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THE DEPENDENCE OF PHYSICAL-MECHANICAL CHARACTERISTICS OF CEMENT ON FLY ASH ORIGIN

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Abstract. *The paper presents the results of an investigation of the potential to use the fly ash as a component of cement mixtures. For this purpose, fly ash from 3 locations has been chosen: from Kragujevac (LP1), Svilajnac (LP2) and Vreoci (LP3). The research was conducted by making cement mixtures with the portions coming up to 10, 20, 30 and 50% of each mentioned type of ash.*
The physical-mechanical characteristics of the cement mixtures created in this way have been determined.
On the basis of the obtained experimental results, the maximum content of fly ash in the cement mixtures has been determined. Also, the areas where the individual mixtures can be optimally applied, depending on their setting time, have been determined.

Key words: *Fly Ash, Portland Cement, Cement Mixture, Compressive Strength, Bending Strength, Specific Surface Area, Fly Ash Composition.*

1. INTRODUCTION

The research up to now has demonstrated that the ash obtained by combustion of coal can be used in various fields of industry. Due to the appropriate chemical and mineralogical composition, fly ash may be used as an integral part of cement production. [1]. Depending on the origin of coal, ash is composed of different minerals that define its contribution in the mass of the cement mixture.

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The usage of fly ash in Serbia and Montenegro does not have a long tradition. Of all the possible fields where it can be applied, it is most frequently used in cement industry, building materials industry, road building industry and at the research level in several other fields [2]. Since the coal used in the territory of Serbia and Montenegro is mostly of lignite origin (with a high content of mineral admixtures), the occurrence of the large quantity of fly ash, estimated at around $6,6x10^6$ t/year [3] is not surprising.

The experience in the usage of fly ash varies from country to country and ranges between several percents and several tens of percents. Our country, despite the very high production of fly ash per unit of produced energy, has a very low degree of its utilization. The economic and environmental damage resulting from such a passive behavior [4] needs not be specially emphasized.

As has already been mentioned, fly ash may be added to cement, prior to the addition of clinker, due to the similar chemical composition [5]. The reason for this is to lessen the total cost of cement, but the strict care must be taken about its share in the total percentage, so as not to alter significantly the cement quality. The basic regulations of the application of the said additives are defined by the world and national standards [6].

The standards define the quality of cement, reflected in bending and compressive strength, specific surface area, setting time and water consumption. In respect to the numerous values of the said characteristics, the classification of cement has been carried out [7].

For the application in cement industry, the American standard defines the ash classification as C class and F class according to the minimal content of the sum of oxides $SiO_2+Al_2O_3+Fe_2O_3$=SAF, which has up to 50% at C class, and 70% at F class [8].

Due to the experience, several criteria defining fly ash quality that may be used as binder in cement have been established [9]. Those are

- reactive SiO_2 in range 10-50%,
- content of Fe_2O_3 <10%,
- small content of CaO,
- ratio $SiO_2/Al_2O_3 \approx 2$,
- content of non-combusted carbon < 5%,
- content of vitreous phase content (i.e. content of micro spheres) should be high, and,
- distribution of particle size - 80-90% < 45μm.

There are several limiting factors for the usage of ash as an integral component of cement, and it is primarily the content of hazardous matter. Also, the reactivity of fly ash might present a problem, because with respect to Portland cement, fly ash is less reactive, so that the increased content of fly ash in cement mixtures adversely affects early hardening of cement. However, the small reactivity of fly ash can have as a consequence some changes which may be useful: decrease of concrete setting time rate and insurance of more favorable hydration. This may be important in the cases when a slower setting of concrete is desired (in hot climate). The solution surely should be sought for in the appropriate balance of economic, ecological and technical requirements that primarily pertain to the later application of cement [10].

Regarding this paper, the given objective is to determine the areas of application in which it is possible to use cement containing fly ash, the maximum quantity of fly ash (that will not change the characteristics below the permissible limit) and the most favorable type of fly ash.

