PROCES HIDRATACIJE I ČVRSTOĆA PRI PRITISKU CEMENTNIH PASTA KOJE SADRŽE PRIRODNI ZEOLIT

HYDRATION PROCESS AND COMPRESSIVE STRENGTH OF CEMENT PASTES CONTAINING NATURAL ZEOLITE

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ORIGINALNI NAUČNI RAD
ORIGINAL SCIENTIFIC PAPER
UDK: 666.942:549.67
doi:10.5937/grmk1602029R

1 UVOD

Beton je jedan od najznačajnijih građevinskih materijala, koji bolje nego bilo koji drugi materijal može da prilagodi svoja svojstva unapred definisanim zahtevima, ukoliko su oni definisani kao realan skup performansi. Ali upravo zbog njegove atraktivnosti često se zanemaruje činjenica da beton ima enorman uticaj na životnu sredinu. Prvo, ogromna količina prirodnih resursa je potrebna za proizvodnju milijardi tona betona godišnje. Drugo, cement predstavlja komponentu betona koja se u svetu najviše proizvodi i koristi (1.6 milijardi tona godišnje) [1]. Zatim, cementna industrija ima vodeću ulogu u globalnom zagrevanju, i odgovorna je za 7% ukupne emisije CO₂ [1]. Kako bi se smanjila potrošnja električne

1 INTRODUCTION

Concrete is up to now the most significant engineered building material whose properties could be tailored to satisfy almost any reasonable set of performances, more than any other building material. But this attractiveness very often entails the neglect of the fact that it has an enormous impact on the environment. First, there are huge amounts of natural resources needed to produce billions of tones of concrete each year. Then, cement as one of the concrete components is worldwide the most produced and used material (1.6 billion tons per annum) [1]. Therefore, the cement industry has a leading role in global warming, with responsibility of 7% of the total CO₂

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energije i emisija CO₂, uvodi se delimična zamena portland cementa (PC) dopunskim cementnim materijalima (u daljem tekstu DCM). Njihova upotreba ima ekonomsku, ekološku i tehničku prednost. DCM obuhvataju širok spektar prirodnih pucolana i nusprodukata iz industrije. Prirodni zeoliti pripadaju grupi prirodnih pucolana, kao i grupi DCM.

Prirodni zeoliti (PZ) jesu mikroporozni, kristalni, hidratizirani aluminosilikatni minerali sa otvorenom, trodimenzionalnom kristalnom rešetkom koja se sastoji od tetraedara silicijum-oksida [SiO₄]⁴⁻ i aluminijum-oksida [AlO₄]⁵⁻ [2, 3]. Kristale karakteriše „sačasta“ struktura s malim porama i kanalima, koja obezbeđuje veliku unutrašnju i spoljašnju specifičnu površinu [4, 5]. Upravo ta velika specifična površina jeste osnova za veliku reaktivnost PZ [5].

Kada se voda doda u suhu mešavinu cementa i DCM, počinje hidratacija cementa i formiranje različitih produkata hidratacije kao što su C-S-H i C-A-H gelovi, AFm, Aft faze, kalcijum-hidroksid (CH), i tako dalje. Pucolanska reakcija DCM predstavlja kompleksan proces koji se odvija u prisustvu kalcijum-hidroksida (Ca(OH)₂) ili Ca²⁺ jona i vode. Razlaganje DCM počinje od površine njihovih zrna pod uticajem hidroksilnih jona (OH⁻). Pokretačku snagu čini razlika u Gibbs-ovoj energiji između reaktanata i produkata hidratacije. Otpuštanje ili razlaganje prvenstveno silike iz DCM u nekom trenutku dovodi do zasićenja pornog rastvora. Tada započinje proces heterogene nukleacije, koji je praćen rastom C-S-H produkata na površini zrna DCM-a. Formiranje C-S-H sloja, koji obavlja površinu zrna utiče na dalju brzinu reakcije. Naime, rast i povećanje gustine sloja koji čine produkti hidratacije može da spreči difuziju hidroksilnih jona ka neizreagovanoj fazi i dovede do smanjenja brzine reakcije. Produkti hidratacije veziva koje se sastoji od običnog portland cementa i DCM, razlikuju se od produkata hidratacije PC-a. Produkte hidratacije mešavine PC-a i DCM po pravilu čine C-(A)-S-H, AFm faze i etringit. U slučaju DCM bogatih MgO, mogu da se jave i hidratirane faze na bazi hidrotalcita. C-S-H faza značajno je drugačija od one nastale u pastama/malterima/betonima na bazi PC-a. Odnos Ca/Si manji je usled smanjenja količine portlandita, kao i zbog veće raspoloživosti Si i Al jonima koji potiču iz rastvorenih DCM. C-S-H faza s nižim odnosom Ca/Si obično ima strukturu nalik tobermoritovom gelu [6]. Prosečna dužina lanca se povećava sa smanjenjem odnosa Ca/Si. U tom slučaju, aluminijum može ući u strukturu tobermorita i formirati C-(A)-S-H. Upravo formiranje C-(A)-S-H faze dovodi do povećanog vezivanja alkalija, zbog negativnog naelektrisanja strukture i u skladu s navedenim, smanjuje se pH vrednost pornog rastvora. Značajan pad pH vrednosti pornog rastvora ispod 10 može u velikoj meri da utiče na smanjenje brzine pucolanske reakcije što dalje može da dovede do destabilizacije AFm i Aft produkata reakcije. Takođe, sa smanjenjem odnosa Ca/Si menja se morfologija C-S-H faze, od vlaknastih čestica do listaste forme [7].

Kada se upotrebljava prirodni zeolit kao DCM, treba očekivati pucolansku reakciju koja se razlikuje od ostalih iz sledećih razloga:

- struktura zeolita apsorbuje značajnu količinu vode;
- difuzija negativno naelektrisanih hidroksilnih jona kroz pore zeolita otežana je zbog negativno naelektri-

emission [1]. In order to reduce energy consumption and CO₂ emission, partial replacement of Portland cement (PC) with supplementary cementitious materials (which will be referred to as SCMs) has been used. The advantages of their use are economic, environmental and technical. SCMs comprise a wide variety of natural pozzolans and by-products of industries. Natural zeolites belong to the group of natural pozzolans, and the group of SCMs.

Natural zeolites (NZs) are microporous, crystalline, hydrated aluminosilicate minerals with an open, three-dimensional framework of silicon-oxygen [SiO₄]⁴⁻ and aluminium-oxygen [AlO₄]⁵⁻ tetrahedra [2,3]. Crystals are characterized by a honeycomb-like structure with small pores and channels that provide large internal and external surface areas [4,5]. The high specific surface area of NZ represents the base of its high reactivity [5].

When water is added to dry mixture of cement and SCM it initiates cement hydration and formation of different hydrated products like C-S-H and C-A-H gels, AFm, Aft phases and calcium hydroxide (CH), etc. The pozzolanic reactions of SCMs represent a complex process which starts in the presence of calcium hydroxide (Ca(OH)₂) or Ca²⁺ ion and water. The decomposition of SCMs begins on the surface of their grains under the attack of hydroxyl ion (OH⁻). The driving force is the difference in Gibbs energy between the reactants and hydrated products. The release or dissolution primarily of silica from the SCMs will lead to saturation of pore solution at some point. Consequently, heterogeneous nucleation starts and it is followed by the growth of C-S-H products at the SCMs grain surface. The formation of the C-S-H layer, which encircles the surface of the SCM grain, will influence further the rate of reaction. Namely, the growth and densification of the layer made of hydrated products would hamper the diffusion of hydroxyl ions towards the unreacted phases and cause the decrease of the rate of reaction. Hydration products of binder that contain ordinary Portland cement (PC) and a SCM differ in comparison with hydration products of PC. The hydration products of the binders consisting of PC and SCM generally contain C-(A)-S-H, AFm-type phases and ettringite. Those SCMs abounding in MgO could have hydrotalcite-type hydrated phases. The C-S-H phase is significantly different than in pastes/mortar/cement based on PC. The ratio of Ca/Si is lower due to the decrease of the amount of portlandite and due to the larger availability of Si and Al ions originating from dissolving of SCMs. The C-S-H phase with lower Ca/Si ratio usually has tobermorite-like structure [6]. The average chain length increases when the Ca/Si ratio decreases. In such case the uptake of aluminium is increased and C-(A)-S-H is formed. The formation of C-(A)-S-H phase leads to an increased uptake of alkalis due to negatively charged structure and, accordingly, to the decrease of pore solution pH value. A significant drop in pore solution pH below 10 could affect a decrease in pozzolanic reaction rate, furthermore it can also lead to the destabilization of AFm and Aft reaction products. Also, the morphology of C-S-H phase is changed from fibrillar particles to sheet-like two dimensional foils when the Ca/Si ratio decreases [7].

