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A. GÜNEY, A. A. SİRKECİ, A. E. YÜCE, K. T. PEREK

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Güven Önal, Neşet Acarkan, M. Sabri Çelik, Fatma Arslan, Gündüz Ateşok, Ali Güney, A. Ali Sirkeci, A. Ekrem Yüce, K. Tahsin Perek

İstanbul Technical University, Mining Faculty, Turkey

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Mechanical activation of solids in processing of minerals and wastes

S.P. Mehrotra
National Metallurgical Laboratory, Jamshedpur, India

Rakesh Kumar
National Metallurgical Laboratory, Jamshedpur, India

Sanjay Kumar
National Metallurgical Laboratory, Jamshedpur, India

ABSTRACT: Recently, there has been an increasing interest in mechanical/mechanochemical activation of solids for developing new materials and metallurgical processes. In this paper, a brief overview of our research in this area is presented. Select applications of mechanical activation are discussed with emphasis on characterisation of activated materials, and the prospects and possibilities of developing improved/novel processes. The main applications covered include the Bayer process of alumina production, and blended cement manufacturing.

1 INTRODUCTION

Mechanochemistry is the branch of chemistry that has primarily evolved in the twentieth century (Boldyrev, 1986, Juhasz & Opoczky, 1994, Fernandez-Bertran, 1999). It deals with the field of reactions caused by mechanical energy, often referred to as Mechanical or Mechanochemical Activation. The process of activation depends on the breakage process, e.g. compression, shear, impact etc, and the rate at which energy is supplied to the system (Boldyrev, 1986, Juhasz & Opoczky, 1994, Boldyrev et al. 1996, Steinike & Hennig, 1998, Takacs, 1998, Gorobets et al. 2004). In contrast to coarse grinding, where the objective is primarily confined to size reduction, mechanical activation is concerned with structural changes that are brought about by application of mechanical energy. Fine grinding is an intermediate case between coarse grinding and mechanical activation (Juhasz & Opoczky, 1994, Boldyrev et al. 1996). The solid state reactions during mechanical activation are generally believed to be favoured due to increase in surface area, stresses and defects induced in the solid structures, phase transformations, localised and overall thermal effects, repeated welding of interfaces and fracture leading to dynamic creation of fresh surfaces for reactions etc. Besides bulk activation, 'surface activation', may contribute towards mechanically induced reactivity (Juhasz & Opoczky, 1994, Kumar et al. 2005a). Presence of water during milling and mechanical activation can lead to number of additional phenomena, for example, stress induced polarisation of surface water and OH^- species, change in the nature of electrical double layer, material transport through surface water, etc (Avvakumov 1994, Senna 1996, Kumar et al. 2005b). Mechanically induced reactivity of solids offers newer possibilities in materials development and metallurgical processing. The notable areas of applications include mechanical alloying, mineral processing, leaching, sintering, catalysis, paints and pigments, cements, geopolymers, pharmaceutical, hydrogenation etc (Boldyrev, 1986, Juhasz & Opoczky, 1994, Murty & Ranganathan, 1998, Balaz, 2000, Balaz, 2003, Grigorieva et al. 2003, Boldyrev, 2004, Kumar et al. 2005c).

The capacity of mechanical activation device is an important consideration in extractive metallurgy and other applications requiring processing of large amount of materials for successful commercial applications (Johansson et al. 1999, Kumar et al. 2004a, b, Kumar et al. 2005a, c). This paper is an overview of our recent research on the applications of mechanical activation in the development of: (a) an eco-friendly Bayer process for alkali leaching of bauxite and, (b) improved blended cements containing blast furnace slag and fly ash. Mechanical activation of bauxite, slag and fly ash is carried out using high energy mills, such as attrition mill and vibratory mill, which have good prospects for applications requiring large scale processing. The focus of the paper is on the physicochemical changes and mechanically induced reactivity of solids, and processing using mechanically activated solids.

2 DEVELOPMENT OF ECOFRIENDLY BAYER PROCESS FOR ALUMINA PRODUCTION

2.1 *The red mud problem*

The Bayer process accounts for majority of world's production of alumina. The process involves digestion of bauxite in a caustic soda solution. The leach residue produced after filtration, washing and thickening, is commonly known as 'Red mud'. Typically, 1-1.5 tonnes of red mud is generated per tonne of alumina produced. It is estimated that nearly 90 million tonnes of red mud is generated worldwide, and India alone contributes about 3 million tonnes (Kumar et al., in press). Red mud may contain 10-25 % Al_2O_3 and 2-8 % Na_2O, and considering large volume of red mud generation, these represent huge resource and financial losses.