2. Experiment Description

Ash from three locations, namely, Kragujevac (LP1), Svilajnac (LP2) and Vreoci (LP3) is chosen for our experiment. Clinker, as the standard product of the cement factory of Novi Popovac, and gypsum from the Gruza deposit are used. The chemical and physical characteristics of these initial samples are presented in Table 1. Out of the mentioned raw materials, three series of the cement mixtures samples are made. Each series has four samples, for the portion of 10, 20, 30 and 50% respectively. In this manner, 12 samples are obtained. The samples are marked in the following manner: PCxLPy. PC means Portland cement with x-percent portion of fly ash of y- type. The cement mixtures are examined with the standard methods for examination of physical-mechanical properties. Therefore, binding and compressive strength, setting time, water consumption and the specific surface by Blein are observed. In order to determine the ways in which the fly ash affected the physical-mechanical characteristics of the obtained cement mixtures, the same parameters are observed for Portland cement. The results are presented in Table 2.

Table 1. Chemical and Physical Characteristics of Used Raw Materials

	Clinker	Fly ash		
		LP1 Kragujevac	LP2 Svilajnac	LP3 Vreoci
Chemical properties				
SiO_2	22.54	40.40	44.7	48.4
Al_2O_3	6.11	16.50	18.2	22.6
$(Fe_2O_3)_u$	2.26	5.69	17.80	9.98
CaO	65.27	27.70	11.7	12.9
MgO	2.93	1.93	1.52	3.05
Na_2O	0.32	1.17	0.42	0.91
K_2O	0.38	1.84	2.16	1.11
$S0_3$	–	2.65	0.11	0.204
Physical characteristics				
Specific gravity, g/cm^3		2.24	2.00	1.43
Specific surface are by BleIn, cm^2/g	2200	1564	1826	2213
Pozzolanic activity		9.5	10.5	15.4

SAF LP1 = 40,4 + 16,5 + 5,69 = 62,59 class C
SAF LP2 = 44,7 + 18,2 + 17,8 = 80,7 class F
SAF LP3 = 48,4 + 22,6 + 9,98 = 80,98 class F

3. Discussion of the Results

On the basis of the results presented in Table 2 and in Figure 1, the graphic representation of the bending strength changes for various cement mixtures and in Figure 3, the changes of the compressive strength, depending on the setting time of the cement mixture with the different content of ash, are given. The change of specific surface area is presented in Figure 4, and the values related to the start and the end of setting are in given Figure 6. Water consumption, depending on the portion of fly ash in cement mixture is presented in Figure 5.

Table 2. Physical-mechanical Characteristics of Cement Mixtures

	PC	PCxLP1				PCxLP2				PCxLP3			
Characteristics		10%	20%	30%	50%	10%	20%	30%	50%	10%	20%	30%	50%
Compressive strength, MPa													
2 days	6.3	5.9	6.1	2.8	1.9	5.5	4.5	3.9	3.4	3.9	3.7	2.4	1.5
7 days	15.9	13.7	13.1	7.6	6.3	12.5	11.8	9.2	9.9	12.5	11.0	9.8	7.6
28 days	24.2	19.8	21.8	15.7	14.7	21.8	20.7	17.5	15.5	23.1	22.8	21.4	18.6
Bending strength, MPa													
2 days	1.8	1.7	1.5	1.2	1.0	1.5	1.4	1.1	0.8	0.7	1.1	1.0	1.0
7 days	3.9	3.2	3.0	1.8	1.3	2.6	2.2	2.2	2.2	2.7	2.6	2.3	2.1
28 days	5.7	4.6	4.5	3.7	1.7	4.6	4.1	4.0	4.9	5.2	4.9	4.3	5.1
Setting time, h													
start	4.00	7.30	6.45	7.20	4.45	4.30	9.20	9.00	5.10	5.00	8.40	7.20	9.15
end	5.15	10.40	9.20	9.30	8.35	6.30	13.30	11.00	7.30	8.50	12.10	9.25	13.25
Water consumption %	27.00	29.20	33.20	36.00	37.0	30.0	35.00	37.00	38.00	29.20	35.00	36.00	38.00
Specific surface area, By BLEIN cm^2/g	2200	1511	1581	1978	1780	1620	1654	1643	2261	1519	2114	2820	3240

A) As to the ***compressive strength*** for the cement mixtures with different portion of fly ash it may be observed (Fig. 1) that the compressive strength increases with the hardening time, both with Portland cement (6,3-24,2 MPa) and with the cement mixtures with ash.