When zeolite is used as SCM it should be expected that pozzolanic reaction is going to be more specific due to the following reasons:

sane kristalne rešetke zeolita;

- izmenljivi katjoni koji se nalaze u strukturi zeolita mogu da utiču na pucolansku reakciju zeolita i odnos Ca/Si u C-S-H fazi.

Zeolit može da apsorbuje veliku količinu vode unutar svoje strukture. Priilikom razgradnje kristalne strukture zeolita oslobađa se ova voda koja može da ima dvostruku ulogu u pucolanskoj reakciji. Prva je doprinos procesu hidratacije u slučaju kada je količina vode u sistemu pora kod paste smanjena, a druga je smanjenje pH vrednosti usled efekta razblaživanja.

Pucolanska reakcija pod uticajem hidroksilnih jona odvija se kroz disocijaciju Si-OH i Al-OH u Si-O i Al-O grupe. Ca^{2+} iz rastvora zasićenog portlanditom adsorbuju se na površini. Pretpostavlja se da prisustvo Si-O i Al-O grupa utiče na dalju razgradnju veza Si-O-Si i Al-O-Si grupa koje se nalaze ispod njih u rešetki zeolita. Negativno naelektrisanje rešetke zeolita sprečava difuziju hidroksilnih jona dublje u strukturu zeolita. Ovaj proces prvenstveno zavisi od koncentracije Si-O i Al-O grupe na površini, zbog čega proces rastvaranja zavisi od specifične površine.

Uloga izmenjivih katjona u pucolanskoj reakciji zeolita veoma je značajna. Oni mogu da utiču na stepen hidratacije, nivo polimerizacije kao i na morfologiju C-S-H faze [8]. Na primer, jon Na^+ brže se otpušta u porni rastvor i tako se povećava njegova pH vrednost. Usled toga se povećava rastvorljivost i reaktivnost zeolita. Takođe, prisustvo jona Na^+ može da utiče na formiranje C-S-H faze u obliku lista, s većim stepenom uređenosti rešetke i krupnijim kristalima. Ove pojave dovode do formiranja strukture veće propusnosti, a samim tim zeolit postaje reaktivniji.

Zeolit sa Ca^{2+} kao izmenjivim katjonom imao bi manju potrošnju portlandita nastalog u procesu hidratacije cementa. Neizreagovani portlandit može da iskristališe i formira ogromne kristale koji mogu da smanje mehanička svojstva pastā/maltera/betona [9].

Sve navedene činjenice ukazuju na kompleksnost mehanizma pucolanske reakcije zeolita i potrebu da se ovaj proces ispita kako bi se razumeo i stavio pod kontrolu.

Značaj razumevanja i sticanje dubljeg uvida u mehanizme pucolanske reakcije zeolita proizlazi na prvom mestu iz povećanja trajnosti. Povećanje trajnosti maltera/betona spravljenih sa zeolitom kao DCM-om utvrđuje se preko smanjenja poroznosti, povećanja hemijske otpornosti i većeg sadržaja C-S-H faze. Dodatno, njegov uticaj na životnu sredinu (Cr^{6+} adsorpcija, antibakterijski materijal i materijal za kontrolisanje vlažnosti), katalitičko svojstvo (velika specifična površina, jonoizmenjivački kapacitet i poroznost), ekonomska pogodnost (niski troškovi proizvodnje), kao i široka rasprostranjenost jesu od velikog značaja za njegovu primenu. Glavni depoziti zeolita u Srbiji visokog su kvaliteta i sadrže više od 70% zeolita (npr. Beočin, Igroš, Jablanica 1, Toponica, Zlatokop) [10].

Glavni cilj ovog rada je prikaz rezultata ispitivanja teksturalnih, mineraloških i mehaničkih svojstava cementnih pasta spravljenih s različitim količinama zeolita (0%, 10%, 20% i 30%) kao DCM. Napredak procesa hidratacije kod uzoraka pastā praćen je nakon 28 i 60 dana.

- zeolite structure absorbs significant amount of water,

- diffusion of negatively charged hydroxyl ions into the zeolite pore network is hindered by negatively charged zeolite framework,

- exchangeable cations from zeolite structure could affect the pozzolanic reaction of zeolite and Ca/Si ratio in C-S-H phase.

Zeolite can absorb a great amount of water in pore structure. While zeolite structure framework is being degraded, this water is released and it could have double function in the pozzolanic reaction. The first one is contribution to hydration process in case the amount of water in the pore system of "binder" paste has decreased, and second one could be a decrease of pH value as dilution effect.

The pozzolanic reaction of zeolite under the action of hydroxyl ions proceeds by dissociation of Si-OH and Al-OH into Si-O and Al-O groups. Ca^{2+} cations from the portlandite saturated solution are adsorbed on the surface. The presence of Si-O and Al-O groups is assumed to influence the further degradation of Si-O-Si and Al-O-Si bonds underlying in zeolite framework. The negative zeolite framework charge impedes the diffusion of hydroxyl ions deep into zeolite framework. This process mostly depends on the concentration of Si-O and Al-O groups on the surface, which makes the dissolution process dependent on specific surface area.

The role of the type of exchangeable cations in pozzolanic reaction of zeolite is very important. They may influence the rate of hydration, the degree of polymerization as well as morphology of C-S-H phase [8]. For instance Na^+ ion is faster released into the pore solution and therefore increases pH value. Accordingly, zeolite dissolution and reactivity will increase. Also the presence of Na^+ ion can influence the formation of foil like morphology of C-S-H phase, with a higher degree of ordering and larger crystals. This will lead to the formation of a structure with a higher permeability and consequently a higher zeolite reactivity.

Zeolite with Ca^{2+} as an exchangeable cation will have lower consumption of portlandite produced in the process of cement hydration. Unreacted portlandite may crystallize and form massive crystals which could decrease mechanical properties of paste/mortar/concrete [9].

All the mentioned facts indicate the complexity of the mechanism of zeolite pozzolanic reaction and the necessity to investigate this process in order to understand and control it.

The significance of understanding the process of zeolite pozzolanic reaction and gaining more fundamental insight into the reaction mechanisms arises in the first place from the increased durability. The increased durability of mortar/concrete made of zeolite used as a SCM is recognised through their reduced porosity, increased chemical resistance and higher content of C-S-H phase. Additionally, their environmental impact (Cr^{6+} adsorption, anti-bacterial and humidity-conditioning material), catalytic (high specific area, cation exchange capacity and porosity), economical (low cost of production), as well as widespread presence are very important for their application. The main zeolite deposits in Serbia are of high quality containing more than 70% of zeolites (e.g. Beočin, Igroš, Jablanica 1,

Toponica, Zlatokop) [10].

The aim of this paper is to present the results of textural, mineralogical and mechanical properties obtained for cement based pastes prepared with different amounts of zeolite (0%, 10%, 20% and 30%) as SCM. The progress of hydration process has been followed for paste samples 28 and 60 days old.

2 EKSPERIMENTALNI DEO

2.1 Materijali i sastav mešavina

U okviru istraživanja prikazanog u ovom radu kao material je korišćen portland cement, CEM I 42.5 (Lafarge, Beočin, Srbija) i prirodni zeolit, PZ, ($d < 125 \mu\text{m}$) iz nalazišta Igroš (Brus, Srbija). CEM I 42.5 ispunjava kriterijume standarda SRPS EN 197-1.

Referentna i tri dodatne mešavine portland cementne paste, koje sadrže 10%, 20% i 30% PZ u odnosu na masu cementa (uzorci C, CZ10, CZ20 i CZ30, prema navedenom redosledu) spravljene su sa dejonizovanom vodom, W/B=0.5 (Tab. 1). Uzorci pastā su dimenzija 1x1x6 cm.

*Tabela 1. Sastav mešavina cementnih i cementno-zeolitnih pastā [11]
Table 1. Mixture proportions for cement and cement-zeolite pastes [11]*

Sastav mešavina / Mixture proportions				
	C	CZ10	CZ20	CZ30
CEM I 42.5	450g	405g	360g	315g
Prirodni zeolit <i>Natural zeolite</i>	-	45g	90g	135g
Dejonizovana voda <i>Deionized water</i>	225g	225g	225g	225g
w/b faktor <i>w/b ratio</i>	0.5	0.5	0.5	0.5

2.2 Metode

2.2.1 Hemijska analiza

Hemijski sastav PZ određen je u skladu sa standardom SRPS EN 196-2.

