CARACTERISTICI ALE CIMENTULUI PORTLAND COȚINÂND CENUŞĂ ZBURĂTOARE, TRATATĂ PRIN DIFERITE METODE FIZICE
CHARACTERISTICS OF PORTLAND CEMENT CONTAINING FLY ASH TREATED BY DIFFERENT PHYSICAL METHODS

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This paper presents an overview of laboratory testing carried out to determine the influence of fly ash, as a component in cement mixture, on physical-mechanical properties of cement. Fly ash, used in this testing, was treated by different physical methods – grinding, very fine grinding and classification. The addition of fly ash varied from 10 to 50% by weight in the mixtures with cement. In the first instance, the results were evaluated by the most important criteria, the compressive strenght of mortar containing prepared mixtures. In addition to that, the flexural strength of mortar, soundness of cement pastes, initial and final setting time, as well as the amount of water, required to produce the standard consistency of cement paste, were also investigated. The reported values have completly satisfied the appropriate standard.

Lucrarea de față prezintă rezultatele cercetărilor de laborator care au urmărit determinarea influenței cenuşii de termocentrală, utilizată ca adaos în cimenturi mixte, asupra proprietăților fizico-mecanice ale lianților. Cenuşa utilizată, a fost tratată anterior, prin diferite metode fizice – măcinare, măcinare foarte fină şi clasare, în vederea îmbunătățirii activității hidraulice. Adaosurile de cenuşă au variat între 10% şi 50%.In primă instanță, au fost determinate rezistențele la compresiune ale mortarelor preparate din lianții micşti – ca cel mai important criteriu de apreciere. In plus, au fost determinate rezistența la încovoiere a probelor de mortar, constanța de volum a pastelor liante, necesarul de apă pentru consistența standard şi timpul de priză inițial şi final. Valorile obținute pentru aceste proprietăți satisfac cerințele standard.

Keywords: *Portland cement, fly ash, grinding, classification*

1. Introduction

Different materials are added in the process of cement production, such as limestone, gypsum and slag as well as various pozzolanic admixtures. One of the commonly used pozzolanic additives is fly ash from the coal fired in thermal power plants.

The addition of fly ash can be accomplished in various phases of the cement production process. Fly ash can be added together with feed material in the clinker production (as a substitute material for clay), as one of the admixture in the clinker grinding process and finally as an admixture to the cement [1–3]. The prerequisite for fly ash addition is the quality of produced cement, which must satisfy the requirements considering chemical composition, physical-mechanical properties, especially the compressive strength of mortar.

Similarly, fly ash can be used as an aggregate in concrete production (as a substitute material for sand) whether it is added in its natural form [4-6], or as an ingredient in artificial aggregates [7,8].

Fly ashes generated by the thermal power plants in the territory of the Republic of Serbia (total annual production is about 5 000 000 t [9]) have such quality that they can be successfully applied as a pozzolanic material in cement and concrete production. Despite of this, the current use of fly ash in Serbia is sporadic and unplanned, and the largest quantities of this material are located in the landfills. Therefore, it is necessary to take some efforts to evaluate and provide any possibility of its use. This present study investigates the possibility of gaining the quality mixture of Portland cement and fly ash, according to the Standard EN 197-1:2000.

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The use of fly ash for commercial purposes has multiple advantages. In addition to reducing its negative impact on the environment, applying of fly ash involves a direct contribution to the conservation of natural mineral resources, reducing costs to their exploitation and disposal, as well as reducing costs related to the disposal of ash. Accordingly, it should be noted that during the construction of fly ash landfills the all required statutory provisions must be complied [10], which may also have an impact on the costs of deposition.

2. Experimental procedure

2.1. Raw materials

Raw materials for this investigation were the high quality Portland cement from the Cement Factory Titan - Kosjerić and fly ash from TPP Kostolac.

A Portland cement sample was obtained by grinding of Portland cement clinker with addition of calcium sulfate (5% by mass). This cement accomplished the requirements for chemical, physical and mechanical properties, defined by valid Standard EN 197-1:2000 and belongs to the type PC 52.5N. Chemical composition and physical-mechanical characteristics of this sample are presented in Tables 1 and 2, respectively.

