Mechanical activation of power station fly ash by grinding – A review

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Abstract
Power station fly ash has good application possibilities mainly in the construction industry, nevertheless, significant amount is landfill due to their relatively low reactivity and heterogeneity. Hydraulic properties of fly ashes can be tailored by mechanical activation achieving a higher added value product, for example supplementary cementing materials (SCMs). The improved properties are higher specific surface area and desired particle size distribution (containing submicron size particles) as well as higher amount of reactive components that can be optimized by grinding. The objective of this paper is to investigate the effect of mechanical activation of fly ash by grinding on physico-chemical and mineralogical properties. It can be established that there are numerous techniques for mechanical activation of fly ash, e.g. planetary ball mill, vibratory mill or stirred media mill. On the other hand, most of the results reported in the literature are focusing on material related investigations, but beside this, from energetic point of view the process related evaluation has even higher importance.

Keywords: mechanical activation, grinding, power station fly ash, reactivity, energy efficiency.

1. Introduction
Sustainable raw material management requires the utilization of industrial by-products and waste materials as secondary raw materials. Typical examples are the silicate or aluminosilicate based raw materials, like power station fly ash, mining waste materials and metallurgical slags, which are generated in enormously large amounts worldwide [1], and therefore they are available at a relatively low price. However, the quality of these kinds of materials is very heterogeneous. Therefore, it is necessary to control their characteristics, to improve the performance of the final product which can be conducted by various ways, i.e., mechanical, thermal or chemical methods. The main application field of the above materials is the construction industry.

The goal of this paper is to present a brief description of mechanical activation as a tool for optimizing the quality of secondary raw materials focusing on the preparation of fly ash. The paper deals with the effect of mechanical activation on the physical, physicochemical and mineralogical properties of fly ash. The paper summarizes the application of mechanically activated fly ash reported recently as raw material for geopolymer and hydraulic binder.

2. Mechanical activation
Smekal [2] defined the term mechanical activation as processes affected by mechanical energy, which increase the chemical reactivity of the system without altering chemical composition. However, there are several forms of mechanical activation (MA) and the following techniques can be distinguished [3]: a) mechanical dispersion (size reduction) where the higher reactivity is the result of the increased specific surface area, b) surface activation where mechano-chemical reactions take place on the particle surface, and c) mechano-chemical (structural) activation where inner parts of the particle are transformed to other structure as well.

The primary effect of mechanical activation (MA) is the comminution of particles, which results in changes in a great number of physicochemical properties of a particular system. During mechanical activation, the structure of a material usually becomes disordered and the generation of defects or other metastable forms can be observed [4]. It has been reported that the application of high energy mills (e.g. planetary mills and vibratory mills) allow the change of the structure and surface properties of solid materials [5, 6].

Grinding is defined as work expended against the bonding energy of solid materials (crystal), where bonding energy is equal to theoretical energy demand to remove the atoms or ions from each other to infinite distance. Therefore, the bonding energy can be calculated as follows [3]:

\[ E = n_e \varepsilon_i + n_S \varepsilon_S = (n - n_S) \varepsilon_i + n_S \varepsilon_S = n\varepsilon_i - n_S (\varepsilon_i - \varepsilon_S) \]

where \( n_{e} \varepsilon_{i} \) is the bonding energy in the non-dispersed system (internal term, lattice energy) and \( n_i (\varepsilon_i - \varepsilon_S) = \varepsilon_i \) is the surface energy (surface term). The \( n \) is the number of atoms (internal or surface) and the \( \varepsilon \) is the bonding energy of atoms (internal or surface).

On the other hand, besides grinding, reactivity of the solids can be tailored by further mechanical methods such as classification [7, 8] by air classifiers or separation by physical properties using various separators (magnetic, electrostatic etc.) The drawback of these technologies is that only a certain part of the total mass is utilized and the rest is landfilled. Furthermore, the pozzolanic activity is not improved [9]. A possible option might be the combined application of grinding and classification as a closed circuit by classification of the fine particles, then mechanical activation of the coarse fraction by grinding. There are other activation techniques to tailor reactivity of fly ash like thermal, chemical activation or the combination of the aforementioned methods [10].

In general, mechanical activation affects the dispersity properties of the materials, in terms of particle size distribution.
(PSD) and specific surface area (SSA), as well as particle shape, morphology and mineralogical composition. These characteristics define together the reactivity of the product.

