

# MECHANICAL ACTIVATION OF SOLIDS IN EXTRACTIVE METALLURGY

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## INTRODUCTION

Mechanochemistry is the branch of chemistry that has primarily evolved in the twentieth century. It deals with the field of reactions caused by mechanical energy, often referred to as Mechanical or Mechanochemical Activation [1-3]. The process of activation depends on the breakage process and the rate at which energy is supplied to the system [1-3]. In contrast to coarse grinding, where the objective is 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 [1-3]. Mechanical activation has been attempted in a variety of disciplines, such as extractive metallurgy, waste utilisation, mechanical alloying, advanced ceramics, catalysis, coal gasification, paints and dyes, fertilizers, drugs and pharmaceuticals, organometallic synthesis, and many others. The changes occurring in solids during the course of mechanical activation are listed below:

- (a) Milling of the particles to a very small size
- (b) Generation of large new surfaces.
- (c) Formation of dislocations and point defects in the crystalline structure.
- (d) Phase transformations in polymorphic materials.
- (e) Chemical reactions: decomposition, ionic exchange, oxidation-reduction, complex and adduct formation, etc.

As mentioned earlier, mechanochemistry, as a discipline, has evolved in 20<sup>th</sup> Century and its definition and scope has expanded with time. We have summarized the historical evolution of mechanochemistry in Table 1.

**Table-1** : Evolution of Mechanochemistry

1919	Study of chemical transformations induced by gravitational and kinetic energy, as well as by energies connected with change in volume, surface and shape of material (Wilhelm Ostwald in Handbuch der allgemeinen Chemie)
1943	Study of correlations between chemical bonding and mechanical strength (G.R. Huttigs in Handbuch der Katalyse, Vol. IV Springer)

1952	Processes which were affected by mechanical energy and which involved an increase in the chemical reactivity of the system, but without altering its chemical composition (A.G. Smekal in Proceedings of the International Symposium on the Reactivity of Solids)
1962	"Mechanochemical reactions" are transformations which are accompanied by change in chemical composition of the system through action of mechanical energy (K. Peters: I. Europ. Symp. Zerkleinern, Verlag Chemie)
1971	Mechanochemistry is a science on acceleration and initiation of reactions in gases, liquids and solids by the effect of plastic energy, (P.J. Butjagin Uspechi Chimiji, 40)
1984	Mechanochemistry as a branch of chemistry which is concerned with chemical and physicochemical transformations of substances in all stages of aggregation produced by the effect of mechanical energy. (G. Heinicke, Tribochemistry, Academie-Verlag, Berlin)
1990	Mechanochemistry comprises those structural and physicochemical changes (as well as chemical reactions) which are induced in solids by deformation, disintegration and dispersion as a result of application of mechanical energy or which are consequences of such actions (A.Z. Juhasz & L. Opoczky, Mechanical Activation of Minerals, Ellis Horwood Ltd.,)

### Communion and Mechanical Activation of Solids

Mechanical activation of solids can be explained by the classical Griffith theory of fracture in brittle materials which is derived on the basis that the rate of elastic strain energy released during crack propagation is equal to the work required to generate new surface area accompanying crack propagation [4,5]:

$$\sigma_c = \left[ \frac{E\gamma}{a} \right]^{1/2} \quad [1]$$

(where  $\sigma_c$  is critical tensile strength for crack propagation of flaw size  $a$ ,  $E$  is tensile elastic modulus and  $\alpha$  is the surface energy). The equation shows that a decreasing flaw size requires higher tensile strength to propagate and that there is a critical particle size corresponding to a particular stress level which is greater than the crack length. It may be emphasized that above equation does not take into consideration crack-tip plasticity effect. After the critical size is achieved, energy can be stored in the material only through brittle to ductile transition and plastic deformation of material. The effect of plastic deformation increases with decreasing particle size. Therefore, if fine enough, particles consisting of materials usually regarded as brittle (such as quartz, calcite, cement clinker etc) undergo plastic deformation instead of fracture. To elaborate further on this point, the milling process may be briefly divided into three stages [4,6]. The rittinger stage, that corresponds to the reduction in size with a proportionality relationship between the energy input and the new surface area produced,

aggregation stage, that leads to decrease in size but the particles start to interact with each other through weak and reversible Van der Waals type adhesion forces, and the agglomeration stage, where decrease in size drops to negligible value or stops and size may even increase because of intense particle interaction. Mechanochemical activation mainly occurs during this stage.

Mechanical activation depends on mode(s) of stress (shear, compression, impact etc), the rate of application of stress, absorption of energy and its relaxation by the material. Material properties and mill construction as well as the mode of operation are important in achieving activation. For example, if the milling device can not transfer sufficient energy and impacts to the powder, the particles cannot be ground, though the size of particles is still larger than the brittle to ductile transition [7]. Depending on the mode of transfer of external energy, mechanical activation can be carried out in a variety of mills such as planetary mills, attrition mills, vibratory mill, tumbling mill, jet mill, ball mill etc., both in dry and wet media. The success of the activation treatment depends on judicious selection of activation device.

### **Mechanical Activation in Extractive Metallurgy**

Mechanical activation of minerals can be used in different stages of metal extraction both in pyrometallurgy and hydrometallurgy. Majority of applications so far deals with leaching ores and minerals, minimisation/utilization of wastes from metal extraction or allied industries, such as thermal power plants. We have tried to highlight only a few pyrometallurgical applications to focus on the novelty aspects and deal primarily with applications in leaching and waste utilization.

