

Stirred bead mill grinding of gibbsite: surface and morphological changes

T.C.Alex¹, Rakesh Kumar¹, S.K.Roy², S.P Mehrotra¹

¹ National Metallurgical Laboratory, Jamshedpur, PIN 831 007, India

² Metallurgical & Materials Engineering Department,
Indian Institute of Technology, Kharagpur, India.

*Correspondence author: T.C. Alex. Email: tc_alex@yahoo.com

Abstract: This paper describes the structural and surface changes in gibbsite subjected to mechanical activation using stirred media mill. During milling, the median particle size decreased from 52 μm to $\sim 3 \mu\text{m}$ in 30 min indicating high milling efficiency. SEM studies revealed that gibbsite particles, present in the feed as agglomerates of pseudo-hexagonal platelets, ruptured by attrition at grain joints followed by chipping leading to further fragmentation. During milling, progressive decrease in the intensity of (002) peak of gibbsite in powder X-ray diffraction pattern indicated amorphisation. It was found that the presence of hematite favoured amorphisation of gibbsite. Zeta potential and iso-electric point of gibbsite changed during milling which is indicative of alteration of gibbsite surface.

Keywords: gibbsite, stirred milling, zeta potential, amorphisation

1. Introduction

Recently, there has been increasing impetus on the application of mechanical/mechanochemical activation for developing new materials^[1-3] and metallurgical processes^[4-7]. Effect of the activation as a pretreatment before leaching and also during leaching has been investigated in processing of base metal sulphides^[4,5], titanium minerals^[6,7] etc. Several beneficial effects of activation are reported in terms of moderation in leaching conditions, enhancement in selectivity, improvements in metal recovery, and rheology and settling characteristics of leach residue. Mechanical activation of bauxite^[8-14] improves the performance of Bayer process of alumina production. Judicious selection of activation device in terms of both efficacy and size is, however, critical for successful development of metal

extraction processes. Stirred media mills, also known as attrition mill, beads mill, etc, are ideally suited for the Bayer process application due to their high efficiency and, more importantly, availability in large size (upto 10000 litres) and integration prospects in the existing process practices. Gibbsite is often the dominant mineral present in bauxite and fundamental understanding of its activation is important. Besides mill type and milling conditions, mineral associations in bauxite also influence the process of activation. The present paper focuses on mechanical activation of gibbsite using stirred media mill. Structural changes in gibbsite resulting from its interaction with hematite, a common associated mineral in the bauxite ore, have also been investigated and the results are reported.

2. Materials & Methods

Gibbsite precipitated from Bayer's liquor and having nearly uniform size ($d_{50} \sim 52 \mu\text{m}$) has been used in this study. The milling was carried out in a laboratory stirred media mill (Model: PE-075, Netzsch Feinmahitechnik GmbH, Selb, Germany). 100 g of gibbsite was milled at ambient temperature using stainless steel media (2 mm diameter) at an agitator speed of 1000 rpm. The solid: liquid and ball: powder ratios (by weight) were maintained at 0.5 and ~ 20 , respectively. The milling time was varied from 0-30 minutes. The procedure used for milling gibbsite-hematite mixture was the same as used for pure gibbsite. The amount of hematite used in the mixture was 20%. Slurry samples were withdrawn at fixed time intervals for characterisation.

Particle size distribution was measured using a laser diffraction based size analyzer (Model: Master Sizer S, Malvern Instruments Ltd, U.K.). Morphology of the particles was examined under scanning electron microscope (SEM) (Model JEOL 840, JEOL, Japan). The X-ray powder diffraction patterns were recorded on a Siemens diffractometer (Model: D500) using $\text{Cu-K}\alpha$ radiation. The degree of amorphisation was calculated from the XRD patterns adopting the procedure reported by Kitamura and Senna^[15]. Zeta potential and iso-electric points of gibbsite suspension were measured in de-ionised water using Zeta Probe (Colloidal Dynamics Inc, USA). The conductivity of the water used was $\sim 20 \mu\text{S/cm}$. pH was varied using acid/alkali solutions prepared from analytical grade reagents. All the measurements were carried out on slurries containing 10%

solid.