Table 1

Chemical composition of fly ash and Portland cement samples
Compoziția chimică a cenuşii şi cimentului portland

Component	Content / *Conținut*, %	
	Fly ash *Cenuşă*	Portland Cement
SiO_2	50.38	20.92
Al_2O_3	26.43	5.81
Fe_2O_3	8.77	3.55
CaO	7.18	63.07
MgO	1.94	1.86
SO_3	2.14	1.89
TiO_2	0.42	/
Na_2O	0.21	0.20
K_2O	0.63	0.74
MnO	/	0.09
Cl	/	0.003
CaO free	0.59	/
SiO_2 active	27.87	/
LOI	2.36	0.96

Table 2

Physical-mechanical characteristics of Portland cement sample
Caracteristici fizico-mecanice ale cimentului portland

Flexural strength *Rezistența la încovoiere*, MPa	2 days		5.7
	7 days		7.7
	28 days		9.5
Compressive strength *Rezistența la compresiune*, MPa	2 days		24.9
	7 days		38.3
	28 days		58.1
Setting time *Timpul de priză*	Water requirement for standard consistency *Necesarul de apă pentru consistența standard,* ml		25.8
	initial, h : min		2:35
	final, h : min		3:30
Soundness *Constanța de volum*	Cement specimens *Probe de ciment*	in water *în apă*	without deformations *fără deformații*
		in the air *în aer*	without deformations *fără deformații*
		boiled	without deformations *fără deformații*
	Le Chatelier's method *Metoda Le Chatelier*		without deformations *fără deformații*
Residue on sieve opening size 90 µm *Rezidiu pe sita cu ochiuri de 90 µm, %*			1.2
Density / *Densitate*, g/cm^3			3.15
Specific surface area *Suprafața specifică*, cm^2/g			3850
Wet / *Umiditate*, %			0.43

A fly ash sample belongs to siliceous fly ash, marked as V according to EN 197-1:2000 (also can be classified into the class F according to standard ASTM C 618), that can be seen from the presented chemical analysis in Table 1. Particle size analysis of this sample is presented in Figure 1.

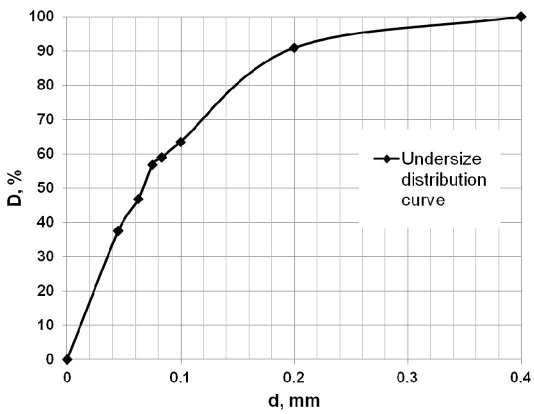

Fig. 1 - Particle size analysis of original fly ash sample / *Analiza dispersională a cenuşii inițiale.*

According to the chemical composition, fly ash fully satisfies the requirements of appropriate standards [11,12].

Particle size analysis of a fly ash sample (Fig. 1) shown that mass content of plus 45 microns class was 62.5%. Considering the standard requirements for pozzolanic admixtures to be finely ground down to minimum 40% more than 45 microns (for N category of fly ash [13]), it is evident that our fly ash sample do not meet the necessary fineness.

2.2. Processing of fly ash samples

In order to obtain the hydraulic binders containing Portland cement and fly ash in different mass ratios, the initial sample of fly ash was treated by different physical processes. One part of the sample was treated in the vibrating ring mill for 35 minutes, in order to achieve a very high fineness of fly ash.

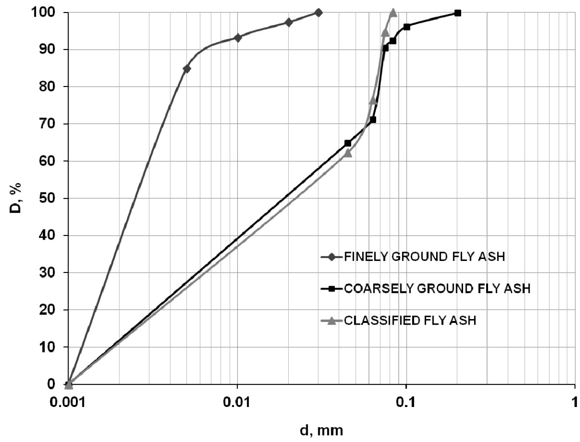

Fig. 2 - Particle size analysis of finely ground, coarsely ground and classified fly ash / *Analiza dispersională a cenuşilor activată, măcinată şi separată.*

Table 3

Physical characteristics of fly ash treated by different methods / *Caracteristici fizice ale cenuşiii tratate în diferite moduri*

Fly ash / *Cenuşa*	Pozzolanic activity index / *Indice de activitate puzzolanică* %	Specific area *Suprafață specifică* cm^2/g
Very fine ground / *Măcinată foarte fin*	97.52	10490
Ground / *Măcinată*	89.14	6380
Classified / *Clasată*	85.27	3440

The second part of the sample was ground in a laboratory ball mill for a 19 minutes, in order to provide the proper fineness of ash, in accordance with the Standard EN 450-1:2005 (maximum 40% class +45 μm for N category of fly ash).

