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ENERGY TRANSFER AND CONVERSION RECORDED ON MECHANICALLY ACTIVATED FLY ASH GRAINS

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Abstract: The fly ash activation through mechanical milling is ussualy applied to improve the ash properties in order to get composite materials with higher characteristics. The activation technology based on mechanical energy action applied on treated materials and is conducted by ultra-fine milling. In order to increase the reactivity of lignite coal fly ash this paper focuses on optimization of mechanical activation period. Also, the influence of the ash activation parameters on the grain-size distribution related characteristics was studied during this research. The ash grain inertia measurement through automatic grain counter (AGC) was performed. Due this mechanically activated grains are the most convenient mineral form for measurement of grain inertia since energy change that occurs in the mill material system is recorded by them. The ash grains energy and properties could be changed by mechanical forces. The ash was thoroughly analyzed, particularly in its activated state, primarily by means of the X-ray diffraction method for a reliable identification of the crystal phases and changes in the crystallinity, followed by comparison of the SEM microphotographs of its initial and activated state.
Key words: milling; grain size; ceramic materials; mechanical activator; recycling.

1. INTRODUCTION

Besides numerous industrial branches where the fly ash is being applied as a secondary raw material, the requests for new appliances are constantly being raised. The activation of the fly ash via mechanical milling is frequently applied in improving of the ash properties for its utilization in the composite materials with advanced characteristics [1-3]. Numerous investigations conducted on a variety of materials highlighted a growing need for raw materials with properties enhanced via mechanical activation [4, 5].
The technology of activation is based on the action of mechanical energy that is applied on a treated material. The activation is conducted via ultra-fine milling [6]. Activation influences the change of the particle size; however it also induces the increase in chemical and surface reactivity and potential energy of the activated system [6, 7]. The reactivity of the powdery material is improving due to the surplus of volume and energy. The odds in energy and volume help in formation of potential centeres which will eventaly grow into a new mineral phase in the treated material [6, 8-10].
The changes in the gravitational and electromagnetic characteristics of the processed powder and subsequent change in entire energy condition are set in motion due to the action of mechanical energy of the activator [11, 12]. Therefore, the change in energy conserved within activated grains takes place. The energetical characteristics that undergo changes due to the action of mechanical forces are usually expressed as the change of the grain inertia [13, 14].
The paper treats the parameters influence of the mechanical activation performed through vibratory mill on the grain-size distribution related characteristics of the fly ash and the possibility of the ash grains inertia measurement by means of an automatic grain counter.

2. EXPERIMENTAL

2.1 The operating hypothesis of the AGC

The response of AGC is in the form of the voltage pulse and is generated as the grain passes through the opening of the AGC. The response value is directly proportional to the grain volume. Mathematical relation between the counter response and the grain coarseness can be determined according to the equation (1). Thus, the response of the electrolyte including the grain is equal to the resistance of two parallel connected resistors [14].

$$\delta R = \frac{1}{\frac{A_o - A_g}{\rho_f \cdot \delta_l} + \frac{A_g}{\rho_g \cdot \delta_l}} \qquad (1)$$

where: ρ_g and ρ_f are resistances of grain and fluid respectively; A_o is the opening cross section; A_g is the

grain cross section and δ_l the thickness of the element or segment.

The element resistance influences the current density (I) and is caused by the grain presence (ΔR). The generated voltage pulse can be expressed as a product of these two elements above mentioned ($I \cdot \Delta R$). The answer does not depend on grain resistance due to presence of the oxide films on the surface, ionic inertia of the Helmholtz double electric layer and solvent molecules adhered on the grains surface, whereby their electric resistance becomes infinite [14]. Thus, the ρ_f / ρ_g ratio can be neglected in the equation (1). The method is based on the assessment of the grain coarseness according to the data obtained for counted grains. The hypothesis that generated voltage is proportional with the grain volume. The practical experience says that one physical value represents change of another, therefore the generated voltage in the AGC represents the change of the grain inertia. The voltage is the measure of the grain inertia, not its volume [14]. Furthermore, the inertia of a spherical grain in its gravity center can be expressed with the equation (2).

$$J = m_g \cdot r_g^{\,2} \tag{2}$$

where: J is the grain inertia, [kg·m^2]; m_g is grain mass, [kg] and r_g is the grain radius, [m].