3. Results and Discussion

The comminution energy (E) in a stirred media mills is defined in terms of product of stress number (SN) and stress intensity (SI) as given below^[16]:

$$SN \propto nt(d_{50}/d_{GM})^2 \quad \dots \quad (1)$$

$$SI \propto d_{GM}^3 \rho_{GM} v_t^2 \quad \dots \quad (2)$$

where n and t are frequency and time of rotation respectively, d_{50} is median particle size of the feed, d_{GM} and ρ_{GM} are the diameter and density of the grinding media respectively and v_t is speed of the stirrer tip. For the same milling media and agitator configuration,

$$E = E(n, t) \propto n^3 \cdot t \quad (3)$$

In the present study, the energy input to the mill was altered by either varying the milling time (t) or the agitator speed (n). Physico-chemical changes in gibbsite are expressed as a function of these variables.

Particle size distribution

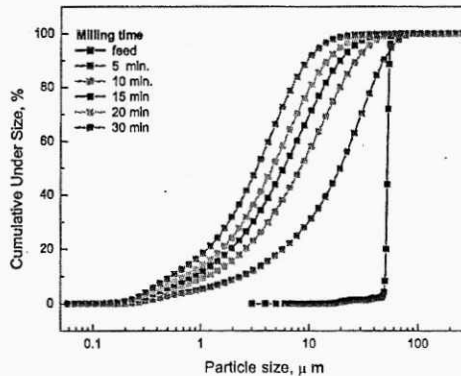


Fig. 1 Variation of size distribution of gibbsite with milling time

Fig. 1 shows the particle size distributions (PSD) of the gibbsite milled for different durations. During milling, the median particle size (d_{50}) decreased from

52 μm to $\sim 3 \mu\text{m}$ in 30 min indicating high milling efficiency. In a ball mill, Kano et al^[17] had to grind a gibbsite sample ($d_{50} = 34.4 \mu\text{m}$) for 3 hours to get similar product size. The size distribution of the feed gets altered very fast with milling. The uni-modal size distribution in the feed changes to bimodal distribution. This may be indicative of multiple breakage mechanisms.

Morphological studies

Fig. 2 depicts the evolution of gibbsite morphologies with milling time. Individual particles in the feed were present as agglomerates consisting of pseudo-hexagonal platelet-shaped crystals. The disappearance of the initial morphology was seen during milling. Particles with platelet like structure seen during the initial stage of milling indicated particle breakage at grain joints. Further increase in milling time resulted in disappearance of platelets and generation of particles having complex shapes. Similar morphological features have also been reported by Frances et al^[18]. Based on extensive image analysis studies, they concluded that the initial stage of grinding is dominated by rupture of grain joints caused by attrition. In the later stages, chipping and the breakage of crystallites were responsible for generation of large amounts of fine fragments.

