

## Properties of Portland-Composite Cements with metakaolin: Commercial and manufactured by Thermal Activation of Serbian Kaolin Clay

A. Mitrovic<sup>1</sup> and D. Nikolic<sup>2</sup>

<sup>1</sup>Institute for testing of materials, Management, Belgrade, Serbia

<sup>2</sup>Institute for testing of materials, Department for materials, Belgrade, Serbia

**Abstract.** Portland-composite cements (CEM II) were prepared with addition of 5 to 35% of metakaolin (MK), manufactured by thermal activation/calcination of Serbian kaolin clay, and commercial metakaolin (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). Setting time (initial and final) is accelerated in Portland-composite cements, for both metakaolins used. The acceleration is higher in cement with addition of commercial metakaolin. Lower compressive strength is obtained after 2 days of curing for all Portland-composite cements in comparison with control cement, since pozzolanic reaction still did not show its effect. After 7 days, pozzolanic reaction show its effect, manifested as compressive strength increase of Portland-composite cements with addition of up to 35% of CMK, and 25% in the case of cements with MK. 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. After 90 days increased compressive strength was noticed with addition of 10 - 20% of CMK, and with 10 and 15% of MK, while after 180 days addition of both metakaolins influences compressive strength decrease. The results of the soundness, 0.5 mm for CEM I, and 1.0 mm in most Portland-composite cements indicate soundness increase with addition of metakaolins. Generally, better performance of Portland-composite cements was obtained with addition of commercial metakaolin, which may be attributed to the differences in the pozzolanic activity of the applied metakaolins, 20.5 MPa and 14.9 MPa for CMK and MK, respectively. By our previous findings pozzolanic activity of the thermally activated clay may be increased by subsequent milling of the metakaolin manufactured by thermal activation process.

## 1 INTRODUCTION

In Serbia, in three cement plants, 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 Portland-composite cements and concrete mixtures has become almost unavoidable owing to their beneficial effects on the ultimate compressive strength, permeability and chemical durability, as well as by the economic and ecologic advantage of their use [1]( R.Siddique, 2009).

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, is 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](B.Ilić, 2010, A.Mitrović, 2009) authors presented the results of preparing metakaolin by thermal activation of several kaolinite clays. The process depends on the raw clays properties, as well as process parameters. The produced metakaolins, in comparison with commercial metakaolin, possess approximately the same pozzolanic activity determined either by Chapelle method or by standard [4](SRPS B.C1.018:2001), 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. In this paper we present the first results on performance of the Portland-composite cement with addition of 5 – 35% by mass of metakaolin manufactured by thermal activation of Serbian kaolin clay.

## 2 EXPERIMENTAL

### 2.1. Starting materials

For the preparation of the Portland-composite cements Lafarž BFC PC (CEM I 42,5R), metakaolin (MK) obtained by thermal activation/calcination of “Garaši” kaolin clay and commercial metakaolin (CMK) were used. Chemical composition and physical properties of the starting materials are shown in table 1 and 2.

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

Chemical composition (% by mass)			
SiO <sub>2</sub>	20,36	Insoluble residue in HCl/Na <sub>2</sub> CO <sub>3</sub>	1,11
Al <sub>2</sub> O <sub>3</sub>	5,83	Insoluble residue in HCl/KOH	0,62
Fe <sub>2</sub> O <sub>3</sub>	2,96	CO <sub>2</sub>	1,04
CaO	62,36	CaO, Free	0,43
MgO	1,32	Physical properties	
SO <sub>3</sub>	2,80		
Na <sub>2</sub> O	0,15		
K <sub>2</sub> O	0,79		
MnO	0,127	Sp (Blaine) (cm <sup>2</sup> /g)	4430
LOI	3,00	γ <sub>s</sub> (g/cm <sup>3</sup> )	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 <sub>2</sub>	55.00	63.91	$\gamma_s$ (g/cm <sup>3</sup> )	2.61	2.42
Al <sub>2</sub> O <sub>3</sub>	40.00	28.71	Sp (Blaine) (cm <sup>2</sup> /g)	-	7400
Fe <sub>2</sub> O <sub>3</sub>	1.40	2.37	Pozzolanic activity (gCa(OH) <sub>2</sub> /g MK)	0.78	0.60
TiO <sub>2</sub>	1.50	-			
CaO + MgO	0.30	1.03	Pozzolanic activity (MPa)	20.5	14.9
Na <sub>2</sub> O + K <sub>2</sub> O	0.80	1.72			
LOI	1.00	1.02			
Sum:	100.00	98.81			

## 2.2. Applied experimental methods

The chemical composition of cement is determined by standard methods [5](SRPS EN 196-2), 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](SRPS EN 196-3, SRPS B.C.8.023), compressive strengths according to the standard [8]( SRPS EN 196-1) and soundness according to [6].

