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PROPERTIES OF COMPOSITE CEMENT WITH COMMERCIAL AND MANUFACTURED METAKAOLIN

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Preliminary notes
Metakaolin composite cements were prepared with 5 to 35 % replacement of ordinary Portland cement with metakaolin (MK), manufactured by thermal activation/calcination of domestic kaolin clay, and commercial matakaolin (CMK) . Performance of the composite cements was evaluated through the setting time (initial and final), compressive strengths (for ages 2, 7, 28, 90 and 180 days) and soundness, and compared with control cement (Portland cement – CEM I). After 28 days, compressive strength was higher than that for control cement for cements prepared with addition of CMK, and with addition of up to 25 % MK.

Keywords: *composite cement, compressive strength, metakaolin, setting time, soundness*

Svojstva kompozitnog cementa s dodatkom komercijalnog i tvorničkog metakaolina

Prethodno priopćenje
Metakaolin kompozitni cementi su pripremljeni zamjenom Portland cementa s dodatkom 5 ÷ 35 % metakaolina (MK), proizvedenog toplinskom aktivacijom / kalcinacijom domaće kaolinske gline, i komercijalnog matakaolina (CMK). Karakteristike metakaolin kompozitnih cemenata ocijenjene su na osnovu ispitivanja vremena (početka i kraja), tlačnih čvrstoća (u starosti od 2, 7, 28, 90 i 180 dana) i postojanosti volumena, te u usporedbi s kontrolnim cementom (Portland cement - CEM I). Nakon 28 dana, veću vrijednost tlačne čvrstoće pokazali su uzorci cementa pripremljeni s dodatkom CMK, te s dodatkom do 25 % MK u odnosu na kontrolne uzorke.

Ključne riječi: *kompozitni cement, postojanost volumena, metakaolin, tlačna čvrstoća, vrijeme vezivanja*

1 Introduction

In three cement plants in Serbia the annual production of Portland-composite cement (CEM II) with blast furnace slag, coal ash and natural pozzolana is approximately 2,5 million tons. As cement industry in the world, Serbian cement industry is facing challenges in terms of increasing durability, improving performance and sustainable production.

The use of pozzolanic materials for partial replacement of clinker or Portland cement in Metakaolin composite cement and concrete mixtures has become almost unavoidable owing to their beneficial effects on the ultimate compressive strength, permeability and chemical durability, as well as to the economic and ecologic advantage of their use [1].

In the last 20 ÷ 30 years, for the partial replacement of the clinker or cement industrial by-products such as fly ash, granulated blast furnace slag and silica fume are used. Beside them, natural pozzolanas and limestone are used. The shares of allowances range from 5 to 35 % by mass, depending on market requirements and product assortment.

Since mid-1990, a highly reactive metakaolin (HRM), a pozzolanic addition for cement and concrete, has been produced in several factories around the world by thermal activation/calcination of previously refined kaolin clay with a high content of kaolinite. Its application in the regular concrete is limited because of the relatively high cost of production.

In previous works [2, 3] authors presented the results of preparing matekaolin by thermal activation of several kaolinite clays. The process depends on the raw clays properties, as weel as the process parameters.

The produced metakaolins, in comparison with commercial metakaolin, possess aproximatelly the same pozollanic activity determined either by Chapelle method or by standard [4], as well as mean diameter. First attempts on making metakaolin encouraged authors to continue their researches. Although manufactured metakaolin possesses high pozzolanic activity, verification of its performance in cement-based systems is necessary.

Serbia has high-quality kaolin clay deposits at the Arandjelovac and Kolubara basin, and thus good potential to produce metakaolin from them. There is currently no industrial production of metakaolin in Serbia. In this paper we present the first results on performance of the Metakaolin composite cement with addition of 5 ÷ 35 % by mass of metakaolin manufactured by thermal activation of Serbian kaolin clay.

2 Experimental work
2.1 Materials

For the preparation of the Metakaolin composite cement with Lafarge BFC PC (CEM I 42,5R), metakaolin (MK) obtained by thermal activation/calcination of "Garaši" kaolin clay and commercial metakaolin ARGICAL-M 1000, produced by AGS Mineraux (France) (CMK) were used. Chemical composition and physical properties of the starting materials are shown in Tabs. 1 and 2.

