

MECHANICAL ACTIVATION OF AL-OXYHYDROXIDE MINERALS – PHYSICOCHEMICAL CHANGES, REACTIVITY AND RELEVANCE TO BAYER PROCESS

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Abstract

Overview of our research on 'structure and reactivity' of gibbsite and boehmite under varied conditions of mechanical activation, e.g. milling energy and presence of a second phase is presented. Bulk and surface changes induced in the solids by milling are characterized in terms of morphology, particle size distribution, specific surface area and nature of porosity, crystallite size and zeta potential. Results on enhanced amorphisation of gibbsite in presence of a second phase (quartz, hematite etc), changes in zeta potential of gibbsite due to loss of texture during milling and anomalous decrease in surface area of boehmite during milling are reported. Reactivity of the activated solids in sodium hydroxide and variation in thermal transformation temperatures is correlated with physicochemical characteristics of the samples and plausible explanation for the observed correlations presented. Significance of the results with specific reference to bauxite and alumina processing in Bayer process is highlighted.

Introduction

In the foreseeable future, the Bayer process, invented more than a century back in 1887 by Karl Joseph Bayer, is projected to remain as the main industrial method of alumina extraction. The process involves two distinct operations: (a) selective alkali leaching of Al-oxyhydroxide minerals [gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), boehmite ($\gamma\text{-AlOOH}$), diaspore ($\alpha\text{-AlOOH}$)] present in bauxite leaving behind leach residue which is popularly known as red mud (red side); and (b) precipitation of pure Al-oxyhydroxide and its calcination to produce alumina (white side). Numerous possibilities exist to integrate mechanical activation in the Bayer process research which is guided by resource conservation, energy and environmental considerations [1-14]. Mechanical activation of bauxite has been used to develop an environmental friendly Bayer process in which alumina and soda losses in red mud are significantly minimized [3-11]. Beneficial effects in terms of moderation in Bayer process conditions, especially temperature and time, are also reported [3,4,9,10]. Fundamental understanding of the effect of mechanical activation in Bayer process is hindered by the multimineralic complex mineralogy of bauxite. To circumvent this problem, the studies on pure Al-oxyhydroxide minerals and their mixtures with other minerals are relevant [12-15]. The objective of this paper is to present an overview of about a decade of our research in this direction with emphasis on the mechanical activation of gibbsite and boehmite. The contents of the paper broadly divided to include: (a) illustrative examples to highlight physicochemical factors involved in the mechanical activation; (b) reactivity and its correlation with physicochemical properties of the activated minerals, and (c) significance of the results presented in the context of Bayer process and other possible applications.

Physicochemical Changes due to Mechanical Activation

The structural unit in gibbsite is $\text{Al}(\text{OH})_6$. These are linked by edges to form octahedral layers perpendicular to c-axis (001 direction). In boehmite, $\text{Al}(\text{O},\text{OH})_6$ are linked with each other along a-axis to form octahedral layers parallel to (010). H-bond exists between layers (Fig. 1) [16]. The weak H-bond makes the minerals amenable to mechanical activation.

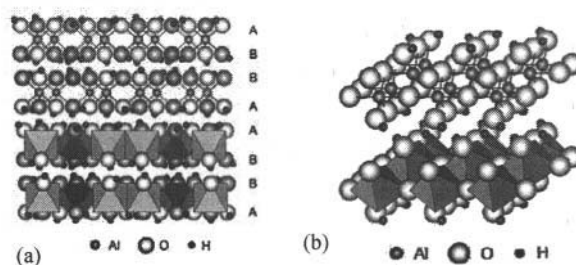


Figure 1. Structure of (a) gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), and (b) boehmite ($\gamma\text{-AlOOH}$).