Knowing the radius and volume of the hypothetical spherical grain, the specific surface area (SSA) is given in the equation (3), [14].

$$SSA = \frac{d_{50}^2 \cdot \pi}{m_g} \tag{3}$$

The hypothesis that automatic grain counter actually measures change of inertia, i.e. the change of the mechanical energy state, is represented by the Eq.(4) [14]:

$$J = \frac{3 \cdot V \cdot d_{50}}{2 \cdot SSA}, \text{ kg·m}^2 \tag{4}$$

2.2 Mechanical activation

The fly ash was activated via vibratory mill with a peripheral comminuting path. The energy is transferred directly onto activating elements of the mill. The "Siebtechnick TS 250" is a screening disc mill with the main operating parameters, as follows: 380V, 50Hz, 750W and 1000rpm. For the experimental research were necessary elements such as: vibrating plate with 155mm diameter and activator with 3×Colmony 250 grinding tools. Also the working parameters took into account were: circumferential velocity, total volume of the activator and rocking amplitude. The variable parameters used in the research are: total ring mass; diameter and number of the activating elements and material structural characteristics. The specific energy consumption (W_e) is defined like a ratio between engine strength (P) and mill capacity (Q). On the beginning the activation period was required 5 minutes and the procedure was then carried out under the same conditions, such as 10, 15, 20, 25 and 30 minutes intervals.

The main parameters of grain size are: d_{50} is the average grain diameter, d_{95} the sieve mesh size that passes 95% of activated product, n the direction coefficient and specific surface. The cumulative characteristics of the activated material grain-size can be presented by functional dependency between the average diameter, cumulative oversize (R) and undersize (D). From the technical literature this dependency is most commonly defined by the Rosin-Rammler-Sperling (RRS) exponential function [8, 15]:

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

where: R represents the cumulative oversize, [%]; e is the basis of natural logarithm (e=2.718); d is applied sieve mesh size, [mm]; and d_{50} is the average of grain diameter, [mm].

Parameters derived and/or calculated from the grinding kinetic model based on RRS equation and depend on the grain size distribution of the activated sample. The parameters d_{50} and n are obtained by analytical procedure which implies selecting of the two farthest points on the grain size composition diagram and fitting new curves through selected points. By double logarithm of RRS resulted a new equation that means a straight line where the direction coefficient is obtained [8, 15]:

$$n = \frac{\log\log\frac{100}{R_1} - \log\log\frac{100}{R_2}}{\log d_1 - \log d_2} \tag{6}$$

As in the case of n parameter the d_{95} is calculated from the RRS [8, 15]:

$$d_{95} = e^{\left(\frac{n\ln d_{50} + \ln\ln 100 - \ln\ln R}{n}\right)} \tag{7}$$

The theoretic specific surface area can be calculated from the average diameter like in equation (8), [8, 15]:

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

(8)

where: S_t is theoretical specific surface area, [m^2/kg] and ρ is the density, [kg/m^3].

2.3 Other instrumental methods

Fly ash grain-size distribution was analyzed by a cyclo-sizer (Warman International LTD, Australia). Chemical analysis was performed via PinAAcle 900 atomic absorption spectrometer (Perkin Elmer, USA). Mineralogical phases and cristalyinty alterantions were analyzed by X-ray powder diffraction analysis on a Philips PW-1710 diffractor. The microstructure of the fly ash was characterized by scanning electron microscopy using a JEOL JSM-5800 microscope [16].

2.4 Material

The fly ash used in the investigation is a by-product of the combustion of lignite coal collected from filter system of a power plant in Serbia [16]. The collected fly ash samples were transported directly to a special closed silo where an initial sample was randomly taken and further re-sampled by the quarter method. Investigated fly ash belongs to F-class according to the chemical analysis. The grain-size distributions of original and activated (5 min) ash samples are illustrated in Fig. 1.

