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INFLUENCE OF THE FLY ASH CHEMICAL COMPOSITION ON THE PORTLAND CEMENT AND FLY ASH MIXTURE HYDRATION MECHANISM

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Abstract. *Knowledge of the Portland cement and fly ash mixture hydration mechanisms is of high importance in the practical usage of fly ash in cement mixtures. The quantity of CaO in the fly ash can determine the course of hydration and influence the strength of cement pastes.*
In this paper the results of the testing of the influence of fly ash composition on the strength of cement mixtures with special emphasis on the content of CaO in the ash have been presented.

Key Words: *Fly Ash, Cement Mixture, Compressive Strength, Fly Ash Content, CaO Content*

1. INTRODUCTION

For the establishment of model of fly as (FA) and Portland cement (PC) mixture hydration, it is important to point out that the pozzolanic reactions, which are primary (the most important) reactions of fly ash in cement (eq. 1-3) in respect to the Portland cement hydration reaction, are much slower reactions and occur in a noticeable extent only after one or two weeks [1].

$$2SiO_2 + 3Ca(OH)_2 = 3CaO \cdot 2SiO_2 \cdot 3H_2O (C_3S_2H_3) \quad (1)$$

$$Al_2O_3 + CaSO_4 \cdot 2H_2O + 3Ca(OH)_2 + 7H_2O = 4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O\ (C_4A\hat{S}H_{12}) \quad (2)$$

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$$Al_2O_3 + 4Ca(OH)_2 + 9H_2O = 4\,CaO \cdot Al_2O_3 \cdot 13H_2O (C_4AH_{13}) \quad (3)$$

The entire Portland cement and fly ash mixture hydration process can be divided into several phases, depending on the time segment of the process. However, there is a difference in the hydration process of the cement mixtures depending on the content of CaO in the fly ash.

If the content of CaO is less than 10% this flying ash is treated as the one with a low content of CaO (FAL) with significant pozzolanic characteristics. Ashes with a high CaO content may have cement characteristics if CaO content is higher than 20%, FAH, but if the presence is within 10 – 20%, then we talk about cement and pozzolanic materials (FAM) (FA with a middle content of CaO).

Pozzolanic materials require the presence of $Ca(OH)_2$ in order to form a solid product, while cement materials contain sufficient quantities of CaO and can present only hydraulic activity. Usually, the content of CaO in ash is not sufficient for the reaction with the total quantity of pozzolanic components, and thus it has a pozzolanic activity (pozzolanic and cement materials).

In the literature, a lot of attention is paid to the cements with low contents of CaO because of their distinctive pozzolanic properties. Having in mind that the ashes from the territory of Serbia and Montenegro are of lignitic origin, and that they can have a high content of CaO, this paper will deal with the explanation of the mixture PC+FAH hydration mechanism.

The hydration process of **PC+FAL** mixture can be divided into early, medium and late period of hydration (Fig. 1). The change of concentration of $Ca(OH)_2$ can be an indicator of the mixture hydration reaction development [2]. In the earliest period of hydration, as soon as after only several minutes, the first hydration, and hydration energy release occur. After that follows a period of rest, during which the hydration energy release is relatively small. Physical changes in the cement paste during this period are demonstrated as its gradual solidification. After the rest period, in the medium phase, the reaction accelerates, and new hydration of cement. The maximum is reached 9-10 hours after the onset of reaction.

