KARAKTERISTIKE PORTLAND CEMENTA SA DODATKOM METAKAOLINA DOBIJENOG KALCINACIJOM DOMAĆE KAOLINSKE GLINE

CHARACTERISTICS OF PORTLAND CEMENT WITH ADDITION OF METAKAOLIN OBTAINED BY CALCINATION OF DOMESTIC KAOLIN CLAY

Aleksandra MITROVIĆ
Dragica JEVTIĆ
Ljiljana MILIČIĆ
Biljana ILIĆ

ORIGINALNI NAUČNI RAD
UDK: 666.942.5.017 = 861

1 UVOD

Cement je jedan od najznačajanijih građevinskih materijala, čija godišnja proizvodnja u svetu prelazi 2.7 milijardi tona. Uprkos uspešnosti koju ima, industrija cementa je suočena sa izazovima u pogledu povećanja trajnosti objekata i poboljšanja njihovih performansi, uz istovremeno povećanje održivosti proizvodnje.

Proizvodnja cementa odvija se u nekoliko faza tehnološkog procesa:

- priprema sirovine (usitnjavanje, mlevenje, sušenje, homogenizacija),
- pečenje klinkera,
- hlađenje klinkera,
- mlevenje i mešanje cementa,
- skladištenje i pakovanje cementa.

Sirovina za proizvodnju portland cementa uglavnom se sastoji od krečnjaka, laporca i/ili gline, uz dodatak komponenata za korekciju sastava klinkera (kvarcni pesak, ruda gvožđa, boksit i dr.).

Nakon procesa usitnjavanja, mlevenja, sušenja i homogenizacije mešavine sirovina, dobija se sirovinsko brašno za pečenje klinkera. Da bi se proizveo klinker, sirovinsko brašno se zagreva na 1450°C.

U temperaturnom intervalu od 100°C do 600°C odvijaju se reakcije dehidratacije sirovinskih komponenti, uz isparavanje vlage hemijski vezane u mineralima gline. Između 600°C i 1100°C odvijaju se reakcije dekarbonizacije:

Dr Aleksandra Mitrović, Institut za ispitivanje materijala, Bulevar vojvode Mišića 43, Beograd, aleksandra.mitrovic@institutims.rs
Prof. dr Dragica Jevtić, Građevinski fakultet Univerziteta u Beogradu, dragica@imk.grf.bg.ac.rs

1 INTRODUCTION

Cement is one of the most important building materials which annual worldwide production exceeding 2.7 billion tons. Despite the success it has, the cement industry is facing challenges in terms of increasing durability of structures and improving their performance and sustainable production.

Cement production is carried out in several stages of technological process:

Preparation of raw materials (crushing, grinding, drying, homogenization),

- Burning clinker,
- Cooling clinker,
- Grinding and mixing cement,
- Storage and packing cement.

Raw materials usually used for the production of Portland cement are limestone, marl and/or clay, with the addition of components to correct the composition of clinker (quartz sand, iron ore, bauxite, etc.).

Raw meal for burning clinker is obtained, after the process of crushing, grinding, drying and homogenizing a mixture of raw materials. In order to produce clinker, raw meal is heated to 1450°C.

During the heating clinker, in the temperature range from 100°C to 600°C, dehydration of raw materials and the evaporation of moisture from clay minerals occur. Between 600°C and 1100°C materials proceeds through the decarbonificaton:

Ljiljana Miličić, dipl. hem. Institut za ispitivanje materijala, Beograd, ljiljana.milicic@institutims.rs
Mr Biljana Ilić, Institut za ispitivanje materijala, Beograd, biljana.ilic@institutims.rs

$$MgCO_3 \rightarrow MgO + CO_2 \quad (1)$$

U temperaturnom intervalu od 1100°C do 1300°C dolazi do egzotermnih reakcija, a u intervalu od 1300°C do 1450°C (zona sinterovanja) dolazi do vezivanja slobodnog CaO sa SiO_2, Al_2O_3 i Fe_2O_3, gde se, osim reakcija u čvrstoj fazi, odvijaju i heterogene reakcije:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2)$$

In the temperature range from 1100°C to 1300°C exothermic reactions occurs, while in the range from 1300°C to 1450°C (sintering zone) free CaO is binding with SiO_2, Al_2O_3 and Fe_2O_3, where, in addition to the solid phase reactions, heterogeneous reactions taking place:

$$2CaO + SiO_2 + CaO \rightarrow 3CaO \cdot SiO_2 \quad (3)$$

Kvalitet klinkera zavisi od sadržaja osnovnih minerala, a na proces stvaranja minerala klinkera utiču i minorne komponente (MgO, SiO_3, K_2O, Na_2O i dr.), naročito kod nastajanja nekih polimorfnih oblika glavnih minerala klinkera. Konačni fazni sastav klinkera zavisi od postupka hlađenja, koji započinje u izlaznoj zoni peći i nastavlja se u hladnjaku klinkera, gde dolazi do ravnotežne ili nezavisne kristalizacije rastopa uz nastajanje staklaste faze.

Cement, kao konačni proizvod, je smeša klinkera, gipsa (regulatora vezivanja) i drugih primesa (dodataka) koje pri hidrataciji cementa ispoljavaju hidraulička svojstva. Takva smeša, u zadatom odnosu za svaku klasu cementa, melje se u cementnom mlinu na određenu finoću čestica.

1.1 Uticaj proizvodnje cementa na životnu sredinu

Približno 5% ukupne globalne emisije CO_2 potiče iz proizvodnje cementa. Emisija gasova je posledica sagorevanja goriva i hemijskih reakcija koje se odigravaju u pojedinim fazama procesa, prvenstveno u fazi pečenja klinkera (jedn. 1 i 2). Proizvodnja cementa spada u red industrijskih grana s najvećom specifičnom potrošnjom električne i toplotne energije po jedinici proizvoda.

U toku procesa proizvodnje cementa, oslobađa se oko 0.92 t CO_2 po toni proizvedenog klinkera. Ova emisija uglavnom potiče od dekarbonizacije krečnjaka (0.53 t) i korišćenja ugljeničnih goriva za grejanje (0.39 t). Srednja emisija CO_2 koja potiče od procesa mlevenja je reda veličine 0.1 t CO_2 po toni cementa i pretežno potiče od proizvodnje električne energije.

Na slici 1. prikazan je pojednostavljen proces proizvodnje cementa sa posebnim naglaskom na emisiju CO_2 [10].

Za smanjenje emisije CO_2 koja potiče iz proizvodnje cementa, u svetu su opšte prihvaćena dva pristupa: (1) smanjenje emisije CO_2 u procesu proizvodnje klinkera i (2) smanjenje sadržaja klinkera u cementu.

Zbog značaja koji u svetu ima cementna industrija, mnoge studije se bave procenama za budućnost, usmeravajući se uglavnom na potencijalno smanjenje emisije CO_2 i povećanje energetske efikasnosti prema očekivanim varijacijama u proizvodnji cementa.

Pored zahteva koji se nameću industriji cementa u pogledu zaštite životne sredine, ona kao i svi drugi industrijski sektori, teži povećanju ekonomičnosti koja se može postići:

- uštedom energije,
- korišćenjem jeftinijih sirovina pri proizvodnji klinkera,
- smanjenjem klinkera u cementu.

Clinker quality depends on the content of primary (main) minerals. The process of formation clinker minerals is affected by content of minor components (MgO, SiO_3, K_2O, Na_2O, etc.), especially for appearance of some polymorphic shapes of main clinker minerals. The final phase composition of clinker depends on the cooling process, which begins at the exit zone of the furnace and continue to the clinker cooler, where reaches equilibrium or the independent crystallization of the melt suived, with appearance of glass phase.