Milling is generally used for mechanical activation [3, 17, 18]. Milling in general results in breakage (increase in surface area) and bulk and surface changes responsible for mechanical activation. Typically, bulk changes in gibbsite and boehmite may involve reduction in micro-crystallite dimensions (MCD), strain (ϵ) and amorphisation, especially in 001 and 010 directions, respectively [12-15]. The overall effect of mechanical activation depends on the material, type of mill, milling mechanism, energy and environment (e.g. dry or wet). Illustrative examples involving mechanical activation of gibbsite and boehmite are presented here.

Mechanical Activation of Gibbsite

Mechanical activation of gibbsite was carried out in an attrition mill (also referred to as stirred media mill or beads mill [19]) which offers specific advantage in terms of scale up prospect [20]. 100 grams of gibbsite ($d_{50} = 124 \mu\text{m}$) was milled in an attrition mill (Model: PE-075, Netzsch Feinmahitechnik GmbH, Selb, Germany) under following conditions: steel media (2 mm dia), solid: liquid ratio (by weight) 0.5, and ball: powder ratios ~ 20 .

Role of energy. Milling energy (E) in attrition mill depends on third power of rotation speed (n) of agitator (i.e. $E \propto n^3$) provided other factors, such as media size, density, solid to liquid ratio, media and solid weight ratio etc, remain constant [13]. Figure 2 shows the results on degree of amorphisation [12,13,21] gibbsite at different milling speeds (250 and 1000 min^{-1}).

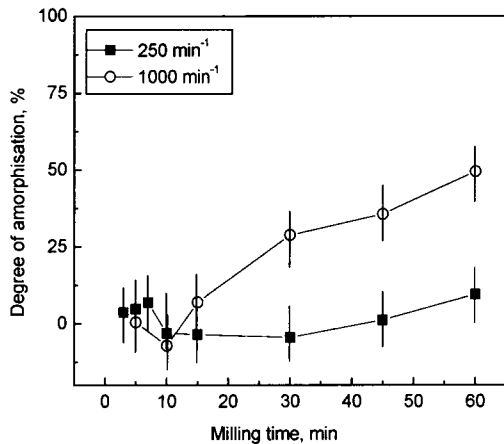


Fig. 2. Effect of milling speed on the degree of amorphisation of gibbsite with milling time

At 250 min⁻¹, no significant amorphisation was observed with milling time. Nearly 50% amorphisation of pure gibbsite was observed at 1000 min⁻¹ after 30 min of milling. Comparison of amorphisation results for pure gibbsite at 250 and 1000 min⁻¹ suggests that mill energy is critical to achieve amorphisation.

Presence of a second phase and amorphisation. Real mineral systems are generally composed of mixture of minerals. In bauxite, hematite and quartz are typical minerals present along with Al-oxyhydroxide minerals. Mixtures containing gibbsite and a second phase, 20% hematite or quartz, were attrition milled and results on degree of amorphisation were compared with pure gibbsite (Fig. 3).

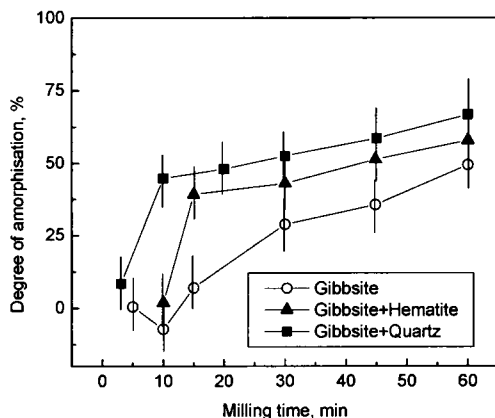


Fig. 3. Effect of second phase, gibbsite or quartz on the degree of amorphisation of gibbsite (milling speed: 1000 min⁻¹)

Higher amorphisation of gibbsite was observed during the milling of gibbsite-hematite and gibbsite-quartz mixtures than pure gibbsite. This indicates that the presence of a second phase favours amorphisation of gibbsite. The hardness of hematite (5-6 on Mohs scale) and quartz (7 on Mohs scale) is much higher than that of gibbsite (2.5-3 on Mohs scale). It is likely that the harder

phase acts as a fine grinding media resulting in increased grinding energy and favouring amorphisation [15, 22].