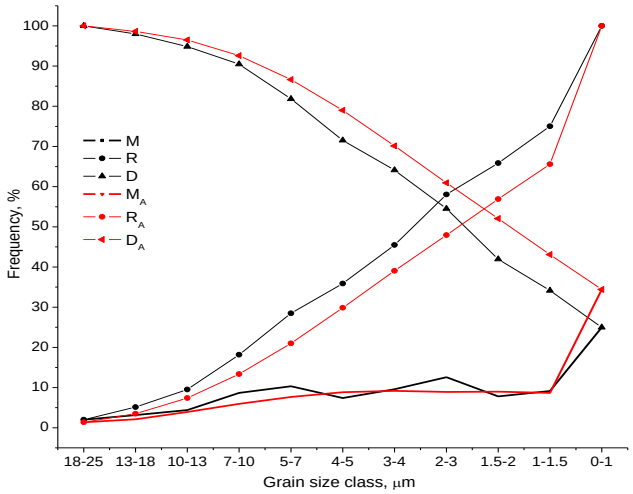

Fig. 1. Grain-size composition of initial and activated ash

3. RESULTS AND DISCUSSION

Parameters of ash activation obtained from Eq.(5)-(8) including specific energy consumption (W_e) are given in Table 1.

Table 1. Parameters of the ash activated in vibratory mill

Activation time, min	d_{50}, μm	d_{95}, μm	S_t, m^2/kg	W_e, kWh/kg	Agglomeration tendency
5	4.25	12.10	350.25	0.81	no
10	3.92	10.25	396.87	0.85	no
15	3.74	9.75	462.35	0.90	no
20	2.95	8.90	525.35	0.95	no
25	2.90	8.80	530.54	0.98	weak
30	2.85	8.80	532.85	1.03	partial

Initial fly ash sample had specific surface area of 295.23 m^2/kg (obtained by Brunauer–Emmett–Teller/BET method); and mean grain diameter of 85.56 μm (obtained by Coulter counter method). As it can be seen from Table 1, the activation significantly influenced the change of the grain-size related parameters. Namely, the activation induced decrease of the d_{50} and d_{95} parameters, and caused the increase in the specific surface area. Specific energy consumption increased with the extension of the activation time. Agglomeration tendency was not present up to 20 min activation periods, however the activated ash exhibited weak and afterwards partial agglomeration tendency for 25 and 30 min long activations, respectively. Values of the parameters presented in the Table 2 lead to conclusion that optimal activation period is 20 min long, because rate of decrease of d_{50} and d_{95} parameters, i.e. increase of S_t rapidly slows down for longer activations. Also longer treatments are more prone to grain agglomerations and require more energy for process.

The ash samples activated for 5, 10, 15, 20, 25 and 30 min were further submitted to the automatic grain counter (AGC) analysis. The experimental sequences in which parameter d_{50} was constant were selected and separated, and the values of inertia were calculated (according to Eq. (4)) on these sequences. Results obtained by AGC are given in the Table 2, and the change of grain inertia momentum is illustrated in Fig. 2.

Table 2. Data obtained by AGC for activated ash samples

Activation time, min	SSA, m^2/kg	d_{50}, μm	Volume, m^3	Number of grains	Grain inertia, kg·m^2
5	345.70	4.13	$6.568 \cdot 10^{-3}$	87865	$6.22 \cdot 10^{-11}$
10	391.55	3.80	$5.999 \cdot 10^{-3}$	100256	$4.60 \cdot 10^{-11}$
15	464.10	3.56	$5.586 \cdot 10^{-3}$	112589	$4.51 \cdot 10^{-11}$
20	524.90	2.95	$4.752 \cdot 10^{-3}$	116545	$3.75 \cdot 10^{-11}$
25	527.20	2.86	$4.564 \cdot 10^{-3}$	118844	$3.61 \cdot 10^{-11}$
30	529.15	2.80	$4.205 \cdot 10^{-3}$	119856	$3.44 \cdot 10^{-11}$

The grain-size related parameters presented in Table 2 confirmed the conclusions regarding RRS parameters analysis given in Table 1. Namely, the changes of the d_{50} and the specific surface area are initiated by the activation of the ash. The all parameters stabilization was carried out during the 20 minutes of treatment, that's why this period of time could be considered as the optimal one.