Cement, as final product, is a mixture of clinker, gypsum (setting regulator) and other additives, which, during the cement hydration, exhibits hydraulic properties. Such a mixture, in the given relation to each class of cement, grinds in the mill to obtain appropriate fineness.

1.1 Influence of cement production on the environment

Approximately 5% of global CO_2 emissions come from cement production. Gas emission is the result of fuel combustion and chemical reactions that take place in different stages of the process, primarily in the clinker burning stage (eq. 1 and 2). Cement production is one of the leaders among the industrial sectors with highest consumption of electricity and thermal energy per unit of product.

During the process of cement manufacturing, around 0.92 t of CO_2 is released per tonne of clinker produced. This emission mainly comes from decarbonization of limestone (0.53 t), and the use of carbon fuels for heating (0.39 t). Average CO_2 emissions associate with milling processes are 0.1 t of CO_2 per tonne of cement and comes from production of electricity.

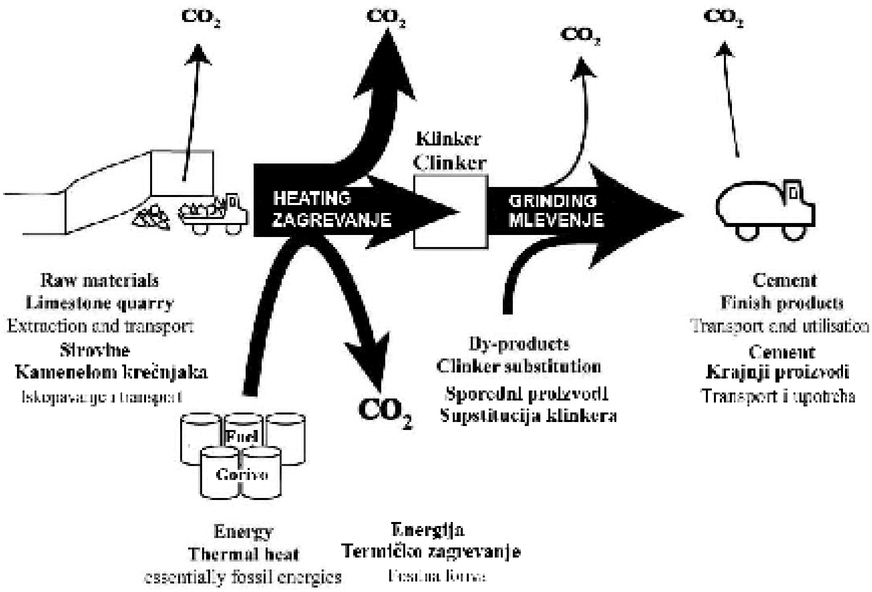
Fig. 1 shows the simplified process of cement production, with special emphases on CO_2 emissions [10].

To reduce CO_2 emissions, originated from the production of cement, in the world are generally accepted two approaches: (1) reducing CO_2 emissions in the production of clinker and (2) reduction content of the clinker in cement.

Owing to importance that worlds cement industry has, many studies dealing with estimates for the future, focusing mainly on the potential reduction in CO_2 emissions and increasing energy efficiency by the expected variations in the production of cement.

In addition to requirements imposed to the cement industry in terms of environmental protection, it tends, like all other industrial sectors, to increase cost-effectiveness, which may be obtained by:

- Saving energy,
- Using cheaper raw materials in the production of clinker,
- Reducing clinker in cement.



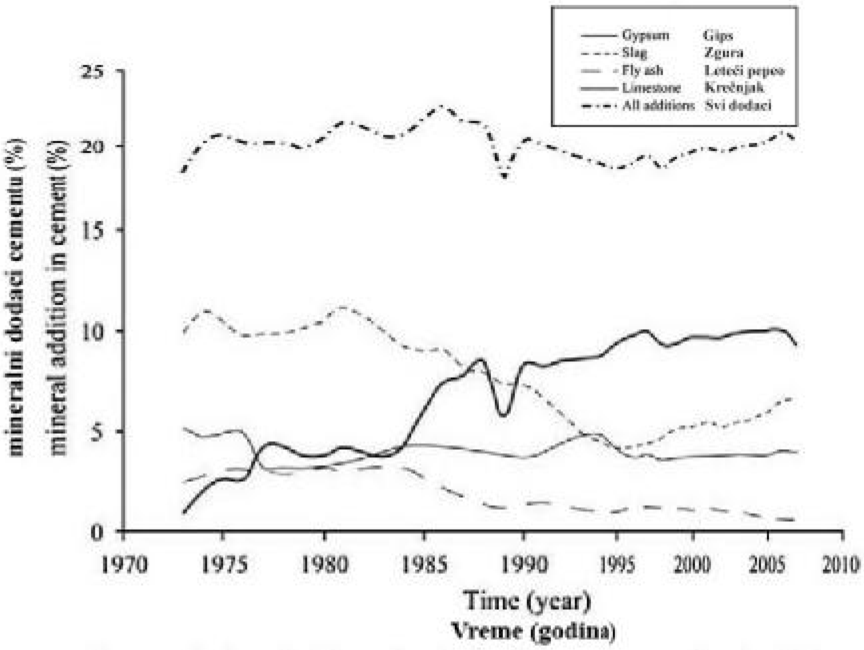
Slika 1. Pojednostavljen proces proizvodnje cementa, sa posebnim naglaskom na emisiju CO_2. Debljina strelica je proporcionalna količini materijala
Figure 1 Simplified process of cement production, with special emphases on CO_2 emissions. The thickness of the arrows is proportional to the amount of material

1.2 Smanjenje udela klinkera u cementu

Poslednjih 20-30 godina, za parcijalnu zamenu klinkera u cementu koriste se industrijski nus-proizvodi leteći pepeo, granulisana zgura visoke peći i silikatna prašina. Pored njih primenjuju se i krečnjaci i prirodni pucolanai. Na slici 2. prikazana je procena zamenjenog klinkera mineralnim dodacima u periodu 1973. do 2007. godine [10].

1.2 Reduction the clinker in cement

In the last 20-30 years, for the partial replacements of clinker are used industrial by-products, such as fly ash, granulated blast furnace slag and silica fume. Beside them, natural pozzolanas and limestone are used. Figure 2. shows estimated replaced clinker with most common used mineral additions in the period 1973. to 2007. [10].



Slika 2. Procena zamene klinkera od 1973. do 2007.
Figure 2 Estimates of replaced clinker from 1973. to 2007.

Korišćenje navedenih, tzv. konvencionalnih dodataka, ima ograničenja i zato se danas u svetu intenzivno istražuju mogućnosti korišćenja novih materijala čijom bi se primenom, pored smanjenja potrošnje energije i emisije gasova, postigla poboljšanja karakteristika cementa, maltera i betona kojima se dodaju, uz sniženje cene finalnog proizvoda. Jedan od mineralnih dodataka nove generacije, koji zadovoljava zahteve održivog razvoja i poboljšava svojstva cementa, maltera i betona, je metakaolin.

Pored toga, sa stanovišta kvaliteta mineralnog dodatka, metakaolin je konzistentan proizvod jer se proizvodi pri kontrolisanim uslovima u pogledu: hemijskog sastava, raspodele veličine čestica, pucolanske reaktivnosti i boje.