When observing the change of the compressive strength according to the hardening time for various portions of fly ash in mixtures, it can be noticed that for the mixtures with 10% of fly ash, PC10LP1 (Fig. 1-a) has the best characteristics in the early period. Namely, the compressive strength increases, from the value of 5,9 MPa (after 2 days of hardening) to 19,8 MPa for 28 days of hardening. At the same time, compressive strength for PC10LP3 has a small value for the period of hardening of 2 days, amounting to 3,9 MPa, but it will reach the value of 23,1 MPa in the later period of hardening.

With the mixtures comprising 20% of fly ash content (Fig. 1-b) PC20LP1 has the best characteristics in the early and medium period of hardening and it amounts to 6,1 MPa after 2 days, that is 13,1 MPa after 7 days of hardening. In the final period of hardening, PC20LP3 has the highest value of the compressive strength, 22,8 MPa.

In Figs. 1-c and 1-d it may be observed that any increase of the ash portion in the mixture of 30% and 50%, the compressive strength significantly increases in time, with the mixtures: PC30LP2, PC30LP3,, PC50LP2 and PC50LP3, whereas for PC30LP1 and PC50LP1 this increase is smaller.

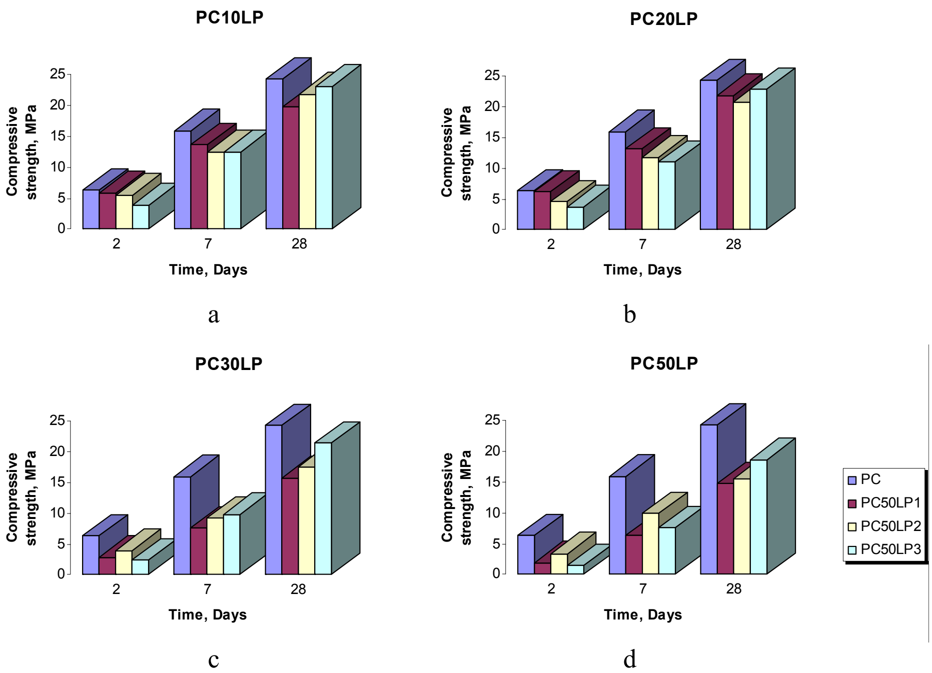


Fig. 1. Comparative Presentation of Compressive Strength of the Examined Cement Mixtures with the Portion of Ash of 10, 20, 30 and 50%.

With the increase of the content of ash in the cement mixture, the compressive strength decreases, while the rate of decrease depends on the hardening time. As fly ash is less reactive than Portland cement, its higher presence in the cement mixtures adversely affects the early hardness, as may be seen in Fig. 2-a. Thus, for PCLP1 it decreases from 5,9 MPa to 1,9 MPa which represents a 67,8% change. For PCLP2 the compressive hardness decreases from 5,5 MPa to 3,4 MPa, which is a 38,2% change, while the change for PCLP3 is 61,5%.

