is not large; available literature mainly deals with dissolution of alumina (arising from enhanced reactivity of bauxite consequent to high energy milling) under Bayer conditions (Kumar et al., 2004a, 2004b, 2005; McCormick et al., 2002; Pawlek et al., 1992; Shumskaya, 2002, Taskin et al., 2009). Physicochemical changes during mechanical

activation responsible for the enhanced reactivity are not discussed in these studies. This study focuses on the reactivity changes of a bauxite ore from India during mechanical activation/high energy milling, on the basis of alterations in its physicochemical characteristics.

2. Materials and methods

Natural bauxite of siliceous type was used for the present study. Broadly it was a gibbsitic ore. However, it contained a small amount of boehmite (~3%) in addition to gibbsite. Chemical analysis (done by standard wet chemical methods) is presented in Table 1. Standard wet chemical methods were used for chemical analysis. Loss on ignition (LOI) was determined using ASTM D7348-13 procedure. Mineral phase compositions (determined using a proprietary software based on data reconciliation involving multiple inputs, i.e. powder XRD, chemical analysis, LOI, etc.) is also included in Table 1; Gan et al. (2013) have quantified phases, including that in low concentrations, present in bauxites and their dissolution products using a similar approach.

Mechanical activation was done in a laboratory scale attrition mill (Netzsch PE-075). Stainless steel balls (SS) of 2 mm diameter were used in all the milling experiments. In each of the run, the quantity of the media was fixed at 1850 g (required to cover the stirrer blades, ~85% by volume of the milling chamber). Ball to Powder ratio (BPR) was maintained at ~20:1. Milling was carried out using distilled water as the dispersing media. Solid (bauxite):liquid ratio was maintained at 100 g:200 ml. The stirrer speed used was 1000 rotations per min

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* Corresponding author.
E-mail address: tc_alex@yahoo.com (T.C. Alex).

Table 1
Chemical and Phase analysis of bauxites used.

Radical	% composition	Phases	Phase composition, %
Al_2O_3	50.15	Gibbsite	70
Fe_2O_3	9.18	Boehmite	3
SiO_2	3.69	Hematite	4
TiO_2	10.93	Goethite	6
LOI	25.79	Anatase	9.5
		Quartz	2
		Kaolinite	3

(peripheral speed = 5.24 m/s, stress number = 0.1/min, stress intensity = 1.7×10^{-3} N·m); and activation time up to 30 min was used.

Particle size distribution was measured using a laser diffraction based size analyzer (Model: MasterSizer S, Malvern Instruments Ltd., U.K.). All particle size measurements were done in wet mode. About 5 drops of 1% Sodium hexametaphosphate solution was used as dispersant. Deagglomeration and dispersion of particles was further ensured through ultrasonic treatment (of 20 s) prior to measurement (Alex et al., 2011a, 2011b). The surface area of the each powder sample was measured using a BET analyzer (model: ASAP2020 make: Micromeritics, US); high purity N_2 gas (Excel grade) at liquid-N_2 temperatures was the adsorbate used in the measurement. Prior to BET measurements, the sample was subjected to degassing/drying under high vacuum for 5 h at 90 °C (Alex et al., 2011a, 2011b). Thermal analysis was done on a Simultaneous TG-DTA instrument (TA Instruments, model SDT-Q600). All measurements were done up to 1200 °C at a heating rate of 10 °C/min under flowing argon atmosphere (100 ml/min) with α-alumina as the reference material. Zeta potential and isoelectric point of bauxite suspensions (in de-ionised water, conductivity ~20 μS/cm) were measured using Zeta Probe (Colloidal Dynamics Inc., USA) maintaining the solid content of the suspensions at 10 wt%. X-ray powder diffraction patterns of samples were recorded on a Siemens diffractometer (Model: D500) using Cu-K_α radiation. Morphological changes are studied using scanning electron microscopy (SEM); samples for SEM analysis are carefully prepared using the recommended procedure for powder samples (Das, 1999).