U Srbiji se godišnje proizvede približno 2.5 miliona tona portland cementa sa dodacima (granulisana zgura visoke peći, pepeo iz proizvodnje uglja, prirodni pucolani) - CEM II. Udeo dodataka u ovim cementima se kreće od 5-35 % težinskih i prvenstveno zavisi od zahteva tržišta za pojedinim vrstama cementa, a definisan je odgovarajućim standardima [9, 16]. Cement se u Srbiji proizvodi u tri cementare, pri čemu nijedna od cementara ne koristi metakaolin kao dodatak cementima, jer se metakaolin ne proizvodi u našoj zemlji.

1.3 Metakaolin, dopunski cementni materijal nove generacije

Od sredine 1990, visoko reaktivni metakaolin (HRM) se proizvodi u nekoliko fabrika širom sveta: AGS Mineraux - Francuska, ČLUZ a.s - Češka, BASF - USA, Advanced Cement Technologies, LLC – USA, Whitmund - Kanada, itd. HRM se konvencionalno proizvodi termičkom aktivacijom/kalcinacijom prethodno prečišćenih kaolinskih glina sa visokim sadržajem kaolinita, i njegova primena u betonima standardnih čvrstoća je ograničena zbog relativno visoke cene proizvodnje (500$/t). Troškovi proizvodnje metakaolin se mogu znatno smanjiti kada se primeni postupak termičke aktivacije kaolinske gline sa nižim sadržajem kaolinita uz izostanak faze prečišćavanja polazne sirovine, čime je primena takvog dodatka opravdana čak i u cementima i betonima standardnih čvrstoća.

Supstitucijom dela klinkera u cementu ili dela cementa u betonskim mešavinama, postižu se značajne tehničke, ekološke i finansijske prednosti [15]. Tako se, zamenom portland cementa sa 8 - 20% (masenih) metakolina u betonu, postiže niz tehničkih prednosti:

- povećanje čvrstoće pri pritisku i pri savijanju,
- smanjenje propustljivosti (uključujući propustljivost hlorida),
- smanjenje eflorescenciju,
- povećanje otpornosti na dejstvo hemijskih agenasa,
- povećanje trajnosti,
- smanjenje alkalno-silikatne reaktivnosti (ASR),
- povećanje obradivosti betona i
- smanjenje ekspanzije zbog gušćeg pakovanja čestica.

Zbog nabrojanih tehničkih prednosti, materijali na bazi cementa sa dodatkom metakaolina, imaju široku primenu za pripremu: betona visokih performansi, visoke

Using these, so called conventional additives, have limitations and that is why in the world today, intensively explore the possibility of using new materials which application would, in addition to reducing energy consumption and gas emission, improve the characteristics of cement, mortar and concrete, and reduce the price of the final product. One of a new generation of mineral additives, which meets the requirements of sustainable development and improving the properties of cement, mortar and concrete, is metakaolin.

Besides, from the standpoint of quality mineral additive, metakaolin is a consistent product, because it is produced in controlled conditions in terms of: chemical composition, particle size distribution, pozzolanic activity and color.

In Serbia, the annual production of composite Portland cement (CEM II) with blast furnace slag, coal ash and natural pozzolana is approximately 2.5 million tons. Content of additions in these cements range from 5 to 35 % by mass. It primarily depends on market demand for certain types of cement and it is defined by the appropriate standards [9, 16]. Cement is produced in Serbia in three cement plants, where none of metakaolin uses, because it is not produced in our country.

1.3 Metakaolin, supplementary cementitious material of new generation

Since mid-1990, a highly reactive metakaolin (HRM) has produced in several factories around the world: AGS Mineraux - France, ČLUZ a.s - Czech, BASF - USA, Advanced Cement Technologies, LLC – USA, Whitmund - Canada, etc. Conventionally HRM has produced by thermal activation/calcination of previously refined kaolin clay, with a high content of kaolinite, and thus application in the regular concrete is limited, because of the relatively high cost of production (500$/t). Metakaolin production cost can be significantly reduced, by applying thermal activation process on kaolin clay with low kaolinite content, without raw materials refining, allowing use of such additive, even in the regular cement and concrete.

Substitution of clinker in cement or the cement in concrete mixes, leads to significant technical, environmental and financial benefits [15]. Thus, replacement of Portland cement with 8 - 20% by mass metakaolin in concrete, achieved a number of technical advantages:

- Increased compressive and flexural strengths,
- Reduced permeability,
- Reduced potential for efflorescence,
- Increased resistance to chemical attack,
- Increased durability,
- Reduced effects of alkali-silica reactivity (ASR),
- Enhanced workability of concrete, and
- Reduced shrinkage due to particle packing.

Because of the enumerated technical advantages of cement-based materials with addition of metakaolin, these materials are widely used for preparation: high-performance concrete, high strength and lightweight concrete, precast concrete, glass fiber reinforced čvrstoće i lakih betona, prefabrikovanih betona, prednapregnutih betona sa staklenim vlaknima, umetničkih skulptura, i maltera.

Pri primeni metakaolina ekološke prednosti se u najvećoj meri manifestuju kroz:

- smanjenje potrošnje energije u procesu proizvodnje cementa: u procesu kalcinacije kaolinske gline troši se manje energije, jer se proces kalcinacije odvija na nižim temperaturama od onih koje treba primeniti za proizvodnju portland cementa (između 600-800 ^oC za metakaolin, 1450 ^oC za portland cement),
- izostanak emisije CO_2, jer na temperaturama kalcinacije ne dolazi do dekarbonizacije polaznih sirovina,
- smanjenje korišćenja prirodnih resursa, jer građevinski materijali koji sadrže metakaolin poseduju povećanu trajnost [14], kao i konstrukcije u koje su ugrađeni, i time smanjuju zahteve u pogledu održavanja,
- povećane trajnosti materijali, kao što su cement i beton sa dodatkom metakaolina, smanjuju probleme vezane za odlaganje čvrstog otpada.

1.4 Cilj istraživanja

U okviru projekta TR 19206, finansiranog od strane Ministarstva za nauku i tehnološki razvoj, u Institutu IMS razvijena je tehnologija za proizvodnju metakaolina iz domaće kaolinske gline.

Polazna glina Vrbica klasifikuje se u kategoriju sirovina visokog kvaliteta, jer je sadržaj kaolinita oko 80% i gubitak žarenjem 12.30%.

Osnovne karakteristike proizvedenog metakaolina su: zbir oksida $SiO_2+Al_2O_3+Fe_2O_3 \geq$ 94,68%, pucolanska aktivnost određena prema Chapelle metodi 0.76 g $Ca(OH)_2$/g MK, i srednji prečnik čestica d_{50}= 5.236 µm. Karakteristike proizvedenog metakaolina upoređene su sa tipičnim karakteristikama HRM ($SiO_2+Al_2O_3+Fe_2O_3 \geq 90\%$, srednji prečnik čestica d_{50} =5 µm, specifična masa 2.5 g/cm, bela boja) [13], na osnovu kojih se proizvedeni metakaolin može svrstati u kategoriju visoko reaktivnog metakaolina.

U istraživanjima vezanim za primenu dodataka cementu neophodno je ispitati uticaj dodatka na fizičko-mehaničke karakteristike. U ovom radu prikazani su rezultati ispitivanja fizičko-mehaničkih karakteristika portland cementa sa dodatkom 5-20% proizvedenog metakaolina.

2 EKSPERIMENTALNI DEO

2.1 Polazne sirovine

Za pripremu portland cementa sa dodatkom metakaolina korišćeni su Portland cement (CEM I 42,5R), proizvođača Lafarge BFC iz Beočina i metakaolin, dobijen termičkom aktivacijom/kalcinacijom kaolinske gline Vrbica.