Texture induced Zeta potential changes. The Zeta potential (ξ) and isoelectric point (IEP) of gibbsite in suspension (10% solid (w/w)), prepared using deionised water (conductivity $\sim 20\mu\text{S/cm}$) was measured by ZetaProbe (Colloid Dynamics, USA) after different duration of milling. The results given in Fig. 3 indicate that Zeta potential increases with increasing duration of milling. Milling also results in the shift of IEP to a lower pH value.

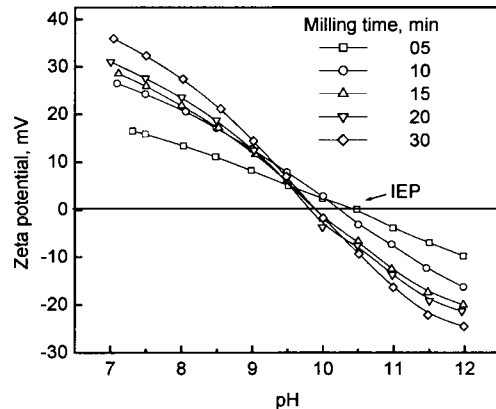


Fig. 4. Effect of milling time on Zeta potential and iso-electric point (IEP) of gibbsite after different milling time

An attempt was made to give a plausible explanation for these results in terms of breakage mechanism and amorphisation of gibbsite during milling. Gibbsite particles comprise of agglomerate of hexagonal platelets (flat surface (001) plane and edge (100), (110) plane). Attrition milling of gibbsite involves separation and breakage of platelets [23] resulting in an increase in edge surface area with respect to face surface area [Fig. 5(a), (b)].

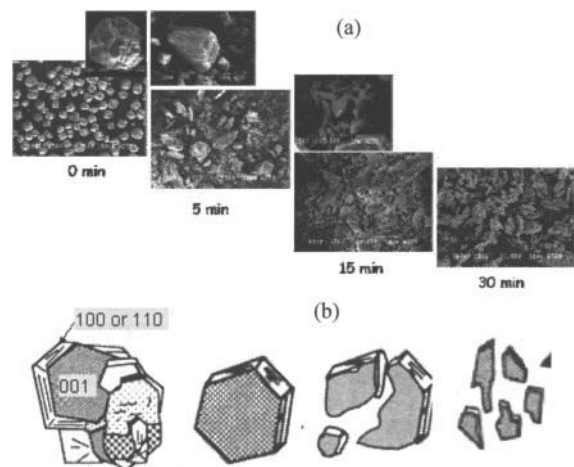
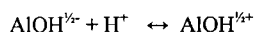


Fig. 5. (a) SEM micrograph showing change in morphology of gibbsite particles with milling time, and (b) schematic representation of particle breakage during milling

In addition to particle breakage, gibbsite also undergoes amorphisation during milling (Fig. 2 and 3). Recently published literature [24-28] suggests that the doubly coordinated basal plane $\equiv\text{Al}_2\text{OH}$ is nearly neutral (except at very low pH) as compared to the doubly and singly coordinated (in equal proportion) edge planes ($\equiv\text{AlOH}$) which can easily get charged according to the following reaction:



It has also been reported that amorphous gibbsite shows greater surface charge as compared to crystalline gibbsite [24]. Thus, the change in surface charge and IEP during milling may be the result of platelet breakage along the edge plane (Fig. 3) and amorphisation of gibbsite.