2.2 Applied experimental methods

The chemical composition of cement is determined by standard methods [5], while chemical composition of metakaolin is determined by silicate analysis.

Cement physical properties, such as standard consistency, setting time, specific gravity were determined according to the standards [6, 7], compressive strengths according to the standard [8] and soundness according to [6].

Pozzolanic activity is determined according to the standard [4].

2.3. Preparation of the cement with addition of metakaolin

In order to determine the characteristics of Metakaolin composite cement with the addition of metakaolin cement samples were prepared with the metakaolin addition of 5, 10, 15, 20, 25, 30 and 35 % by mass. To test the compressive strength after 2, 7, 28, 90 and 180 days mortar mixes were prepared according to the standard [8] with water-cement factor (w/c) 0,5; and the ratio of binder-sand=1:3.

3 Results and discussion

The influence of addition of metakaolin, in quantities 5 to 35 % by mass, to the Portland cement was determined through the examination of setting times, compressive strengths and soundness.

3.1 Setting time

The influence of the metakaolin addition on setting time is shown in Tab. 3.

The results indicate that Metakaolin composite cement requires a larger amount of water to achieve a standard consistency of the control Portland cement (CEM I 42,5R), which is in agreement with results published by other authors [9, 10].

All blended cements showed lower setting time (initial and final) than that of control cement, in other words they accelerated initial and final setting time. The higher acceleration occurs by adding commercial metakaolin. Essentially, one of the most important factors which cause a decrease in the setting time is the higher surface area metakaolin.

Table 1 Chemical composition and physical properties of the Portland cement (CEM I 42,5R)

Chemical composition (% by mass)			
SiO_2	20,36	Insoluble residue in HCl/Na_2CO_3	1,11
Al_2O_3	5,83	Insoluble residue in HCl/KOH	0,62
Fe_2O_3	2,96	CO_2	1,04
CaO	62,36	CaO, Free	0,43
MgO	1,32		
SO_3	2,80		
Na_2O	0,15	**Physical properties**	
K_2O	0,79	Residue on siev 0,09 mm / %	0,3
MnO	0,127	S_p / cm^2/g	4430
LOI	3,00	γ_s / g/cm^3	3,10
Sum:	99,70		

Table 2 Chemical composition and physical properties of the metakaolin (CMK) and (MK)

Chemical composition (% by mass)			Physical properties		
	CMK	**MK**		**CMK**	**MK**
SiO_2	55,00	63,91	γ_s / g/cm^3	2,61	2,42
Al_2O_3	40,00	28,71	S_p (Blaine) / cm^2/g	-	7400
Fe_2O_3	1,40	2,37	PA (Chapelle) $Ca(OH)_2$/g MK	0,78	0,60
TiO_2	1,50	-			
CaO + MgO	0,30	1,03	PA / MPa	20,5	14,9
$Na_2O + K_2O$	0,80	1,72			
LOI	1,00	1,02			
Sum:	100,00	98,81			

Table 3 The influence of metakaolin on the setting time of the Metakaolin composite cement

Sample	Metakaolin (% by mass)	Standard consistency (%)	Setting time (min)	
			Initial	**Final**
CEM I	-	30,0	260	320
CMK 5	5	30,6	240	300
CMK 10	10	31,2	185	240
CMK 15	15	32,8	185	240
CMK 20	20	34,6	185	245
CMK 25	25	36,6	185	235
CMK 30	30	38,4	165	215
CMK 35	35	40,6	165	215
MK 5	5	30,4	220	280
MK 10	10	30,8	220	280
MK 15	15	31,8	200	250
MK 20	20	34,2	210	250
MK 25	25	35,2	210	270
MK 30	30	36,4	190	240
MK 35	35	38,0	180	230