Hemijski sastav i fizičke karakteristike polaznih sirovina (cementa i metakaolina) prikazane su u tabelama 1. i 2.

concrete, art sculptures, and plaster.

In applying metakaolin, environmental benefits are largely manifested through:

- Reduction of energy consumption in cement production process: the process of calcination kaolin clay uses less energy, because calcination process takes place at lower temperatures than those that should be applied for the process for production for Portland cement (between 600-800 ^oC for metakaolin, 1450 ^oC for Portland cement),
- Absence of CO_2 emission, because the calcination temperature are low to affect decarbonization of raw materials,
- Reduce the use of natural resources, because building materials with metakaolin has increased durability [14], as well as structures in which they are installed, thereby reducing the requirements in terms of maintenance,
- Increased durability of materials such as cement and concrete with the addition of metakaolin, reduce the problems associated with disposal of solid waste.

1.4 The aim of the research

The result of project TR 19206, funded by the Ministry for Science and Technological Development, is technology for obtaining metakaolin from domestic kaolin clay.

The starting clay Vrbica classifies into the category of high-quality raw materials, with content of kaolinite about 80% and loss of ignition 12.30.

The main characteristics of the produced metakaolin are: the sum of oxides $SiO_2+Al_2O_3+Fe_2O_3 \geq$ 94,68%, pozzolanic activity (Chapelle method) 0.76 g $Ca(OH)_2$/g MK, and medium particle diameter d_{50} = 5.236 µm. Characteristics of the produced metakaolin are compared with typical characteristics of HRM ($SiO_2+Al_2O_3+Fe_2O_3 \geq 90\%$, medium particle diameter d_{50} = 5 µm, specific density 2.5, and white color) [13]. According obtained characteristics, produced metakaolin may classify into the category of high reactive metakaolin.

In researches related to the application of cement additives is necessary to examine the influence of the addition to the physical and mechanical characteristics. This paper presents the results of the physical and mechanical characteristics of Portland cement with addition of 5-20% produced metakaolin.

2 EXPERIMENTAL

2.1. Starting materials

Portland cement (CEM I 42,5R) of the producer Lafarge BFC and metakaolin, obtained by thermal activation/calcination of kaolin clay Vrbica, were used for the preparation of the samples.

Chemical composition and physical properties of the starting materials (cement and metakaolin) are shown in Table 1. and Table 2.

Tabela 1. Hemijski sastav i fizičke karakteristike cementa
Table 1 Chemical composition and physical properties of the cement

Hemijski sastav (%, m/m) ***Chemical composition* (% by mass)**			
SiO_2	20,36	Gubitak žarenjem Loss of ignition	3,00
Al_2O_3	5,83	Nerastvorni ostatak u HCl/Na_2CO_3 Insoluble residue in HCl/Na_2CO_3	1,11
Fe_2O_3	2,96	Nerastvorni ostatak u HCl/KOH Insoluble residue in HCl/KOH	0,62
CaO	62,36	CO_2	1,04
MgO	1,32	Slobodan CaO Free CaO	0,43
SO_3	2,80	Zbir: Sum:	99,70
Na_2O	0,15	**Fizičke karakteristike** ***Physical properties***	
K_2O	0,79	R (%), ostatak na situ 0,09 mm R on sieve 0.09 mm (%)	0,3
MnO	0,127	S_p (cm^2/g)	4430
Cl^-	0,007	γ_s (g/cm^3)	3,10

Tabela 2. Hemijski sastav i fizičke karakteristike metakaolina
Table 2 Chemical composition and physical properties of the metakaolin

Hemijski sastav (%, m/m) ***Chemical composition*** **(% by mass)**		**Fizičke karakteristike** ***Physical properties***	
SiO_2	55,08	R (%) ostatak na situ 0,43 mm R(%) on sieve 0,43 mm	45
Al_2O_3	34,50		
Fe_2O_3	5,10		
CaO	0,67	S_p (Blaine), (m^2/g)	0.88
MgO	1,20	γ_s (g/cm^3)	2.61
Na_2O	0,29	Pucolanska aktivnost (Chapelle), (g $Ca(OH)_2$/ g MK) Pozzolanic activity (Chapelle) (g $Ca(OH)_2$/ g MK)	0,76
K_2O	1,24		
Gubitak žarenjem Loss of ignition	1,73		
Zbir: Sum:	99,45	d_{50} srednji prečnik čestica, (μm) d_{50} mean particle diameter, (μm)	5,236

2.2 Primenjene eksperimentalne metode

Hemijski sastav portland cementa određen je u skladu sa standardnim metodama [19], dok je hemijski sastav metakaolina određen klasičnom silikatnom analizom.

Fizičke karakteristike cemenata, kao što su standardna konzistencija, vreme vezivanja, finoća mliva, zapreminska masa i specifična površina su određene prema standardima [20, 21]. Mehaničke karakteristike cemenata određene su u skladu sa standardnim metodama [18], a linearne deformacije prema standardu [17].

2.2 Applied experimental methods

The chemical composition of Portland cement was determined by standard methods [19], while the chemical composition of metakaolin was determined by silicate analysis.

Physical properties of cement, such as standard consistence, setting time, fineness, specific gravity and specific surface were determined according to the standards [20, 21]. Mechanical characteristics of the cement were determined according to the standards [18] and shrinkage of the mortar – linear deformations according to standard [17].

Pucolanska aktivnost metakaolina određena je Chapelle metodom [12].
Raspodele veličine čestica metakaolina određena je laser granulometrijskom metodom.

Pozzolanic activity was determined by Chapelle method [12].

Particle size distribution of metakaolin was determined by laser granulometry.

2.3 Priprema cementa sa dodatkom metakaolina

U cilju određivanja karakteristika portland-cement sa dodatkom metakaolina pripremljeni su uzorci cementa sa dodatkom 5, 10, 15 i 20 % (m/m) metakaolina.

Za ispitivanje čvrstoća pri savijanju i pri pritisku malterne mešavine su pripremljene prema standardu [18], vodo-cementni faktor (v/c) 0,5; standardni pesak (odnos vezivo : pesak=1 : 3).

2.3 Preparation of the cement with addition of metakaolin

In order to determine the characteristics of Portland cement with the addition of metakaolin, cement samples were prepared with the addition of 5, 10, 15 and 20% by mass metakaolin.

Mortar mixes, for the test of the flexural and compressive strengths, were prepared according to standard [18], with water-cement ratio (w/c) 0,5 and the ratio of binder : sand=1 : 3.

3 REZULTATI I DISKUSIJA

Uticaj dodatka 5, 10, 15 i 20% metakaolina portland cementu i karakteristike portland cementa određeni su kroz ispitivanje vremena vezivanja, čvrstoće pri savijanju, čvrstoće pri pritisku i skupljanja maltera, u svemu prema [17], [18] i [20].