2.2.2 Mineraloška karakterizacija

XRD difrakcioni praškasti paterni snimani su na Philips-ovom difraktometru tipa PW-1710 pri čemu je korišćena bakarna antikatoda sa $\text{CuK}\alpha=1.54128\text{\AA}$ i grafitni monohromator. XRD analiza je izvedena pod uglom od $2\theta(^{\circ})$ u opsegu od 5° do 50° s korakom 0.02° . Identifikacija postojećih mineralnih faza izvedena je upoređivanjem interpolirane razdaljine (d) i relativnog intenziteta (I) s podacima iz literature, ili odgovarajuće kartice iz JCPDS fajlova.

Za spektroskopsku karakterizaciju pripremljeni su uzorci pastā i izvedeno je snimanje infracrvenom spektroskopijom s Furijeovom transformacijom (Thermo-Nicolet Nexus 670 FTIR spektrometar), s ciljem da se izuče vibraciona svojstva navedenih uzoraka. FTIR

2 EXPERIMENTAL

2.1 Materials and mixture proportions

The materials used in this study are Portland cement, CEM I 42.5 (Lafarge, Beočin, Serbia) and natural zeolite ($d < 125 \mu\text{m}$) from Igroš quarry (Brus, Serbia). CEM I 42.5 meets the criteria of standard SRPS EN 197-1.

Reference and three additional mixtures of Portland cement paste, containing 10%, 20% and 30% of NZ per cement weight (samples C, CZ10, CZ20 and CZ30, respectively) have been prepared with the addition of deionized water, W/B=0.5, Tab. 1. The dimensions of paste samples have been 1x1x6 cm.

2.2 Methods

2.2.1 Chemical analysis

The chemical composition of NZ has been determined according to SRPS EN 196-2.

2.2.2 Mineralogical characterization

The XRD powder diffraction patterns have been acquired on Philips X-ray powder diffractometer type PW-1710 using copper anticathode with $\text{CuK}\alpha=1.54128\text{\AA}$ and graphite monochromator. Powder XRD analyses have been performed in the $2\theta(^{\circ})$ angle range from 5° to 50° with a 0.02° step in experiments. The identification of the existing mineral phases has been acquired by comparing interpolate distances (d) and relative intensities (I) with literature data, or the appropriate card from the JCPDS files.

For the spectroscopic characterization of the prepared paste samples, the Fourier Transform Infra-Red (FTIR) analyses have been carried out (Thermo-Nicolet Nexus 670 FTIR spectrometer) in order to study vibration properties of the prepared samples. The FTIR

spektri snimljeni su sa spektralnom rezolucijom od 4 cm^{-1} u opsegu od 400 do 4000 cm^{-1} , s prosečno 32 skeniranja po jednom merenju. Spektri svih ispitanih uzoraka određeni su korišćenjem tehnika KBr pastille. Jedna od prednosti upotrebe FTIR spektroskopije jeste mogućnost izučavanja vibracionih svojstava kako amorfnih tako i kristalnih uzoraka [12].

2.2.3 Teksturalna karakterizacija

Niskotemperaturna adsorpcija azota, model 2000, (ASAP Micrometrics, USA) korišćena je za određivanje teksturalnih svojstava (specifične površine, zapremine pora i prosečnog prečnika pora). Uzorci u prahu (prirodni zeolit-Z, portland cement-CEM I) sušeni su na 100°C .

Raspodela veličine pora i kumulativna zapremina pora određene su metodom živine porozimetrije (Hg Porozimetar Carlo Erba 2000 WS, Italija), s prečnikom u opsegu od 0.002 do $200\text{ }\mu\text{m}$. Uzorci pastā (C, CZ10, CZ20, CZ30, stari 28 i 60 dana) sušeni su i degasirani na 50°C . Pri datoj temperaturi ne dolazi do razaranja strukture C-S-H, etringita i drugih produkata hidratacije.

2.2.4 Čvrstoća pri pritisku

Za određivanje čvrstoće pri pritisku korišćeno je deset uzoraka pastā po mešavini. Svi uzorci su negovani u skladu sa standardom SRPS EN196-1 [13], izuzev u pogledu uslova u vezi s kvalitetom vode u kojoj su negovani (umesto vode iz česme korišćena je dejonizovana voda).

3 REZULTATI I DISKUSIJA

3.1 Hemijska analiza

Hemijski sastav PZ prikazan je u tabeli 2. Na stabilnost strukture zeolita utiče više faktora. Jedan od njih je odnos Si/Al koji za korišćeni zeolit iznosi 4.95. Što je prethodno navedeni odnos manji, to je veći stepen izomorfne zamene Si sa Al u tetraedrima kristalne rešetke [14].

Tabela 2. Hemijski sastav prirodnog zeolita [11,14]
Table 2. Chemical composition of natural zeolite [11, 14]

Hemijski sastav prirodnog zeolita iz Igroša (%) / Chemical composition of natural zeolite from Igros [%]												
SiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O	K ₂ O	P ₂ O ₅	L.I.*	L.H.**	SO ₃
62.30	12.59	0.23	1.20	4.80	1.94	0.22	0.70	0.63	0.016	11.06	4.59	0.05
* Gubici žarenjem / Loss on ignition												
** Gubici pri zagrevanju / Loss by heating												

Jonoizmenjivački kapacitet PZ prikazan je u tabeli 3. Najveći jonoizmenjivački kapacitet u korišćenom PZ ima katjon kalcijuma.

spectra have been recorded with a spectral resolution of 4 cm^{-1} in the range of 400 – 4000 cm^{-1} , with 32 averaged scans per one measurement. The spectra of all investigated samples have been measured using the KBr pellet technique. One of the advantages of using FTIR spectroscopy is a possibility to study vibration properties of both amorphous and crystalline samples [12].

2.2.3 Textural characterization

Low temperature nitrogen adsorption, Model 2000, (ASAP Micrometrics, USA) has been used for the determination of textural properties (specific surface area, pore volume and average pore diameter). Powder samples (natural zeolite, ordinary Portland cement-CEM I) have been oven-dried at 100°C .

The pore size distribution and the cumulative volume of pores have been determined by mercury intrusion porosimetry (Hg Porosimeter Carlo Erba 2000 WS, Italia), diameter range of 0.002– $200\text{ }\mu\text{m}$. Paste samples (C, CZ10, CZ20, CZ30, 28 and 60 days old) were oven-dried and degassed at 50°C . At a given temperature there is no destruction of the structure of C-S-H, ettringite and other products of hydration.

2.2.4 Compressive strength

The compressive strength of pastes has been determined on 10 samples per mixture. All the samples have been cured in accordance with standard SRPS EN196-1 [13], except for the condition related to the quality of curing water (deionized water has been used instead of tap water).

3 RESULTS AND DISCUSSION

3.1 Chemical analyses

Chemical composition of NZ is shown in Table 2. The stability of zeolite structure depends on several factors. One of them is ratio Si/Al and for the used NZ the value of this ratio is 4.95. The smaller the ratio, the greater is the extent of isomorphous substitution of Al for Si in the tetrahedral framework [14].

The ion exchanged capacity of NZ is shown in Table 3. The highest value has had calcium cation.

Tabela 3. Jonoizmenjivački kapacitet i izmenjivi katjoni nakon tretiranja sa NH_4^+ [14]
Table 3. Cation-exchange capacity and exchanged cations after treatment by NH_4^+ [14]

CEC (meq/100g)	K	Na	Ca	Mg
180	4.4	7.3	147.5	20.8

3.2 Teksturalna karakterizacija komponenti u prahu

Vrednosti specifične mase, specifične površine i zapremine pora date su u tabeli 4. Navedeni rezultati potvrđuju da zeolit ima poroznu strukturu.

3.2 Textural characterization of powder components

The results of true density, specific surface area and the volume of pores are presented in Table 4. They confirmed the porous structure of zeolite.

Tabela 4. Specifična masa, BET specifična površina, zapremina pora [14]
Table 4. True densities, BET surface area, Volumes of pores [14]

	Specifična masa True density (kg/m^3)	BET specifična površina BET surface area (m^2/g)	Zapremina pora Volumes of pores (cm^3/g)
CEM I 42,5	3126	1.5474	0.008483
Natural zeolite	2312	78.1586	0.230315

3.3 Mineraloška karakterizacija

3.3.1 XRD analiza

3.3.1.1 Prirodni zeolit

Prirodni zeolit sadrži klinoptilolit kao glavni mineral $(Na,K,Ca)_5Al_6Si_{30}O_{72}18H_2O$ i glinoviti mineral smektit $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2nH_2O$ u manjoj količini [15].