As can be seen from Table 2 and Figure 2, the lower values of the grain inertia can be correlated with longer activation periods. This because the fact that activation treatment extension influences the increasing of the tribo-mechanical interaction

between grains i.e. supports the loss of electrons. In that way, the grain mass is being reduced. Thus, the grain mass is assessed indirectly through measuring/calculating the grain-size parameters and the grain inertia by means of AGC (Table 2.) The AGC analysis can be considered as average of the rationalization of grain-size related data. Namely, variations of average statistical diameter, specific surface area, total volume and number of grains, as variables which appear in equation (4), determine one physical parameter - the grain inertia momentum which reflects the expected regularity during the variation of the grains mechanical properties after mechanical activation.

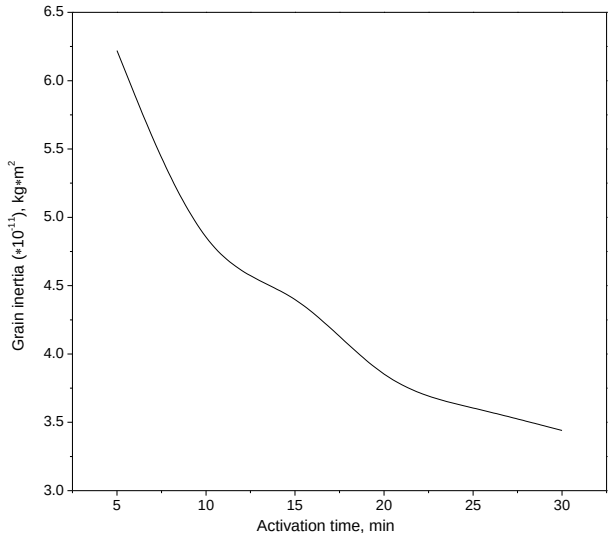

Fig. 2. Change of grain inertia momentum depending on mechanical activation time

The main results from this investigation are supported by theoretical explanations provided by the model of grain which lost electrons due to tribo-mechanical effect and remained positively charged with smaller mass, [14]. The fly ash contains three groups of mineral oxides, thus: the first one includ minerals with metal element in the crystal lattice: Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O, MnO and K_2O and the participation in the composition of the ash sample is 47.93 %; the second group of minerals is represented by SiO_2, with Si being a metalloid and the participation of Si oxides is 47.15 % and the last one of minerals includ nonmetallic oxides P_2O_5, SO_3 and CO_2, with 1.67 % participation percentage. After the composition analyzing it can be assumed that a grain that lost electrons either remains positively charged with reduced mass or the electrons remain built in the structure of the crystal lattice composed of nonmetallic crystallites and the mass increases [14]. Took into account the composition of the ash, its activated stage fits into the model which assumes that metals remain positively charged due to loss of electrons and nonmetals remain negatively charged due to acceptance of electrons. Activated ash analysis through AGC proves that mass of the grains is more often reduced (inertia decrease) then increased (inertia increase) relative to participation of minerals "divided" in the fly ash. Therefore, the tendency of the grain inertia decrease, accompanied by mass reduction is depending on activation time as it was shown in table 2. According to model presented, grains lost electrons due to tribo-mechanical effect and remained positively charged with reduced mass and lower grain inertia momentum. Prolonging of of the activation period enhances this effect. However, the analysis pointed out on the relative stabilization of decreasing of the inertia momentum at approximately 20 min of treatment which can be accepted as the optimal activation period.

