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Variability of Coal Fly Ash for use in the Cement Industry

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Abstract

Fly ash is widely used in the construction industry, and its quality and quantity varies greatly about the thermal power plant from which it is obtained. This paper reviews the test results for six fly ash samples generated by lignite combustion in different thermal power plants. The aim of this paper is to compare the properties of different samples using laser diffraction, X-ray fluorescence spectroscopy (XRF) and scanning electron microscopy (SEM) methods, to determine which fly ash would be the best choice as a mineral additive, for concrete composition design as part of a project entitled "*Concrete development for sustainable construction in the marine environment*". The use of fly ash improves the durability properties because it reduces permeability while improving the microstructure of concrete. Due to the variability of fly ash properties, and with the high demands that come with construction in the marine environment, it is very important to conduct tests for the purpose of their characterization.

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Keywords: fly ash, laser diffraction, marine environment, SEM, XRF.

1. Introduction

Fly ash is a finely divided mineral additive for cement and concrete produced by the combustion of coal dust in power plants [1]. The following combustion technologies are used in thermal power plants: high-temperature combustion, dry combustion and fluidized bed combustion [2]. Particles float in a stream of gases, and their separation is done by electrostatic or mechanical precipitation and filtration [3]. Fly ash consists of amorphous [1], spherical particles with average sizes from 1 to 100 µm, low to medium bulk density and very fine texture [4]. Hollow particles filled with smaller particles of material and irregular unburned remains are also characteristic. The size, shape and color of the particles depend on the technology and temperature of combustion, the source and type of coal, the cooling rate, etc. [3]. Fly ash particles have a hydrophilic surface and are extremely porous, due to their shape they have a large specific surface, and their reactivity is determined by their size. Fly ash is an alkaline material with a pH in the range of 8,5 – 11,5 [4]. A lighter color of fly ash indicates the presence of a larger amount of calcium, while a darker color indicates a higher content of organic matter (unburned coal) [5]. In terms of chemical composition, it consists mainly of aluminium-silicate compounds, and to a lesser extent of calcium and metal oxides [6]. According to the mineral composition, it consists mainly of the amorphous phase, mullite, quartz, hematite, magnetite and a small amount of unburned carbon particles [7].

According to the composition and properties, fly ash is divided into two types depending on the calcium content: fly ash with low calcium content, obtained by burning anthracite and bituminous black coal and fly ash with high calcium content, obtained by burning lignite and subbituminous coal. The American standard, ASTM C 618:2019, designates ash with low CaO content (< 18 % by mass) as class "F", and those with high

CaO content (> 18 % by mass) as class “C” [8]. Class F ashes have pozzolanic properties, while class C ashes have hydraulic and / or pozzolanic properties [9]. According to HRN EN 197-1, fly ash is divided into: silicon fly ash (V), corresponding to class F ash and calcium fly ash (W), corresponding to class C ash. For class F, the proportion of reactive CaO must not exceed 10,0 % by mass, and the free CaO content must not exceed 1,0 % by mass; while for class C the proportion of reactive CaO must not be less than 10,0 % by mass. Calcium fly ash containing 10,0 to 15,0 % reactive CaO must contain at least 25,0 % reactive SiO_2 [10].

According to the European Coal Combustion Products Association, Europe produced close to 40 million tonnes of CCW in 2016 and reused more than 90 % in the construction industry and for reclamation [11]. First of all, the use of fly ash is a more environmentally friendly option because the production of one ton of ordinary Portland cement emits 930 kg CO2 per ton, while the achieved content of fly ash is 4 kg CO2 per ton. It is also possible to reduce the economic costs of purchasing materials, as this reduces the amount of cement in the mixes. The maximum allowable proportion of fly ash as a replacement for cement in concrete is prescribed by national standards, and for Europe it is 35 % [6]. The most important properties of fly ash for concrete production are particle fineness, moisture content, annealing loss and chemical composition. Fly ash affects the properties of concrete in a fresh and hardened state by filling the structure with small particles, and actively participates in the hydration process. Its addition reduces the need for water and water separation and improves workability. Fly ash releases less heat during hydration compared to ordinary cement and is therefore often used in solid concrete [12]. The initial strengths of mixtures are reduced and the setting time is extended, but the late strengths of mixtures with ash can achieve higher values compared to mixtures without fly ash [9]. It is known that after the age of more than 28 days, the concrete continues to harden, even up to 90 days of age. Also, the use of fly ash reduces the permeability of concrete and increases the resistance to chloride penetration [12].