3 RESULTS AND DISSCUSION

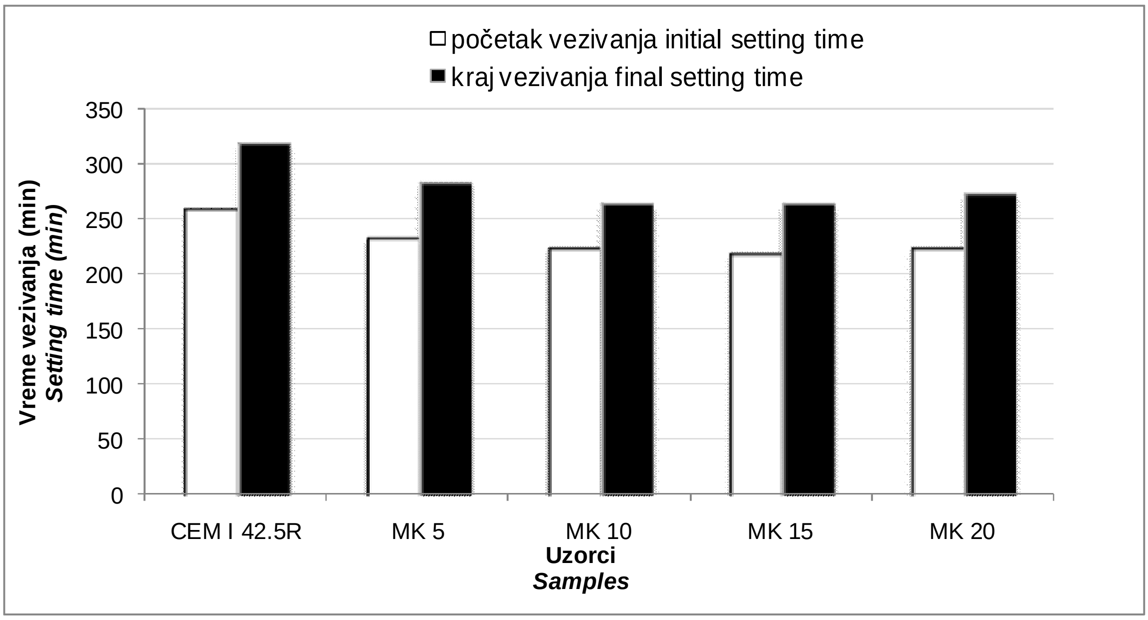
The influence of addition 5, 10, 15 i 20% by mass metakaolin to the Portland cement were determined through examination of setting time, flexural and compressive strengths and shrinkage of the mortars, according [17], [18] and [20].

3.1 Vreme vezivanja

Uticaj dodatka metakaolina na vreme vezivanja kompozita portland cement - metakaolin prikazan je na slici 3.

3.1 Setting time

The influence of the metakaolin on setting time of composites Portland cement - metakaolin is shown in Fig. 3.



Slika 3. Uticaj metakaolina na vreme vezivanja kompozita portland cement – metakaolin
Figure 3 Influence of metakaolin on the setting time of the composites Portland cement-metakaolin

Dobijeni rezultati ukazuju da kompoziti portland cement - metakaolin zahtevaju veću količinu vode za postizanje standardne konzistencije od referentnog portland cementa (CEM I 42,5R), što je u saglasnosti sa istraživanjima drugih autora [1, 2].

The results indicate that composites Portland cement - metakaolin require a larger amount of water to achieve a standard consistence of the control Portland cement (CEM I 42,5R), which is in line with research by other authors [1, 2].

Svi kompoziti portland cement - metakaolin pokazali su skraćeno vreme vezivanja (početak i kraj vezivanja) u poređenju sa referentnim portland cementom, odnosno ubrzavaju početak i kraj vremena vezivanja. Najveće ubrzanje vezivanja se javlja dodatkom 15% metakaolina (MK 15), gde je početak vremena vezivanja kraći oko 40 min u odnosu na referentni uzorak.

Dobijeni rezultati su u skladu sa rezultatima istraživanjima do kojih je došao Justice [11], koja ukazuju da dodatak metakaolina ubrzava vreme vezivanja, kao i da vreme vezivanja kompozita portland cement - metakaolin zavisi od količine dodatog metakaolina.

U istraživanjima [4, 22] razlika između početka i kraja vezivanja za kompozite portland cement – metakaolin je veća i iznosi 60 min i više.

3.2 Čvrstoće pri savijanju

Rezultati uticaja metakaolina na čvrstoće pri savijanju kompozita portland-cement - metakaolin prikazani su na slici 4.

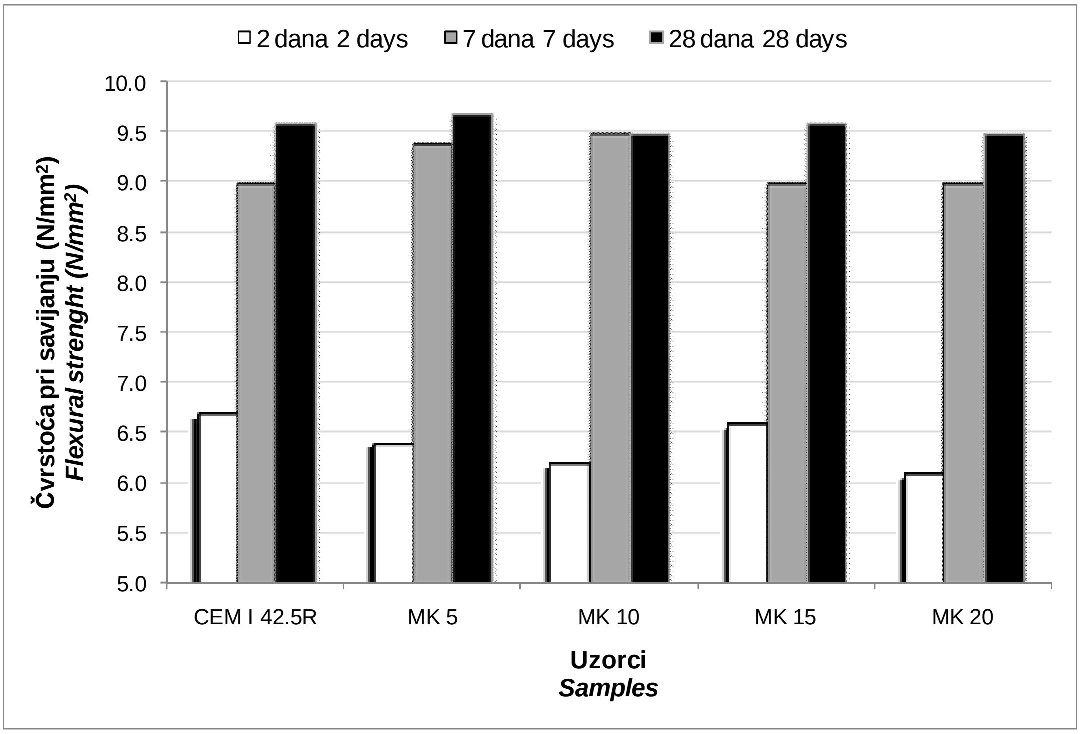
All composites Portland cement - metakaolin were showed shorter setting time (initial and final) in comparation to the control Portland cement, in other words, they accelerate initial and final setting time. The greatest acceleration occurs by adding 15% by mass metakaolin (MK 15), where the initial setting time is less than 40 minutes compared to the control sample.

The results are in line with the results of Justice [11], which indicate that addition metakaolin accelerates setting time, and that setting time of Portland composite cement depends on the amount of added metakaolin.

In researches [4, 22] difference between initial and final setting time of Portland composite cements is higher, about 60 min or more.

3.2 Flexural strengths

The influence of added metakaolin on flexural strengths of composite Portland cement - metakaolin is shown in Fig. 4.