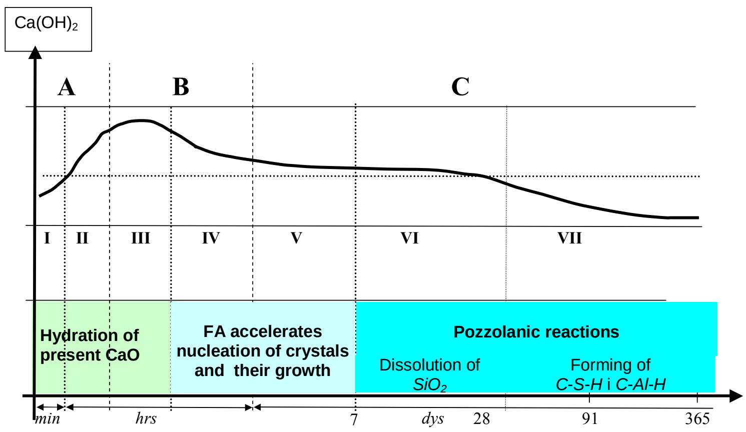


Fig. 1. Physical Model of Hydration Process of PC+FAL Mixture

A Early period	1. *preinduction*- hydration of portland cement and creation of products C-S-H, C-Al-H, and $Ca(OH)_2$. 2. *Induction*- period of rest
B Medium period	3. *acceleration phase* 4. *nucleation phase*
C Late period	5. *crystal growth* 6. *dissolution of amorph SiO2* 7. *pozzolanic reactions*

Due to the increase of ion $(OH)^-$, concentration, which is a consequence of the creation of $Ca(OH)_2$, the environment becomes more and more alkali. The fly ash which is activated in this early period to a negligible extent exhibits the behavior of an inert material which accelerates the hardening of cement paste by acting as nucleus for sedimentation of C-S-H and C-Al-H and $Ca(OH)_2$ created upon the cement hydration.

Fig. 2a displays SEM appearance 3 days after hydration, and Fig. 2b after 14 days. It is obvious that in the early period there are no traces of a pozzolanic reaction. In the nucleation phase, the final cement paste structure is formed.

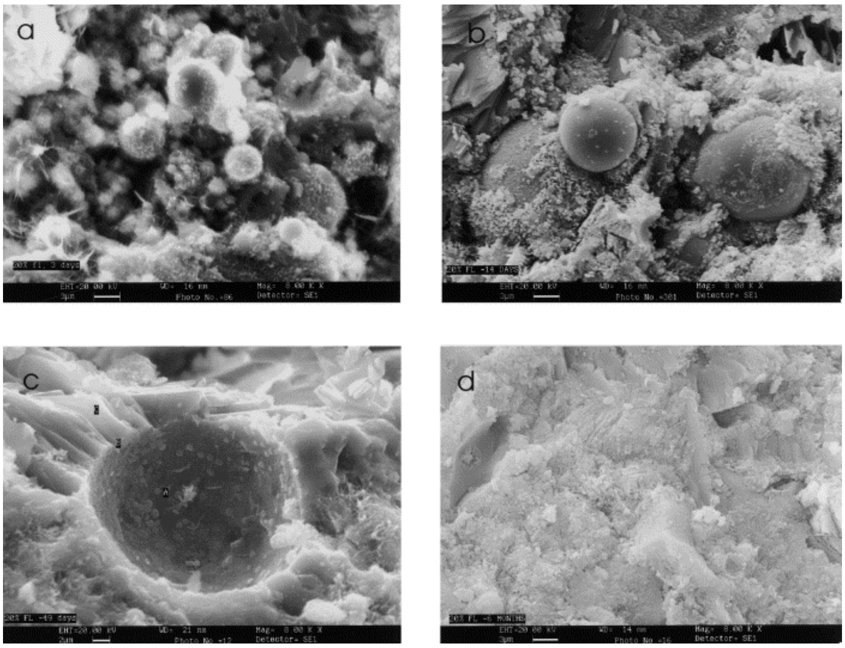


Fig. 2. SEM Appearance of Cement Paste with 20% of FAL after (a) 3, (b) 14, (c) 49 and (d) 182 Days of Hydration. [Pap99]

In the late period, the cement paste solidifies, and the pH value which affects the dissolution of molecules of amorphous SiO_2 increases in the pores of cement paste. Along with the increase of pH value, the dissolubility of the amorphous phase increases. [3]. After 28 days the particles of fly ash are grooved and surrounded with hydration products, but still retain the spherical shape (Fig.2c). As the pozzolanic reactions start to develop, the fly ash particles lose the spherical form, become covered with a layer of the product and after a period of 6 months cannot be identified any longer (Fig.2d).

As has already been emphasized, the case of hydration of mixture of Portland cement and fly ash with a high content of CaO (PC+FAH) is much more complex than the hydration of mixture of Portland cement and fly ash with low content of CaO (PC+FAL) because of the simultaneous pozzolanic and cement activity of this kind of ash. The activity of fly ash with a high content of CaO (FAH) begins from the very start of mixture hydration because of the presence of free CaO oxide in the ash, which has as a consequence the increase of early hardness of cement mixture. Figure 3 presents a typical SEM image of mixture sample, where 20 % of cement is substituted with FAH in various periods of hydration.