3.3 Mineralogical characterization

3.3.1 XRD analyses

3.3.1.1 Natural zeolite

Zeolite tuff contains mineral clinoptilolite $(Na,K,Ca)_5Al_6Si_{30}O_{72}18H_2O$ as a main and clay mineral smectite $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2nH_2O$ as a minor component, [15].

3.3.1.2 Uzorci pasta

Svi uzorci pasta ispitani su pomoću XRD analize kako bi se identifikovali produkti hidratacije, kao i smanjenje količine minerala klinoptilolita, glavne komponente zeolita, u odnosu na proteklo vreme hidratacije (28 i 60 dana), slike 1 i 2. Napredovanje pucolanske reakcije dovodi se u vezu s formiranjem novih hidratiranih jedinjenja i smanjenjem količine $Ca(OH)_2$ u pastama. Formirani produkti hidratacije isti su kod uzoraka starih 28 i 60 dana i navedeni su kao: portlandit, etringit, C-S-H i C-A-H faze.

Očekivano je da se s povećanjem udela PZ u pastama postepeno smanjuje intenzitet pikova koji odgovaraju portlanditu ($Ca(OH)_2$). Međutim, ova pretpostavka se ispostavila nevalidnom kada je reč o rezultatima XRD analize uzoraka starosti 28 dana (sl. 1). Tačnije, pikovi koji odgovaraju portlanditu ($d \sim 4.9, 2.6 \text{ \AA}$) u pasti CZ20 starosti 28 dana imaju najveće intenzitete. Najverovatnije je da je ovaj rezultat posledica svojstva PZ poznatog kao sadržaj *extraframework* katjona. Zamena datih katjona katjonima koji potiču iz rastvora koji ispunjava pore paste može da dovede ili do povećanja ili do smanjenja koncentracije alkalija u pornom rastvoru. Do čega će doći, zavisi od jonoizmenjivačkog kapaciteta PZ. U ovom slučaju, prihvatljivo objašnjenje je da je nakon cepanja strukture PZ i njegovog ulaska u pucolansku reakciju došlo do otpuštanja *extraframework* katjona u porni rastvor. Kao

3.3.1.2 Paste samples

All paste samples have been examined by the means of XRD in order to identify hydration products as well as the degradation of mineral clinoptilolite, zeolite main component, in relation to the age of hydration (28 and 60 days), Figs. 1, 2. The progress of pozzolanic reactions has been coupled with the formation of new hydrated compounds and reduction of the amount of $Ca(OH)_2$ in the paste. The formed hydration products are the same for both 28-day and 60-day old samples and they are specified as: portlandite, ettringite, C-S-H and C-A-H phases.

The reduction of the peak intensity related to portlandite ($Ca(OH)_2$) has been expected to gradually decrease as the amount of zeolite has increased. This statement is not valid for the results of XRD analysis of samples aged 28 days, Fig 1. Exactly, the greatest intensities have the peaks of portlandite ($d \sim 4.9, 2.6 \text{ \AA}$) for paste CZ20 28 days old. Most probably this result is a consequence of the zeolite property known as *extraframework* cation content. The exchange of the zeolite *extraframework* cations with the cations present in the pore solution can either increase or lower the alkali concentration in the pore solution. This depends on zeolite ion exchange capacity. In this case, a reasonable explanation is that after zeolite structure has been partly broken down and taken part in pozzolanic reaction, the *extraframework* cations have been released

posledica navedenog javila se povećana koncentracija alkalija i zbog jonskog efekta zaustavlja se rastvaranje $\text{Ca}(\text{OH})_2$. To je moglo da utiče na strukturu C-S-H, što je i potvrđeno FTIR analizom – polimerizacija SiO_4^{4-} grupa manje je zastupljena u formiranoj C-S-H fazi (sl. 3).

Kao što se može uočiti sa slika 1 i 2, pikovi koji odgovaraju klinoptilolitu, glavnoj komponenti PZ, nisu nestali tokom procesa hidratacije, što implicira da proces razgradnje PZ nije završen ni nakon 60 dana.

Ni kod uzoraka starih 60 dana nije zabeleženo značajno smanjenje intenziteta pikova koji odgovaraju portlanditu pri porastu udela zeolita u pastama (sl. 2).

into the pore solution. Consequently, alkali concentrations have increased and, due to ionic effect, they have suppressed $\text{Ca}(\text{OH})_2$ dissolution. This also might have influenced the structure of C-S-H, which has been confirmed by FTIR analysis (polymerization of the SiO_4^{4-} units is less pronounced in formed C-S-H phase), Figs. 3, 5a.

As seen from Figures 1 and 2 the peaks corresponding to clinoptilolite, the main component of zeolite, have not disappeared during the hydration process. It clearly implies that the process of zeolite degradation is still unfinished even after 60 days.

The intensities of portlandite peaks for samples at the age of 60 days also failed to present a remarkable decrease with the enhancement of the zeolite content, Fig 2.

Slika 1. XRD paterni očvrslih cementnih pastā i cementnih pastā koje sadrže PZ kao DCM, nakon 28 dana hidratacije (P-portlandit, Et-etringit, C-S-H-kalcijumsilikatni hidrati, C-A-H-kalcijumaluminatni hidrati, Clp- klinoptilolit) [11, 14]

Figure 1. XRD patterns of the hardened cement paste and cement pastes containing NZ as SCM, after 28 days of hydration (P-portlandite, Et-ettringite, C-S-H-calcium silicate hydrate, C-A-H-calcium aluminium hydrate, Clp-clinoptilolite) [11, 14]

Slika 2. XRD paterni očvrslih cementnih pastā i cementnih pastā koje sadrže PZ kao DCM, nakon 60 dana hidratacije (P-portlandit, Et-etringit, C-S-H-kalcijumsilikatni hidrati, C-A-H-kalcijumaluminatni hidrati, Clp- klinoptilolit, Gl-glina, G-gips, C-kalcit)

Figure 2. XRD patterns of the hardened cement paste and cement pastes containing NZ as SCM, after 60 days of hydration (P-portlandite, Et-ettringite, C-S-H-calcium silicate hydrate, C-A-H-calcium aluminium hydrate, Clp-clinoptilolite, Gl-clay, G-gypsum, C-calcite)

Formiranje kalcijum-siliko-hidrata (C-S-H) evidentirano je kod uzoraka obe starosti i pripisuje se postojanju postepenog povećanja pozadinskog zračenja u opsegu 20: 25-35° (sl. 1, 2).

3.3.2 FTIR analiza

Glavni cilj primene FTIR spektroskopije bio je analiza produkata hidratacije pripremljenih pasta nakon 28 i 60 dana hidratacije. Uporedni prikaz dobijenih FTIR spektara dat je na slikama 3 i 4.

Na osnovu dobijenih FTIR spektara prikazanih na slikama 3 i 4, može se uočiti pojava apsorpcionih traka na $\sim 3640\text{ cm}^{-1}$, $\sim 3435\text{ cm}^{-1}$ i $\sim 1646\text{ cm}^{-1}$, koje se pripisuju postojanju vibracija različitih oblika O-H molekulske grupe. Naime, apsorpcione trake na $\sim 3640\text{ cm}^{-1}$ upućuju na prisustvo valentnih vibracija Ca-OH iz portlandita, dok se apsorpcione trake na $\sim 3435\text{ cm}^{-1}$ i $\sim 1646\text{ cm}^{-1}$ dovode u vezu s prisustvom vodonične veze OH grupe u molekulima H_2O koji su adsorbovani na površini ispitanih uzoraka. Pojava apsorpcionih traka na $\sim 1421\text{ cm}^{-1}$, $\sim 876\text{ cm}^{-1}$ i $\sim 711\text{ cm}^{-1}$ dovodi se u vezu s prisustvom karbonata u strukturi ispitanih uzoraka [12]. Postojanje apsorpcione trake na $\sim 1111\text{ cm}^{-1}$ može se pripisati prisustvu SO_4^{2-} molekulske vibracije koja može da ukaže na postojanje faze etringita ili gipsa. Postojanje apsorpcione OH trake na $\sim 3435\text{ cm}^{-1}$ koja se prepisuje vodoničnoj vezi OH grupe i dovodi se u vezu s prisustvom vode u strukturi etringita, dodatno potvrđuje činjenicu da je etringit prisutan.

The formation of calcium silicate hydrate (C-S-H) has been evident for the samples at both ages and is attributed to the existence of the gradual increase of background in the range 20: 25-35°, Figs.1, 2.

3.3.2 FTIR analyses

The main objective of the FTIR study has been to analyze the hydration products of the prepared pastes after 28 and 60 days of hydration. The comparison of the obtained FTIR spectra of the pastes is presented in Figs 3 and 4.