Particle size analysis of the initial sample (Fig. 1) has showed that the satisfactory fineness of fly ash [11] can be achieved by sieving on the screen with opening size of 0.083 mm. Therefore, the third part of sample was sieved on the mentioned sieve. Particle size analyses of each sample, obtained after appropriate treatment are shown in the Figure 2. Pozzolanic activity indices were determined by standard method (outlined in ASTM C311 [14] and specified by ASTM C618 [12]). In this test method, the 28 days compressive strengths of a mortar, prepared with 20 % fly ash substitution for cement on a mass basis, are compared to those of control mortar (with the Portland cement only). The results are presented in Table 3. The same Table presents the specific surface areas of fly ashes, determined by Blain method.

2.3. Testing procedure of cement mixtures

Further experimental procedure was carried out through the three series of experiments. In the first series of experiments, the finely ground fly ash was added to the Portland cement in quantities of 10, 30 and 50%, and then the resulting mixtures were homogenized for a good uniformity of chemical composition. Samples are marked as FFA10, FFA30 and FFA50. In the second series of experiments, the analog amounts of coarsely ground fly ash were added to the Portland cement and after that the homogenization of mixtures was also performed. Samples were marked as GFA10, GFA30 and GFA50. The same procedure was repeated in the third series of experiments, where the substitute for Portland cement was classified fly ash. Samples were marked as CFA10, CFA30 and CFA50.

Mortars were prepared according to the standard procedure from the obtained cement mixtures. Compressive and flexural strengths were determined after 2, 7, and 28 days of hardening the mortar prisms in aqueous medium (standard procedure [15]). Water consumption for standard consistency and setting time of cement pastes were determined using the Vicat apparatus in accordance with the Standard [16]. Soundness of cement pastes was determined by Le Chatelier's method (according to [16]).

3. Results and discussion

The compressive and flexural strengths of studied mortar samples are presented in Table 4.

Based on the data in Table 4, it can be

Table 4

Compressive and flexural strength (MPa) of fly ash and cement mixtures
Rezistențe la compresiune şi tracțiune ale cimentului portland şi cimenturilor cu cenuşă

Sample /*Proba*	Compressive strength (MPa) *Rezistența la compresiune*			Flexural strength (MPa) *Rezistența la tracțiune*		
	2 days	7 days	28 days	2 days	7 days	28 days
PC(wt.0% fly ash)	24.9	38.3	58.1	5.7	7.7	9.5
FFA10(wt.10% fly ash)	24.3	39.9	62.7	5.7	7.5	9.2
FFA30(wt.30% fly ash)	17.6	34.7	55.4	3.7	6.0	7.8
FFA50(wt.50% fly ash)	11.6	21.4	43.1	2.8	4.4	6.3
GFA10(wt.10% fly ash)	22.2	41.5	59.3	4.2	7.3	9.1
GFA30(wt.30% fly ash)	15.8	31.3	50.9	3.4	6.0	7.7
GFA50(wt.50% fly ash)	9.8	19.0	40.8	2.6	4.0	6.3
CFA10(wt.10% fly ash)	22.0	37.4	56.1	4.5	7.9	8.3
CFA30(wt.30% fly ash)	14.5	32.8	47.6	3.3	5.8	7.7
CFA50(wt.50% fly ash)	9.9	17.8	36.4	2.4	3.8	5.9

concluded that the addition of fly ash to the Portland cement up to 10% can cause an increase of its compressive strength after 28 days of hardening (standard strength [13]). The increase in strength is achieved by addition of finely and coarsely ground fly ash, while cement mixture containing the classified fly ash, gives a lower standard strength than the Portland cement (CEM I). This can be explained by the fact that far-reaching comminuting of fly ash affects rapid progress of pozzolanic reaction [17,18]. Therefore, cement mixture with very finely ground fly ash (which has very high fineness, Fig. 2) achieved the highest strength.

Regardless, it can be generally concluded that these samples belong to the high quality cement mixtures and can be classified into the certain type of Portland cement with addition of siliceous fly ash up to 20%. They have a normal early strength, and after 28 days they achieve a compressive strength higher than 50 MPa. These cements can be labeled as PC 20V 52.5 N, according to the Standard [13].

Cement mixtures containing 30% fly ash developed lower standard strengths than the Portland cement (Table 4).

If the standard strengths of cement mixtures containing fly ash are compared mutually, the highest strength is achieved by a mixture containing very finely ground fly ash (55.4 MPa). All cement mixtures meet the standard requirements in terms of compressive strengths and belong to the type of Portland cement with addition of siliceous fly ash in quantity of 20 - 35%. These cements can be marked as PC 35V 42.5N [13]. It should be noted that the samples FFA 30 and GFA 30, could be classified into higher class of cements (according to the standard compressive strength and considering the limit value for single results of tests [11]). However, it is not possible, due to relatively low initial strength of 17.6 MPa and 15.8 MPa, respectively. (Minimum compressive strength of mortar after 2 days of hardening in water (early strength) should be 18 MPa [13]).

