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THE TYPE OF MECHANO-ACTIVATOR EFFECT ON MECHANICAL ACTIVATION OF FLY ASH

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Abstract

In this study, the results of mechanical activation of fly ash from thermal power plant "Nikola Tesla"- Obrenovac are presented. This study aimed high degree of fly ash reactivity by different types of mechano-activators. The mechanical activation of fly ash in the three types of mechano-activators: vibratory ring mill, planetary ball mil and conventional ball mill was investigated.

The all mechanical activation experiments were based on kinetic model. The mechanically activated fly ash, from each type of mechano-activator, was examined particularly by application of different analyses: the X-ray diffraction method, specific surface area, as well as, particle size distribution.

The obtained results of mechanically activated fly ash by vibratory ring mill were indicated on slight tendency of agglomerates, while this tendency is more pronounced in the planetary ball mill. The best experimental results were achieved by vibratory ring mill, where decreasing crystal state, gross distortion and enhanced reactivity were occurred. Enhanced reactivity is less prominent at the mechano-activators such as planetary and conventional ball mill.

Key words: *mechanical activation, fly ash, reactivity, distortion.*

1. Introduction

Coal have been playing a key role as a world primary energy source for decades, due to its availability, security of supplies and relative inexpensiveness [1]. Nowadays, the special attention is paid to minimize either its environmental impact, or to the safe and economical disposal of residues generated by coal-fuelled power plants. Ash disposal has recently risen to a renewed interest, triggered by the increas-

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ing concern associated with conventional disposal of ash in landfills and ponds [1]. Disposal of fly ash in a landfill enhances the risk of ground water contamination by leaching of heavy metals. The potential hazard associated with disposal of wet ash in lagoons (ash ponds) has been recently perceived after a major environmental disaster occurred in the US following the collapse of a pond-containing dam. The need for more environmentally friendly and economical disposal of ash has gained today high priority in the clean coal technologies agenda. Industrial use of fly ash in the cement and concrete manufacture offers the largest and more feasible opportunity for extensive ash utilization as an alternative to disposal [2].

Mechanical activation of fly ash can be used to develop improved blended cements with higher proportion of fly ash from the current 15–25% to 50–60% without degradation in cement properties. In addition by introducing mechanical activation as the pre-processing has greater merit as compared to air classification since the former permits utilization of entire fly ash along with superior reactivity [3].

Huge number of investigation has been conducted with aim to find sustainable solutions and applications of fly ash. The special attention is paid to mechanical activation process in a various types of mechano-activators. The term “mechanical activation” refers to enhanced reactivity of fly ash from combined effects of increased surface area and physic-chemical changes induced in the bulk as well as on the surface through high energy milling by vibratory mill, attrition mill, etc. [4]-[7].

Senneca et al. (2011) showed that noticeable modification of DTG profiles of fly ash, indicative of enhanced reactivity, is observed as a result of mechano-chemical activation by ball milling in a lab-scale apparatus at 500 rpm and duration variable between 5 and 30 min [8]. On the other hand, Mechanical activation of fly ash in a vibration mill with milling media to powder ratio of 10:1 leads to a reduction of particle size and change in particle shape but little change in mineralogical composition. However, mechanical activation in eccentric vibratory mill increases the reactivity of fly ash. The reactivity of fly ash varies with median particle size and increases vary rapidly when the particle size is reduced to less than 5–7 mm. The improvement in physical properties is related to the intrinsic structure developed due to enhanced geopolymerisation [9], [10].

The new opportunities for utilizing coal fly ash in environmental protection applications like the stabilization/ solidification treatment of hazardous waste and contaminated soil could be achieved by mechano-chemical activation of with a high energy mono-planetary ball mil. On this way, the adsorption characteristics of coal fly ash have been enhanced [11].

This study aimed enhanced reactivity fly ash by mechanical activation with a vibratory ring mill, planetary ball mill and conventional ball mill as well. At the same time, the best mechanical activation technique finding for mechanical activation of fly ash could be the aim of this study.