According to the obtained FTIR spectra presented in Figures 3 and 4, the appearance of the absorption bands at $\sim 3640\text{ cm}^{-1}$, $\sim 3435\text{ cm}^{-1}$ and $\sim 1646\text{ cm}^{-1}$ has been noted. These bands are ascribed to the existence of the vibration of different modes of O-H molecular group. Namely, the absorption bands at $\sim 3640\text{ cm}^{-1}$ indicate the presence of stretching vibrations of Ca-OH from portlandite, while the absorption bands at $\sim 3435\text{ cm}^{-1}$ and $\sim 1646\text{ cm}^{-1}$ are associated with the presence of hydrogen bonded OH group in molecules of H_2O which are adsorbed on the surfaces of the tested samples. The occurrence of the absorption bands at $\sim 1421\text{ cm}^{-1}$, $\sim 876\text{ cm}^{-1}$ and $\sim 711\text{ cm}^{-1}$ is associated with the presence of the carbonates in the structure of the tested samples [12]. The presence of the absorption band at the $\sim 1111\text{ cm}^{-1}$ could be attributed to the presence of the SO_4^{2-} molecular vibration which could be assigned to the presence of the ettringite mineral phase or gypsum. The existence of the OH absorption band at $\sim 3435\text{ cm}^{-1}$ is attributed to hydrogen bonded OH group and could be related to the water present in ettringite structure which additionally supports the fact that ettringite is present.

Slika 3. FTIR spektri pasta nakon 28 dana hidratacije
Figure 3. FTIR spectrum of pastes after 28 days of hydration

Prisustvo produkata hidratacije kao što su kalcijum-siliko-hidrati (C-S-H) može da se poveže sa apsorpcionom trakom na $\sim 970\text{ cm}^{-1}$ zbog postojanja Si-O valentine vibracije Q^2 tetraedara SiO_2 . Dodatno, apsorpcione trake na $\sim 660\text{--}670\text{ cm}^{-1}$ i na $450\text{--}500\text{ cm}^{-1}$, u kojima je utvrđeno prisustvo Si-O-Si savijajuće vibracije i deformacionih vibracija SiO_4 tetraedra, prema navedenom redosledu, mogu se takođe prepisati prisustvu C-S-H faze [16].

Upoređujući FTIR spektre referentnog uzorka (cementna pasta bez zeolita) i pastā koje sadrže različitu količinu zeolita u oba slučaja (nakon 28 i 60 dana hidratacije), primećene su značajne promene u dobijenim FTIR spektrima, što bi moglo da ukaže na izvesne izmene u strukturi. Naime, primetno se smanjio intenzitet apsorpcionih traka koje upućuju na prisustvo Ca(OH)_2 , CaCO_3 i SO_4^{2-} s porastom udela zeolita (sl. 3, 4), nakon 28 i 60 dana hidratacije. Dodatno, postoji razlika u vezi s pomeranjem apsorpcione trake na $\sim 970\text{ cm}^{-1}$ koja se odnosi na postojanje Si-O valentnih vibracija Q^2 tetraedra u C-S-H (sl. 3, 5).

The presence of the hydration products such as calcium silicate hydrates (C-S-H) could be related to occurrence of absorption bands at $\sim 970\text{ cm}^{-1}$ due to the existence of the Si-O stretching vibrations of Q^2 tetrahedra of the SiO_2 . Additionally, the absorption bands at $\sim 660\text{--}670\text{ cm}^{-1}$ and at $\sim 450\text{--}500\text{ cm}^{-1}$, which are designated to the presence of Si-O-Si bending vibration and deformation of SiO_4 tetrahedra vibrations, respectively, could be ascribed to the presence of the C-S-H, as well [16].

Comparing the FTIR spectra of the reference sample (cement pastes without zeolite) and pastes with different amount of zeolite in both cases (after 28 and 60 days of hydration), certain changes of the obtained FTIR spectra have been noticed, which could indicate the existence of certain alteration of the structure. Namely, there has been a notable gradual decrease of absorption bands intensities related to the presence of Ca(OH)_2 , CaCO_3 and SO_4^{2-} with the increase of the wt% of zeolite in the structure, Figs. 3, 4, both after 28 and 60 days of hydration. Moreover, there is a difference regarding the shift of the absorption band at $\sim 970\text{ cm}^{-1}$ related to the existence of Si-O stretching vibrations of Q^2 tetrahedra of the C-S-H, Figs. 3 and 5.

Slika 4. FTIR spektri pastā nakon 60 dana hidratacije
Figure 4. FTIR spectra of pastes after 60 days of hydration

Na primer, u slučaju pastā nakon 28 dana hidratacije može se uočiti pomeranje ka nižim vrednostima talasnih brojeva kod pastā CZ10 i CZ20 (974.05 cm^{-1} , 981.09 cm^{-1} , prema navedenom redosledu) u poređenju s referentnom cementnom pastom C (990.05 cm^{-1}), što se može pripisati smanjenju stepena polimerizacije C-S-H strukture (sl. 3). S druge strane, na osnovu poređenja talasnih brojeva uzoraka CZ10, CZ20 i CZ30 opaža se pomeranje ka većim talasnim brojevima (974.05 cm^{-1} , 981.09 cm^{-1} , 990.05 cm^{-1} , prema navedenom redosledu)

For example, in the case of the pastes after 28 days of hydration the shift toward the lower wavenumber values for CZ10 and CZ20 pastes (974.05 cm^{-1} , 981.09 cm^{-1} , respectively) has been noted in comparison with the reference cement paste, sample C (990.05 cm^{-1}), which could be attributed to the decrease of polymerization level of the C-S-H structure, Fig. 3. On the other hand, the comparison of the wavenumbers among the samples CZ10, CZ20 and CZ30 has been perceived the shift toward the higher wavenumber

što upućuje na povećani nivo polimerizacije. Najveće pomeranje pozicije pomenute Si-O valentine trake bilo je kod uzorka CZ10 (sl. 5a), sugerišući da razlaganje zeolita utiče na sastav C-S-H faze tokom procesa hidratacije.

Drugim rečima, povećanje količine zeolita utiče na hemijski sastav pornog rastvora, generalno na porast sadržaja alkalija, Si i Al, i istovremeno na opadanje koncentracije Ca. Na koncentraciju alkalija u kontaktnoj tečnosti utiču sadržaj *extraframework* katjona u zeolitu kao i njegove jonoizmenjivačke karakteristike. Usled jonskog efekta povećanje sadržaja alkalija smanjuje se sadržaj Ca, dok se koncentracije Si i Al generalno povećavaju u toku vremena. U skladu s tim, smanjenje Ca/Si odnosa dovodi do produženja silikatnog lanca (povećava se stepen polimerizacije). To bi moglo da bude prihvatljivo objašnjenje dobijenih rezultata (sl. 3, 5).

values (974.05 cm^{-1} , 981.09 cm^{-1} , 990.05 cm^{-1} , respectively) indicating the increase of polymerization level. The largest shift of the mentioned Si-O stretching band position has been found in the case of CZ10, Fig. 5a, suggesting that zeolite decomposition has influenced the composition of C-S-H phase during the hydration process.

This points out that the increase of zeolite amount thoroughly influences pore solution chemistry, generally increasing alkali, Si and Al contents and at the same time decreasing Ca concentrations in the pore solution. The alkali concentration in the contact fluid has been affected by the extra-framework cation content and cation exchange characteristics of zeolite. Due to the ion effect the increasing alkali content decreases Ca content while concentrations of Si and Al generally increase through time. Accordingly, the decrease of Ca/Si ratio leads to lengthening of silicate chains (increase of polymerization). That could be a reasonable explanation for the obtained results, Figs 3-5.

Slika 5. FTIR spektri apsorpcione trake na $\sim 970\text{ cm}^{-1}$ kod pastā nakon a) 28 i b) 60 dana hidratacije
Figure 5. FTIR spectra of the absorption band at $\sim 970\text{ cm}^{-1}$ of pastes after a) 28 and b) 60 days of hydration

Nakon 60 dana hidratacije, drugačija je situacija u pogledu položaja apsorpcione trake koja se odnosi na postojanje Si-O valentnih vibracija Q^2 tetraedara. Naime, došlo je do mnogo manjeg pomeranja apsorpcione trake prema većim talasnim brojevima u odnosu na referentni uzorak, sl. 5b. Ova činjenica upućuje na veći stepen polimerizacije C-S-H strukture sa dodatkom zeolita, sl. 4, 5b, u poređenju s referentnim uzorkom nakon 60 dana hidratacije.

Na osnovu rezultata FTIR analize može se bez ikakve sumnje zaključiti da uvođenje zeolitne faze utiče na sastav i strukturu C-S-H faze tokom procesa hidratacije.

