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TOWARDS SUSTAINABLE SOLUTIONS FOR FLY ASH REAPPLICATION THROUGH MECHANICAL ACTIVATION

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ABSTRACT *– The aim of investigation was to find sustainable solution for coal fly ash reapplication by increasing its reactivity through mechano-activation. For obtaining complete insight into activation process an understanding of theoretical principles of activator operation is necessary. The vibratory mill was used in experiments. The characteristics of activated ash and possibility of grain inertia measurement by automatic grain counter were analyzed. Following proposed AGC operating hypothesis, energy and properties of ash grains induced by mechanical force were expressed as grain inertia change. The ash used in experiment was thoroughly analyzed by XRD and SEM methods. The final result was establishing of the upper limit of activation period.*

Key words: *coal ash; energy conversion; vibratory mill; activation.*

ODRŽIVA REŠENJA ZA REAPLIKACIJU LETEĆEG PEPELA POSTIGNUTA KROZ PROCES MEHANIČKE AKTIVACIJE

REZIME *– Cilj istraživanja je bio da se pronađe održivo rešenje za reaplikaciju letećeg pepela poreklom iz uglja povećanjem reaktivnosti uz pomoć mehano aktivacije. Da bi se proces aktivacije potpuno sagledao neophodno je razumeti teorijske principe na kojima se zasniva rad aktivatora. U eksperimentu je korišćen vibracioni mlin. Karakteristike aktiviranog pepela i mogućnost merenja inercije zrna pomoću automatskog brojača zrna su analizirani. Na osnovu predložene hipoteze rada ABZ, energija i svojstva zrna su uslovljeni delovanjem mehaničke sile i izražavaju se u obliku promene inercije zrna. Pepeo koji je upotrebljen u eksperimentu je detaljno analiziran popoću XRD i SEM metoda. Konačni rezultat je bilo uspostavljanje gornje granice aktivacionog perioda.*

Ključne reči: *pepeo iz uglja; konverzija energije; vibracioni mlin; aktivacija.*

INTRODUCTION

Despite wide area of engineering branches where fly ash is applied as secondary raw material the demands for new applications, as well as the improvement of ash as a component material are being raised on daily basis. Mechanical activation is a procedure which is often applied in order to improve the characteristics of fly ash as component in the design of a composite material. In material science, there is a growing need for mechanically activated raw materials which have advanced properties and can significantly influence performance of the composites in which they are built-in [1-3]. Technology of mechano-activation is based on action of mechanical energy applied on a certain material. The activation of solid substance is accomplished by ultra-fine activation of material in specially designed high-energy mills [4, 5]. Activation does not only effect simple change of particle size, it is a complex physical-chemical process which brings about increase of potential energy, chemical activity and surface reactivity of the system [6]. The increase of material reactivity can be used in rationalization of a process and making the basic technologies cheaper. A thorough study in this area imposes a need to define thermo-dynamical, mechanical, physical and physico-chemical processes occurring within the material which is comminuted to micron or nano dimensions under influence of mechanical energy [7]. The energy properties induced by mechanical force are best expressed as change of grain inertia [8]. The characteristics of activated ash and the possibility of grain inertia measurement by means of AGC were investigated and presented in this paper.

EXPERIMENTAL

The fly ash used in the investigation is by-product of combustion of lignite coal. The ash was collected directly from filter and transported to a special closed silo where it was resampled by quarter method. Investigated ash, having less than 20 % of Ca oxide, belongs to F-class. The grain size of the original ash sample varied from several µm up to 1 mm. The fly ash was mechanically activated by means of a laboratory activator – vibratory disc mill RS 200 (Retsch, Germany) which comminutes by impact and friction. Batch size of the mill is 75 ml. The grinding set is firmly attached to the vibration plate. Material of grinding tools is hardened steel. Grinding jar size is 100 ml. Working parameters of the mill are: total volume of space for activation; circumferential velocity; and rocking amplitude. The variable parameters are: total ring mass; number and diameter of activating bodies; and structural characteristics of material. With kinetic energy generating in activating bodies, vibration, amplitude, impact and contact surface between grinding bodies and processed material are increasing.

AGC provides response in form of voltage pulse, generated as grain passes through opening, its value directly proportional to grain volume. Mathematical relation between the counter response and grain coarseness can be determined as:

$$\delta R = \frac{1}{\dfrac{A-a}{\rho_f \cdot \delta_\lambda} + \dfrac{a}{\rho_s \cdot \delta_\lambda}} \tag{1}$$

Where: ρ_s and ρ_f are resistances of grain and fluid; A is cross section of the opening; a is the cross section of the grain; δ_λ is thickness of the element or the segment.