2. Material and experimental works

According to the project plan, in addition to testing on real samples taken from buildings in the marine environment, the tests will include cements. Mineral additives that represent a potential basis for the development of new concrete for construction in the marine environment will also be tested. Part of these mineral supplements is also six fly ashes from different thermal power plants whose properties are compared in this paper. Table 1 shows the data on selected production raw materials, and Figure 1 shows the macroscopic appearance of all samples.

Table 1. Fly ash tested within the project “*Concrete development for sustainable construction in the marine environment*” [13, 14, 15, 16, 17]

Industry	Sample mark	Type of raw material	Coal location	Technology of collection
RiTE Stanari	M1	Lignite	Stanari, B&H	Bag filter
RiTE Gacko	M2	Lignite	Gatačko polje, B&H	Bag filter
RiTE Ugljevik	M3	Black coal	Bogutovo selo, B&H	Electrofilters
TE „Kakanj”	M4	Black coal	Kakanj, B&H	Electrofilters
TE „Nikola Tesla B”	M5	Lignite	Kolubarski bazen, Serbia	Electrofilters
TE „Kolubara”	M6	Lignite	Kolubarski bazen, Serbia	Electrofilters

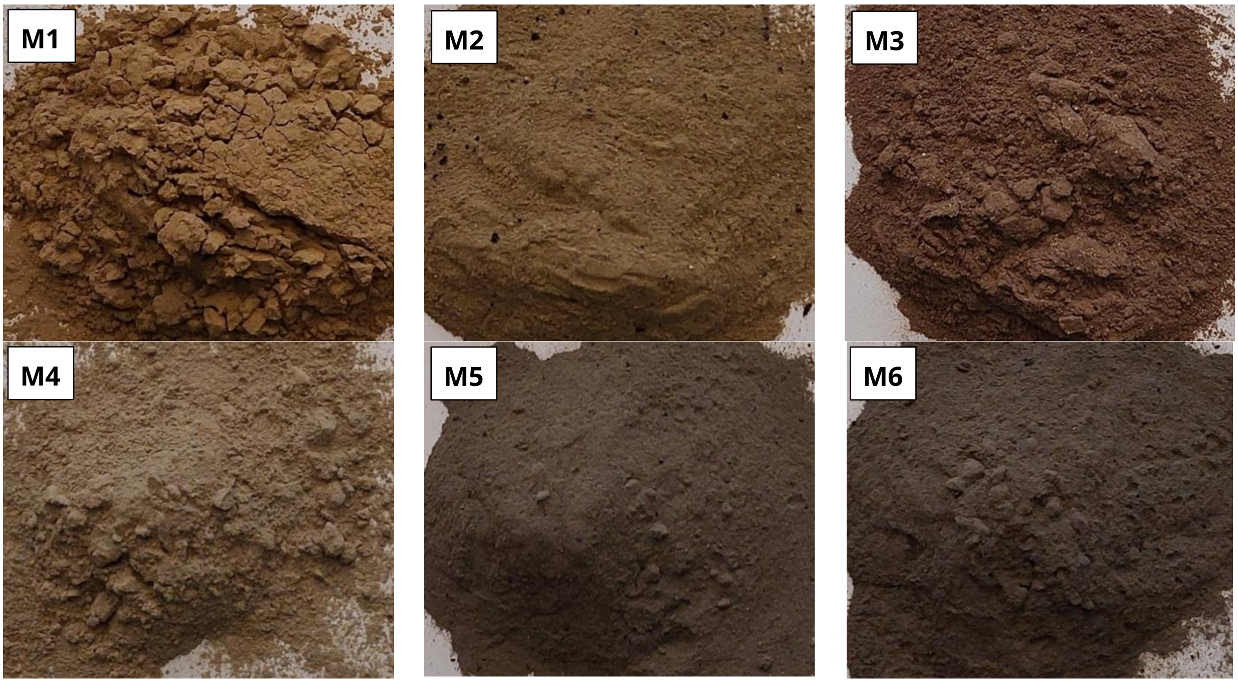

Figure 1. Comparison of fly ash obtained by burning coal from different locations

Using the method of laser diffraction, the characterization of coarsely dispersed systems was performed, which involves determining the size of particles as well as their distribution, which is important for understanding the physical and chemical properties of fly ash. Mie's theory was applied to calculate the particle size based on the diffraction angle. The SALD 3101 (*Shimadzu*) was used. X-ray fluorescence spectroscopy (XRF) is an analytical method used to determine the chemical composition of fly ash. This test was performed according to ISO / TS 16996:2015, on a NEX CG device (*Rigaku*) with a Pd anode. Also, the test of loss by annealing at a temperature of 950 °C according to the standard HRN EN 15169: 2008 was performed, and the device TGA 701 (*Leco*) was used for testing. Insight into the morphology, microstructure and texture of the samples was obtained using the scanning electron microscopy (SEM) method performed on the device *Tescan*, FE MIRA, II LMU.