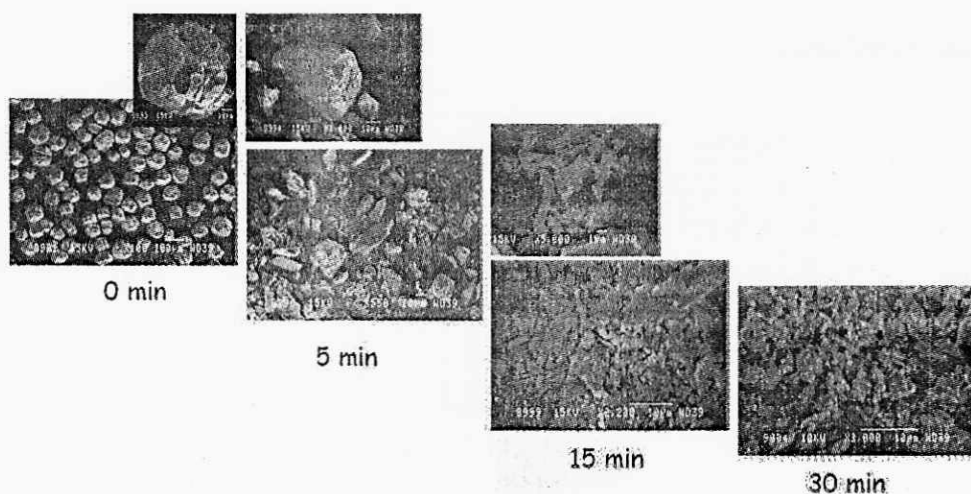


Fig. 2 Morphological changes with milling

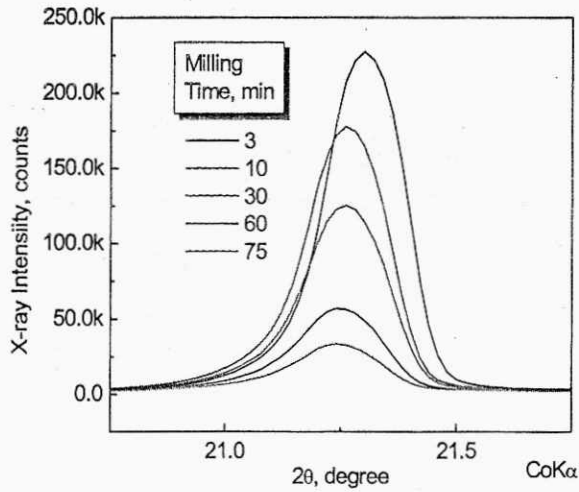


Fig.3 Changes in x-ray intensity of gibbsite (002 peak) with increasing milling time

X-ray diffraction studies

Changes occurring during stirred media milling can go beyond the realm of size reduction. A progressive decrease in the intensity of (002) peak of gibbsite was observed (Fig. 3) and this was used to calculate the degree of amorphisation^[12].

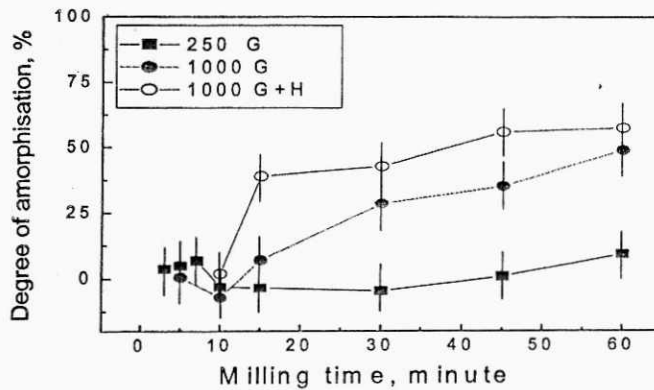


Fig.4 Degree of amorphisation of gibbsite with milling time for pure gibbsite (G) and gibbsite-hematite (G+H) mixture

Fig. 4 shows the results on degree of amorphisation of gibbsite during milling of pure gibbsite and gibbsite-hematite mixture. During milling of pure gibbsite at 250 rpm, no significant amorphisation was observed with milling time. Nearly 50% amorphisation of pure gibbsite was observed at 1000 rpm after 30 min of milling. Comparison of amorphisation results for pure gibbsite at 250 and 1000 rpm suggests that mill energy ($E \propto n^3$, Eq. 3) is critical to achieve amorphisation. At 1000 rpm, higher amorphisation of gibbsite was observed during the milling of gibbsite-hematite mixture than pure gibbsite. This indicates that the presence of hematite favours amorphisation of gibbsite. The hardness of hematite (5-6 on Mohs' scale) is higher than that of gibbsite (2.5-3 on Mohs' scale). It is likely that the harder hematite phase acts as a fine media resulting in increased grinding energy (Eqs. 1 and 2) and favouring amorphisation.

Zeta potential of milled slurries

Fig. 5 shows the variation of zeta potential (ξ -potential) of gibbsite with pH at different milling times. Iso-electric points, that is pH corresponding to ξ equal to zero, for the different milled samples are also shown in Fig. 6. An increase in ξ -potential and shift of iso-electric point with milling time suggest alteration of gibbsite surface during milling.