Measuring method is based on determination of grain coarseness using data obtained for counted grains and assumption that generated voltage is proportional to the grain volume and that the voltage is the measure of grain inertia. Inertia of spherical grain in its gravity center can be calculated according to the following equation:

$$J = m \cdot r^2 \quad (2)$$

Where: m is mass of the grain, kg; and r is grain radius. Radius of the sphere r can be written as $d_{av}/2$, thusly specific surface area for the sphere is:

$$SSA = \frac{d_{av}^2 \cdot \pi}{m} \quad (3)$$

The hypothesis that AGC measures change of inertia, i.e. change of the mechanical energy state, can be represented as:

$$J = \frac{3 \cdot V \cdot d_{av}}{2 \cdot SSA}, \ \mathrm{kg \cdot m^2} \quad (4)$$

Fly ash grain fraction content was analyzed by means of cyclo-sizer (Warman International LTD, Australia). Mineralogical changes in fly ash were tracked by XRD (Philips PW-1710 automated diffractometer). The microstructure of the fly ash samples was characterized by SEM (JEOL JSM-5800 microscope).

RESULT AND DISCUSSION

Fly ash underwent mechanical activation in the vibratory mill. The initial activation time was 10 minutes. Characteristics of activation product are function of the activator type, namely the strain intensity and number of impulses are basic variable parameters which influence activator operation kinetics and activation product. Figure 1 shows results of grain-size analysis performed after ash initial activation.

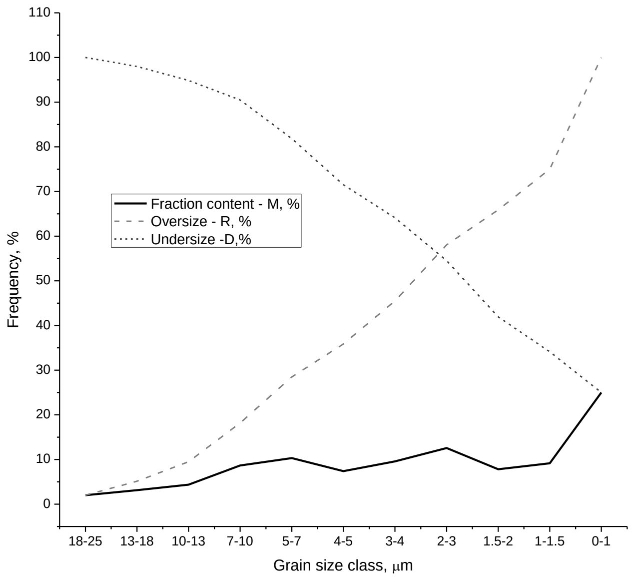

Figure 2 The ash granulometric composition after 10 minutes activation.

The main granulometric parameters are: mean particle diameter, d_{50}; sieve opening through which passes 95 % of the activated product, d_{95}; direction coefficient, n; specific surface, S; and specific energy consumption W_e (obtained as ratio of engine strength and mill capacity). Dependence is described by Rosin-Rammler equation [9]:

$$R = 100 \cdot e^{-\left(\frac{d}{d_{50}}\right)^n} \tag{5}$$

Where: R is cumulative oversize; %; e is basis of natural logarithm (e= 2.718); d is sieve opening; mm; d_{50} is mean grain diameter; mm.

Specific surface, S can be calculated from the mean diameter as:

$$S_t = \frac{6.39}{\rho \cdot d_{50}} e^{\frac{1.795}{n^2}} \tag{6}$$

Results of obtained by Rosin-Rammler method are given in Table 1.

Table 1. Table caption Parameters of the fly ash mechano-activation in vibro mill.

Activation time, min	d_{50}, μm	d_{95}, μm	S, m^2/kg	W_e, kWh/kg	Agglomeration tendency
10	3.88	12.02	369.35	0.85	no

Initial ash sample had specific surface area of 112.50 m^2/kg (obtained by BET method); volume of $8225 \cdot 10^{-3}$ m^3 (obtained by Coulter counter method); and mean grain diameter of 75.23 μm. The samples were afterwards activated for 30, 45, 60, 120 and 180 minutes and subsequently submitted to the AGC analysis. Results obtained by means of AGC after activation for 10, 30, 45, 60, 120 and 180 min are given in Table 2. As seen from Table 2, the values of inertia were lower if the activation times were longer. It can be explained by the fact that extension of mechanical activation time increases tribo-mechanical interaction between the grains, i.e. it supports the loss of electrons. In that way, the grain mass is reduced. In this case, the grain mass is assessed indirectly, by measuring grain inertia at automatic grain counter.

Table 2 Survey of the analysis data for activated fly ash samples obtained by means of AGC

Activation time, min	SSA, m^2/kg	V, m^3	d_{50}, μm	Number of grains	V/SSA, kg·m	Grain inertia, J, $kg \cdot m^2$
10	365.23	$6.068 \cdot 10^{-3}$	3.85	97865	$1.03 \cdot 10^{-5}$	$8.26 \cdot 10^{-11}$
30	526.25	$5.599 \cdot 10^{-3}$	3.00	100256	$0.82 \cdot 10^{-5}$	$6.60 \cdot 10^{-11}$
45	530.54	$5.586 \cdot 10^{-3}$	2.96	102589	$0.74 \cdot 10^{-5}$	$6.51 \cdot 10^{-11}$
60	540.12	$5.352 \cdot 10^{-3}$	2.92	116545	$0.61 \cdot 10^{-5}$	$6.25 \cdot 10^{-11}$
120	545.30	$5.164 \cdot 10^{-3}$	2.86	125844	$0.54 \cdot 10^{-5}$	$5.91 \cdot 10^{-11}$
180	549.15	$5.005 \cdot 10^{-3}$	2.085	139856	$0.45 \cdot 10^{-5}$	$5.54 \cdot 10^{-11}$