Slika 4. Uticaj metakaolina na čvrstoće pri savijanju kompozita portland-cement – metakaolin
Figure 4 Influence of the metakaolin on the flexural strengths of the Portland composite cements

Dodatak metakaolina neznatno utiče na smanjenje čvrstoće pri savijanju kompozita portland-cement - metakaolin tokom prvih dana odležavanja (2 dana). Nakon 7 dana odležavanja kompoziti portland-cement sa dodatkom 5 % i 10 % metakaolina pokazuju više vrednosti od referentnog uzorka, dok su rezultati sa dodatkom 15 % i 20 % metakaolina identični. Nakon 28 dana, rezultati čvrstoća pri savijanju su ujednačeni, što je u saglasnosti sa rezultatima istraživanja Courard i dr [7].

Procenat dodatka metakaolina se nije pokazao kao značajan parametar za pravljenje razlike u rezultatima.

The addition of metakaolin slightly decreases flexural strengths of Portland cements composite after 2 days of curing. After 7 days, composites Portland cement with the addition of 5 and 10 % by mass metakaolin, have higher values than control sample, while the results with the addition of 15 and 20 % by mass metakaolin are identical. After 28 days, results for flexural strengths are balanced, which is in accordance with the results of Courard at all [7].

Percent of addition metakaolin did not show as a relevant parameter for making differences in the obtained results.

3.3 Čvrstoća pri pritisku

Naučna literatura jasno pokazuje da, zahvaljujući svojim pucolanskim svojstvima, metakaolin kao dodatak portland-cementu pozitivno utiče na njegove mehaničke karakteristike.

Rezultati uticaja metakaolina na čvrstoće pri pritisku kompozita portland-cement - metakaolin prikazani su na slici 5.

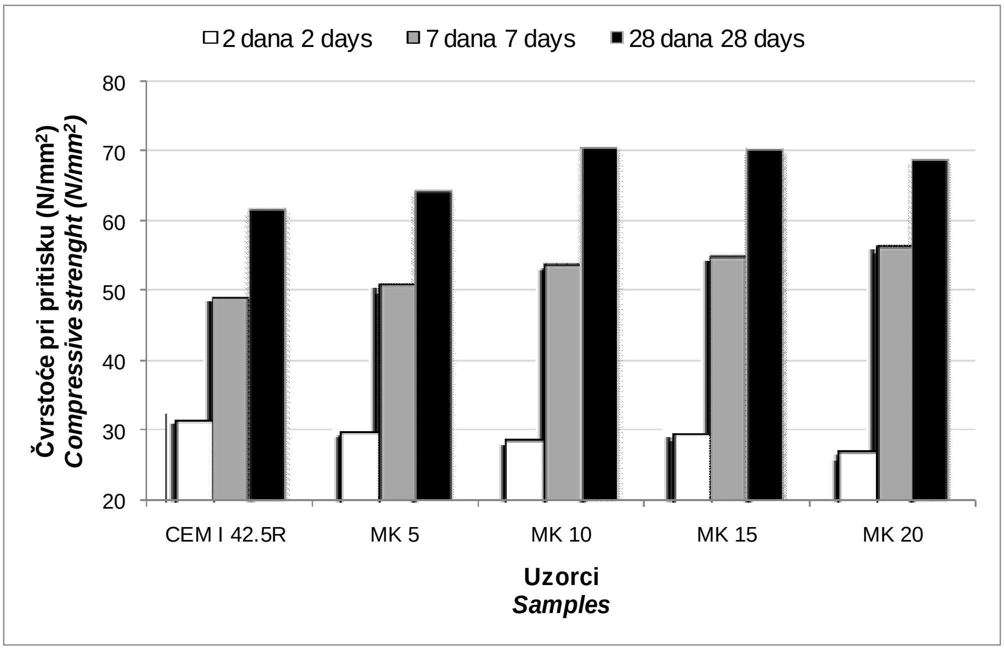
Rezultati ukazuju da dodatak metakaolina ima negativan efekat na čvrstoće pri pritisku nakon 2 dana. Ovo se objašnjava činjenicom da pucolanska reakcija još uvek nije pokazala svoj efekat. Najmanji uticaj na smanjenje čvrstoća pri pritisku nakon 2 dana ima dodatak metakaolina od 5 %, dok se dodatak 20 % metakaolina pokazao kao najnepovoljniji.

3.3 Compressive strengths

Scientific literature clearly shows that, owing to its pozzolanic properties, metakaolin addition to Portland-cement has positive influence on the mechanical characteristics.

The influence of the metakaolin addition on compressive strengths of Portland composite cements is shown in Fig. 5.

After 2 days of curing, all Portland composite cements show lower compressive strengths in comparation to the control cement. This might be explained by the fact that pozzolanic reaction still did not show its effect. After 2 days, the lower influence on compressive strength is observed with addition of 5%, while addition of 20% metakaolin is shown unfavorable.



Slika 5. Uticaj metakaolina na čvrstoće pri pritisku kompozita portland-cement – metakaolin
Figure 5 Influence of the metakaolin on the compressive strengths of the Portland

Nakon 7 dana, svi kompoziti portland-cement - metakaolin pokazuju veće čvrstoće pri pritisku od referentnog uzorka. Sa porastom dodatka metakaolina, povećava se čvrstoća pri pritisku, pa dodatak od 20 % metakaolina povećava čvrstoće za 15 % u odnosu na referentni uzorak (Slika 6).

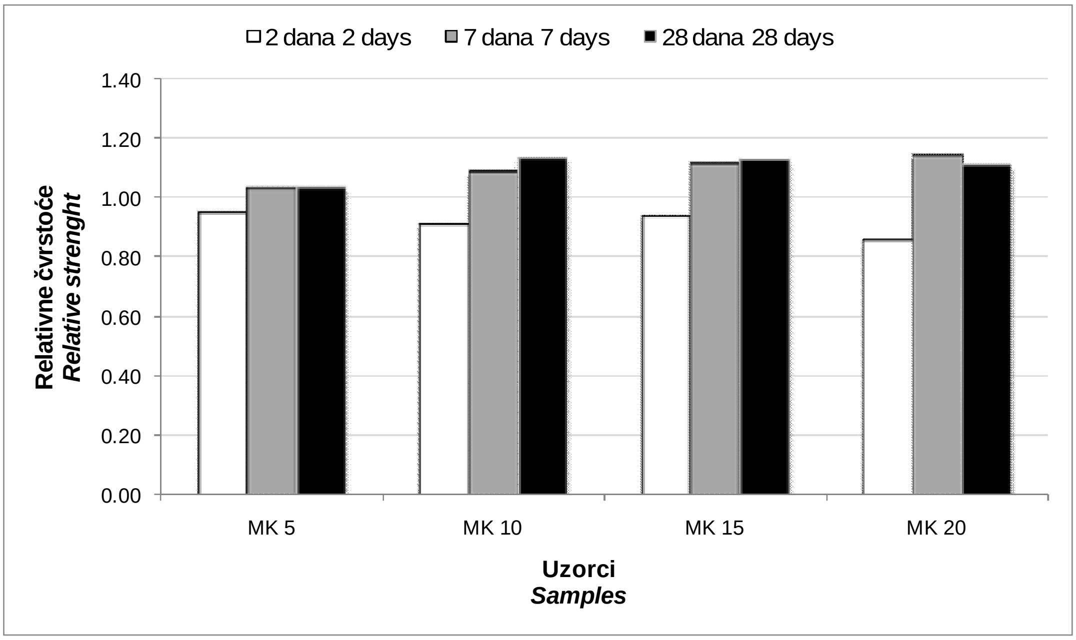
Svi kompoziti portland-cement - metakaolin pokazali su veće čvrstoće pri pritisku nakon 28 dana u odnosu na referentni uzorak. Najbolje rezultate čvrstoća pri pritisku pokazali su kompoziti portland-cementa sa 10 % i 15 % dodatka metakaolina koji povećavaju čvrstoće pri pritisku do 15 %. Već pri dodatku 20 % metakaolina, čvrstoće pri pritisku opadaju.