![Schematic diagram of grinding kinetics](image)

**Fig. 1.** Schematic diagram of the stages of grinding, based on [11]

I. **Rittinger stage** where considerable increase of SSA appears, comminution takes place relatively quickly due to the high number of material defects (dislocations, pores, inclusions, lattice defects); in this case grinding energy is proportional to the produced increase in SSA.

II. **Aggregation stage** where the intensity of size reduction is moderated, adhesion of particles to the surface of the grinding media, to the lining, or to each other begins. In this stage the flattening of the curve shows that the energy efficiency decreases. The energy is used for deformation of the adhering layer of the particles.

III. **Agglomeration stage** which means apparent coarsening of the material after a certain maximum fineness. Crystal structure and mechano-chemical changes take place.

Most of the silicate and alumino-silicate based materials (e.g. cement clinker, quartz, fly ash, slags) are susceptible to aggregation and agglomeration. Therefore, it is crucial to eliminate the adhesion forces between particles which can be realized by various surface-active materials, by dosing so called grinding aids [3, 39].

### 3. Materials

Coal Combustion Products (CCP) or Coal Utilization By-products (CUB), including fly ash (FA), are industrial by-products generated in enormous high quantity worldwide, almost 800 million t/y [1], as a result of the coal based energy production which represents significant contribution to the electricity production worldwide, for example: 80% in China, 47% in Australia, 42% in United Sates of America, almost 30% in Europe [12].

Fly ash is a finely dispersed granulated material with spherical shape of particles and approx. 100-150 µm maximum particle size, generated by burning of coal in the boiler of power stations and collected by mechanical separators (electrostatic and bag filters). The main chemical components are SiO₂, Al₂O₃, Fe₂O₃, and CaO besides minor components such as Na₂O, K₂O, TiO₂, MgO,... [17]. Based on the oxide composition, class C and class F fly ash can be distinguished, latter one has lower CaO and higher SiO₂ content than the previous one [23]. Their characteristic mineralogical phases are quartz, mullite, lime and hematite [13, 14]. Beside these minerals fly ash usually contains amorphous constituents as well which are responsible mainly for the reactivity.

The relatively high amorphous content is a required parameter from utilization point of view. However, it is well known that significant amount (about 50%) of the by-products is landfilled [1], causing a serious environmental risk [44]. In this way the composition of these materials change due to weathering conditions resulted in a lower reactivity. Muluken et al [15] investigated the chemical, mineralogical and geochemical properties of landfilled fly ash and revealed the formation of secondary minerals (calcite and ettringite) mainly due to hydration, carbonation and pozzolanic reactions. Kusnierova et al [16] found devitrification in case of previously landfilled fly ash, i.e. the reduced in the ratio of glassy phase: amorphous content of initial fresh fly ash reduced by 20% after 5 years, and by additional 12% after 20 years.

On the other hand, the reactivity of these by-products can be controlled by mechanical activation (grinding) [17-19].

### 4. Methods

Since mechanical activation alters the physicochemical properties (particle size distribution, specific surface area, surface energy, phase composition of powders), the exact determination of these properties is of great importance. Concerning the particle size distribution (PSD), it can be determined by various ways: dry or wet sieving, sedimentation or laser scattering methods. The most widely used apparatus is the laser particle size analyzer (LPSA) which is carried out generally in distilled water or in alcohol media using dispersing agent to desagglomerate secondary particles.

Specific surface area (SSA) of solids can be referred as either outer surface or total surface, which can be determined by Blaine or BET (Brunauer-Emett-Teller) methods, respectively. The Blaine method is based on air permeability of material bed, and it is widely used in the cement industry [45]. The BET method represents the inner pores (micro- and mezo pores) of the particles as well, based on gas adsorption on the surface of the investigated solid material. The difference between the value of Blaine and BET surface might be as high as several magnitudes, i. e. a Hungarian power station fly ash (from Tiszajúváros) was characterized with 2724 cm²/g Blaine and 82000 cm²/g BET specific surface area [20].

Material structure can be identified by fourier transform infrared spectroscopy (FTIR) in transmission or reflectance mode (ATR). The X-ray diffraction (XRD) technique is used for mineral phase analysis. Morphology and particle shape of the ground material can be investigated by optical or scanning electron microscopy (SEM) or by transmission electron microscopy (TEM).