After 60 days of hydration, there is a different situation regarding the position of the absorption band related to the existence of the Si-O stretching vibrations of Q^2 tetrahedra. Namely, there has been a much smaller shifting of the absorption band towards the higher wavenumber values in comparison with the reference sample, Fig. 5b. This indicates a better polymerization of the C-S-H structure with addition of zeolite, Figs. 4, 5b, in comparison with the reference sample after 60 days of hydration.

According to the performed FTIR analysis it can be undoubtedly concluded that introduction of the zeolite phase has influenced the composition and structure of the CSH phase during hydration process.

3.3.3 Teksturalna karakterizacija pastā

U okviru ovog istraživanja, živina porozimetrija (ŽP) korišćena je za karakterizaciju strukture pora. Određivanje strukture pora je od izuzetnog značaja za razumevanje hemijskih, fizičkih i mehaničkih svojstava. Analiza koja je ovde data polazi od klasifikacije koja je data prema IUPAC-u (mikropore < 2 nm, mezopore između 2-50 nm, makropore > 50 nm). Ako se uzme u obzir da uz pomoć ŽP metode nije moguće meriti količinu pora sa $d < 2$ nm, onda je razumljivo da se rezultati u ovom radu odnose samo na mezoporoznost i makroporoznost. U okviru ovog istraživanja očekivalo se da kapilarna poroznost (IUPAC nomenklatura, 10 nm-10 μ m) zavisi samo od količine produkata hidratacije, naročito C-S-H faze koja se pri formiranju taloži u porama pošto njegovo formiranje vodi ka smanjenju prečnika pora i smanjenju kapilarne poroznosti.

Kapilarne pore s prečnikom u opsegu od 10 nm do 50 nm (mezopore) utiču na skupljanje usled sušenja i tečenja, dok makropore s prečnikom većim od 50 nm, utiču na čvrstoću i na smanjenje propustljivosti pastā, maltera i betona [17].

Opšte je prihvaćeno stanovište da dodavanje DCM dovodi do povećanja ukupne poroznosti, ali i smanjenja prosečnog prečnika pora.

3.3.3 Textural characterization of pastes

Mercury intrusion porosimetry (MIP) has been used to characterize pore structure. In general, determination of the pore structure has become important in understanding chemical, physical and mechanical properties. The following analysis has been based on a general classification of the pores that has been given by the IUPAC (micropore- up to 2 nm, mesopore 2-50 nm, macropore > 50 nm). If one takes into account that MIP method is inappropriate to measure the pores with $d < 2$ nm, then it is logical that the results of the study relate only to meso- and macroporosity. In this study, it has been expected that capillary porosity (IUPAC nomenclature, 10 nm-10 μ m) is dependent only on the amount of hydrated products, particularly due to the precipitation of C-S-H phase since its formation leads to the reduction of the pore diameter and capillary porosity.

The capillary pores with diameters in the range from 10 nm to 50 nm (mesopores) influence drying shrinkage and creep, while macropores, with diameters greater than 50 nm, influence the strength and impermeable characteristics of paste, mortar and concrete [17].

It is commonly observed that the addition of SCMs results in an increase of total porosity as well as a decrease in mean pore size.

Tabela 5. Rezultati teksturalne analize
Table 5. The results of textural analysis

Uzorak Sample	Ukupna poroznost Total porosity (%)	Srednji polupreč.pora Average pore radius (μ m)	Udeo makropora Macroporosity (%)	Udeo mezopora Mesoporosity (%)
28 dana stari uzorci				
C	17.22	0.50	3.88	13.34
CZ10	30.13	5.30	2.02	28.11
CZ20	26.67	3.80	2.71	23.89
CZ30	31.45	3.80	3.17	28.28
60 dana stari uzorci				
C	26.43	3.80	3.12	23.31
CZ10	21.04	3.80	3.15	17.89
CZ20	2.87	237	2.71	0.16
CZ30	9.98	0.90	1.35	8.63

U tabeli 5 prikazane su vrednosti ukupne poroznosti, srednjeg prečnika pora, makroporoznost i mezoporoznost. Količine makropora izračunate su u odnosu na vrednost ukupne poroznosti i izražene u procentima.

U okviru ovog istraživanja, uticaj zeolita kao DCM u uzorcima starosti 28 dana u skladu je s pomenutim trendom samo u pogledu ukupne poroznosti (tabela 5). Kod pastā starosti 28 dana, koje sadrže zeolit, došlo je do povećanja umesto očekivanog smanjenja prosečnog prečnika pora kao i do smanjenja udela makropora u odnosu na referentnu pastu. S porastom količine zeolita raste i makroporoznost (poređenje između uzoraka CZ10, CZ20 i CZ30). Ustanovljeno je da su pore prečnika do 0.06 μ m dominantne u cementnim pastama sa zeolitom, dok su u referentnoj pasti naročito izražene pore do 0.03 μ m (sl. 6).

Uzorci pastā starosti 60 dana, koji sadrže cement i zeolit, imaju manju ukupnu poroznost u odnosu na referentnu pastu, tab. 5. Kod uzoraka C, CZ10 i CZ30

In Table 5, the results of total porosity, average pore radius, macro- and mesoporosity are presented. The quantities of macropores were calculated in relation to the total porosity and are expressed in percentages.

In this study, the influence of zeolite as a SCM for the samples 28 days old is in accordance with the mentioned course just regarding total porosity, Table 5. For the pastes with zeolite, 28 days old, opposite to the expected decrease in the average diameter, there has been an increase in relation to reference paste. Macroporosity has been increased when the amount of zeolite has been increased (comparison among samples CZ10, CZ20 and CZ30). Dominant pore diameter interval has been in the range, up to 0.06 μ m for cement pastes with zeolite, while it has been particularly prevailing with pores up to 0.03 μ m for reference paste, Fig. 6.

The pastes made of cement with zeolite, 60 days old, have had lower values of total porosity than referent paste, Table 5. For samples C, CZ10, and CZ30 the

preovlađuju pore do 0.03 μm , sl. 7. Vrednosti dobijene za uzorak CZ20 potpuno su drugačije nego kod ostalih uzoraka. Ukupna poroznost je veoma mala (2.87%), prosečni poluprečnik pora ekstremno velik (237 μm) kao i udeo makropora ($2.71/2.87=94.42\%$). Za ovako neuobičajene rezultate potrebno je dodatno pojašnjenje. Preciznije, za posmatrani uzorak teško je prihvatiti ovako nisku vrednost ukupne poroznosti, naročito ako uzmemo u obzir dobijenu vrednost čvrstoće pri pritisku (tab. 6). U ovom slučaju, izgleda da nisu sve pore registrovane metodom ŽP, kao što se dešava u slučaju prisustva pora s gustim površinskim slojem (eng. *hollow-shell* pore) [18]. Obično se *hollow-shell* pore formiraju tokom procesa hidratacije u unutrašnjosti zrna klinkera, dok se na površini formira C-S-H produkt hidratacije. Vrlo često ih zovu Hadlijeva zrna (eng. *Hadley grains*), a veličine su između 1 i 15 μm . Osim toga, smeštena su u deo sa gelskom strukturom te proizlazi da su povezana s mrežom kapilarnih pora preko manjih gelskih pora. Zbog *ink-bottle* efekta koji se pritom javlja, nije ih moguće registrovati pomoću ŽP metode. Slična situacija može se desiti kada su u pitanju zrna izreagovanog zeolita. Naime, *ink-bottle* efekat može se pojaviti kao rezultat formiranja C-S-H faze na površini zeolita, dok je unutrašnjost zrna zeolita šuplja. Ako je struktura formiranih produkata hidratacije bila previše gusta, onda je pore u unutrašnjosti zrna teško registrovati.

Slika 6. Raspodela veličine pora za paste starosti 28 dana
Figure 6. Pore size distribution for the pastes 28 days old

Generalno, uzorci pastā CZ20 i CZ30 pri starosti od 60 dana imaju značajno manju poroznost u poređenju sa uzorcima C i CZ10, kao i u poređenju sa svim uzorcima starim 28 dana (tab. 5). Na osnovu rezultata ŽP za uzorke ispitane nakon 28 dana hidratacije, može se zaključiti da su mezopore dominantne. Kod uzoraka C, CZ10 i CZ30 koji su ispitani nakon 60 dana hidratacije, može se zaključiti da preovlađuju mezopore dok su kod paste CZ20 makropore dominantne.