3. Results and discussion

3.1. X-ray fluorescence spectroscopy (XRF)

The chemical compositions of fly ash obtained by XRF analysis are shown in Table 2. According to ASTM C618:2019, the total oxide content (SiO_2+Al_2O_3+Fe_2O_3) determines the pozzolanic properties of fly ash. Guided by this, samples M1, M4, M5 and M6 belong to class F, while samples M2 and M3 can be described as class C. However, this does not agree with the standard definition for fly ash for samples M1, M3, M5 and M6. All the above also applies to the results of the CaO content in the samples. (Halstead, 1986.) indicates that class F ash can be produced from non-bituminous coal, and bituminous coal can be produced from non-bitumen ash. Also, according to [5], ash from thermal power plants in Serbia (M5 and M6) although it was formed by the combustion of lignite, it has a low content of Ca, and a high content of Si and Al, and is classified in class F fly ash. All samples show the value of LOI within the permissible limits prescribed by the standards HRN EN 197-1 (max. 5 % by mass) and ASTM C618:2019 (max. 6 % by mass). The SO3 content in samples M2 and M3 is higher than the upper limit, while in other samples it is within the allowed limit (< 5 % by mass, ASTM C618:2019). If the SO_3 content of fly ash exceeds the allowed upper limit for the sulphate content of cement, this must be considered for cement production by appropriate reduction of calcium sulphate-containing ingredients [10].

Table 2. Chemical composition of fly ash from different locations

Sample mark	M1	M2	M3	M4	M5	M6
Compound			Content, % wt			
SiO_2	50,54	30,54	29,27	51,36	55,65	56,51
Al_2O_3	19,72	9,93	7,84	20,03	24,9	22,59
Fe_2O_3	8,59	5,32	11,44	8,59	6,42	5,62
CaO	13,59	42,24	25,47	13,03	6,04	7,40
SO_3	2,35	8,93	19,18	1,51	1,07	1,24
MgO	3,22	1,48	2,54	1,91	2,42	2,35
K_2O	0,62	0,56	0,94	2,1	1,88	1,70
Na_2O	0,20	0,53	2,42	0,69	0,91	1,90
SiO_2+Al_2O_3+Fe_2O_3	78,85	45,79	48,55	79,98	86,97	84,72
LOI	0,70	0,80	0,50	0,10	1,20	1,10