Dobijeni rezultati su u saglasnosti sa rezultatima drugih autora [3, 22] i podacima da dodavanje metakaolina cementu smanjuje rane čvrstoće pri pritisku, da nakon 7 dana svi uzorci pokazuju veće čvrstoće pri pritisku od referentnog uzorka (bez dodatka metakaolina), kao i da se trend rasta nastavlja i nakon 28 dana. Isti autori [3, 5] su zaključili da je optimalna količina 10 %, odnosno 15 % metakaolina.

After 7 days, all composites Portland cement - metakaolin have higher compressive strengths than control cement. The increase of addition metakaolin, increases compressive strength, so the addition of 20 % metakaolin increase compressive strength for 15 % compared to the control sample (Fig. 6).

After 28 days, all composites Portland cement - metakaolin showed higher compressive strengths than control sample. Best results of compressive strengths are showed composites with addition of 10 and 15 % by mass metakaolin, where compressive strengths increases up to 15 %. The addition of 20 % leads to compressive strengths decrease.

The results are consistent with the results of other authors [3, 22] and data, which show reduction of early compressive strengths with addition metakaolin. After 7 days all samples showed higher strength than control sample, as well as the trend of increase continues after 28 days. The same authors [3, 5] have concluded that the optimal content of metakaolin are 10% and 15%.



Slika 6. Relativne čvrstoće (u odnosu na CEM I 42,5 R) kompozita portland-cement - metakaolin u zavisnosti od količine dodatog metakaolina

Figure 6 Relative strengths of Portland composite cement (in regard to CEM I 42,5 R) dependence on added metakaolin

3.4 Skupljanje maltera

Skupljanje predstavlja deformacije koje se ispoljavaju u vidu smanjenja dimenzija u toku vremena, približno proporcionalno u svim pravcima usled zapreminskih razlika između reaktanata i proizvoda reakcije hidratacije cementa, usled isparavanja vode tokom perioda vezivanja cementa ili skupljanja nakon završetka procesa vezivanje cementa.

Rezultati skupljanja usled sušenja u zavisnosti od vremena odležavanja uzoraka prikazani su na slici 7.

Rezultati uticaja dodatka metakaolina na skupljanje maltera ukazuju da se skupljanje smanjuje sa povećanjem udela metakaolina do maksimalnih 10 % u odnosu na referentni uzorak (CEM I 42,5R), dok dalje povećanje udela metakaolina izaziva povećanje skupljanja.

Primetno je da u ranim danima odležavanja, svi kompoziti portland-cement - metakaolin pokazuju manje skupljanje u odnosu na referentni uzorak.

Ovi rezultati su u saglasnosti sa istraživanjima do kojih su došli Caldarone i dr. [6], a koji su smanjuje skupljanja sa dodatkom 10 % metakaolina, objasnili činjenicom da metakaolin utroši mnogo više slobodne vode iz sistema, ostavljajući manje vode koja bi isparavala tokom skupljanja.

Povećanje skupljanja sa porastom dodataka metakaolina (15 % i 20 % metakaolina) može se objasniti relativnim povećanjem zapremine reakcionih proizvoda, što je u skladu sa rezultatima [23].

Svi kompoziti portland-cement - metakaolin pokazuje veću brzinu skupljanja tokom prve nedelje, nakon čega dolazi do smanjenja brzine skupljanja, što je u saglasnosti sa rezultatima istraživanja Ding i Li [8].

3.4 Shrinkage of the mortars

Shrinkage represents deformations that are manifested in the form of reduced dimensions in the course of time, roughly proportional in all directions due to the volume difference between reactant and products of cement hydration reaction, by evaporation of water during the period of cement setting or shrinkage after the finishes of cement binding.

Shrinkage, as result of drying, vs. curing time is shown in Fig. 7.

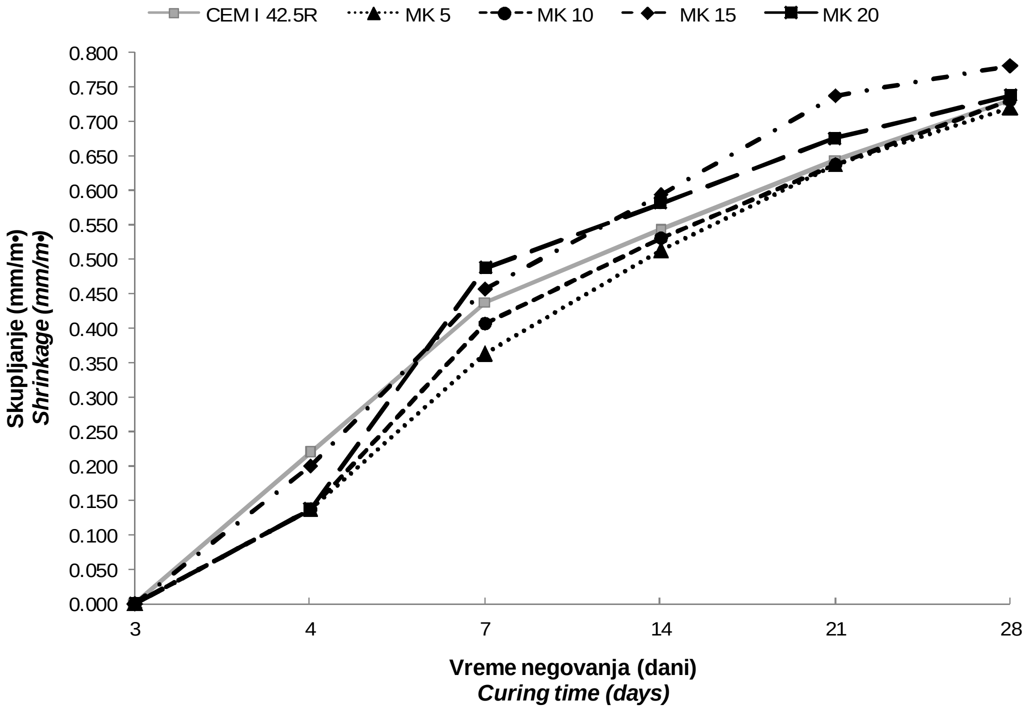
The results of the mortar shrinkage indicate that shrinkage decreases with increasing metakaolin share up to maximum of 10 %, compared to the control sample (CEM I 42,5R), while further increase of metakaolin addition, causes increased shrinkage.

It is notable that in early days of curing, all composites Portland cement –metakaolin show less shrinkage compared to the control sample.

These results are consistent with studies of Caldarone and others [6], in which decrease in shrinkage with addition of 10 % metakaolin, is explained by fact that metakaolin consumes more free water from system, living less water to evaporate during shrinkage.

Increase in shrinkage with increase metakaolin addition (15 % and 20 %) can be explained by the relative increase in volume of reaction products, which is in line with the results [23].

All composites Portland cement -metakaolin show larger shrinkage rate during the first week, after which there is a reduction in shrinkage rate, which is in accordance with the results of research of Ding and Li [8].



Slika 7. Skupljanje kompozita portland-cement - metakaolin u zavisnosti od vremena negovanja i količine dodatog metakaolina

Figure 7. Shrinkage of composite Portland cement vs. Curing time and added metakaolin

4 ZAKLJUČAK

Kompoziti portland-cement - metakaolin zahtevaju veću količinu vode od referentnog portland-cementa za postizanje standardne konzistencije.

