

ABSTRACT

Reactivity of the industrially important Al-oxyhydroxides minerals, particularly of gibbsite [γ -Al(OH)₃] and boehmite (γ -AlOOH) is the focus of this study. Mechanical activation using planetary and attrition mills has been used to enhance the reactivity of these minerals. Industrial gibbsite and boehmite prepared by thermal decomposition of the gibbsite have been used. The mineral samples, both unmilled and milled, are characterised in terms of their particulate (particle size distribution, specific surface area, pore size distribution, morphology and zeta potential), structural (XRD, TEM and FTIR) and thermal (TG-DTA) characteristics. The reactivity has been assessed in terms of their dehydroxylation characteristics and leachability in NaOH solutions. As gibbsite is more reactive vis-à-vis boehmite, more emphasis has been given to the latter.

Breakage mechanism of gibbsite in planetary mill involves separation and breakage of the platelets constituting the particles followed by aggregation of particles. The structural disordering has increased with milling, and mostly an amorphous phase is obtained after 240 min of milling. The energy stored in the structural defects enhances the reactivity of gibbsite in terms of decrease in the dehydroxylation temperature and increase in dissolution in NaOH solutions. During attrition milling, the particle aggregation has been negligible, unlike in planetary mill. During attrition milling, the ζ -potential of gibbsite is observed to increase with milling time; the increase has been ascribed to the generation of reactive singly coordinated OH species on the gibbsite surfaces.

Large surface area (264 m²/g) and unique pore structure have been the characteristics of the boehmite used in this study. Severe aggregation and fusion of particles are observed from the early stages of planetary milling, whereas, aggregation has been negligible during attrition milling. An anomalous decrease in the specific surface area is observed during planetary milling, ~75% decrease in 240 min, due to changes in the pore structure and pore size distribution. Analyses of XRD data has shown that the microcrystalline dimension decreases with milling time while the microstrain is increased; both signify accumulation of energy in the solid structure which enhances the reactivity of boehmite, in spite of a decrease in the specific surface area. Partial rehydration of boehmite to bayerite [α -Al(OH)₃] is observed during attrition milling of boehmite, and is explained on the basis of Al₂O₃-H₂O phase diagram.

With planetary milling, the thermal transformation profile has been found to change; the removal of physisorbed water is delayed, whereas, its transformation temperatures to γ -Al₂O₃ and subsequently to α -Al₂O₃ are lowered with milling time. This has been explained on the basis of changes in the Al-OH and hydrogen bond strengths with the decreasing microcrystalline dimension (MCD) as the milling time is increased. The kinetics of γ -Al₂O₃ transformation has been analysed as a two step process since it involves removal of two energetically different equatorial and axial type hydroxyls. It is observed that the activation energy for the second step continuously decreases with milling time indicating enhancement of reactivity. The changes observed for the first step has been unsystematic, possibly due to the delayed removal of physically adsorbed water.

The structural changes observed during planetary milling have enhanced the leachability of boehmite in NaOH solutions; more than 90% boehmite dissolution is possible at 90 °C and ambient pressure for 240 min milled boehmite. Kinetic analysis has revealed that the dissolution mechanism changes with milling; shrinking core model describing the dissolution of unmilled boehmite changes to mostly a second order mechanism for the milled boehmite. The ratio k^*/k , where k and k^* are, respectively the rate constants of unmilled and milled samples, has increased indicating reactivity enhancement. The activation energy of the dissolution has decreased from ~ 65 kJ/mol for the unmilled boehmite to ~ 40 kJ/mol for 240 min milled boehmite. The nature of the increase in surface area normalised rate constants with milling time shows role of structural changes, and possibly a complex role of specific surface area on the reactivity.

The reactivity of boehmite has been found to have strong correlations with the microcrystalline dimension and microstrain.

Key words: aluminium oxyhydroxides, mechanical activation, reactivity, microcrystalline dimension, microstrain, activation energy, zeta potential, specific surface area, pore size distribution, dehydroxylation, leaching kinetic models.