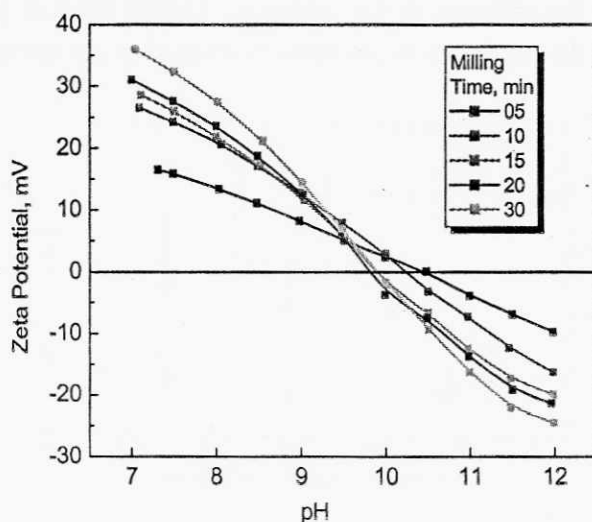


Fig.5 Variation of zeta potential changes with increase in milling time

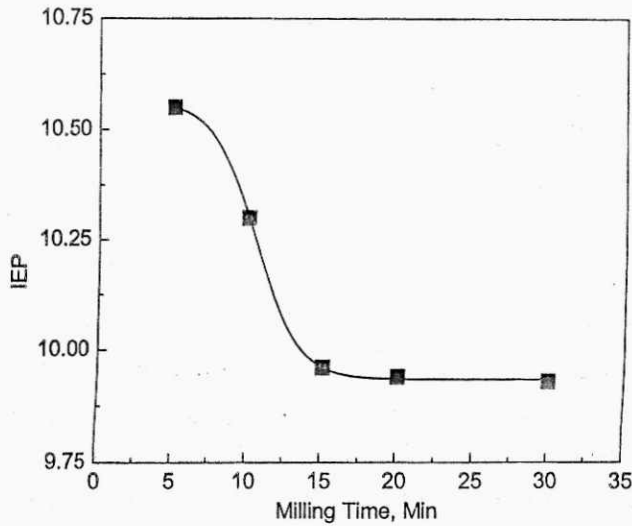


Fig. 6 Variation of iso-electric point (IEP) of gibbsite with increase in milling time

SEM studies show that the gibbsite particles undergo breakage initially through breakage at grain joints and this was followed by chipping. During breakage at grain joints more of flat platelet surface is exposed to the surrounding media. Chipping which leads to the formation of finer fragments of particles involves creation of more edge surface. Roseqvist et al^[19] and Hiemstra et al^[20] have reported that both doubly coordinated OH groups ($\equiv\text{Al}_2\text{OH}$) and singly coordinated OH groups ($\equiv\text{AlOH}$) are available in gibbsite surfaces. Mostly the basal planes (001 plane) are occupied by the $\equiv\text{Al}_2\text{OH}$ groups, whereas $\equiv\text{AlOH}$ and $\equiv\text{Al}_2\text{OH}$ groups are equally distributed on the edge sides (100, 010, 110 planes). It is likely that the alteration of the surface and charge generation on the gibbsite surface is linked with breakage mechanisms; however, further studies are required to corroborate this hypothesis.

4. Conclusions

Major conclusions that follow from the present study are:

- 1 Stirred media milling of gibbsite is characterized by high efficiency vis-à-vis ball mill.
- 2 The milled gibbsite shows bimodal size distribution after stirred media

milling. Multiple mechanisms, breakage at platelets joints during initial stages followed by chipping, are involved during milling.

3 Milling energy is critical to achieve amorphisation of gibbsite. Presence of hematite during milling favours amorphisation of gibbsite.

4 Milling results in an increase in ξ -potential and shift of iso-electric point towards lower pH value indicating alteration of gibbsite surface during milling.

Acknowledgement

The authors are grateful to National Aluminium Company (NALCO), Bhubaneswar, India, for providing the gibbsite samples for the study.