2. Experimental

2.1. Material characterization

Three samples EFP-1, EFP-2 and EFP-3, from the electro-filter of the Thermo power plant Obrenovac - (TPO) were used for experimental investigations. The particle size distributions, physico-chemical and mineralogical analyses of the initial samples are listed in the Tables 1, 2 and 3, at the same time, chemical analyses in the three-component diagram and X-ray analyses of fly ash on Figs. 1, 2, 3 and 4 are shown respectively.

The initial samples of fly ash have relatively high value of specific surface area. This is good predisposition for further chemical activation and chemical activity. The achieved result of chemical analyses of fly ash is graphically presented in the three-component diagram SiO_2+Al_2O_3, Cao+MgO and Fe_2O_3 on Fig. 1.

Table 1. *Particle size distributions of the initial samples EFP-1, EFP-2 and EFP-3*

Flying ash TPO	Sample label								
	EFP-1			EFP-2			EFP-3		
Size classes in mm	M%	R%	D%	M%	R%	D%	M%	R%	D%
-0.833+0.589	1.37	1.37	100.00	1.37	1.37	100.00	1.37	1.37	100.00
-0.589+0.418	2.12	3.49	98.63	2.12	3.49	98.63	1.82	3.19	98.63
-0.418+0.295	3.91	7.40	96.51	2.75	6.24	96.51	3.05	6.24	96.81
-0.295+0.295	5.94	13.34	92.60	6.06	12.30	93.76	4.01	10.26	93.76
-0.208+0.147	7.67	21.01	86.66	7.35	19.65	87.70	3.84	14.10	89.74
-0.147+0.104	8.84	29.85	78.99	8.60	28.25	80.35	12.28	26.38	85.90
-0.104+0.074	9.19	39.04	70.15	9.79	38.04	71.75	9.06	35.43	73.62
-0.074+0.053	8.90	47.94	60.96	10.90	48.94	61.96	9.10	44.54	64.57
-0.053+0.037	8.97	56.91	52.06	7.87	56.81	51.06	10.90	55.43	55.46
-0.037+0.025	8.67	65.58	43.09	9.97	66.78	43.19	11.68	67.11	44.57
-0.025+0.000	34.42	100.00	34.42	33.22	100.00	33.22	32.89	100.00	32.89
Total	100.00			100.00			100.00		

Table 2. *The average values of physico-mechanical properties of the initial samples EFP-1, EFP-2 and EFP-3*

Physical-mechanical parameters	Numerical value
Density (with no pores and cavities) (g/cm^3)	2.25
Specific surface (m^2/g)	0.672
Bulk density, Δ (kg/m^3)	
- Loosen state	650
- Closed state	950
Mechanical strength, σ (MPa)	
- on bending	1.5
- on pressure	2.5

Table 3. *The chemical composition of the initial samples EFP-1, EFP-2 and EFP-3*

Type of oxide	Sample label EFP-1	EFP-2	EFP-3
SiO_2	58.52	60.72	55.16
Al_2O_3	24.03	22.20	28.30
$(Fe_2O_3)_u$	6.23	6.43	6.33
FeO	3.70	4.55	3.00
CaO	3.31	4.11	2.49
MgO	2.11	2.15	2.18
Na_2O	0.32	0.36	0.32
K_2O	1.08	0.11	1.04
TiO_2	0.87	0.83	0.65
P_2O_5	<0.02	<0.02	<0.02
S	0.33	0.32	0.11
F	<0.02	<0.02	<0.02
LOI	3.16	2.73	3.38
Total	100.00	100.00	100.00