3.2. Laser diffraction

Each sample was tested three times and mean values were considered. Table 3 shows the values of the characteristic size of the median, d_{50}, and the values mean V, x_g. The median divides the population into two equal parts and indicates the particle size of which 50 % is less than the declared value of *d*. Mean V represents the mean geometric diameter calculated from all particle distribution data. In Figure 2 the distribution of particle sizes in cumulative form for all fly ash samples is shown graphically. Considering the different technologies of coal combustion in thermal power plants, more pronounced differences in the granulometric composition of samples from M1 to M6 are also observed. According to the obtained data, it is evident that by far the smallest (finest) particles of all samples have the M1 sample, while the largest particles have the M5 sample. Sample M1 is known to be formed by burning coal in a circular fluidized bed at a temperature of 850 °C. [13]

Considering that according to [18] the particle size of fly ash can be around 150 μm, and for a typical size particle below 20 μm can be taken, it can be concluded that somewhat larger particle sizes of samples M5 and M6 (whose coals are of the same origin) caused by incomplete combustion of coal.

Table 3. Granulometric composition of fly ashes

Sample mark	M1	M2	M3	M4	M5	M6
d_{50} (μm)	18,80	148,47	117,10	106,38	180,00	152,72
x_g (μm)	15,60	107,36	74,03	54,07	148,86	115,58

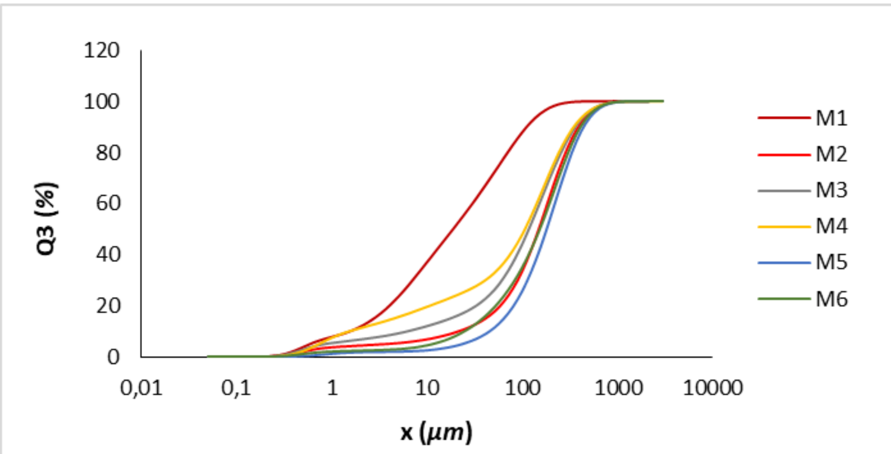

Figure 2. Particle size distribution characteristics for six different samples of fly ash

3.3. Scanning electron microscope (SEM)

Figure 3 shows micrographs obtained on fly ash powder samples at 2000x magnification. Micrographs show morphological diversity of particles, which vary from spherical to irregular shapes. The particles are mostly of non-uniform structure, have an inhomogeneous surface and are of different dimensions. In samples M2, M5 and M6, pieces of unburned coal are visible, so sieving is necessary before use in concrete. The micrograph of the M1 sample mostly shows characteristic irregular particles formed by combustion in a fluidized bed, which are most often highly crystalline. Mostly spherical particles, which are visible on the micrographs of samples M4 and M5, are formed during high-temperature combustion and these particles are extremely amorphous structures [2]. According to [19], particles have a porous structure, and according to [9], irregularly shaped and porous fly ash particles are prone to water absorption, which can have a negative effect on the workability of cement pastes. The micrograph of the M4 sample shows a characteristic hollow spherical particle of fly ash, which contains several smaller spherical particles (*plerospheres*) [20].