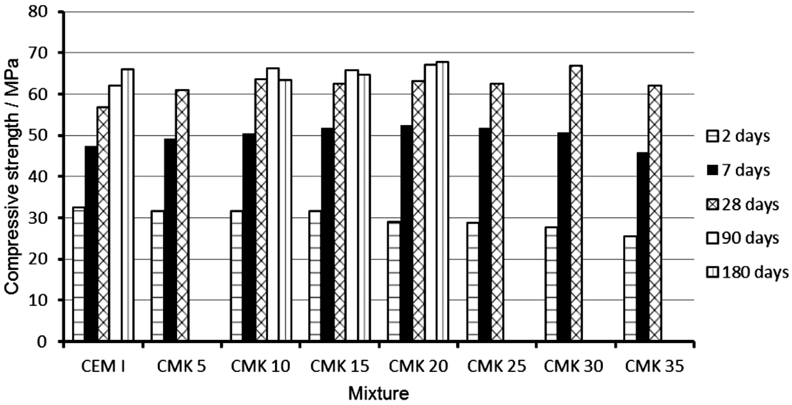

Figure 1 Compressive strengths for various quantities of added commercial metakaolin

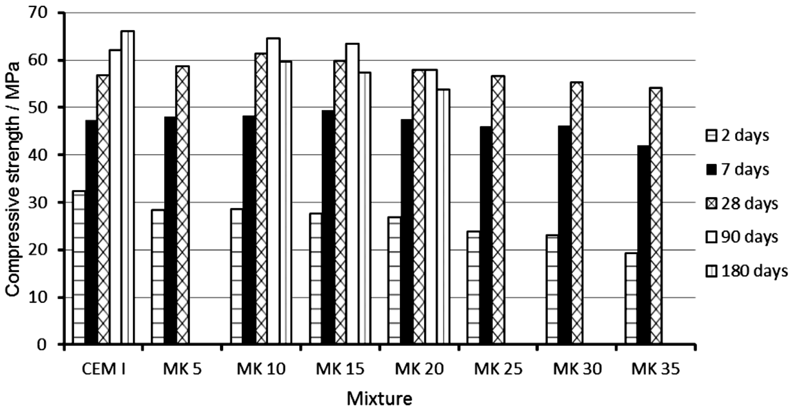

Figure 2 Compressive strengths for various quantities of added metakolin produced by thermal activation

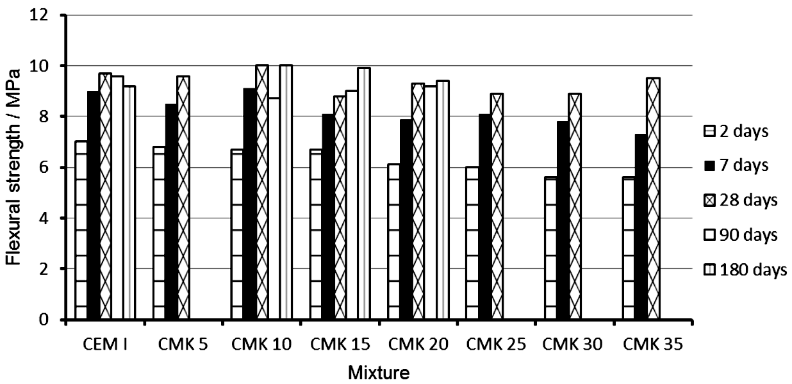

Figure 3 Flexural strengths for various quantities of added commercial metakaolin

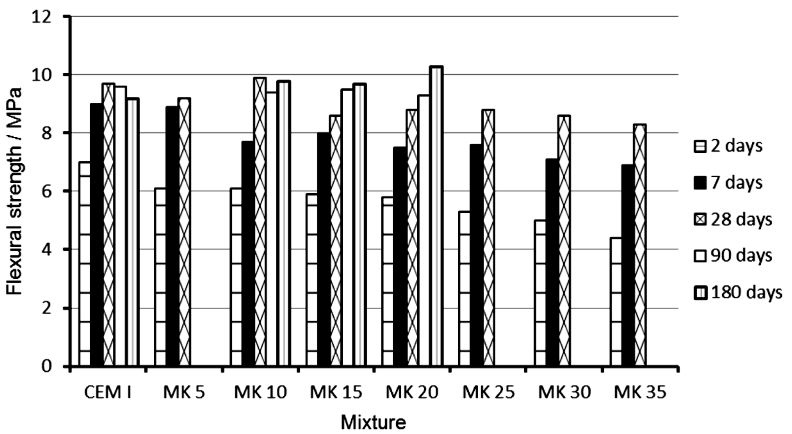

Figure 4 Flexural strengths for various quantities of added metakolin produced by thermal activation

3.2 Mechanical properties

Scientific literature clearly shows that, owing to its pozzolanic properties, metakaolin addition to portland cement has positive influence on the compressive strengths.