Mechanical Activation of Boehmite

Boehmite (hardness 3-3.5) is relatively difficult to activate as compared to gibbsite (hardness 2.5-3.0). Planetary mill (specific mill power 9000-36000 kWt^{-1}) characterized by higher specific mill power as compared to an attrition mill (900-14000 kWt^{-1}) [18] was used for mechanical activation of boehmite. Mechanical activation was carried out in Pulverisette P6 planetary mill (Fritsch GmbH, Germany) under following condition: boehmite sample taken -30 g, ball to powder ratio - 10:1, rotational speed - 400 min^{-1} [14]. Boehmite used was synthesized by thermal transformation of gibbsite at 350 °C for 2 h. The sample retained the morphology of the parent phase and was characterized by very high specific surface area ($\sim 260 \text{ m}^2/\text{g}$) due to channels of pores formed during thermal transformation (Fig. 6).

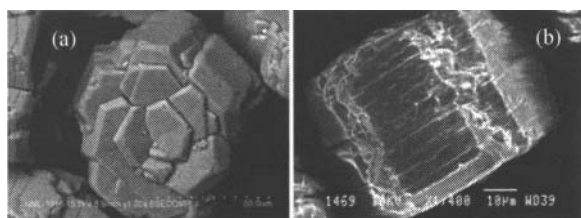


Fig. 6. SEM micrograph showing (a) morphology of boehmite, and (b) channels of pores formed due to the escape of water during thermal transformation of gibbsite to boehmite

Earlier studies on mechanical activation of boehmite have been carried out on synthetic boehmite formed under hydrothermal conditions or on samples of unspecified origin [29-30]. In general, mechanical activation results in a decrease in particle size (or increase in surface area) [3, 18] as reported by Tsuchida and Horigome [30] for the boehmite sample investigated by them.

Anomalous decrease in surface area. After an initial decrease in particle size up to 15 min, the particle size of boehmite used in our study showed an increase with further milling; the median size (d_{50}) increased from 1.8 to 5 μm during 15 and 240 min of milling. Quite unexpectedly, the BET specific surface area of the sample (N_2 adsorption method) decreased continuously from $\sim 260 \text{ m}^2/\text{g}$ to $\sim 60 \text{ m}^2/\text{g}$.

Changes in pore structure during milling. A detailed analysis of N_2 adsorption /desorption isotherms indicated that the decrease in

surface area is associated with a change in pore structure of the sample (Fig. 7). It was observed that the maxima in pore size distribution plot at $\sim 2 \text{ nm}$ and $\sim 4 \text{ nm}$ shift to dominantly $\sim 23 \text{ nm}$.

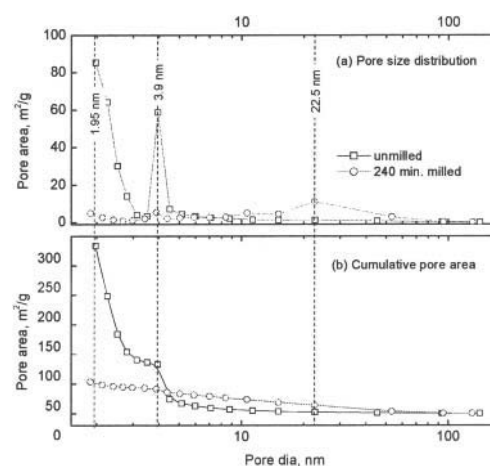


Fig. 7. (a) Pore size distribution and (b) cumulative pore area for unmilled and 240 min milled boehmite [14].

Scanning electron microscopy (SEM) studies revealed that during milling, initial breakage is followed by agglomeration/fusion of particles with consequent loss in porosity (Fig. 8). These are significant observations since mechanical activation of porous solids have not been paid any attention.