At the same time, the value of the compressive hardness for the pure Portland cement is 6,3 MPa. As the time of hardening reaches 7 days, this effect diminishes so that the compressive hardness for PCLP1 cement mixtures decreases from 13,7 MPa to 6,3 MPa (54%), for LP2 from 12,5 MPa to 9,9 MPa (20,8%), and for LP3 from 12,5MPa to 7,6 MPa (39,2%) (Fig. 2-b).

When the hardening period of 28 days (Fig. 2-c) is in question, the influence of the content of fly ash upon compressive hardness is even less, so that for LP1 hardness decreases from 19,8 to 14,7MPa (25,8%), for LP2 from 21,8 to 15,5 MPa (29,6%) and for LP3 from 23,1 to 18,6MPa (19,5%).

On the basis of the preceding result, it can be concluded that PCLP1 is the most sensitive to the content of ash in the mixture.

In the hardening period up to 2, that is 7 days, for little content of ash, (maximum 25%) PCLP1 mixtures have the best compressive strength characteristics (Fig. 2-a,-b).

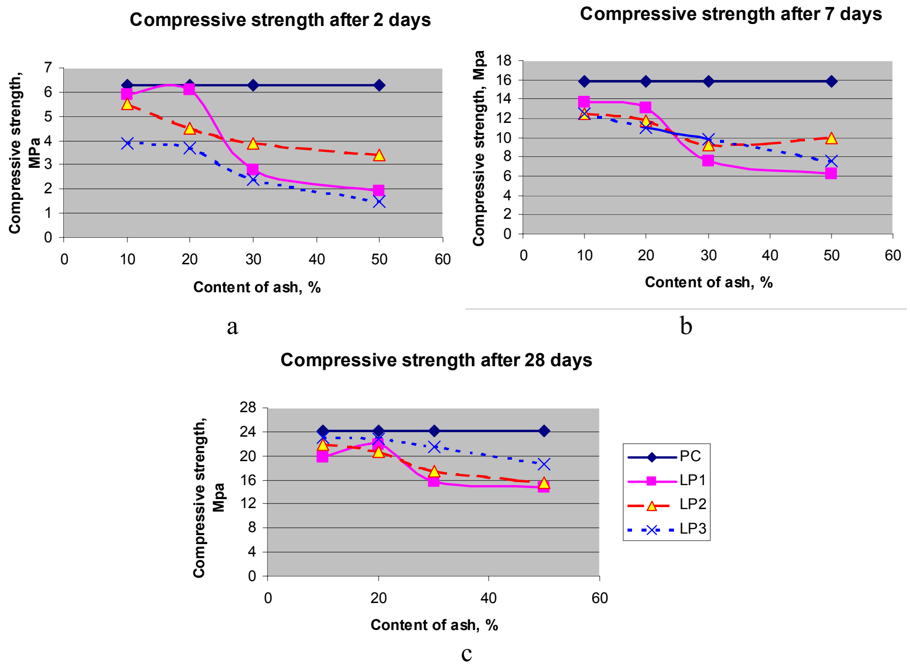


Fig. 2. Comparative Representation of Compressive Strength for Cement Mixtures with Different Ash Content for Hardening Periods of 2, 7 and 28 Days

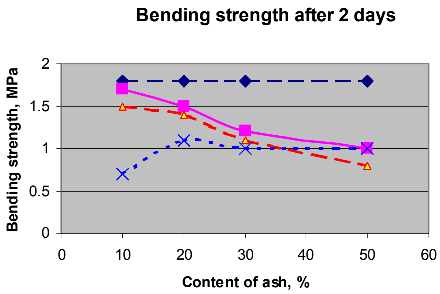
As the hardening period gets longer PCLP3 gets ever better characteristics, and for the longest hardening period it has the best characteristics of all the ash contents in the mixtures, ranging between 23,1 and 18,6 MPa (Figure 2-c).