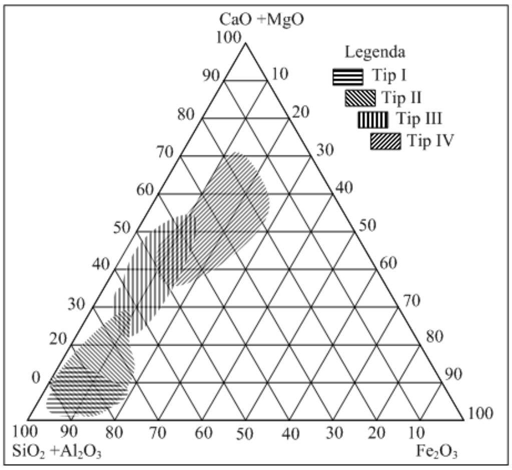

Figure 1. *The three-component diagram SiO_2+Al_2O_3, Cao+MgO and Fe_2O_3 of fly ash*

Explanation:

Type I - Acidic: 50% SiO_2, 25% Al_2O_3, 7-9% Fe_2O_3, 5-7% CaO, 1-33% SO_3

Type II - Aluminum-Silicate: with lower content of SiO_2 40-50%, 17-25% Al_2O_3, 8-12% Fe_2O_3, 9-22% CaO, 0.5-5% SO_3,

Type III - Alkaline: flying ash with high content of CaO 40-50%, where 10% of free CaO, 2-5% SiO_2, 7-8% Al_2O_3, 6-8% Fe_2O_3 i 9% SO_3 and

Type IV – High sulphate and high alkaline: ashes with high content of SO_3 26% and CaO 33% (where 23% of free CaO), 4% MgO, 4% Al_2O_3, and 3% SiO2.

The fly ash from thermal power plant "Nikola Tesla"- Obrenovac consists a high content of SiO_2 and Al_2O_3. This kind of ash is classified as acid ashes. Contents of sulfate and free CaO in this kind of ash are low.

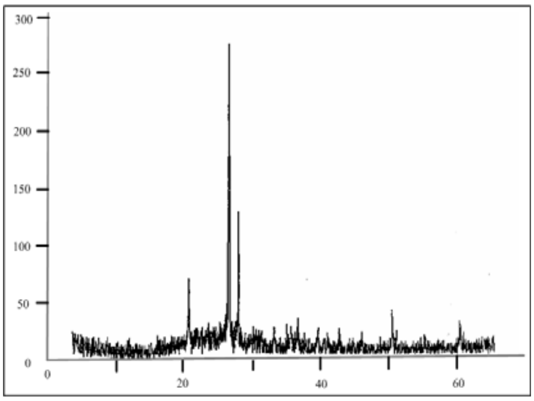

Figure 2. *The X-ray analysis of initial sample EFP-1*

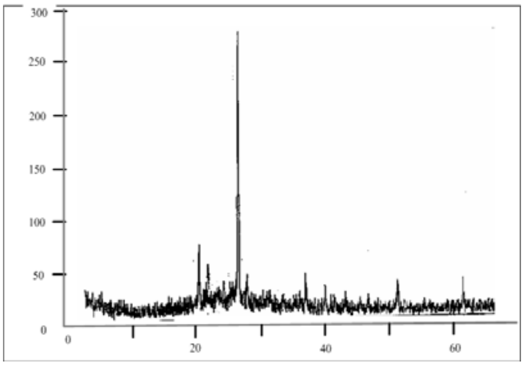

Figure 3. *The X-ray analysis of initial sample EFP-2*

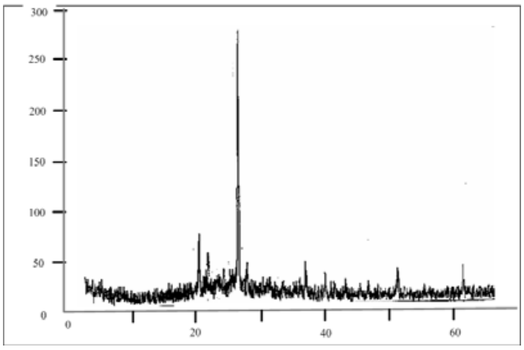

Figure 4. *The X-ray analysis of initial sample EFP-3*

These figures show the samples are the mixtures of glass and crystalline phases. This is consequence of contaminations of samples with quartz, christobalite, feldspar, hematite, and magnetite. Furthermore, the initial samples were subjected to the microscopic analysis by the "Jenapol".