3.4 Čvrstoća pri pritisku

Smatra se da su čvrstoće cementnih pastā određene brzinom hidratacije cementa, dok se u cementno-zeolitnim pastama uticaj zeolita ogleda kroz efekat razređivanja (smanjena količina cementa u odnosu na

dominant pore interval has been up to 0.03 μm , Fig 7. The values obtained for sample CZ20 have been completely different from the others. In this case the total porosity has been very low (2.87 %), average pore radius extremely high (237 μm) and the ratio of macropores extremely high ($2.71/2.87=94.42\%$). These uncommon results need further clarification. To be precise, for this sample it has been difficult to accept that the total porosity is so low, especially if we take into account the obtained values for compressive strength, Table 6. It seems that in this case some pores are not registered by MIP, like hollow-shell pores [18]. Usually, hollow-shell pores are formed during hydration process within the clinker grains, while hydrated product (C-S-H) is usually formed on the surface. They are often called Hadley grains and are in the size range from 1 to 15 μm . Furthermore, they are embedded in cement gel resulting that they are connected to the continuous capillary pore system through smaller gel pores. Because of their "ink-bottle" effect, they may not easily be detected by MIP. A similar situation may appear when reacted zeolite grains have been in question. Namely, the "ink-bottle" effect may be the result of formation of C-S-H phase on the surface of zeolite, while the inside of zeolite grain is hollow. If the structure of the formed hydrated products is too dense, pores in the interior of the grain can be difficult to detect.

Slika 7. Raspodela veličine pora za paste starosti 60 dana
Figure 7. Pore size distribution for the pastes 60 days old

Generally, samples CZ20 and CZ30 at age of 60 days have a significantly lower porosity compared to C and CZ10 samples as well as in comparison to all the samples at age of 28 days, Table 5. According to the obtained MIP results for the samples tested after 28 days of hydration, it was concluded that mesopores have been dominant. In samples C, CZ10 and CZ30 which were tested after 60 days of hydration, mesopores have been prevailing, while macropores has been dominant for CZ20 sample.

3.4 Compressive strength

The strength development in cement pastes is conceived to be determined by the hydration rate of cement, while in cement-zeolite pastes the influence of zeolite inclusion is determined by dilution effect (cement

paste sa čistim cementom), efekat pakovanja, ubrzanje procesa hidratacije i pucolansku reakciju. Uobičajeno je shvatanje da prva tri parametra najviše utiču na razvoj čvrstoće do 28 dana, a poslednji na čvrstoću nakon 28 dana. Prema literaturnim podacima [17] čvrstoće dobijene na pastama moguće je dovesti u vezu s makroporoznošću uzoraka. Ova korelacija zasnovana je na činjenici da su pore veće od 50 nm, koje se smatraju makroporama, najverovatnije veoma značajne za svojstva čvrstoće i nepropustljivosti [17]. Zato su u ovom radu predstavljeni, analizirani i poređeni rezultati čvrstoće pri pritisku i makroporoznosti.

Na slici 8. i u tabeli 6. prikazane su srednje vrednosti čvrstoće pri pritisku ($f_{cm,28}$, $f_{cm,60}$) određene na 10 uzoraka za svaku pastu, starosti 28 i 60 dana. Zbog rasipanja rezultata određene su i standardne devijacije (σ_{28} , σ_{60}), tabela 6.

content decreases in comparison with pastes containing ordinary cement), the filler effect, the hydration acceleration effect and pozzolanic reaction. The first three parameters are regarded to govern the strength development up to 28 days, while the last one is assumed to influence the strength after 28 days. According to literature [17] it is possible to correlate the strength value of pastes with the macroporosity of the samples. This correlation is based on the fact that the pores larger than 50 nm, referred to as macropores, are most likely to be rather significant for the strength and impermeability properties [17]. Therefore, the results of compressive strength and macroporosity have been presented, analysed and compared in this article.

The average compressive strength values ($f_{cm,28}$, $f_{cm,60}$) of 10 tested samples per each paste, at the age of 28 and 60 days, are shown in Figure 8 and Table 6. Due to the scattering of the obtained compressive strength results the standard deviations (σ_{28} , σ_{60}) have been additionally determined, Tab. 6.

Tabela 6. Čvrstoća pri pritisku ($f_{cm,28}$, $f_{cm,60}$) pastā C, CZ10, CZ20 i CZ30 nakon 28 i 60 dana, i njihove standardne devijacije (σ_{28} , σ_{60})

Table 6. 28-day and 60-day compressive strengths ($f_{cm,28}$, $f_{cm,60}$) of C, CZ10, CZ20 and CZ30 pastes and their standard deviations (σ_{28} , σ_{60})

Vrsta paste / Paste type	C	CZ10	CZ20	CZ30
$f_{cm,28}$ [MPa]	34.821	37.783	39.137	30.411
σ_{28} [MPa]	± 5.211	± 7.288	± 5.523	± 6.832
$f_{cm,60}$ [MPa]	39.946	39.500	37.445	34.207
σ_{60} [MPa]	± 7.170	± 5.160	± 7.348	± 6.357

Čvrstoće pri pritisku takođe su iskazane u odnosu na čvrstoće pri pritisku referentne paste starosti 28 dana i date su u procentima (tab.7).

The compressive strength values have also been expressed as relative percentages of the 28-day compressive strength of the reference paste, Tab. 7.

Tabela 7. Čvrstoće pri pritisku ispitanih pastā ($\Delta f_{cm,28}$, $\Delta f_{cm,60}$) u poređenju sa čvrstoćom pri pritisku referentne paste starosti 28 dana (%)

Table 7. Compressive strength of tested pastes ($\Delta f_{cm,28}$, $\Delta f_{cm,60}$) compared to the 28-day strength of reference mortar [%]

Vrsta paste / Paste type	C	CZ10	CZ20	CZ30
$\Delta f_{cm,28}$ [%]	100.00	108.51	112.40	87.34
$\Delta f_{cm,60}$ [%]	114.718	113.437	107.536	98.237

Nakon 28 dana nege, paste CZ10 i CZ20 imale su za 8.51% i 12.40%, veću čvrstoću pri pritisku, prema navedenom redosledu, u odnosu na referentnu pastu. Međutim, nakon 60 dana, primetan je blagi pad (tab. 7, sl. 8).

S porastom udela zeolita, smanjuje se čvrstoća pri pritisku pastā, CZ20 i CZ30, starosti 60 dana, u odnosu na čvrstoću referentne paste. Suprotno pomenutim pastama, uzorak CZ10 jedini je skoro dostigao vrednost čvrstoće pri pritisku referentne paste.

After 28 days of curing the results of compressive strength values have shown that pastes CZ10 and CZ20 by 8.5% and 12.40%, respectively, have had higher compressive strength than the reference sample. However, after 60 days a slight decline is shown, Tab. 7, Fig 8.

With an increase of zeolite content, the compressive strength of paste samples CZ20 and CZ30 at the age of 60 days has been reduced compared to the strength of the reference paste. In contrast, the sample CZ 10 has been the only one which has almost reached the compressive strength value of the reference sample.

Slika 8. Čvrstoće pri pritisku pastā C, CZ10, CZ20 i CZ30 starosti 28 i 60 dana
Figure 8. 28-day and 60-day compressive strengths of C, CZ10, CZ20 and CZ30 pastes

S ciljem utvrđivanja u kojoj meri je makroporoznost uticala na vrednosti čvrstoća, analiziran je redosled po kom se smanjuju vrednosti čvrstoća s redosledom po kom se povećava količina makropora za uzorke starosti 28 i 60 dana (tab. 5, 7). Dobijeni rezultati su prikazani u tabeli 8.

In order to determine how the amount of macropores has influenced the compressive strength values, the order of compressive strength decrease has been analysed in comparison with the order of macroporosity values increase for the samples 28 and 60 days old, Tabs. 5, 7. The obtained results are presented in Table 8.

Tabela 8. Korelacija između čvrstoće pri pritisku i makroporoznosti
Table 8. Correlation between compressive strength and macroporosity

	28 dana stari uzorci 28 days old samples	60 dana stari uzorci 60 days old samples
Pravac smanjenja čvrstoće pri pritisku The order of decrease of comp. strength values	CZ20→CZ10→C→CZ30	C(CZ10)→CZ20→CZ30
Pravac povećanja vrednosti makroporoznosti The order of increase of macroporosity values	CZ10→CZ20→CZ30→C	CZ30→CZ20→C(CZ10)

Analiza rezultata prikazanih u tabeli 8 pokazuje da postoji izvestan stepen korelacije za uzorke starosti 60 dana. Naime, uzorak CZ20 ima središnji položaj u oba analizirana niza, dok uzorci C i CZ10 imaju slične vrednosti čvrstoće pri pritisku i makroporoznosti. Zato imaju isti položaj u oba analizirana niza (tabela 8).