Dodatak metakaolina skraćuje vreme vezivanja kompozita portland-cement - metakaolin, neznatno utiče na čvrstoće pri savijanju, povećava čvrstoće pri pritisku (do 15%) i smanjuje skupljanje kompozita portland-cement - metakaolin (sadržaj metakaolina do maksimalnih 10 %).

Optimalna količina metakaolina u kompozitu portland-cement - metakaolin je između 10 i 15 %.

4 CONCLUSION

Composites Portland cement - metakaolin require larger amounts of water from the control Portland cement to achieve standard consistence.

The addition of metakaolin reduces the setting time, it has a slight influence on flexural strength, increases compressive strength (up to 15%) and reduce shrinkage of the composite Portland cement - metakaolin (content of metakaolin up to a maximum of 10%).

Optimal content of metakaolin in the composite Portland cement – metakaolin is between 10 and 15%.

Zahvalnost

Autori se zahvaljuju Ministarstvu za nauku i tehnološki razvoj Srbije na finansijskoj podršci projekta TR 19206.

Acknowledgements

The authors wish to thanks Serbian Ministry for Science and Technological Development for financial support of research project TR 19206.

5 LITERATURA
REFERENCES

[1] Badogiannis E, Kakali G, Dimopoulou G, Chaniotakis E, Tsivilis S. Metakaolin as a main cement constituent: exploitation of poor Greek kaolins. Cem. Concr. Compos. 2005;27(2):197–203

[2] Batis G, Pantazopoulou P, Tsivilis S, Badogiannis E. The effect of metakaolin on the corrosion behavior of cement mortars. Cem. Concr. Compos. 2005;27(1):125–130.

[3] Bensted J, Barnes P. Structure and Performance of Cements. 2nd ed. New York: Spon Press; 2002.

[4] Brooks JJ, Johari MAM, Mazloom M. Effect of admixtures on the setting times of high-strength concrete. Cem. Concr.Compos. 2000;22(1):293-301.

[5] Cabrera J, Rojas MF. Mechanism of hydration of the metakaolin-lime-water system. Cem. Concr. Res. 2001;31(2):177–182.

[6] Caldarone MA, Gruber KA, Burg RG. High reactivity matakaolin: new generation mineral admixture. Concrete Int. 1994; 37-40

[7] Courard L, Darimont A, Schouterden M, Ferauche F, Willem X, Degeimbre R. Durability of mortars modified with metakaolin. Cem. Concr. Res. 2003;33(9):1473–1479.

[8] Ding JT, Li ZJ. Effects of metakaolin and silica fume on properties of concrete. ACI Materials Journal. 2002;99(4):393-398.

[9] EN 197-1:2000, Cement - Part 1: Composition, specifications and conformity criteria for common cements.

[10] Habert G, Billard C., Rossi P., Chen C., Roussel N., Cement technology improvement compared to factor 4 objectives, Cem. Concr. Res. 2010;40 820-826.

[11] Justice JM. Evaluation of metakaolins for use as supplementary cementitious materials. A Thesis Presented to The Academic Faculty: Georgia Institute of Technology;2005.

[12] Largent R. Estimation de l'activite pouzzolanique. Bull. Liaison Lab. Pont Chausees. 1978;93:61.

[13] Mindess S, Young FJ, Darwin D. Concrete. 2nd ed. Upper Saddle River: Prentice Hall: 2003

[14] Mitrović A, Đuričić R, Ilić B, Živanović B, Metakaolin: nova generacija dopunskih cementnih materijala, Materijali i konstrukcije 48, 2005, 48-54.

[15] Mitrović A, Miličić Lj, Ilić B, Benefits of use metakaolin in cement-based systems, Internacionalni Naučno-Stručni skup Građevinarstvo – Nauka i praksa, Žabljak, 15-19. februar 2010, 753-757.

[16] SRPS B.C1.011:2001, Cement. Portland-cement, portland-kompozitni cement, metalurški cement, pucolanski cement, kompozitni cement. Definicije, klasifikacija i tehnički uslovi.

[17] SRPS B.C8.029:1979, Linearne deformacije - Skupljanje maltera usled sušenja.

[18] SRPS EN 196-1:2008, Metode ispitivanja cementa-Ispitivanje čvrstoće.

[19] SRPS EN 196-2:2008, Metode ispitivanja cementa-Hemijske analize cementa.

[20] SRPS EN 196-3:2007, Metode ispitivanja cementa-Određivanje vremena vezivanja i stalnosti zapremine.

[21] SRPS EN 196-6:1995, Metode ispitivanja cementa-Određivanje finoće mliva.

[22] Vu DD, Stroeven P, Bui VB. Strength and durability aspects of calcined kaolin-blended Portland cement mortar and concrete. Cem. Concr. Compos. 2001;23(6):471-478.

[23] Wild S, Khatib JM, Roose LJ. Chemical and autogenous shrinkage of Portland cement-metakaolin pastes. Adv. Cem. Res. 1998;10(3):109-119.

REZIME

KARAKTERISTIKE PORTLAND CEMENTA SA DODATKOM METAKAOLINA DOBIJENOG KALCINACIJOM DOMAĆE KAOLINSKE GLINE

Aleksandra MITROVIĆ
Dragica JEVTIĆ
Ljiljana MILIČIĆ
Biljana ILIĆ

U Institutu za ispitivanje materijala IMS-Beograd razvijena je tehnologija za dobijanje pucolanskog dodatka - metakaolina iz domaće kaolinske gline Vrbica. Verifikacija pucolanskog ponašanja proizvedenog metakaolina izvršena je određivanjem karakteristika portland cementa sa dodatkom 5 - 20 % metakaolina i upoređenjem sa karakteristikama portland cementa. Upoređenjem karakteristika portland cementa (CEM I) i cementa sa dodatkom metakaolina (CEM II) utvrđeno je da se dodatkom metakaolina skraćuje vreme vezivanja (početak i kraj) i postižu niže vrednosti čvrstoća pri pritisku nakon 2 dana. Nezavisno od udela metakaolina, čvrstoća pri pritisku nakon 7 i 28 dana je veća od čvrstoća portland cementa. Utvrđeno je da se pri dodatku 10 i 15 % metakaolina cementu, čvrstoća pri pritisku povećava približno 15 %.

Ključne reči: kaolinska glina, metakaolin, cement, mehaničke karakteristike.

SUMMARY

CHARACTERISTICS OF PORTLAND CEMENT WITH ADDITION OF METAKAOLIN OBTAINED BY CALCINATION OF DOMESTIC KAOLIN CLAY

Aleksandra MITROVIĆ
Dragica JEVTIĆ
Ljiljana MILIČIĆ
Biljana ILIĆ

The technology for obtaining pozzolanic additive – metakaolin, from domestic kaolin clay Vrbica, is developed in the Institute for testing of materials IMS-Belgrade. Pozzolanic behavior of the produced metakaolin is verified by determining the characteristics of Portland cement made with addition of 5 to 20 % by mass metakaolin. The characteristics of Portland cement made with addition of metakaolin (CEM II) were compared with Portland cement (CEM I), which was used as a control sample. The composite cements have lower setting time (initial and final) as well as compressive strengths after 2 days. Compressive strengths after 7 and 28 days are greater than compressive strengths obtained for the control cement, independently on the metakaolin content. The addition of 10 and 15 % by mass metakaolin increases compressive strengths for approximately 15 %.

Key words: kaolin clay, metakaolin, cement, mechanical characteristics.