The results of microscopic analysis show that in all samples the most frequent crystalline phases are the quartz and degraded feldspar, which appear as the broken and thermally corroded grains. In feldspar grains, melting processes along the edges have been perceived. The fireclay in larger quantities and forms bigger aggregates (sponge-like and hollow) which contain integrated coal and iron oxide was occurred. The glass mass in pearls up to 1 mm in diameter and in various colors is occurred.

The fly ash particles are rich with quartz and possess the smooth surface, while some particles have rugged edges of irregular isometric shape. This is confirmed by SEM analysis of initial samples. This fly ash almost does not contain aggregates. Aggregates are basically made of quartz sand, and ash particles smaller than 5 μm are mostly adhesively connected to the quartz particles.

Based on chemical, X-ray and microscopic analysis, the quantitative mineralogical analysis of the initial samples is shown in Table 4.

Table 4. *Quantitative mineralogical analysis of the initial samples of fly ash EFP-1, EFP-2 and EFP-3*

Phase type	Quartz	Fireclay	hematite	magnetite	feldspar	glass	coal	other phases	∑
Content (%)	7.20	46.10	5.30	0.80	3.40	32.60	2.50	2.10	100

Further investigations of the initial fly ash samples EFP-1, EFP-2 and EFP-3, were based on thermal and thermo-gravimetric analysis. The DTA curve of the tested flying ash shows weak endothermic effects at 90 and 750ºC and slightly more prominent exothermic effect with the characteristic peak at 500ºC. The first endothermic effect is in connection with the presence of the small amounts of moisture, while other effect with the presence of aluminum-silicates. The Exothermic effect relates to the transformation of the organic matter in the tested samples. The DTA curve is shown in the Fig. 5.

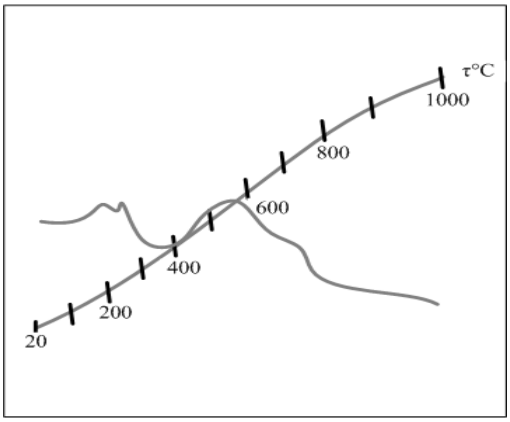

Figure 5. *DTA diagram of the initial fly ash samples EFP-1, EFP-2 and EFP-3*

The thermal characteristics of the flying ash have been tested by the thermo-microscope and the characteristic temperature changes during heating are shown in Table 5.

In the framework of thermal tests, dilatometric analysis performed, on the "Netzsch" brand dilatometer, where the change of sample dimensions in function of temperature was observed. The following characteristic temperatures were identified: start of shrinking 815ºC, start of sintering 1170ºC and the end of sintering 1250ºC.

The fly as samples have cohesive propertise and can influence negatively on mechanical activation process. In this case, It was expected that fly ashes particles can adhered and attached on grinding medias and on the walls of mechano-activator. As a result could be occured high level of agglomeration which negatively affects on the proess.

Table 5. *Thermal characteristics of initial fly ash samples EFP-1 EFP-2 and EFP-3*

Characteristic temperatures	EFP-1, T^0C	EFP-2, T^0C	EFP-3, T^0C
Start of sintering	1180	1170	1160
Fusion point	1270	1280	1260
Halfsphere point	1320	1310	1320
Dissolution point	1330	1330	1330
Interval of sintering condition	80	80	80

2.2. Experimental method

The initial fly ash samples EFP-1, EFP-2 and EFP-3 were tasted on the following types of mechano-activators: planetary ball mill "Retsch PM 4", vibratory ring mill "Siebtechnick TS 250" and conventional ball mill. The quantitative characterisation of the product is determined by the modern techniques such as: "Coulter Electronics-Coulter Multisizer" for physical characterisation; "Reidhammer Gradient oven G 100/9" and Netsch, for thermal determination; "Philips PW 1710", for x-ray testing; SEM and "JEOL JSM T20", electronic microscope for shape factor, average particle diameter and specific surface area.