References

1. Puclin T., Kaczmarek W.A., Synthesis of alumina-nitride nanocomposites by successive reduction nitridation in mechanochemically activated reactions, *Journal of Alloys and Compounds*, **1998**, 266, 283–292.
2. Senna M., Recent development of materials design through a mechanochemical route *International Journal of Inorganic Materials*, **2001**, 3509–514.
3. Temuujin J., MacKenzie K. J. D., Jadambaa T., Namjildorj B., Olziiburen B., Smith M. E and Angerer, Effect of mechanochemical treatment on the synthesis of calcium dialuminate *J. Mater. Chem.*, **2000**, 10, 1019–1023.
4. Maurice D., Hawk J.A., Ferric chloride leaching of mechanically activated chalcopryrite, *Hydrometallurgy*, **1998**, 49, 103–123.
5. Balaz P., Achimovicova M., Bastl Z., Ohtani T., Sanchez M, Influence of mechanical activation on the alkaline leaching of enargite concentrate *Hydrometallurgy*, **2000**, 54, 205–216.
6. Amer A.M., Alkaline pressure leaching of mechanically activated Rosetta ilmenite concentrate, *Hydrometallurgy*, **2002**, 67, 125–133.
7. Sasikumar C., Rao D.S., Srikanth S., Ravikumar B., Mukhopadhyay N.K., Mehrotra S.P., Effect of mechanical activation on the kinetics of sulfuric acid leaching of beach sand ilmenite from Orissa, India, *Hydrometallurgy*, **2004**, 75, 189–204.
8. Pawlek F., Kheiri M.J., Kammel R., *Light Metals*, **1991**, 91–95.
9. Mc Cormick P.G., Picaro T., Smith P.A.I., *Minerals Engineering*, **2002**, 15, 211–214.
10. Shumskaya L.G., *J. Mining Science*, **2002**, 38, 299–304.

11. Shumskaya L.G., Yusupov T.S., *J. Mining Science*, **2003**, 39(6), 610-615.
12. Rakesh Kumar, Alex T.C., Srivastava J.P., Ravi Kumar B., Khan Z.H., Mahapatra S.P., Misra C.R., Mechanochemical activation of bauxite: on the nature of physicochemical changes and reactivity of bauxites. *Metals Materials and Processes*, **2004**, 16(2-3), 171-180.
13. Rakesh Kumar, Alex T.C., Khan Z.H., Mahapatra S.P., Misra C.R., *Light Metals*, **2004**, 31-34 (ed. P. Crepeau (Minerals, Metals & Materials society, Warrendale).
14. Rakesh Kumar, Alex T.C., Jha M.K., Khan Z.H., Mahapatra S.P., Mehrotra S.P., Mechanical Activation of Bauxite – Potential and prospects in the Bayer process. *Light Metals*, **2005**, 77-79 (ed. P. Crepeau (Minerals, Metals & Materials society, Warrendale).
15. Kitamura M., Senna M., Electrorheological properties of mechanically activated gibbsite, *International Journal of Inorganic Materials*, **2001**, 3(6), 563-567.
16. Kwade A., Schwedes J., Breaking characteristics of different Materials and their effect on stress intensity and stress number in stirred media mills, *Powder Technology*, **2002**, 122, 109-121.
17. Kano J., Mio H., Saito F., Correlation of grinding rate of gibbsite with impact energy of balls. *AIChE Journal*, **2000**, 46(8), 1964-1967.
18. Frances C., Le Bolay N., Belaroui K., Pons M.N., Particle morphology of ground gibbsite in different grinding environments. *Int.J.Minor.Process*, **2001**, 61, 41-56.
19. Roseqvist R., Persson P., Sjöberg S., Protonation and charging of nanosized gibbsite (α -Al(OH))₃ particles in aqueous suspension, *Langmuir*, **2002**, 18, 4598-4604.
20. Hiemstra T., Yong H., Van Riemsdijk W.H., Interfacial charging phenomena of aluminium (hydr)oxides. *Langmuir*, **1999**, 15, 5942-59