Equipment of mechanical activation might be traditional tumbling ball mill or high energy density mill (HEM) like planetary ball mill, vibratory mill or stirred media mill.
5. Mechanical activation of FA

Based on the results of mechanical activation of fly ash in stirred media mill, Molnár et al. [21] reached submicron fine fly ash product at 7 m/s circumferential speed (stress intensity \( SI = 2.14 \times 10^4 \, \text{Nm} \)) for 10 minutes grinding time (SSA = 7.76 \( \text{m}^2/\text{g} \); \( x_{10} = 0.8 \, \mu\text{m}; x_{80} = 1.98 \, \mu\text{m} \)). The amount of mullite 2:1 decreased, parallel to mullite 3:2 increased at 5 and 7 m/s as function of grinding energy. Increasing the grinding time has decreased, parallel to mullite 3:2 increased at 5 and 7 m/s as function of grinding energy. Increasing the grinding time has increased X-ray amorphicity. A crystalline particle is coated with an amorphous layer (5-15 nm thickness) is shown in Fig. 2 that is expected to be generated by the mechanical activation process.

Mucsi et al. [22] evaluated the variation of particle density of raw and ground fly ash. Significant increase in the particle density was observed as function of grinding time. Namely, from the initial value of 1.94 g/cm\(^3\) the density increased to 2.26 g/cm\(^3\) after grinding time of 20 minutes in a tumbling ball mill. It can be explained by the porous structure of fly ash. A plateau in the particle density-grinding time curve is reached after grinding time of 20 minutes and only slight increase was detected afterwards – in spite of that the material fineness is remarkably changed further. It can be found that the fly ash reached its material density (2.27 g/cm\(^3\)).

Terzic et al. [24] realized that the mechanical activation in vibratory mill promoted the amorphization of the fly ash product, induced the changes in its microstructure, reduced the size of the fly ash particles and increased the specific surface area, which are together prerequisites for increasing the reactivity of the material. Optimal residence time of MA process was 20 minutes.

Paul et al. [25] carried out high energy ball milling on class F fly ash. The particle surface of the nanostructured fly ash is more uneven and rough, the shape is irregular, as compared to fresh fly ash which has particles mostly spherical in shape. They achieved significant reduction in crystallinity (from 35% down to 16%) in high energy milled fly ash after 60 h (!) residence time by the destruction of quartz and hematite crystals. As a result, the median particle size was reduced from 60 \( \mu\text{m} \) to 148 nm.

Fu et al. [26] investigated the physico-chemical characteristics of mechanically-treated circulating fluidized bed combustion (CFBC) fly ash. The water requirement decreased with prolonged grinding time, and slightly increased during the last stage of grinding. The pH of ground CFBC fly ash is greater than that of the original fly ash, indicating that ground samples react more rapidly with water. The intensity of the crystalline phases of ground CFBC fly ash decreases, which means that ground fly ash has higher reactivity than that of the original fly ash.

Sharma et al. [27] studied the variation in silica composition as function of milling time which indicates that the silica percentage is increased marginally after milling for 5 to 15 hours, and the specific surface area (BET) is increased from 9 to 17 m\(^2/g\). The increase in SiO\(_2\) content was in agreement with the results of [25, 38] which reasons are not explained in details in their studies. The crystallite size is reduced from the original 33 nm to 21 nm as milling time was increase up to 15 hours [27]. The FTIR spectra showed broad band between 3400-3000 cm\(^{-1}\), was attributed to surface -OH groups of Si-OH and adsorbed water molecules on the surface. The broadness after ball milling for 15 hours is an evidence for the breaking down of the quartz structure and formation of Si-OH groups [28]. The FTIR studies clearly showed changes in the broadening of IR peaks corresponding to Si-O-Si asymmetric stretching vibrations (1101 to 1090 cm\(^{-1}\)) indicating structural rearrangement during mechanical treatment for 15 hours.

FA can be transformed; the initial FA turns to a nanostructured material through high energy planetary ball milling for 30 hours as reported by Rao et al. [29]. The crystallite size was reduced from 92 nm to 29 nm and the percentage of crystallinity reduced from 63% to 38%. The original spherical shape changed to irregular after 30 hours residence time and the surface morphology was rough.