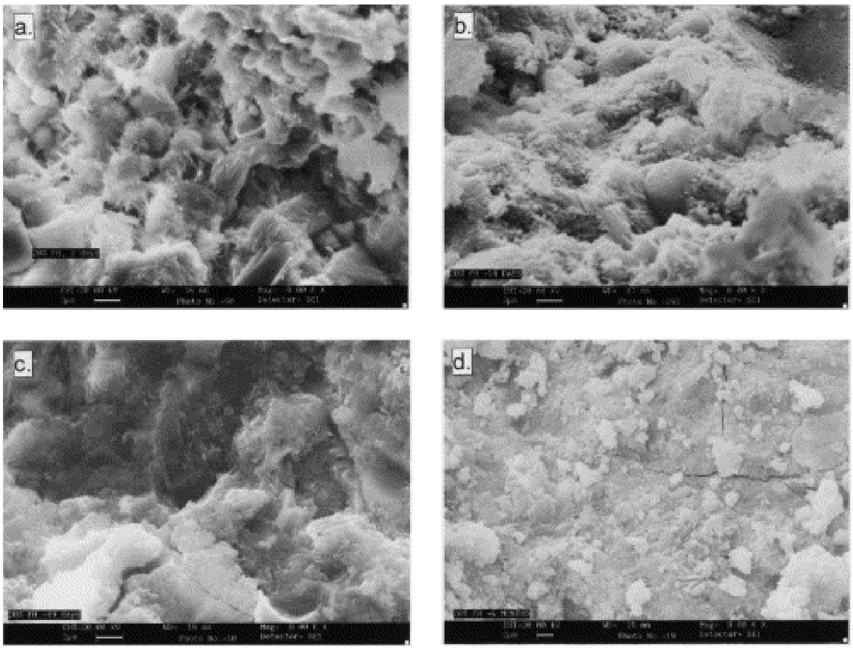


Fig. 3. SEM Appearance of Portland Cement Paste with 20% FAH after (a) 3, (b) 14, (c) 49 and (d) 182 Days of Hydration [Pap00]

Since the very start of reaction (3 days), product of reaction is identified on the surface of fly ash particle. However, after 2-3 weeks, it is hard to differ the FAH in the created micro-structures. After a longer period (6 months), a solid structure is formed.

Hardness of such mixture (as opposed to PC+FAL) increases from the very beginning of hydration. It can be said that the presence of free CaO in this kind of ash affects the increase of early hardness of cement paste.

If the chemical composition of fly ash is compared to cement, FA with a high content of CaO is much more similar to cement than the ash with low content of CaO. The pozzolanic reactions in one and the other kind of ash are similar, but their beginning and scope of action are different, and thus it gives the different characteristics to the cement pastes.

The cement mixtures that contain flying ash with a middle content of CaO will have characteristics somewhere in between of the previously mentioned mixtures.

2. Experiment Description

Three types of fly ashes have been chosen for the experimental research: Kragujevac (FA1), with a high content of CaO and Svilajnac (FA2) and Vreoci (FA3) ashes with the medium content of CaO.

Ash from three locations was chosen for the experimental research: Kragujevac (FA1), Svilajnac (FA2) and Vreoci (FA3). Clinker, which is the standard product of the cement factory of Novi Popovac, and gypsum from the Gruza deposit were used. The chemical characteristics of these initial samples are presented in Table 1.

Table 1 Chemical Characteristics of Used Raw Materials

Compounds	Portland cement	Fly ash		
		FA1 Kragujevac	FA2 Svilajnac	FA3 Vreoci
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
Pozzolanic activity		9,5	10,5	15,4

Out of the mentioned raw materials, three series of the cement mixtures samples were made. Each series has four samples, for the portion of as of 10, 20, 30 and 50% respectively. In this manner, 12 samples were obtained. The samples were marked in the following manner: PCxFAy. PC means Portland cement with x-percent portion of fly ash of y- type. The cement mixtures were examined with the standard methods for examination of compressive strength. The results have been presented in Table 2.