2.2 *Use of mechanical activation in Bayer process*

The presence of soft oxyhydroxide minerals in bauxite, for example gibbsite etc, characterised by weak M-OH bonding makes bauxite a suitable material for mechanical activation (Pawlek et al. 1992, Shumskaya, 2002, Shumskaya & Yusupov, 2003, Kumar et al. 2004a, b). Mechanical activation of bauxite has been carried out to achieve moderation in leaching conditions and minimise loss of soda and alumina in red mud (Pawlek et al. 1992, Li et al. 1991, McCormick et al. 2002). Recent studies by Kumar et al. (2004a, b, 2005a) have focused on systematic characterisation of original and activated gibbsitic bauxite, role of mechanical activation in leaching, efficacy of mechanical condition vis-à-vis temperature and alkali concentration during leaching, and coupling of milling and leaching processes. The major findings of these studies are summarised in the following sections. Justification for the use of attrition mill as a device of choice for mechanical activation is presented as a prelude to the findings.

2.3 *Attrition mill as a device of choice for mechanical activation of bauxite*

The process of grinding depends on 'stress intensity (SI)' and 'stress number (SN)' as defined below (Kolb & Ott, 1992, Kwade & Schwedes, 2002):

$$SI = D_{M^3} \cdot \rho_M \cdot v_t^2 \qquad \ldots \quad [1]$$

$$SN = n \cdot t \cdot \left(\frac{X_{50}}{D_M}\right)^2 \qquad \ldots \quad [2]$$

(where, v_t = circumferential speed of rotor (discs or pegs or smooth surface), D_M = diameter of the grinding media, ρ_M = density of the media, n = number of revolutions of the rotor, and X_{50} = characteristic particle size of the material to be ground). In physical terms, stress intensity is the intensity of each impact on one or more particles during the grinding process, and stress number is a value for the number of impacts between the grinding media in a mill. The product of stress intensity and stress number is directly proportional to grinding energy. High grinding energy in attrition mills (typically SI = $1.6x10^{-4}$, SN = 2.2.t for ρ_M = 7.1 g/cm^3, D_M = 0.2 cm, n = 1000 rpm, v_t = 1.7 m/s and X_{50} = 94.5μm) makes them ideally suited for fine grinding as compared to ball mills (SI = $4x10^{-3}$, SN = $6x10^{-4}$.t for ρ_M = 7.1 g/cm^3, D_M = 2.5-3.0 cm, n = 40 rpm, v_t = 0.17 m/s and X_{50} = 94.5μm) (Kumar et al. 2004c). Present availability of large capacity mills, upto 10000 L, is a favourable factor for potential application of attrition mills in the Bayer process of alumina production. Wet milling in an attrition mill offers the possibility of combining milling and leaching operations in a single step.

2.4 *Mechanical activation of bauxite*

Bauxite undergoes particle breakage and structural changes during attrition milling. The particle breakage dominates during early stages (3-5 min) of milling. In a typical milling experiment, the initial values of median particle size (X_{50}), 34 μm, changed to 4.75 and 2.35 μm after 3 and 30 min of milling, respectively. Structural changes in gibbsite, which is a soft mineral and present as a dominant mineral, can be detected by powder X-ray diffraction (XRD) technique (Fig. 1). Gibbsite does not transform into new mineral phase(s) but undergoes amorphisation during milling. The loss in the X-ray intensity of (002) peak of gibbsite is attributed to breakage of Al-OH bond or amorphisation (Kitamura & Senna, 2001, Shumskaya, 2002, Shumskaya & Yusupov, 2003, Kumar et al. 2004a).

The interaction of minerals during attrition milling is not completely understood. It has been observed that presence of minerals, such as hematite, can

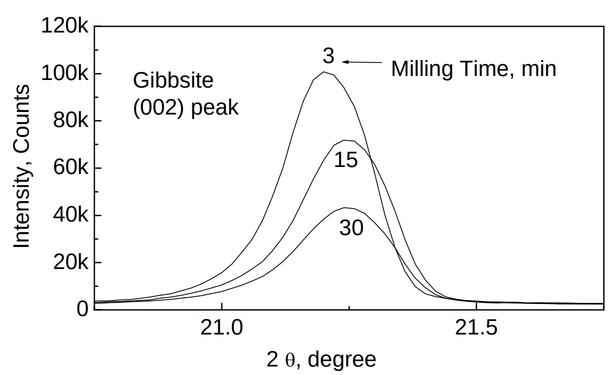

Figure 1. Effect of attrition milling time on the X-ray intensity of (002) peak of gibbsite

facilitate the activation of relatively soft gibbsite under milder milling conditions (Kumar et al., unpublished results). Effect of milling/mechanical activation on minerals other than gibbsite is difficult to characterise by XRD techniques due to their presence in smaller amount and interference by other minerals.