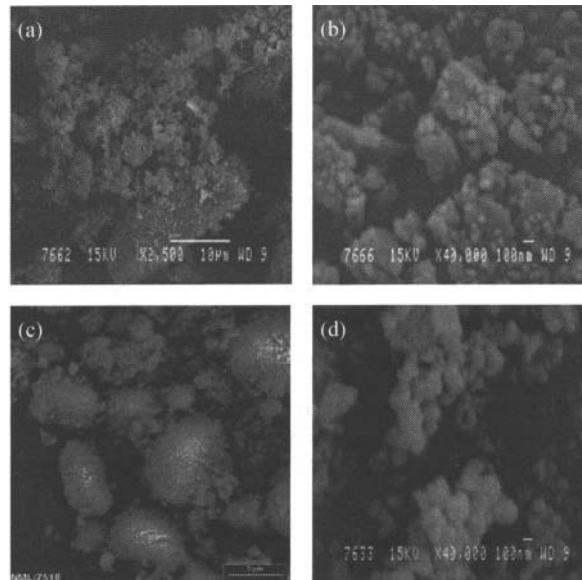


Fig. 8. SEM micrograph showing morphology and pore structure: (a) (b) after 3 min, (c), (d) after 240 min

Detailed analysis of XRD pattern and Fourier Transform Infrared (FTIR) spectra of unmilled and milled samples also indicated amorphisation, decrease in microcrystallite dimension (MCD) and increase in strain (ϵ) during milling [14, 15].

Mechanically Induced Reactivity

Earlier papers by Kumar *et al* [9,10,12] have discussed the reactivity of mechanically activated gibbsite. Enhanced reactivity of gibbsite results due to the combined effect of particle breakage and amorphisation. The mechanically induced reactivity of high specific surface area boehmite, synthesized by thermal transformation of gibbsite to boehmite showed interesting correlation with its physicochemical properties and these results are presented here in detail.

For the unmilled sample, the percentage of boehmite dissolved (%R) in 250 g/l Na₂O solution at 90 °C after 30 min was 44%. The boehmite to γ -Al₂O₃ transformation temperature ($T_{(AlOOH \rightarrow \gamma-Al_2O_3)}$) was 522 °C for the unmilled sample. Figure 9 shows the variation of $T_{(AlOOH \rightarrow \gamma-Al_2O_3)}$ and %R, with milling time. It is evident from Fig. 9 that milling results in an increase of reactivity which is manifested by an increase in boehmite dissolved (%R) and lowering of transformation temperature ($T_{(AlOOH \rightarrow \gamma-Al_2O_3)}$). The % R increased to ~ 90% and $T_{(AlOOH \rightarrow \gamma-Al_2O_3)}$ decreased to 478 °C after 240 min of milling.

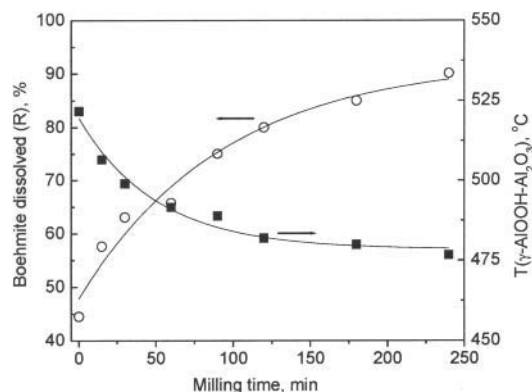


Fig. 9. Variation of $T_{(AlOOH \rightarrow \gamma-Al_2O_3)}$ and %R, with milling time

In order to study the nature of correlation between reactivity and physicochemical characteristics of the sample, reactivity was defined as: (a) a decrease in the boehmite to γ -Al₂O₃ transformation temperature ($\Delta T_{(AlOOH \rightarrow \gamma-Al_2O_3)}$); and (b) percentage increase in the boehmite dissolved (ΔR) with reference to the unmilled sample. Binary correlations (r_{xy}) were calculated between reactivity (i.e. $y = \Delta T_{(AlOOH \rightarrow \gamma-Al_2O_3)}$ or ΔR) and physicochemical characteristics (x) of the samples, namely, median size (d_{50}), Specific surface area ($SSA_{\text{geometrical}}$, SSA_{BET}), Microcrystalline dimension (MCD) and strain (ϵ), and the values are given in Table 1.