The fly ash mineralogical composition and the changes in crystalline structure induced by activation are illustrated via XRD diffractograms in Fig. 3-4.

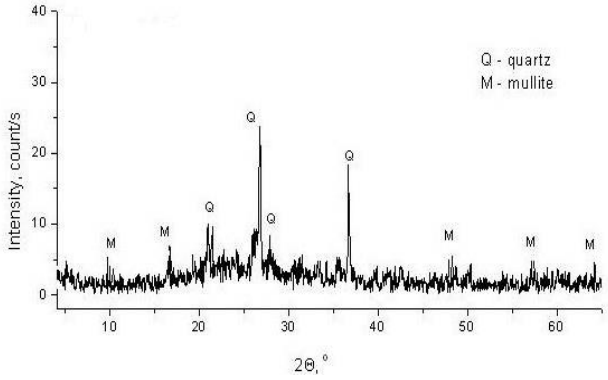

Fig. 3. XRD diffractogram of ash activated for 5 min

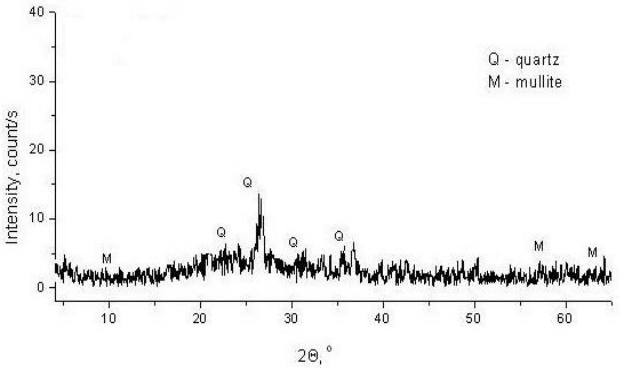

Fig. 4. XRD diffractogram of ash activated for 20 min

In all ash samples can be found quartz and mullite as major crystalline phases while calcite, magnetite, hematite, fluorite and anhydrite are negligible amounts. The background hump between (10-40)° corresponds to the presence of the glassy phase, [16]. The crystallinity of activated ash is lower in comparison to the initial sample. The decrease of the crystallinity can be considered as an effect of activation. The significant changes in the crystal

structure appeared within 5 minutes of activation. Comparison of the ash samples before activation and after 5 minutes and 20 minutes of activation implies that the length of treatment significantly influences the crystallinity of the ash. The crystallinity level is decreasing with the extension of the activation time. On its turn the activation has an influence on disordered structure formation of the treated material and generated crystal lattice defects and meta-stable forms which are potential centers for creation of new mineral phases. The activation treatment promoted the amorphization of treated ash, induced changes in microstructure, reduced the grain-size and increased specific surface area, which are together prerequisites for increasing of the material reactivity.

The previously identified changes in the ash mineral composition and crystalline structure are further supported by the SEM analysis. The figures 5 and 6 presents the microphotographs of initial ash and ash activated for 20 minutes.