2.3. Operating conditions of mechano-activators

For successfully mechanical activation of fly ash, based on kinetic model, it is necessary to determine the operating parameters for each type of mechano-activator. The stress intensity and number of stresses (number of impulses) are the basic variable parameters which affect on operation conditions of mechano-activator. These two parameters are calculated by the basic equations, for each type of mechano-activator. The basic equations are listed in Table 6.

***Table 6**. The basic equations for operating parameters determination, for each type of mechano-activator*

Mechano-activator type	N	v	W_T
Vibratory ring mill	$N = n \cdot t$	$v = 4 \cdot \pi \cdot n \cdot a$	$W_T = m_1/2m_2 \cdot n \cdot t \cdot (4 \cdot \pi \cdot n \cdot a)^2$
Planetary ball mill	$N = n \cdot t$	$v = \sqrt{2 \cdot b \cdot D}$	$W_T = m_1/m_2 \cdot b \cdot n \cdot t \cdot D$
Conventional ball mill	$N = n \cdot t$	$v = \sqrt{2 \cdot g \cdot D}$	$W_T = m_1/m_2 \cdot n \cdot \pi \cdot t \cdot g \cdot D$

Where: n-speed; t-milling time; v-stress intensity; g-gravity acceleration; b-acceleration; D-diameter; a-amplitude; m_1-weight of ball (ring), m_2-weight of material.

These factors can be considered after election of the mechano-activator type and its operating parameters. However, specific energy consumption is very important parameter during mechanical activation process. This parameter plays the key role in mechanical activation process of fly ash.

Specific energy consumption is directly proportional to consumed energy during the mechanical activation of fly ash ($P_{el}\ t$), at the same time is inversely proportional to weight of fly ash. Specific energy consumption can be calculated by the next equation:

$$W_m = P_{el} \cdot t/m \text{, (kWh/kg)} \quad (1)$$

Where:

W_m - Specific Energy Consumption, kWh/kg

P_{el} - Engine power of mechano-activator, kW

t - Mechanical activation time, h

m - Weight of fly ash to be mechanically activated, kg

The mechano-activator type is elected that the present properties of the fly ash can be achieved. This step aimed the mechano-activator type with high stress intensity and low specific energy consumption. The operating conditions and technical characteristics of each type of mechano-activator are presented in Table 7.

***Table 7**. Technical characteristics and operating conditions of mechano-activators*

Type of mechano-activator	The filling ratio, (%)	Material /balls	Ambient	Optimal pulverisation conditions Type of Loading	Effect	Undersize , d_{50} (μm)
Vibratory	70-80	0,15-0,40	damp dry	compression at high frequency	Mixing speed	<0,5 20
Planetary	60-80	0,20-0,40	dry	attritional	Low and high acceleration	Narrow particle size range
Conventional ball mill	45	0,1	dry	compression at low frequency	gravity acceleration	From 10 to 100

In order, to achieve high stress intensity in a shorter mechanical activation time, it is necessary to conduct the experiments with high filling ratio (~ 80%), light weight of material to be activated (~30%) and high value of amplitude (>8mm) at vibratory ring mill. This conditions have been set in order to be approximate to operational conditions of the industrial vibratory ring mill. Also the mechanical activation time does not depend on the stress conditions (pressure, friction, shearing etc), which prevalent in the high-energy mechano-activators.

3. Results

The achieved experimental results of particle size distributions for each mechanically activated fly ash sample are presented in Table 8.

The comprehensive results of mechanical activation kinetic experiments are listed in Table 9.