Table 2 Physical-mechanical Characteristics of Cement Mixtures

Compounds	Content of fly ash, %	Compressive strength, MPa 2 days	7 days	28 days
PC		6,3	15,9	24,2
PCxFA1	10	5,9	13,7	19,8
	20	5,9	13,1	19,7
	30	4,1	9,9	15,7
	50	2,4	7,6	14,7
PCxFA2	10	5,5	12,5	21,8
	20	4,5	11,8	20,7
	30	3,9	9,2	17,5
	50	3,4	9,1	15,5
PCxFA3	10	3,9	12,5	23,1
	20	3,7	11,0	22,8
	30	2,4	9,8	21,4
	50	1,5	7,6	18,6

3. Discussion of Results

On the basis of results presented in Table 2, in Figure 4, a graphic representation of compressive strength variation for the cement mixtures with various presence of fly ash in their mass (10 and 30%) is given. As is obvious in the figure, the compressive strength increases in time, both in Portland cement and fly ash mixtures.

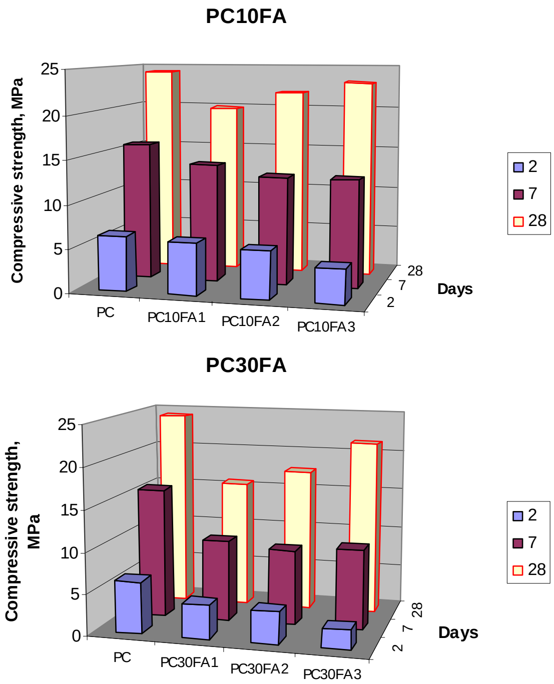


Fig. 4. Comparative Representation of Compressive Strength of the Tested Cement Mixtures, with the 10 and 30%of Ash

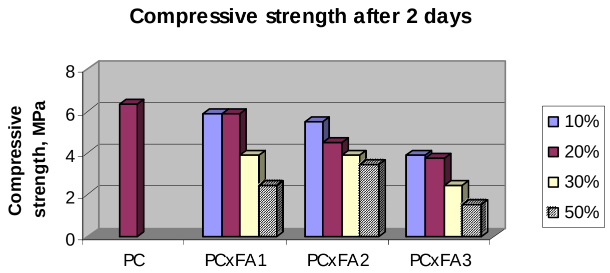
With the increase of content of ash in cement paste, the compressive strength decreases, since fly ash is less reactive than Portland cement (Fig. 4). The results of the examination of the impact fly ash content has to physical and mechanical characteristics of the cement pastes are given in detail in paper (6)

Analyzing the ash according to content of CaO (Table 1), ash FA1 containing 27,70% of CaO can be classified into the ashes with a high content of CaO (FAH) which thus has very distinct cement characteristics. The ash FA2 has 11,70% CaO, and ash FA3 12,90%, so they can be classified into the ashes with cement and pozzolanic characteristics, FAM .

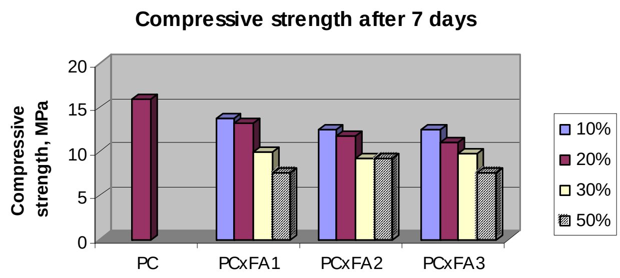
In the earliest period (2 days) the mixtures containing the fly ash with a high content of CaO (FA1), develop early hardness very soon upon the contact with water owing to the cement behavior of such fly ash. Mixtures with 10% and 20% of FAH have the compressive strength characteristics which are similar to the characteristics of Porland cement. With an increase of the fly ash content upon 20%, the value of hardness decreases (Fig. 5a).