2.5 *Alkali leaching of mechanically activated bauxite*

Figure 2 shows the strongest (002) peak of gibbsite in the XRD patterns of leach residue obtained after alkali leaching of non-activated bauxite, bauxite milled for 3 min (mostly particle breakage), 15 min (particle breakage and structural changes), and a typical plant red mud produced using the same bauxite. It is interesting to note that the combined effect of particle breakage and structural changes (referred to as mechanical activation) results in complete leaching of gibbsite and its elimination from the leach residue.

Under similar alkali to caustic ratio conditions, the residue obtained after alkali leaching of mechanically activated bauxite at 90 °C contained ~ 10% Al_2O_3 and < 1% Na_2O as compared to typical plant red mud that contained 15-30 Al_2O_3 and 3-4%. Na_2O. Unlike plant red mud which contained gibbsite as a major mineral, hematite was present as dominant mineral in the leach residue of mechanically activated bauxite.

2.6 *Efficacy of mechanical activation*

Efficacy of mechanical activation has been investigated as a function of the leaching temperature and alkali concentration (Kumar et al. 2005a). Figure 3 shows the effect of mechanical activation on extractable Al-trihydrate (ATH %) at 90, 106 and 145 °C under alkali concentration of 180 g/l and 250 g/l. The effect of mechanical activation on ATH% at 90 °C and 180 g/l Na_2O is quite noticeable. The effect becomes less pronounced at higher Na_2O concentration. At the leaching temperature of 106 and 145 °C, the effect of milling

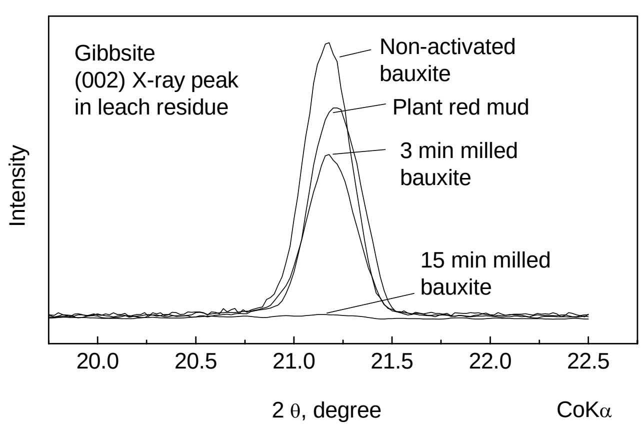

Figure 2. Effect of mechanical activation on (002) XRD peak of gibbsite in leach residue of bauxite

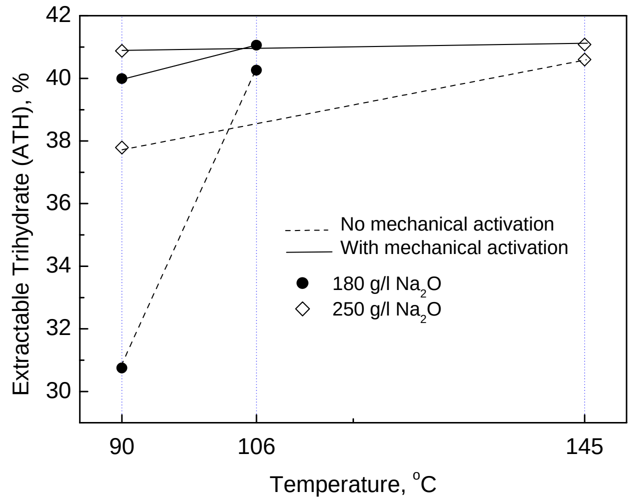

Figure 3. Effect of mechanical activation on extractable Al-trihydrate (ATH %)

is not as significant, irrespective of Na_2O concentration and temperature. ATH % similar or better than 106 and 145 °C can be achieved at 90 °C with mechanically activated bauxite. The results presented in Figure 3 are quite interesting and show the combined effects of mechanical activation and thermal activation at different concentrations of Na_2O. Mechanical activation represents extra energy in bauxite being leached due to particle breakage and structural changes in mineral such as gibbsite. While no quantification of this energy is possible at this stage, the stored energy is enough to manifest itself at lower temperature resulting in enhanced dissolution.