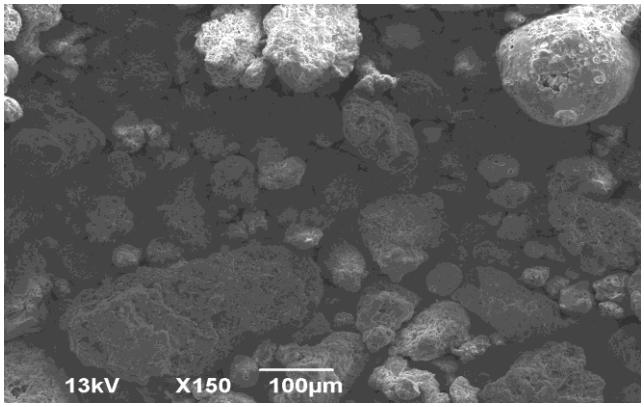

Fig. 5. SEM microphotograph of initial ash sample

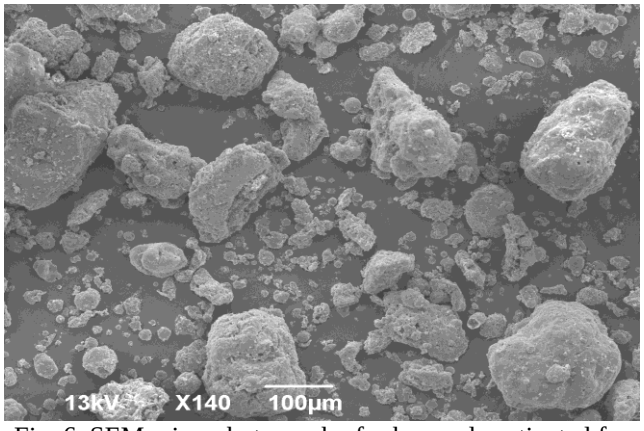

Fig. 6. SEM microphotograph of ash sample activated for 20 min

The microphotograph given in Fig. 6 highlights that the initial ash sample is composed of various grains of different sizes and shapes which correspond to different inorganic phases and possibly certain quantity of unburned organic matter. Majority of the ash grains are spherical and hollow, characterized by increased superficial porosity. Internal porosity is also present, namely smaller internal pore channels are visible within superficial pores in the SEM recording. Extremely porous grain might correspond to the unburned coal [16]. Irregularly shaped particles of different sizes correspond to quartz crystals. As it can be seen from the microphotograph given in Fig. 6 certain changes occurred in the microstructure of ash after 20 min long activation. Precisely, the size of the grains is visibly reduced, as well as the percentage of characteristic spherically shaped grains. More irregularly shaped grains, including needle-like structures that correspond to the mullite crystals immersed in the fly ash mixture. Pseudospheres, that is, spherical particles composed of various layers or grains were also notice. Agglomerations as a specific form of grouping of reduced ash grains are characteristic for long-term periods of activation and they were not noticed after 20 min of activation. The agglomerations can be expected for prolonged activation periods; therefore 20 min was adopted as upper limit of the treatment duration.

4. CONCLUSIONS

The study of the influence of the procedure parameters of mechanical activation conducted via vibratory mill on the grain-size distribution related characteristics of the fly ash was successfully conducted. The insight in the applied mechanical activation procedure was created by correlating the theoretical principles of the mill operation kinetics and the grain inertia measurement in the mill-material system recorded via an automatic grain counter (AGC). The major findings are summarized below:

The activation of ash in vibratory mill significantly influenced the change of the grain-size related parameters which can be ascribed to the strain increase due to the friction, compression and impact forces occurring in the activator. The decreasing of d_{50} and d_{95} parameters is due to the activation which leads to increasing of the specific surface area. The specific energy consumption increase with the extension of the activation time. The optimal activation period is 20 minutes because of the decreasing rate for d_{50} and d_{95} and the increasing of S_t rapidly slows down for longer activations. Also, longer treatments are more prone to grain agglomerations and require more energy for the process.

The proposed kinetic model for the activation in vibratory mill combined with the RRS equation and the AGC operation hypothesis gave approximately same grain-size related parameters for 20 minutes treatment: d_{50} = 2.95µm and S_t=525m^2/kg. The starting hypothesis that AGC measures the grain inertia not the grain volume was confirmed. The analyze of the measured/calculated experimental

AGC data pointed that they comply with the model of the grain that lost electrons due to tribo-mechanical effect and remained positively charged with reduced mass. The grain inertia decrease accompanied by the mass reduction is promoted by the extension of the mechanical activation.

The activation treatment promoted the amorphization of treated ash, induced the changes in the ash micro-structure, reduced the size of the ash grains and increased the specific surface area, which are together prerequisites for increasing of the material reactivity. The 20 min long activation is established as the optimal period for the mechanical treatment.

Even though mechanical activation might appear as an expensive process due to low mill capacity and/or high energy consumption, it is a perfect means for reduction of negative effect of ash inherent properties on the final product quality and manufacturing technology economic sustainability.

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