At the mixtures with the fly ash FAM, the values of an early hardness are reduced due to a lower content of CaO.

In the course of time, the compressive strength values increase, but remain the highest at the FAH (Fig. 5b).



a)



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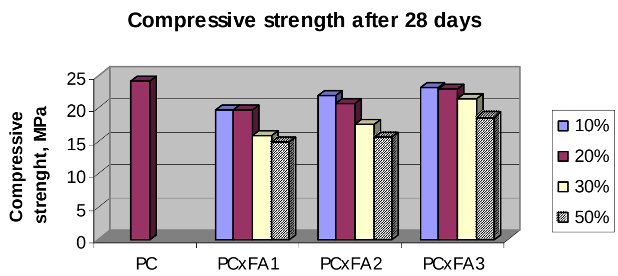

c)

Fig. 5. Comparative Representation of Compressive Strength for Cement Mixtures with Different Content of Ash for the Hardening Periods of 2, 7 and 28 Days

After the free CaO has been consumed, the compressive strength of mixtures with FA1 decreases in respect to the mixtures with FA2 and FA3.

As the hardening period continues, the active components (SiO_2 and Al_2O_3) of ash, react with $Ca(OH)_2$ in the pozzolanic reactions (Eq. 1-3), so the mixtures with FA3 which have a higher content of active components and the highest pozzolanic activity, 15,4 (Tab.1), have the best characteristics of compressive strength for all the contents of ash in mixtures (Fig. 5c).

By comparing the values of compressive strength on mixtures with FA3 and hardness of Portland cement, it can be determined that there is 11,5% difference of the ash presence in the mixture of 30%, and for the share of ash of 50% that difference is 23%. This explains the possibilities of use of fly ash FA3 in higher percentage.

The mixture with FA2 that has reduced value for the pozzolanic activity, 10,5 (Tab.1) also has reduced value of compressive strength which is especially perceived with the increase of ash content.

The compressive strength at mixtures with FA1 is even lower compared to mixtures with FA3 adequate to the smallest value of the pozzolanic activity.

4. Conclusion

The results of the conducted experimental research have shown that the cement mixtures containing fly ash with variable content of CaO have the different mechanical properties which can affect their application.

- The rate of hardening of cement mixtures in the early period is higher at the mixtures with fly ash FAH than at the mixtures with fly ash FAM.
- The cement mixtures with fly ash FAH have the best compressive strength characteristics in the conditions of short time of setting with the maximum content of fly ash up to 20%.
- The compressive strength of the cement mixtures containing the fly ash with medium content of CaO, PC+FAS, in the earliest period of hardening is smaller in respect to the Portland cement, primarily because of the weak activity of the fly ash particles. In time, due to the pozzolanic activities, the value of the compressive strength of the mixtures with FAM becomes higher in respect to the mixtures with FAH.
- The fly ash FA3 can be used in the cement mixtures with a content higher than 30% due to a high content of SiO_2 and Al_2O_3.

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UTICAJ HEMIJSKOG SASTAVA LETEĆEG PEPELA NA MEHANIZAM HIDRATACIJE SMEŠE PORTLAND CEMENTA I LETEĆEG PEPELA (PC+LP)

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Poznavanje mehanizama hidratacije smeše Portland cementa i letećeg pepela je od velikog značaja za praktično korišćenje letećeg pepela u cementnim mešavinama. Količina CaO u letećem pepelu može odrediti tok hidratacije i uticati na čvrstoću cementnih pasti.

U ovom radu su prikazani rezultati ispitivanja uticaja hemijskog sasatava letećeg pepela na čvrstoću cementnih mešavina sa posebnim osvrtom na sadržaj CaO u pepelu.

Ključne reči: *Leteći pepeo, cementna smeša, čvrstoća na pritisak, sadržaj letećeg pepela, sadržaj CaO.*