All leaching experiments were carried out using simultaneous milling and leaching process, acronymed SMILE (Kumar et al., 2005). In SMILE, leaching is carried out while milling is in progress; the commonly used dispersing media (in wet milling operation), water is replaced with the leachate, NaOH solution in the present study. 100 g of bauxite ($d_{50} = 17$ μm) was subjected to SMILE in an attrition mill using 250 g/l of Na_2O as leachate cum dispersant at 90 °C for a time period of 0–30 min. Recovery, expressed in terms of Al_2O_3 dissolved, was computed based on original ore and residue analysis. In some cases, recovery values are cross checked with that computed from solution analysis as well. The residue and solution analysis gave similar values of recovery.

3. Results and discussion

3.1. Particle breakage

Particle size distributions (PSD) of the feed and milled (1000 rpm) products, obtained using laser diffraction based particle size analyzer, are depicted in Fig. 1. On attrition milling, the multimodal distribution (of feed particle) transforms into a bimodal distribution; the bimodal nature remains unaltered during the course of milling. The median particle size, d_{50} of the bauxite gets reduced to ~4 μm from ~17 μm in about 5 min of attrition milling at 1000 rpm. With further increase in milling time, median size, d_{50} continued to decrease (as presented in Table 2) as the mode is shifted to lower size; however, the rate of decrease has reduced considerably. It is to be noted that the mode at the finer size (~0.5 μm) remains more or less intact at its original position in spite of high energy milling; this indicates that these fines in the submicron
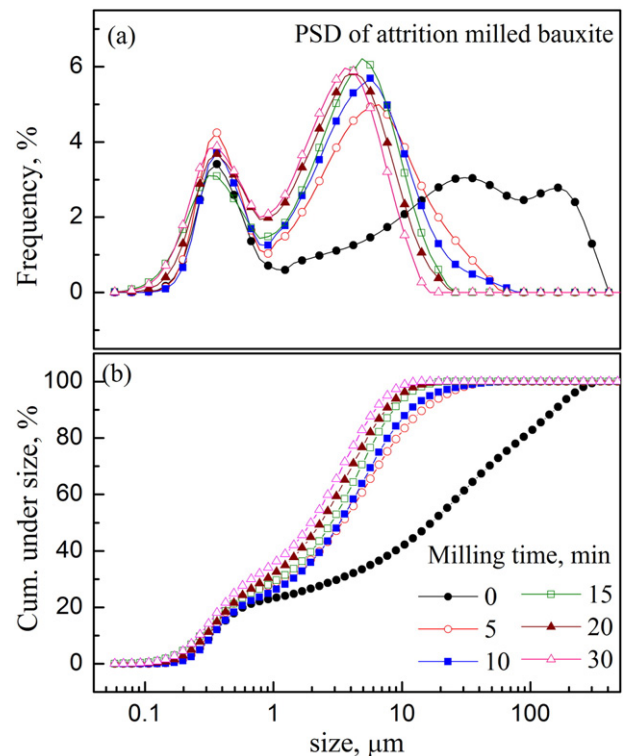

Fig. 1. Particle size distribution of bauxite after milling for different durations. (a) frequency distribution and (b) cumulative undersize.

size do not effectively participate in the breakage process. Decrease in momentum transfer (stress intensity and stress number) as a consequence of the changes in the rheological characteristics (Kwade and Schwedes, 2002) and increased critical energy requirement for breakage as the particles become finer (Boldyrev et al., 1996) are responsible for the reduced rate of decrease of the median size with the progress of milling time. Neither the evolution of PSD (Fig. 1) nor the median size (Table 2) at various milling time suggests any sort of aggregation.

The surface area of milled bauxites measured using BET method is presented in Fig. 2 as a function of milling time. The surface area has increased significantly in the early stages, but slowly died out and eventually attained its equilibrium value; such increase necessitates generation of fine pores. However, the pore generation/increase in specific surface area is quite unlikely from mechano-dehydr(oxyl)ation as reported for gibbsite during dry planetary milling (Alex et al., 2014a), as the milling in this study is carried out in presence of water. Selective dissolution of certain elements/radicals during wet milling from activated mineral surface can be a reason for such increase in specific surface area.

3.2. Morphological changes

Figure 3 presents the changes in morphological features as the milling time is increased. The focus has been on the finer size. Individual grain can be seen in the micrograph (Fig. 3(a)) of unmilled bauxite. After attrition milling for 5 min, the particles have become smaller

Table 2
Evolution of median size with milling time.

Milling time, min	Median size (d_{50}), μm
0	17.21
5	3.44
10	3.30
15	2.80
20	2.33
30	1.94