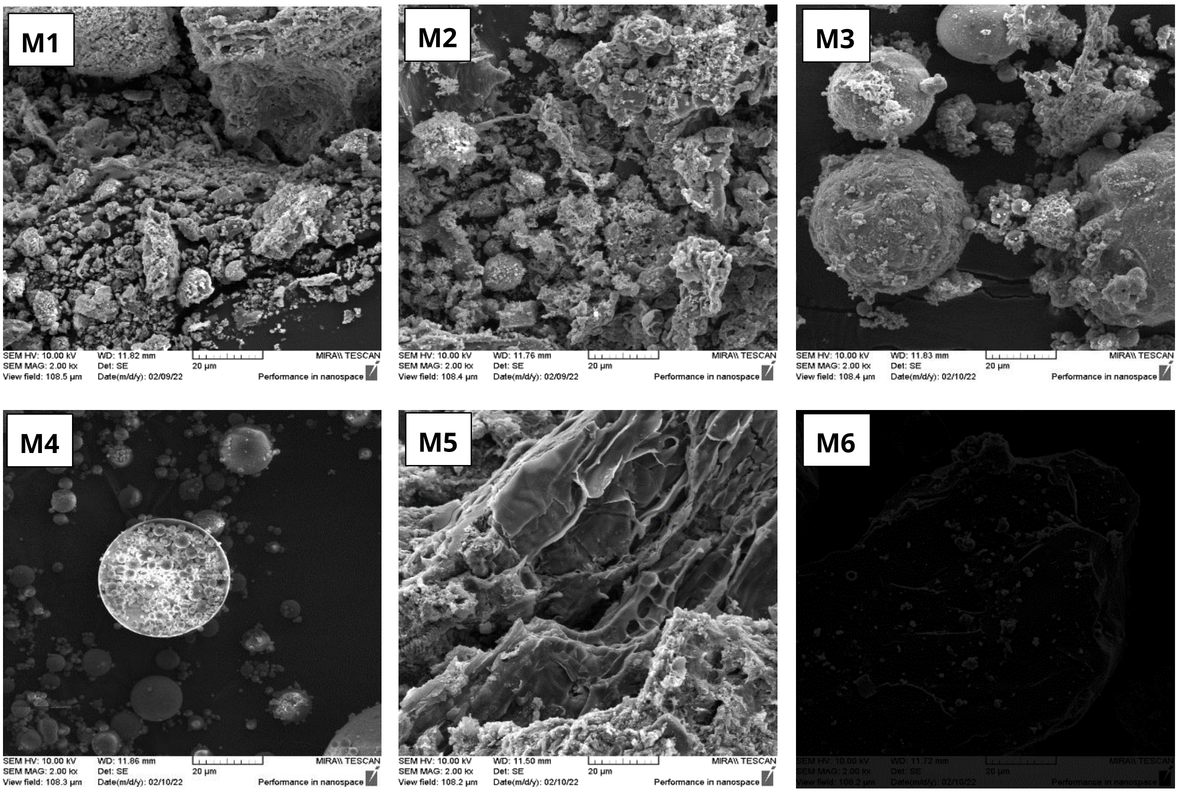

Figure 3. Micrographs obtained by powder of different samples of fly ash (magnification SEM_MAG = 2000x)

4. Conclusion

In this paper, the characteristics of fly ash, obtained by different technologies of lignite and black coal combustion, from different locations are analyzed. The addition of fly ash directly affects the properties of fresh and hardened concrete in a way that fills the structure, and actively participates in the hydration process. According to the obtained results, the differences between the six examined samples are significant. Therefore, depending on the final requirements of concrete, to design its composition it is important to know the detailed characteristics of fly ash to ensure satisfactory quality of the final product. For fly ash to be used as a mineral additive, its physical and chemistry characteristics must meet the prescribed international standards. For this reason, it is necessary to create conditions in thermal power plants for the separation of ash of appropriate and continuous quality, and the quality of coal should be considered.

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