As to PCLP2, in the hardening period of 7 days, this cement mixture has worse compressive strength characteristics with respect to PCLP1 for the ash content less than 25%, but for the content higher than 25% those characteristics are the best. The characteristics in the longest period of hardening are similar to PCLP1 mixtures.

- Therefore, it can be concluded that the cement mixture PCLP1 has the best compressive strength results in the hardening period up to 7 days for the ash content up to 25%. For the ash contents higher than 25% in the same hardening period, PCLP2 mixtures have better characteristics. Further on, better bending strength results are obtained in the mixtures containing LP3 ash.
- For the low content of ash in cement, the compressive strength is slightly altered with respect to the compressive strength for pure Portland cement.

B) As to the influence of type and content of ash on the ***bending strength*** value, if the results displayed in Table 2 are analyzed, it may be seen that with the increase of the hardening time, the bending strength of all the examined samples increases, while it decreases as the content of ash in the cement mixture increases.

In Fig. 3-a it may be seen that PCLP1 mixtures in the hardening period up to 2 days have the best bending strength characteristics for all the given contents of ash, as well as in the hardening period of up to 7 days for the maximum ash content in the mixture of 25%.



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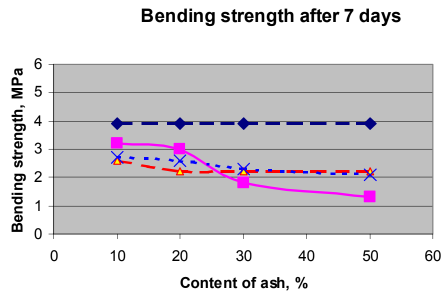

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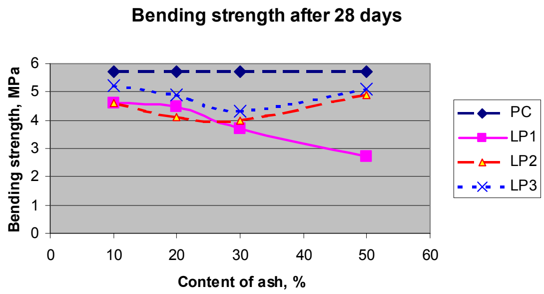

c

*Each picture contains the limit values for Portland cement (PC) as rough values.

Fig. 3. Comparative Representation of Bending Strength for Cement Mixtures with Different Ash Content for Hardening Periods of 2, 7 and 28 Days

Further, mixtures PCLP2 and PCLP3 have improving bending strength characteristics, and for the longest period PCLP3 mixtures have the best characteristics for all the ash contents.

If the bending and compressive strength of the cement mixtures are analyzed, it can be concluded that:

- PCLP1 is the most sensitive to the ash content.
- Cement mixture PCLP1 has the best characteristics in the hardening period up to 7 days with maximum ash content of 25%.
- For the ash content higher than 25% in the hardening period of up to 7 days, PCLP2 mixtures have the best characteristics.
- In the final hardening period, PCLP3 has the best characteristics with the maximum portion of ash up to 50%.
- Also, it may be observed that PCLP2 in all the hardening periods, for all the ash contents in the mixtures, has good characteristics which are only slightly weaker than those of PCLP1 or of PCLP3

The explanation for the said behavior of the cement mixtures with the different types of fly ash lies in, among other things, the chemical composition of the said types of fly ash.

Cement mixtures comprising fly ash from the location of Vreoci (LP3) have the best compressive and bending strength characteristics in the longest period of hardening which may be accounted for by the chemical composition of this type of fly ash. If Table 1 is observed, it can be seen that the LP3 ash has the highest content of SiO_2 (48,4%) which is crucial for the binding properties of cement. As to the presence of the undesirable component of CaO, it amounts to 12,9% , which is a large difference in relation to the presence of CaO of 27,7% in the ash of the location of Kragujevac (LP1). Good characteristics of these mixtures are influenced by the presence of Fe_2O_3 which stays below 10% as well as the favorable ratio $SiO_2/Al_2O_3 = 48,4/22,62 = 2,14 \approx 2$.