Pozzolanic activity is determined according to the standard [4](SRPS B.C1.018:2001).

## 2.3. Preparation of the cement with addition of metakaolin

In order to determine the characteristics of Portland-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]( SRPS EN 196-1) 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 were 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 table 3.

**Table 3.** The influence of metakaolin on the setting time of the Portland-composite cements.

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

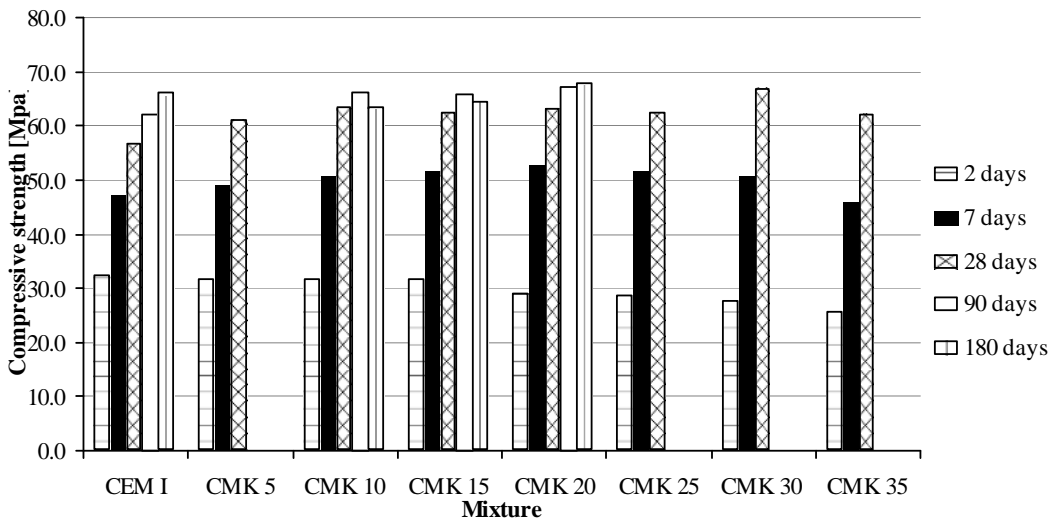
The results indicate that Portland-composite cements requires a larger amount of water to achieve a standard consistency of the control Portland cement (CEM I 42,5R), which is in agreement with results published by other authors [9, 10](E.Badogiannis, 2005, G.Batis, 2005). They concluded that the composite cement demand more water than the relatively pure cement and that this phenomenon is attributed to the high fineness of metakaolin.

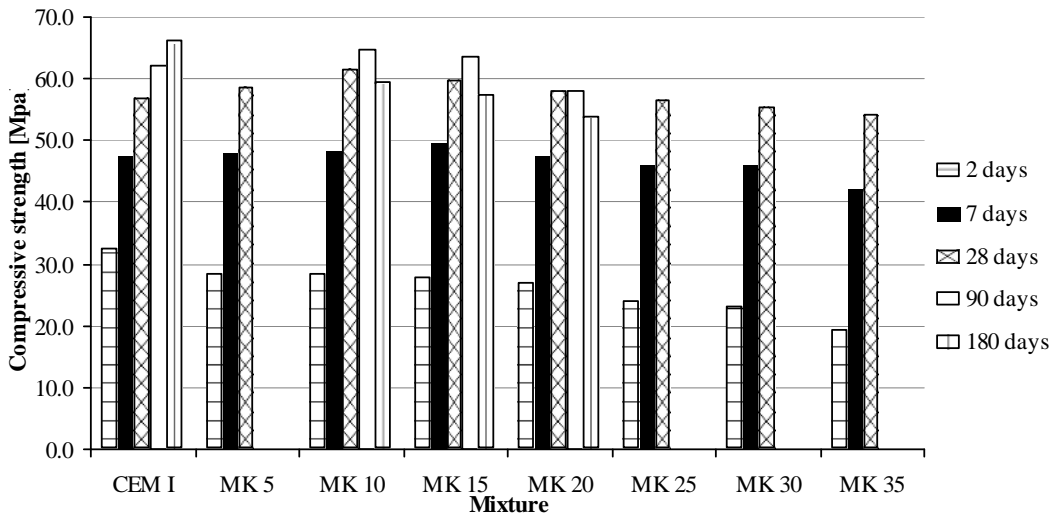
All blended cements showed slow setting time (initial and final) than that of control cement, in other words they accelerate initial and final setting time. The higher acceleration occurs by adding commercial metakaolin. The results are in line with the results of Justice [11](JM.Justice, 2005), which indicate that addition metakaolin accelerates setting time, and that setting time of Portland composite cement depends on the amount of added metakaolin.