The analysis of the results presented in Table 8 has shown that there is a certain degree of correlation for 60 days aged samples. Namely, sample CZ20 has had a medial position in both analysed sequences, while samples C and CZ10 have similar values of compressive strength as well as microporosity. Therefore, they have taken the same position in both analysed sequences, Tab. 8.

4 ZAKLJUČCI

Na osnovu rezultata ovog rada mogu se izvesti sledeći zaključci:

- Prirodni zeolit, iz Igroša, Srbija, najvećim delom sastoji se od minerala klinoptilolita. Odnos Si/Al je 4.95. Specifična površina je 78.1586 m²/g.
- Rendgenostrukturalna analiza potvrdila je prisustvo minerala portlandita, etringita, C-S-H, C-A-H. Osim toga, u pastama s prirodnim zeolitom identifikovan je klinoptilolit za uzorke obe starosti. Semikvantitativna analiza intenziteta pikova portlandita, za uzorke pastā starih 28 dana, ukazuje na nedostatak korelacije između pravca u kom opada intenzitet pikova portlandita i pravca u kom raste sadržaj zeolita. Sličan odnos je

4 CONCLUSION

The following conclusions can be drawn from the results of this study:

- The main mineral of natural zeolite from Igroš, Serbia, is clinoptilolite. Ratio Si/Al is 4.95. Specific surface area is 78.1586 m²/g.
- XRD analysis of the pastes has confirmed the presence of minerals portlandite, ettringite, C-S-H, C-A-H. Additionally, clinoptilolite has been identified in pastes with zeolite, for both ages. Semiquantitative analysis of portlandite peak intensities, for paste samples 28 days old, has indicated the absence of correlation between the sequence of decrease of portlandite peak intensities and the sequence of

dobijen za uzorke starosti 60 dana. Postojanje *extraframework* katjona kao i jonsko-izmenjivačka sposobnost smatraju se odgovornim za sprečavanje rastvaranja portlandita.

- Na osnovu FTIR analize može se zaključiti da je dodavanje zeolita u cementnu pastu uticalo na sastav i strukturu C-S-H faze u toku procesa hidratacije. Kod pasta koje su sadržale zeolit zabeleženo je pomeranje vrednosti talasnih brojeva za paste CZ10, CZ20 (974.05 cm^{-1} , 981.09 cm^{-1} , prema navedenom redosledu) u poređenju s referentnom cementnom pastom, što se može pripisati opadanju stepena polimerizacije C-S-H faze. Nakon 60 dana hidratacije primetno je pomeranje absorpcione trake vezane za Si-O valentine vibracije Q^2 tetraedara C-S-H faza prema većim talasnim brojevima u poređenju s referentnom pastom. Ovo ukazuje na bolji stepen polimerizacije C-S-H strukture sa dodatkom zeolita i produženim vremenom hidratacije.

- Uzorci CZ20 i CZ30 starosti 60 dana imali su mnogo manju ukupnu poroznost u poređenju sa uzorcima C i CZ10. Uzorci CZ10, CZ20, CZ30 starosti 60 dana imali su manju ukupnu poroznost u poređenju sa uzorcima negovanim 28 dana. Kod svih uzoraka starosti 28 dana dominantne su mezopore. Kod uzoraka C i CZ10 i CZ30 starih 60 dana, dominantne su mezopore dok su za uzorak CZ20 dominantne makropore.

- Nakon 28 dana negovanja, vrednosti čvrstoća pri pritisku pokazuju da paste CZ10 i CZ20 imaju za 8.5% i 12.40%, respektivno, veće vrednosti čvrstoća pri pritisku u odnosu na referentnu pastu.

S porastom količine zeolita, čvrstoća pri pritisku uzoraka CZ20 i CZ30 starosti 60 dana, smanjena je u poređenju sa čvrstoćom referentne paste. Nasuprot tome, uzorak CZ10 jedini je koji je skoro dostigao čvrstoću referentnog uzorka.

ZAHVALNOST

U radu je prikazan deo istraživanja koje je pomoglo Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije u okviru tehnološkog projekta TR 36017 pod nazivom: „Istraživanje mogućnosti primene otpadnih i recikliranih materijala u betonskim kompozitima, sa ocenom uticaja na životnu sredinu, u cilju promocije održivog građevinarstva u Srbiji”.

increase of zeolite amount. Similar relation has been obtained for 60 days old samples. The *extraframework* cations and exchanged capacity have been held responsible for hindering portlandite dissolution.

- According to the performed FTIR analysis, it can be concluded that introduction of the zeolite phase in cement pastes has influenced composition and structure of the C-S-H phase during the process of hydration. The pastes with zeolite after 28 days of hydration have had the shift towards the lower wavenumber values for CZ10 and CZ20 pastes (974.05 cm^{-1} , 981.09 cm^{-1} , respectively) in comparison with the reference paste, which could be attributed to the decrease of polymerization level of the C-S-H phase. After 60 days of hydration, there has been the shifting of the absorption band related to the existence of the Si-O stretching vibrations of Q^2 tetrahedra of the C-S-H phase towards the higher wavenumber values in comparison with the reference paste. This indicates better polymerization of the C-S-H structure with the addition of zeolite with prolonged hydration time.

- Samples CZ20 and CZ30 at the age of 60 days have had a significantly lower total porosity compared to C and CZ10 samples. Samples CZ10, CZ20, CZ30 at the age of 60 days have had lower total porosity compared to the samples cured for 28 days. For all 28 days old samples mesopores are dominant. For C, CZ10 and CZ30 60 days old samples mesopores are dominant, while for CZ20 macropores are dominant.

- After 28 days of curing, the results of compressive strength values have shown that pastes CZ10 and CZ20 by 8.5 % and 12.40%, respectively, have had higher compressive strength than the reference sample.

With an increase of zeolite content, the compressive strength of paste samples CZ20 and CZ30 at the age of 60 days has been reduced compared to the strength of the reference paste. In contrast, the sample CZ10 has been the only one which has almost reached the compressive strength value of the reference sample.

ACKNOWLEDGEMENTS

The research work reported in this paper is a part of the investigation within the research project TR 36017 "Utilization of by-products and recycled waste materials in concrete composites in the scope of sustainable construction development in Serbia: investigation and environmental assessment of possible applications", supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia. This support is gratefully acknowledged.

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REZIME

PROCES HIDRATACIJE I ČVRSTOĆA PRI PRITISKU CEMENTNIH PASTA KOJE SADRŽE PRIRODNI ZEOLIT

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U ovom radu prikazani su rezultati studije ispitivanja uticaja prirodnog zeolita iz Igroša, Srbija, na proces hidratacije i čvrstoću pri pritisku portland cementnih pastā, kod kojih je jedan deo cementa zamenjen prirodnim zeolitom. Eksperimentalni deo istraživanja sastojao se iz tri faze. U okviru prve faze dat je hemijski sastav prirodnog zeolita i ispitana su teksturalna svojstva prirodnog zeolita i portland cementa. U drugoj fazi, spravljani su uzorci portland cementnih pastā koji sadrže 0%, 10%, 20% i 30% prirodnog zeolita u odnosu na masu cementa, i negovani su 28 i 60 dana. Potom su ispitana mineraloška svojstva i čvrstoće pri pritisku pastā. Proučavani su i produkti hidratacije kao i relativne promene potrošnje portlandita u toku procesa hidratacije pomoću rendgenske strukturne analize i infracrvene spektroskopije s Furijeovom transformacijom. Dodatno je metodom živine porozimetrije urađena karakterizacija strukture pora.

Ključne reči: prirodni zeolit, cementna pasta, produkti hidratacije, XRD, FTIR, živina porozimetrija, čvrstoća pri pritisku

SUMMARY

HYDRATION PROCESS AND COMPRESSIVE STRENGTH OF CEMENT PASTES CONTAINING NATURAL ZEOLITE

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This paper presents the results of the study examining the effect of natural zeolite from Igroš, Serbia, on the hydration and compressive strength of Portland cement based pastes, in which a part of cement has been replaced by natural zeolite. The experimental part comprises three stages. In the first stage, the chemical composition of natural zeolite and the textural properties of both natural zeolite and Portland cement have been examined. In the second stage, Portland cement based pastes incorporating 0%, 10%, 20% and 30% per weight of natural zeolite have been prepared and cured for 28 and 60 days. Finally, mineralogical properties and compressive strength of pastes have been examined. The products of hydration and relative changes of portlandite consumption throughout hydration process (28 and 60 days) have been studied by the means of X-ray diffraction and Fourier transform infrared spectroscopy. Additionally, mercury intrusion porosimetry has been used to characterise pore structure.

Key words: natural zeolite, cement paste, hydration products, XRD, FTIR, mercury intrusion porosimetry, compressive strength