The influence of the metakaolin addition on compressive strength of Metakaolin composite cement is shown in Fig. 1 and Fig. 2.

The strength development in Portland cement is mainly dependent on the hydration rate of clinker, while in Metakaolin composite cement is dependent on the combination of portland cement hydration and the pozzolanic activity of metakaolin.

After 2 days of curing all composite cements showed lower compressive strength in comparison with control cement. This might be explained by the fact that pozzolanic reaction still did not show its effect. The compressive strength of cements with MK was lower than those obtained with commercial MK, particular with addition of more than 25 % of MK. After 7 days composite cements with CMK, with exception of cement with 35 %, had higher compressive strength than control cement. Composite cements with MK up to 25 % had higher compressive strength than control cement.

After 28 days all composite cements with CMK showed higher compressive strength than control cement. Addition of MK up to 25 % showed positive effect on strength, but this effect was lower than that obtained with commercial MK.

The main factors that affect the contribution of metakaolin in strength are: the filler effect, the dilution effect and the pozzolanic reaction of metakaolin with Calcium Hydroxide (CH) [9].

The influence of prolonged curing, 90 and 180 days, was investigated on the composite cements with addition of 10, 15 and 20 % of metakaolin, as literature suggests that those quantities give the best results. After 90 days addition of 10 and 20 % of CMK showed increase in strength, as well as cements with 10 and 15 % of MK. After 180 days both metakaolins showed compressive strength decrease.

A decrease of the relative strength between 28 and 180 days can be explained by cessation of the pozzolanic reaction.

The results are consistent with the results obtained by other authors [11, 12] where data shows reduction of early compressive strength with addition of metakaolin. In papers [11, 13] authors have concluded that the optimal amounts of addition of metakaolin are 10 % and 15 %.

The influence of the metakaolin addition on flexural strength of composite cement is shown in Fig. 3 and Fig. 4. Results of flexural strength at 2 days showed slight decreasing tendency with increasing amount of CMK. This trend is more noticeable at samples with addition of thermal activated metakaolin.

After 28 days, the results showed quite equal values of the flexural strength from 8,9 to 10,0 MPa with addition up to 35 % of CMK. Addition up to 35 % of thermal activated metakaolin resulted in only a marginal decrease of the flexural strength from 9,7 to 8,3 MPa.

3.3 Soundness

The consistency of the mix was kept constant for all samples. Le Chatelier soundness tests were performed on the paste to assess the possibility of deleterious expansion due to the hydration of uncombined calcium oxide and/or magnesium oxide. No evidence of significant possible late expansion was found.

The mortar soundness (expansion) of 0,5 mm for CEM I, and in most Metakaolin composite cement of 1,0 mm indicates shrinkage increase. Increase in soundness with addition of metakaolin can be explained by the relative increase in volume of reaction products.

4 Conclusion

The results obtained in this study allow us to draw the following conclusions:

- Metakaolin composite cement requires a larger amount of water to achieve a standard consistency of the control Portland cement,
- Addition of commercial metakaolin and metakaolin manufactured by thermal activation in a quantity 5 – 35 % by mass accelerates initial and final setting time,
- Compressive strength for all ages is higher in cements with addition of commercial metakaolin,
- Compressive strength for both metakaolins after 2 days is lower than that of control cement as pozzolanic reaction still did not show its effect,
- After 180 days both metakaolins show compressive strength decrease, but without bad influence in use of metakaolin in cement and concrete,
- Addition 5 ÷ 10 % of commercial metakaolin and metakaolin manufactured by thermal activation has no negative impact on flexural strength at 28 days. Addition of up to 35 % of CMK and MK slightly decreases flexural strength.
- In most Metakaolin composite cements soundness is constant, 1 mm but higher than that in control cement.

The lower values for compressive strength of the composite cements manufactured from Serbian kaolinite clay were expected as metakaolin MK has lower pozzolanic activity.

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