Sharma et al. [30] established that mechanical activation in high energy planetary ball mill results in increase in silica percentage, amorphous nature, specific surface area and surface roughness. Furthermore, thermal activation results changes in phase mineralogy, removal of amorphous carbon and enhances the silica amount. The intensity of IR peaks corresponding to Si-O-Si symmetric stretching vibrations (697 cm\(^{-1}\)) and T-O-Si (\( T = \text{Si}, \text{Al} \)) asymmetric stretching vibrations (1161 cm\(^{-1}\)) after milling that indicates structural rearrangement during mechanical activation.

In the work of Patil and Anandan [31] a class-F fly ash was subjected to planetary ball milling induced mechano-chemical activation aided by a surfactant. The nanostructured fly ash was characterized by dynamic light scattering, BET surface area analysis, X-ray diffraction, FTIR spectroscopy, scanning electron microscopy, field emission scanning electron microscopy and transmission electron microscopy. The ball-to-powder weight ratio and the surfactant type are the major influencing factors on lower crystallite size and average particle size and higher specific surface area. The surface modification of fly ash was confirmed by FTIR spectroscopy.
6. Applications of mechanically activated FA

The mechanically activated fly ash can be utilized mainly as raw material for hydraulic binder (Portland cement) or for geopolymer concerning mass production worldwide. Fly ash utilization in Portland cement has a very detailed literature from the beginning of the last century [32], however, geopolymers just come to the front a few decades ago [33].

Somna et al. [34] studied NaOH-activated ground fly ash geopolymers, cured at room temperature. Ground fly ash with a median particle size of 10.5 μm, was used as raw material mixed with NaOH as an alkali activator. Results indicated that ground fly ash gave higher strength geopolymer compared to the original fly ash. Compressive strengths at 28 days of 20.0–23.0 MPa were obtained.

Investigations carried out by Kumar and Kumar [14] used mainly high energy density mills, such as vibratory and stirred media mill. It was revealed that beside the particle size distribution or the specific surface area the reactivity depended on the mill type used for the mechanical activation of the raw material. Sample with the same fineness activated in different type of mill resulted in different mechanical and structural properties of the geopolymer. The effect of mechanical activation of fly ash on geopolymers was investigated also by [14, 18, 19].

Santrysky et al. [35] investigated the effect of ground fly ash on concrete properties, the flowability of the concrete mix increases to 240 mm without strength loss by 114%, the compressive strength is higher by 62%, furthermore, it gives the possibility to reduce costs by reducing the cement content by 20%.

Marjanovic et al. [36] investigated mechanically activated FA in planetary ball mill. Geopolymerization was conducted by use of sodium silicate at 95 ºC for 4 hours. It was observed that mechanical activation of FA for 15 min resulted in increase of geopolymer compressive strength (ten times higher). High strength values were associated with improved FA reactivity obtained mainly by the reduction in particle size and reduced water/binder ratio.

Another work [37] reported the results of mechanical activation of fly ash conducted in a planetary ball mill, while blends of fly ash and blast furnace slag were prepared with different ratios. Alkali activation was carried out at 95 ºC by use of sodium silicate solution as an activator. Significant increase of geopolymer strength was observed in respect to the geopolymer activated by stirred media mill which resulted in advantageous properties of the geopolymer products (e.g. ten times higher compressive strength).

Mucsi et al. [19] established relationship between the grinding process, the ground material properties and the geopolymer characteristics, i.e. strength of the specimen strongly depends on the grinding conditions, i.e. type of mill, grinding stresses and residence time. The variation of the uniformity factor of ground FA was investigated as well. It was demonstrated that fly ash with a much wider particle size distribution can be generated by stirred media mill which resulted in advantageous properties of the geopolymer products (e.g. ten times higher compressive strength).

Kumar et al. developed geopolymer with 120 MPa compressive strength by grinding of fly ash in vibratory mill [17]. Based on the reported data it can be concluded that most of the research work is based on material related investigations, however the product properties of raw materials are strongly depend on the mill types and parameters [14, 19]. Therefore, the mechanical activation can be controlled consciously by using e.g. the stress model [41, 42, 43].

7. Conclusions

The fundamentals of mechanical activation of fly ash were presented in this paper based on a comprehensive literature review in terms of effects of mechanical treatment on the fly ash characteristics.