As to the LP1 fly ash from the location of Kragujevac, the content of SiO_2 is lower than in LP3 and amounts to 40,40%, but is high enough so that it can be used as a binder. Also, the low content of Fe_2O_3 of 5,69% contributes to the good binding properties. The high content of CaO of 27,7% is the reason for the limited use of this ash in the cement mixtures, and is also responsible for the unfavorable behavior of the cement mixtures in the later period of hardening. Also, the ratio of SiO_2/Al_2O_3 is above the optimal value of 2 and amounts to 2,45.

As indicated by the experimental results, when the cement mixtures from the location of Svilajnac (LP2) are in question, these mixtures have the medium values of mechanical characteristics in all the hardening periods as can be confirmed with the chemical composition. So, the contents of SiO_2 is 44,7% as the medium value between LP1 and LP3. Better behavior of PCLP2 in the later period of hardening in comparison to PCLP1 and the potential application in the medium period of hardening with the content of ash higher than 25% can be accounted for by the far lower content of CaO in LP2 than 11,7% comparing to 27,7% at LP1. The ingredient which has the most negative influence on the mechanical characteristics of PCLP2 mixtures is Fe_2O_3 whose presence amounts to as much as 17,8%.

C) In the chart given in Fig. 4 it may observed that the ***specific surface area*** of the cement mixtures increases with the increase of the portion of ash in the mixture.

In PCLP1 and PCLP2 this increase is smaller and ranges between 1511cm^2/g (for 10% portion) through 1978 cm^2/g (for 30% portion) and 1780 cm^2/g (for 50%) for PCLP1, constituting an increase of 17,8% and between 1620 cm^2/g (for 10% portion) and 2261 cm^2/g (for 50%) which for PCLP2 constitutes an increase of 39,6%. In PCLP3, the increase of the specific surface area is very prominent and ranges between 1519 cm^2/g (for 10% portion) and 3240 cm^2/g (for 50%). This increase of 113% agrees with the values of their pozzolanic activities: 9,5, 10,5 and 15,4, respectively (Table 1).

In Fig. 4 it can be seen that the specific surface area PCLP3 for the ash content over 22% is higher than the specific surface of clinker (amounting to 2200 cm^2/g) and increases to 3240 cm^2/g.

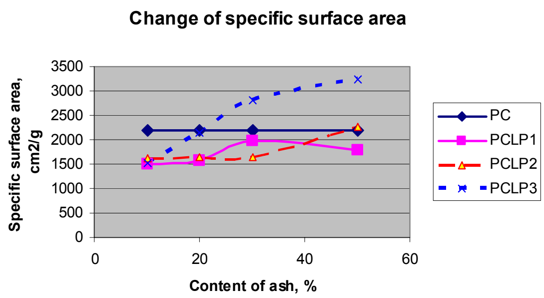

Fig. 4. Specific Surface Area of the Examined Cement Mixtures

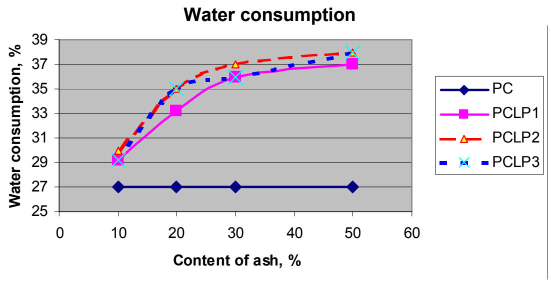

Fig. 5. Water Consumption for Normal Consistency of Cement Mixtures

D) In the results displayed in Fig. 5 it is clearly visible that the water ***consumption*** in all the cement mixtures increases with the increase of the fly ash content in them. So, for PCLP1 mixtures, it grows from 29,2 to 37,0%, for PCLP2 from 30,0 to 39,0%, while for PCLP3 mixtures it grows from 29,2 to 38,0%. Also, it may be observed that all these values are higher than those of water consumption for Portland cement which amounts to 27%.