### 3.2. Compressive strengts

Scientific literature clearly shows that, owing to its pozzolanic properties, metakaolin addition to portland cement have positive influence on the compressive strengths. In paper [12](M.Arikan, 2009) reported that the application of thermally activated kaolin provides a 15% improvement of the compressive strength of cement.

The influence of the metakaolin addition on compressive strength of Portland-composite cements is shown in fig. 1.





**Fig. 1** Compressive strengths for various quantities of added metakaolin; (a) commercial metakaolin CMK, and (b) metakolin produced by thermal activation MK.

After 2 days of curing all composite cements shows 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 is 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%, has higher compressive strength than control cement. The increase is approximately 10% with addition of 15 - 25% of CMK. Composite cements with MK up to 25% have nearly the same compressive strength as control cement.

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

The influence of prolonged curing, 90 and 180 days, were investigated on the composite cements with addition of 10, 15 and 20% of metakaolin, as literature suggests that those quantities gives the best results. After 90 days addition of 10 - 20% of CMK shows increase in strength, as well as cements with 10 and 15% of MK.

After 180 days the increase was noticed only with addition of 20% of CMK.

Lower values for compressive strength in Portland-Composite cement with MK might be explained through the differences in pozzolanic activity and specific surface of the applied metakaolins. Commercial metakaolin have pozzolanic activity of 20.5 MPa or 0.78 gCa(OH)<sub>2</sub>/gMK (Chapelle method), while metakaolin obtained by thermal activation have significantly lower values, 14.9 MPa or 0,60 gCa(OH)<sub>2</sub>/gMK. Also, the specific surface couldn't be measured by Blaine, indicating higher values than those obtained for MK. We expect that pozzolanic activity of thermally activated

clay could be increased by subsequent grinding of MK, and thus to obtain compressive strength comparable with cement prepared with commercial metakaolin.

The results are consistent with the results obtained by other authors [13,14](J.Bensted, 2002, D.Vu, 2001) where data shows reduction of early compressive strength with addition of metakaolin. In papers [13,15](J.Bensted, 2002, J.Cabrera, 2001) authors have concluded that the optimal amounts of addition metakaolin are 10% and 15%.

Our investigations show that the optimal amount of addition of CMK is 20%, and 5-10% of MK.

### 3. 3. Soundness

The influence of CMK and MK on the soundness is shown in table 4. The mortar soundness (expansion) of 0.5 mm for CEM I, and in most Portland-composite cements 1.0 mm indicate shrinkage increase in composite cement. Increase in soundness with addition of metakaolin can be explained by the relative increase in volume of reaction products.

**Table 4.** The influence of CMK and MK on the soundness

Metakaolin (% by mass)	Soundness, Le Chatelier, mm	
	CMK	MK
-	0.5	0.5
5	1.0	1.0
10	1.0	1.0
15	0.5	1.0
20	1.0	1.0
25	1.0	1.0
30	1.0	0.5
35	1.0	1.0

## 4 CONCLUSION

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

- Portland-composite cements 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 accelerate initial and final setting time,
- Compressive strength after 2 days for both metakaolins is lower than that of control cement as pozzolanic reaction still did not show its effect,
- For 7, 28, and 90 days addition CMK up to 30% increases compressive strength of composite cement,
- Increase in compressive strength for 7, 28, and 90 days was observed for addition, up to 15% of MK,
- After 180 days only cement with 20% of CMK show compressive strength increase,

In most Portland-composite cements soundness is constant, 1 mm but higher than that in control cement.

The lower values for compressive strength of the composite cements prepared with addition of metakaolin produced by thermal activation of Serbian kaolinite clay were expected as metakaolin (MK) have lower pozzolanic activity and specific surface than commercial metakaolin (CMK).

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