It is reported in most papers that due to the mechanical activation, beside the physical properties of fly ash (particle size distribution, specific surface area), the morphological and mineralogical characteristics are varied as well, for example amorphisation takes place.

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These modified fly ash properties resulted in favourable effect on the performance of hydraulic binder and geopolymer (improved consistency, higher density and compressive strength). Since the reactivity of fly ash can be tailored, the importance of the conscious control of the mechanical activation of fly ash by grinding parameters is highlighted.

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References


http://dx.doi.org/10.1016/0301-7516(95)00028-3


http://dx.doi.org/10.1016/j.jmatprotec.2009.03.016


http://dx.doi.org/10.1016/j.minpro.2015.08.010


http://dx.doi.org/10.12693/APHysPolA.126.988


http://dx.doi.org/10.1016/s11671-008-9704-7


http://dx.doi.org/10.1016/j.cemconcomp.2007.08.006


http://dx.doi.org/10.4314/ijest.v2i5.25577


http://dx.doi.org/10.1016/j.powtec.2015.04.078
of the absorbed products. A fine grained material resulting from dry flue gas is to 900°C. FBC ash is rich in lime and sulfur.

Fluidized Bed Combustion (FBC) Ash

The essential raw material is coal, burnt in power stations to temperatures of 1500 to 1700°C, followed by wet ash derivation from coal combustion in boilers at temperatures of 1100 to 1200°C. Ashes of furnaces fired with coal or lignite at these temperatures, which is much coarser than FA though also formed in similar processes, is a granular material resulting from coal combustion in boilers at temperatures of 1500 to 1700°C, followed by wet ash derivation from coal combustion in boilers at temperatures of 1100 to 1200°C.

Pulverized Fuel Ash (PFA) of powdered coal. It is the product of coal combustion in fluidized bed combustors. PFA is a fine grained material composed of spherical glassy particles. Depending on the type of furnace and the amount of fly ash produced, PFA can be very fine or quite coarse. PFA is a natural gypsum like product which is obtained by desulfurisation with lime as a sorbent.

Coal ash is a granular material resulting from coal combustion in boilers at temperatures of 1500 to 1700°C, followed by wet ash derivation from coal combustion in boilers at temperatures of 1100 to 1200°C. Ashes of furnaces fired with coal or lignite at these temperatures, which is much coarser than FA though also formed in similar processes, is a granular material resulting from coal combustion in boilers at temperatures of 1500 to 1700°C, followed by wet ash derivation from coal combustion in boilers at temperatures of 1100 to 1200°C.

Furnace (Furnace) Bottom Ash (FBA, BA) is another term for the same material.

Fly ash (floaters) are recovered from the ash of coal-fired power stations as valuable recoverable resources.

Fly ash is also a component of fly ash-blastfurnace slag blends.

ECOBA was founded in 1990 by European energy producers to deal with matters related to the usage of construction raw materials from coal. The initial membership consisted of 10 companies and associations from across Europe, all producers of electricity and heat. Since then more companies have been elected as members giving the association 24 full members from 15 countries across Europe.

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ECOBA members represent over 86 % of the CCP production in the EU 28 countries. ECOBA has associations with other international institutions providing a vast network of contacts and experience. ECOBA has been particularly active in the development of European standards and is represented on a number of CEN committees.

Mission

ECOBA members consider coal combustion products (CCPs), that is combustion residues and desulphurisation products generated in coal-fired power plants, to be valuable raw and construction materials which can be utilised in various environmentally compatible ways. It is the task of ECOBA to propagare this message especially amongst legislative and standardizing institutions and to communicate the economic and ecological benefits of CCP utilisation.

The mission of ECOBA is

- to encourage the development of the technology for the use of all-by-products from coal-fired power stations, both on the industrial and the environmental level, with regard to relevant industrial and environmental demands;
- to promote the mutual interests of its members, internationally and particularly within the framework of the European organisations, which are of scientific, technical, ecological and legal nature;
- to establish and/or develop necessary legal/regulatory measures for recognition, acceptance and promotion of the use of all-by-products from coal-fired power stations as valuable recoverable resources;
- to participate in international cooperation, including co-operation within the framework of the European organisations, and
- to ensure the exchange of information and documentation among the various national and international bodies.

In order to accomplish these aims, ECOBA maintains and develops close links with all parties interested in the earth’s resources - from governments to end-users and in construction.