All the samples containing 50% fly ash have a noticeably smaller of early and standard compressive strengths than the Portland cement, which was expected. However, it should be mentioned that the quality of these cements is relatively high considering the mass ratio of fly ash) and they completely satisfy the requirements of corresponding standard. They can be classified into the type of pozzolanic cements with 11-55% of admixture. According to the compressive strength that they reach after 2 and 28 days of setting, the samples FFA 50 and GFA 50 can be defined as cements with the standard mark P55 42.5N, and the sample CFA 50 as cement with the standard mark P55 32.5R [13].

Water consumption values for the standard consistency pastes are shown in Figure 3, while Figure 4 presents the initial and final setting times of cement pastes.

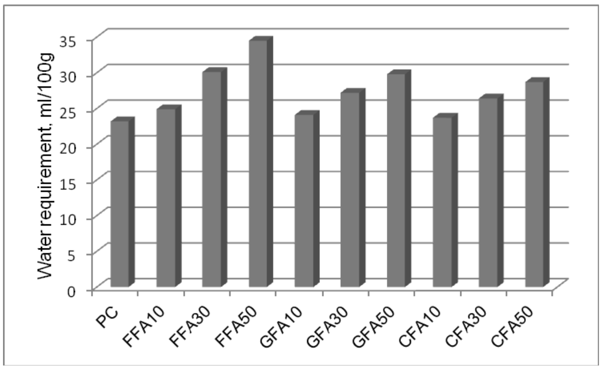

Fig. 3 - Water requirement for standard consistency of cement pastes / *Necesarul de apă pentru pastele liante de consistență standard.*

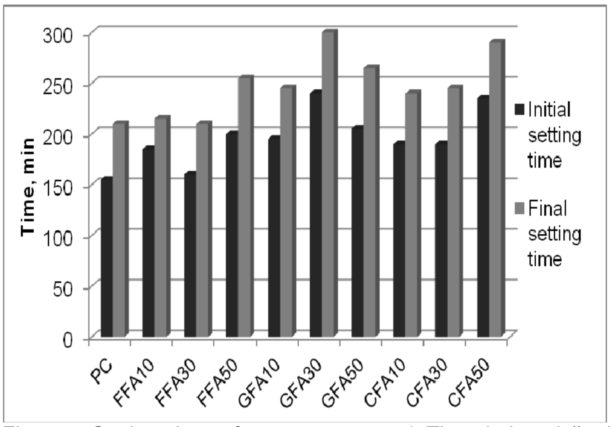

Fig. 4 - Setting time of cement pastes / *Timpul de priză al pastelor liante.*

Based on the data in the Figure 3, it is obviously that water requirement for standard consistency pastes depends on the amount of fly ash in mixtures. Minimum amount of water to attain the standard consistency is required by the Portland cement (CEM I) and maximum amount of water is required by the cement containing 50% finely ground fly ash, as expected. High fineness of finely ground fly ash determined a large consumption of water for standard consistency paste (Figure 3) [19].

Tests of soundness have shown that expansion of all cement pastes was within the limits prescribed by the standard. Initial and final setting time of cement pastes ranges between 160 and 300 minutes. It should be noted that all these cement pastes begins and ends their setting later than the Portland cement, but these values are within the standard limits (Figure 4).Since the setting time does not depends on the fly ash treatment method, it can be concluded that the amount of ash influences the setting time. Cements containing 50% fly ash begin and end their setting later than the most other cements.

4. Conclusion

Investigation has shown that fly ash from TPP Kostolac B can be successfully used as an admixture in the cement production at the Cement Factory Titan-Kosjerić. In other words, it is possible to obtaint high quality cements with ash content up to 50%, which completely satisfy the requirements of the Standard EN 197-1:2000, using the procedures that are described in this paper.

Fly ash complies with the necessary quality requirements considering the chemical composition, but fineness is too low for usage in the cement mixture. Therefore, in order to fulfill the fineness requirement and to improve its quality, fly ash was treated by different physical processes. Procedure of fly ash treatment as well as amount of fly ash in cement mixtures affects the properties of cement mixtures.

Addition of fly ash to the Portland cement up to 10% can cause an increase of its compressive strength after 28 days of hardening.

Cement mixtures containing 30% fly ash developed lower standard strengths than the Portland cement.

Cement mixtures containing 50% fly ash have a noticeably smaller of early and standard compressive strengths than the Portland cement.

Water requirement for standard consistency pastes significantly depends on the amount of fly ash in mixtures.

Initial and final setting time of cement pastes ranges between 160 and 300 minutes.

Generally, it can be concluded that the best results were obtained using the very fine ground fly ash (FFA) as an admixture (i.e. the highest quality cements were obtained using this procedure).

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