***Table 8**. Particle size distributions of each mechanically activated fly ash samples*

Flying ash (TPO)	Mechano-activator type Vibratory ring mill			Planetary ball mill			Con. Ball mill		
Size classes in μm	M%	R% Over.	D% Unde.	M%	R% Over.	D% Under.	M%	R% Over.	D% Under.
-25+18	1.99	1.99	100.00	1.85	1.85	100.00	3.00	3.00	100.00
-18+13	3.14	5.13	98.01	3.19	5.04	98.15	3.17	6.17	97.00
-13+10	4.38	9.51	94.87	5.78	10.82	94.96	4.89	11.06	93.83
-10+7	8.66	18.17	90.49	6.59	17.41	89.18	6.44	17.51	88.94
-7+5	10.31	28.48	81.83	10.99	28.40	82.59	7.55	25.06	82.49
-5+4	7.41	35.89	71.52	11.34	39.74	71.60	8.93	33.99	74.94
-4+3	9.59	45.48	64.11	7.46	47.20	60.26	9.96	43.96	66.01
-3+2	12.58	58.06	54.52	9.05	56.25	52.80	8.03	51.99	56.04
-2+1.5	7.80	65.87	41.94	11.11	67.36	43.75	7.37	59.36	48.01
-1.5+1	9.14	75.01	34.13	6.53	73.89	32.64	5.41	64.77	40.64
-1+0	24.99	100.00	24.99	26.11	100.00	26.11	35.23	100.00	35.23
Total	100.00	-	-	100.00	-	-	100.00	-	-

***Table 9**. Achieved results of mechanically activated fly ash samples*

Mechano-activator Type	Time of mech. activation t, min	Average particle diameter d_{50}, μm	d_{95}, μm	Specific surface S, m^2/g	Specific energy consumption, W_m, kWh/kg	Agglomeration tendency
Initial sample	-	82.66	334.33	0.67	-	-
Vibratory ring mill	15	4.00	12.00	5.06	0.93	Weak
Planetary ball mill	15	5.00	17.00	3.44	0.95	Strong
Con. Ball milll	520	33.00	153	2.92	10.40	No

Where: Time of mech. Activation - duration of mechanical activation process, t (minutes); Average particle diameter d_{50}, μm - determined by "JEOL JSM T20" device; d_{95}, μm - square opening of sieve trough which passes 95% of material; Specific surface S, m^2/g - determined by "JEOL JSM T20" device; Specific energy consumption, W_m, kWh/kg - calculated by Eq. 1; Agglomeration tendency - tendency of material to be attached and adhered for the wall of mechano-activators and grinding media.

According to the results in Table 9 can be seen the highest value of specific surface area and the lowest value of average particle diameter of mechanically activated fly ash (5.06) was achieved by vibratory ring mil. At the same time, the vibratory ring mill has consumed the lowest amount of electrical energy during the mechanical activation process of fly ash. Also in this mechano-activator type, weak agglomeration of fly ash particles is observed. The results are described in relation to other achieved results by planetary and conventional ball mill.

4. Conclusion

The mechanical activation process has realized the following results: the changes in microstructure of particles, energy state, enhanced reactivity, deterioration of the crystal state, and size of crystallites (irregular crystals) as well.

The best results of mechanical activation process are obtained by vibratory ring mill. In this type of mechano-activator, the reduction of crystal state and the enhanced distortion and reactivity were observed. The enhanced reactivity of fly ash, as a key parameter, is less prominent at the planetary and conventional ball mill. The significant reduction of particle size during the mechanical activation process in vibratory ring mill and planetary ball mill can be explained with high stress intensity. High stress intensity in these two types of mechano-activators was caused by friction and impact forces as well as compression.

The mechanically activated fly ash samples have shown slight agglomeration tendency in the vibratory ring mill. On the other hand, the same samples have shown strong agglomeration tendency in the planetary ball mill.

The mechanically activated fly ash from thermo plant "Nikola Tesla"-Obrenovac could be applied in production of fume gases purification filters (desulphurization), production of binders, bricks, roof-tiles, paving and wall bricks etc.

5. Acknowledgement

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