2.5 *Coupling of leaching and mechanical activation and future prospects*

In spite of encouraging results on the effect of mechanical activation on leaching of bauxite in terms of reduction in alumina and soda content of red mud and prospects of moderation in leaching conditions, a number of issues remain to be considered further, e.g.. coupling of mechanical activation with leaching operation. It has been found that in batch type experiments both 'separate milling and leaching (SEMIL)' and 'simultaneous milling and leaching (SMILE)' result in similar alumina extraction. However, higher soda content is observed in the case of SEMIL depending upon the duration of leaching. SMILE is a better proposition from the point of view of reduction in processing step and effective utilisation of energy lost during milling for the purpose of leaching (Kumar et al. 2005a). Other issues that need further probing are settling behaviour of red mud, behaviour of impurities during the leaching of mechanically activated bauxite and the testing of SMILE concept in continuous operation.

3 IMPROVED BLENDED CEMNTS

3.1 *Resource conservation in cement manufacture*

Typically, 1-1.5 tonnes of limestone and 0.5 tonnes of coal are used per tonne of clinker produced Specific energy consumption in cement manufacturing amounts to 4000 MJ/tonne of cement with nearly 80% contributions arising from thermal energy (mostly for clinker formation) and rest from electrical energy (major contribution arising from grinding). Similarly, 0.8-1 tonne of CO_2/tonne of clinker is generated during clinker formation. Replacement of clinker with industrial wastes, such as fly ash and granulated blast furnace slag is practised world over for resource conservation, reduce energy consumption and minimise CO_2 emissions. In India, blended cements containing 20-25% fly ash, and nearly 40% blast furnace slag are produced (Kumar et al. 2005c, Kumar et al, in press). The fly ash and the slag produced in the country amount to ~110 and 12-15 million tonnes. 10-12% fly ash and 40-50% slag are utilised in blended cement manufacturing and there is significant scope to increase the utilisation of these wastes in blended cement manufacturing. Recently, usage of large volume of slag and fly ash in blended cements has attracted intensive research attention (Olorunsogo, 1998, Dongxum et al. 2000, Kumar et al. 2004c, Kumar et al. 2005c). The higher usage in the blended cements is restricted by the low pozzolonic and/or latent hydraulic activity, consequently resulting in slow development of compressive strength as compared to Ordinary Portland Cement (OPC). High-energy milling is suggested to improve the reactivity of the blended cement constituents, namely the clinker, fly ash and the slag (Boldyrev, 1986, Juhasz & Opoczky, 1994, Johansson et al. 1999). Recent studies by the authors (Kumar et al. 2004c, d, Kumar et al. 2005b, c) have focussed on the mechanically induced reactivity and the use of the activated slag and fly ash in blended cement formulations to increase replacement of clinker. One of the highlights of these studies has been the comparison of different types of high energy milling devices.

3.2 *Mechanically induced reactivity of blast furnace slag and fly ash*

Ground granulated blast furnace slag (GGBFS) is a glassy granular material consisting essentially of silicates and aluminosilicates of calcium and other oxides. The slag possesses latent hydraulic activity, i.e. it shows cementitious properties in contact with water over a long period of time. It has been recently shown (Kumar et al. 2005b) that complete hydration of slag is possible in short time (days) even without a chemical activator provided the slag is

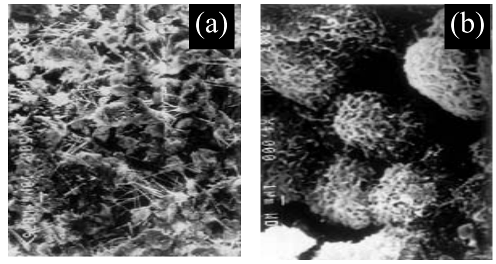

Figure 4. SEM micrographs showing morphology of slag hydration product after 28 days (a) non-activated slag, (b) 30 min attrition milled slag

mechanically activated by attrition milling (Fig.4). The process of activation, and consequent hydration, is mill specific and ball milled slag of same fineness does not behave in the same manner. The hydration is facilitated by combined effect of particle breakage and surface activation during milling as manifested by change in zeta potential of the slag. Isothermal conduction calorimetric studies revealed that during hydration, the formation of impervious hydrous surface film that inhibits hydration of neat ball milled slag (Taylor, 1998) is prevented in the case of attrition milled slag (Kumar et al. 2005b). Unlike the poorly crystalline hydration product formed by the non-activated slag even after prolonged hydration for years, the mechanically activated slag forms a crystalline product and the crystallinity can be improved with increasing mechanical activation.