Variations of mean statistical diameter, specific surface area, total volume and number of grains obtained are variables which appear in Eq. (4), and they determine one physical parameter - the grain inertia momentum. This momentum reflects expected regularity in variation of mechanical properties of grains after activation. Fly ash contains three groups of mineral oxides. The first group includes the minerals whose crystal lattice contains metal element (Al_2O_3, Fe_2O_3, TiO_2 CaO, MgO, Na_2O, MnO and K_2O): participation in the sample was 47 %. The second group of minerals is represented by metalloid SiO_2 (45%). The third group of minerals includes nonmetallic oxides P_2O_5, SO_3 and CO_2, their participation being 2 %. It can be assumed that the grain which lost its electrons due to tribo-mechanical effect either remains positively charged, with reduced mass, or its electrons remain built in the structure of the crystal lattice composed of nonmetallic crystallites, so its mass increases. Having in mind the composition of the fly ash, its mechanical activation is interesting for the analysis using model which assumes that metals remain positively charged due to electron losses, while nonmetals remain negatively charged due to acceptance of electrons. Mechanically activated fly ash was analyzed using AGC in order to prove that mass of the grains is more often reduced (inertia decrease) then increased (inertia increase), relative to participation of minerals in fly ash. The criterion for this conditional division is the element group involving the element contained in the mineral crystal structure. Thus, tendency of grain inertia decrease, accompanied by mass reduction is depending on activation duration.

Mineralogical composition and changes in crystal structure of initial fly ash, fly ash activated for 30 minutes, and fly ash activated for 180 minutes were analyzed by XRD. Major identified crystalline phases present in all ash samples were quartz and mullite. Calcite, magnetite, hematite, fluorite, and anhydrite were present in negligible amounts. Crystallinity of activated ash samples was noticeably lower than that of initial sample which can be considered as the effect of activation. The significant changes in the crystal structure appeared within 30 minutes of activation. Comparison of fly ash samples before mechanical activation and after mechanical activation (30 minutes and 180 minutes) implies that the length of mechano-activation influences the crystallinity of fly ash samples, i.e. the level of crystallinity is decreasing with the increasing of the time of mechanical activation. Namely, the mechano-activation treatment might promote amorphization of treated material, noticeable change of micro-structure, size and shape of particles, etc.

The previously named changes occurring in the microstructure of activated ash are investigated by SEM method. It was showed that initial ash sample contained various grains of different sizes and shapes belonging to different inorganic phases and certain quantity of unburned organic matter. Majority of fly ash particles were spherical and hollow. Internal porosity was also present in fly ash grains. Certain changes occurred in the microstructure of fly ash after 30 min of mechanical activation. Namely, the size of the grains was visibly reduced, as well as the percentage of characteristic spherically shaped grains. More irregularly shaped grains, including needle-like shapes which correspond to the mullite crystals immersed in the fly ash mixture. Pseudospheres, that is, spherical particles composed of various layers or grains were noted at 180 minutes of activation time. Agglomerations as form of grouping of reduced ash grains are characteristic for long-term periods of activation; therefore 180 min can be adopted as upper limit of the treatment duration.

CONLUSION

The significant decrease of fly ash particle size during mechanical activation in vibratory mill can be ascribed to the strain increase due to the friction forces as well as the compression and impact forces during the mechanical activation. The samples activated in vibration mill showed no tendency to create agglomerations. Activation of the fly ash influenced its properties, energy state, reactivity, and crystallinity. Consequently it might affect the performing properties of an ash based composite.

In accordance to Rosin-Ramler mathematical equation, parameters of initial 10 min long activation were obtained: d_{50}=3.88 µm; d_{95}=12.02 µm; S=369.35 m^2/kg. The approximately same parameters for 10 minutes long activation are obtained according to the operating hypothesis of AGC: d_{50}=3.85 µm; S=365.23 m^2/kg. Thus, operating hypothesis of AGC is confirmed by Rosin-Ramler model. The starting assumption was that AGC measures the grain inertia, not its volume. By analyzing the obtained data, it was found that grain inertia is showing mechanical changes induced in grain by mechanical activation. Namely, the tendency of the grain inertia decrease, accompanied by mass reduction, is depending on mechanical activation.

X-ray analyses of non-activated and activated fly ash samples confirmed that mechanical activation contributes to the decreasing of crystallinity. Reduction of the original particles of fly ash conducted by mechanical activation procedure appeared to have reached a limit at approximately 30 minutes grinding time and longer activation does not produce significant decrease in particle size nor increase in specific surface area of activated material.

Fly ash was successfully treated by mechanical activation procedure, and even though mechanical activation procedure might appear as an expensive process due to low mill capacity and high energy consumption, activated products have advanced characteristics which open entirely new spectra of their industrial applications. Also, activated minerals significantly improve the performances of standard products in which they are used as raw material.

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