E) Observing the values for the ***start and end of the setting time*** (Figs. 6-a and 6-b), the following conclusions can be made:

- Both the start and the end of the setting time for the examined cement mixtures are higher than the values for Portland cement (4,00 and 5,15h).
- The content of ash affects in the same way both the start and the end of setting for the certain cement mixtures.
- There is no direct dependence of the setting time on the ash content. PCLP1 has a decreasing trend both of the beginning and the ending of setting time, in PCLP3 these values increase, while PCLP2 has a prominent maximum for ash content in mixture between 20 and 25% so that the beginning of the setting time is at 9,8h, and the end at 13,8h.
- If some limitation is imposed, in the form of the maximum setting time of 10 hours, PCLP1 mixtures have the best characteristics, that is, the shortest setting time. In Fig. 6-b it can be seen that the maximum time of setting of PCLP1 mixtures for any given content of ash below the 10 hour limit. PCLP2 mixtures can be used with the ash content of 10-15% and 35-50%, while for PCLP3, this would be for 10-13% and 25-35% of ash content.

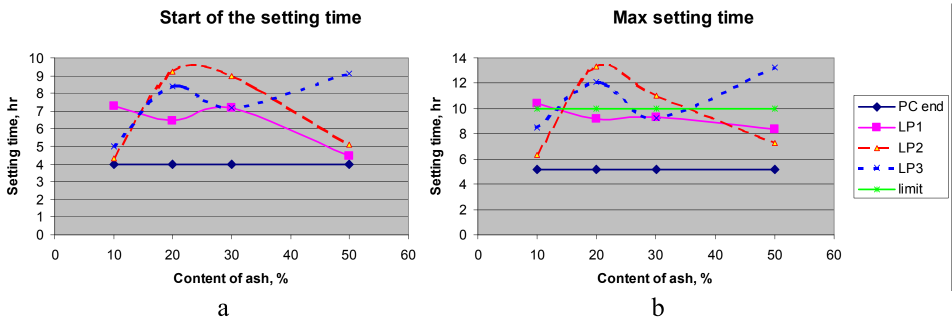

Fig. 6. Setting Time of the Examined Cement Mixtures

4. CONCLUSIONS

The goal of the conducted research has been to determine (on the basis of the analysis of physical-mechanical characteristics of cement mixtures [bending and compressive strength, specific surface area, start and end of setting and water consumption] and on the basis of the chemical analysis of three types of fly ash which are the components of the examined cement mixtures) the fields of application in which it is possible to use the cement with a certain type of fly ash as well as the maximum fly ash quantity that will not change the characteristics below the acceptable quality limit.

On the basis of the carried out research and the obtained results, it can be concluded that:

- Fly ash LP1, from the location of Kragujevac, can be used in the cement mixtures only in the short setting time conditions, with the maximum content of ash of 25% due to the high content of CaO.
- Ash LP2 from the location of Svilajnac can also be used in the short hardening time conditions of up to 7 days due to the low content of SiO_2, but the ash can be present in the mixture from 35 to 50% which is possible due to the low content of CaO in ash.
- Due to the good chemical properties, and especially due to the high content of SiO_2 and low content of CaO, the fly ash from the location of Vreoci (LP3) can be used in cement mixtures in the conditions where a long hardening time is required, with the maximum content of fly ash in the mixture of 35%.

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ZAVISNOST FIZIČKO-MEHANIČKIH KARAKTERISTIKA CEMENTA OD POREKLA LETEĆEG PEPELA

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U ovom radu su dati rezultati ispitivanja mogućnosti korišćenja letećeg pepela kao komponente cementnih smeša. U tom smislu je izabran letećI pepeo sa 3 lokacije: Kragujevac (LP1), Svilajnac (LP2) i Vreoci (LP3). Ispitivanja su urađena tako što su napravljene cementne smeše sa učešćem 10, 20, 30 i 50% od svake navedene vrste pepela.

Određene su fizičko-mehaničke karakteristike tako napravljenih cementnih smeša.

Na osnovu dobijenih eksperimentalnih rezultata utvrđen je maksimalni sadržaj letećeg pepela u cementnim smešama. Takođe su određena i optimalna područja primene pojedinih smeša u zavisnosti od perioda očvršćavanja.

Ključne reči: *Leteći pepeo, portland cement, cementna smeša, čvrstoća na pritisak, čvrstoća na savijanje, specifična površina, sadržaj letećeg pepela*