Table 1. Binary correlations (r_{xy}) between physicochemical characteristics (x) and reactivity (y) of boehmite

x	Binary correlations (r_{xy})	
	$y = \Delta R$	$y = \Delta T_{(AlOOH \rightarrow \gamma-Al_2O_3)}$
d_{50}	-0.65	-0.73
$SSA_{\text{geometrical}}$	0.47	0.56
SSA_{BET}	-0.99	-0.98
MCD	-0.94	-0.98
ϵ	0.96	0.98

In general, solid reactivity correlates positively with surface area. It was intriguing to observe a strong negative correlation between reactivity (ΔR or $\Delta T_{(AlOOH \rightarrow \gamma-Al_2O_3)}$) and SSA_{BET} (Table 1). A detailed explanation for the observed correlations is presented elsewhere [14]. However, it may suffice to state here that the positive effect of stored energy associated with decrease in MCD and increase in ϵ appears to more than offset the negative impact of decrease in surface area. In addition, the pore structure of the boehmite also undergoes changes during milling which may influence reactivity. While there is a decrease in surface area during milling, pores having size < 5 nm are annihilated and average pore diameter increases from 3.23 to 12.9 nm. The bigger pore may be more favourable to mass transfer of reactant/products, i.e. H₂O (g) in the case of thermal decomposition, and NaOH/NaAlO₂ during alkali dissolution.

Significance of Results and Concluding Remarks

The significance of the results presented is highlighted here in relation to: (a) Bayer process, and (b) tailoring properties of Al-oxyhydroxides/oxides.

Bayer Process

Gibbsite is soluble in caustic soda above 100°C, while boehmite is soluble in caustic soda above 200°C and requires longer digestion times. A simultaneous milling and leaching process (SMILE) which exploits mechanically induced reactivity of gibbsite and results in a more environmental friendly red mud (Na₂O < 1%) was reported by Kumar *et al* [9,10]. SMILE was also operated at about 15 °C lower temperature and involved shorter leaching time (15 min). Fortin and Forté [11] pursued similar studies and paid special attention to the behaviour of silica. The results in a batch type attrition mill [9,10] were also confirmed in continuous type attrition mill [33]. Mechanochemical and chemical leaching could be combined in the mill to avoid excessive milling of bauxite [33]. In spite of encouraging results [4,9-11,33], development of a Bayer commercial process based on mechanochemical activation is a distant dream. A number of unresolved issues remain, for example the nature of Al-bearing phases in the laboratory red mud, the opportunity for further improvement in alumina recovery, understanding of the lower soda content of red mud, possibility of the conversion of goethite into hematite under milling condition to improve filtration etc. In addition, since a very critical energy and water balance is maintained in the Bayer process, a pilot scale study involving all operations (milling, leaching, thickening, filtration, precipitation etc) is required for the evaluation of the process.

Based on the leaching studies on mechanically activated bauxites of different mineralogy, Pawlek *et al* [4] concluded that mineralogy did not have any effect on alumina recovery. About 90% dissolution for mechanically activated synthetic boehmite (Fig. 9) is interesting as a direction towards the development of universal Bayer process which is independent of mineralogy.

Tailoring Properties of Al-oxyhydroxides/oxides

Anomalous behaviour of mechanically activated boehmite highlights the immense scope to apply mechanical activation not only to save energy through reduction in thermal transformation ($AlOOH \rightarrow Al_2O_3$) temperatures but also to tailor structure and properties of the Al-oxyhydroxide/oxide phases. Literature on the

subject is still limited. Similarly, the concept of texture induced Zeta potential (Fig. 4 and 5) may be employed to tailor surface charge through mechanical activation. Size dependent surface charge has also been used for classification of particles by electrical field-flow fractionation [34].

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