Unlike blast furnace slag, class F fly ash that is dominant in India consists of more than 70% SiO_2, Al_2O_3 and Fe_2O_3 and shows pozzolanic activity, i.e. it develops cementitious properties after reaction with lime. SEM studies have indicated that the fly ash after mechanical activation, using vibratory or attrition milling, form a denser reaction product as compared to raw fly ash due to increased reactivity (Kumar et al. 2005c).

3.3 *Mechanical activation and cement properties*

Figures 5 and 6, respectively, show the strength development in blended cements as a function of % replacement of clinker by mechanically activated slag and fly ash, using attrition and vibratory mills. Results for commercial cements containing ~ 35 % slag and 25% fly ash are given in Figure 5 and 6, respectively as reference.

The effect of mechanical activation of the slag on clinker replacement is mill specific (Fig.5). The median size of attrition milled and vibratory milled slag was of the order of 13-15 μm. However, it was found that the strength of cement sample containing upto 80% attrition milled slag was comparable or superior to commercial cement containing only 35% slag. Increasing replacement of clinker by vibratory milled slag of similar fineness resulted in

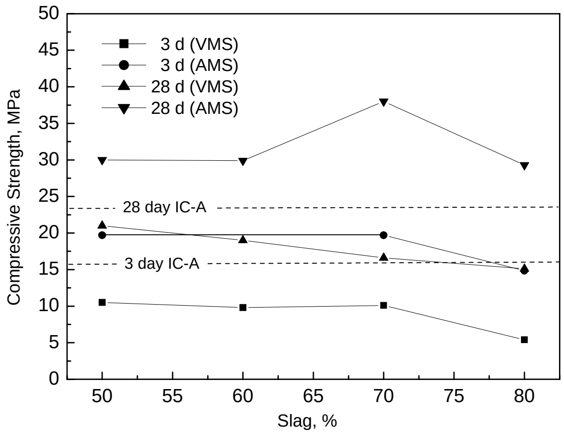

Figure 5. Variation in compressive strength of cement as function of replacement of clinker by mechanically activated blast furnace slag

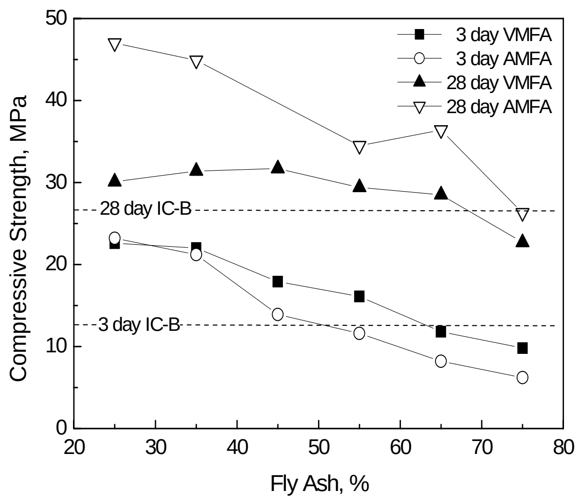

Figure 6. Variation in compressive strength of cement as function of replacement of clinker by mechanically activated fly ash

unacceptable lowering of cement strength and was not effective. Both attrition mill and vibratory mill gave good result in the case of fly ash (X_{50} = 9-12 μm) and 50-60% clinker could be replaced by mechanically activated fly ash (Fig. 7).

3.4 Alternate strategies in cement manufacturing

Alternate strategies need to be evolved based on the results obtained with mechanically activated slag and fly ash. Attrition milling is carried out in wet condition and on-site milling and blending needs consideration. The current practice of fly ash containing blended cements production involves transport of fly ash from power plant to the cement industry since the proportion of fly ash used is less than 25% of cement clinker. However, this may require rethinking for the cement containing 50% or more fly ash and their production in small scale units near coal fired thermal power plants.

4 CONCLUSIONS

Select applications of mechanical activation are presented in the paper to illustrate possibilities of developing environmental friendly processes and minimisation and utilisation of solid wastes. Mechanical activation of bauxite in the Bayer process can be used to minimise soda and alumina losses in the red mud and achieve moderation in process conditions. Similarly, increased utilisation of blast furnace slag and fly ash in blended cements through judicious use of mechanical activation devices, such as attrition and vibratory mills, has interesting resource conservation and waste recycling implications.

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