In pyrometallurgy, the effect of mechanical activation on thermal decomposition and roasting has been studied from three different aspects. The first is the decrease of reaction temperature, the second is the change of reaction mechanisms, and the third, typical of production of active oxides, is the relationship between the structure of solid structure and properties of the resulting product. Some of the good examples are temperature of reaction of zircon ( $ZrSiO_4$ ) with calcium carbonate ( $CaCO_3$ ) to form calcium zirconate ( $CaZrO_3$ ) suitable for HCl leaching is lowered from 1673-1773 K to 1373 through mechanical activation of the mixture in a planetary mill. Typical examples where second aspect is exploited are reaction of zircon with potassium fluorosilicate ( $K_2SiF_6$ ), and oxidative roasting of chalcopryrite. The reaction of zircon with potassium fluorosilicate ( $ZrSiO_4 + K_2SiF_6 = K_2ZrF_6 + 2SiO_2$ ) is feasible in the narrow temperature range of 650-700°C. Mechanical activation of zircon in planetary mill changes the reaction mechanism resulting in formation of reaction product at 580°C and completion at 650°C [8- 13].

The main applications of mechanical activation of minerals are found within the field of hydrometallurgy, e.g. leaching, cementation. Several beneficial effects of activation on leaching are observed in terms of enhancement in selectivity, improvement in metal recovery and kinetics, moderation in leaching conditions, rheology and settling characteristics of the leach residue. Sulphides of base metals have received major attention to develop novel metal extraction flow-sheets for the recovery of base metals (Cu, Ni, Pb, Zn) and/or accompanied precious metals (Au and Ag). Numerous examples on successful application of mechanical activation

to treat difficult to leach ores can be cited: HCl and H<sub>2</sub>SO<sub>4</sub> leaching of titanium minerals (rutile, ilmenite); soda leaching of tungsten minerals (wolframite, scheelite); leaching of silicates in various media [4, 8-13]. Recent developments in soft-mechanochemistry (refers to the solid state reactions between chemically reactive oxy-hydroxide/hydroxide species or compounds resulting in formation of water) are of special significance for ores containing oxy-hydroxide minerals, such as bauxite and laterites [14, 15].

### **Research & Development at NML**

A well thought out comprehensive program on mechanical activation of solids was started at NML encompassing both fundamental and applied research. Mechanical activation was applied for (a) improving the Bayer's process for aluminium extraction, (b) waste minimisation by high volume utilisation of slag and fly ash in blended cement, and (c) development of green building materials by geopolymerisation.

In order to develop an improved Bayer process of alumina extraction from bauxite, two different schemes, namely 'separate milling and leaching (SEMIL)' and 'simultaneous milling and leaching (SMILE)' have been tested by the research group at NML [16]. In a typical SMILE at 90°C for 15 min, combined effect of particle breakage, mechanical activation resulted in about 90-92% alumina recovery and less than 1% soda loss in the leach residue. Both SMILE and SEMIL showed comparable alumina recovery at 90°C under identical condition. However, greater soda loss was observed in SEMIL. The superiority of SMILE over SEMIL is also reflected in terms of leaching time, 15 min and 90 min respectively, energy utilisation and simplicity of operation.

Granulated blast furnace slag generated by Iron & Steel industry is mainly used as blended cement constituent. Normally this slag does not hydrate even after months when used in cement. In a remarkable development, granulated blast furnace slag mechanically activated in attrition mill was studied. It is observed that the attrition milled slag begins to hydrate after 48 h whereas ball milled slag of same particle size does not! It is important to note at this point that while it takes more than an hour to get 12 µm in a ball mill, the attrition mill takes only 20-25% of that time. Quite interestingly, the hydration product (after 28 days) of attrition milled slag has crystalline character and its crystallinity increases with milling time. On the contrary, wet ball milling of slag with simultaneous hydration, even after 28 days shows only a small amount of amorphous hydration product [17]. The improved reactivity of blast furnace slag has been exploited in developing blended cement containing up to 80% BF slag and properties comparable to commercial slag cements [18].

Geopolymers are inorganic polymers consisting of Al-O-Si as essential constituents along with an alkaline activator (Na, K, etc). The chemistry of fly ash, nearly 50-60% SiO<sub>2</sub> and 20-25% Al<sub>2</sub>O<sub>3</sub> makes it an ideal raw material for geopolymers. Reactivity of fly ash is of concern in developing high strength geopolymeric materials and other novel building materials. Mechanical activation is used as a means to enhance the reactivity of fly ash [19]. With the increased reactivity of fly ash, very high strength geopolymer cement has been prepared where 120 MPa compressive strength was achieved in 24 hours [19-21].

## Concluding Remarks

The focus of this lecture is mechanical activation of solids and its applications in extractive metallurgy. Various developments in Mechanochemistry are discussed. However these developments are need to be watched closely to exploit multi-disciplinary character of mechanical activation research and development. People all over are looking into the possibilities of mechanical activation for tailored solid-state reactions under minimum external energy, and the concept of Smart Mechanochemistry is being evolved. While we are able to see beneficial effects of mechanochemical activation in many cases, we are far from predicting or controlling the course of mechanochemical reactions. This calls for intensive basic research, and emphasis on quantification of mechanochemical effects.

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