KARAKTERISTIKE TRANZITNE ZONE BETONA NA BAZI LAKOG AGREGATA

CHARACTERISTICS OF LIGHTWEIGHT AGGREGATE CONCRETE INTERFACIAL TRANSITION ZONE

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1 UVOD

Proizvodnja konstrukcijskih betona s poboljšanim termoizolacionim svojstvima na bazi kvalitetnog lakog agregata (LA) proizvedenog od otpadnih materijala predstavlja novu, dodatnu vrednost koja utiče na racionalno korišćenje prirodnih resursa i upravljanje otpadom. S lakim agregatom mogu se uspešno proizvoditi betoni za monolitne konstrukcije kao i prefabrikovani elementi. Dobre strane upotrebe lakih agregata proizvedenih na ovaj način jesu:

- zamenjuju prirodne sirovine zbog čega se smanjuje količina otpadnog materijala na deponijama;
- povećavaju uštede u izgradnji i eksploataciji objekata smanjenjem opterećenja na temelje (do 25%), čime se povećava otpornost konstrukcije na dejstvo zemljotresa;
- povećavaju toplotno-izolaciona svojstva elementa konstrukcije.

Kao polazna sirovina za proizvodnju ove vrste agregata najčešće se koristi: zgura visokih peći, leteći pepeo, otpadno staklo, silikatni mulj, papirni mulj, itd. [4], koji po svojim karakteristikama uspešno konkurišu lakim agregatima dobijenim od prirodnih sirovina: vermikulit, perlit i glina.

1 INTRODUCTION

The production of construction concrete with enhanced thermal insulating characteristics based on quality lightweight aggregate (LWA) produced from waste materials, represents a new, additional quality which influences rational usage of natural resources and waste management [3,4]. Concrete for monolith constructions along with prefabricated elements can be easily produced with lightweight aggregate. Positive sides of the use of lightweight aggregate produced in this way are:

- Natural materials are replaced in this way, which results in reduced amount of waste material deposited in landfills
- There is a reduction in building expenses by reduction of deadweight of the structure (up to 25%) and increase of overall earthquake resistance
- Thermal insulating properties of construction elements are increased

Mostly used raw materials for production of LWA are: blast furnace slag, fly ash, waste glass, silicate sludge, paper sludge [4] etc., all of which successfully can replace LWA made from natural materials: vermiculit, perlite and clay.

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Beton na bazi lakog agregata ima u svežem i očvrslom stanju osobine drugačije od običnog betona. One su posledica osobina lakog agregata (mala zapreminska masa, dobre termoizolacione karakteristike, sposobnost da upijenu vodu koristi za negu betona u procesu očvršćavanja) [7] po kojim se razlikuje od osobina normalnog agregata. Osobine očvrslog betona na makronivou, na kom se definišu inženjerska svojstva betona, posmatraju se kao osobine homogenog materijala, dok se na mezonivou smatra da se sastoji od tri faze: 1) agregat 2) cementna pasta i 3) tranzitna zona (TZ) između ove dve faze. Uticaj TZ na čvrstoću i propustljivost betona veoma je velika. Teksturalna i mineraloška svojstva površine lakog agregata utiču na formiranje mikrostrukture u ovoj zoni. Iz ove činjenice je proistekao značaj proučavanja mikrostrukture formirane tranzitne zone, jer je prepoznato da interakcija zrna agregata s cementnom pastom u velikoj meri modifikuje osobine betona u pogledu čvrstoća, modula elastičnosti i propustljivosti za gasove i tečnosti [2]. Tranzitna zona koja se formira između agregata normalne težine i očvrslog cementnog kamena je porozna (u betonima normalne težine). Veća poroznost je pripisana „efektu zida", koji vodi ka smanjenju sadržaja zrna nehidratisanog cementa u poređenju s cementnom matricom, usled čega dolazi do rasta poroznosti [12a]. To znači da za isti vodocementni faktor u tranzitnoj zoni ima manje nehidratisanih zrna nego u cementnoj matrici. Ako je vodocementni faktor u celoj masi 0.4, u cementnoj matrici će biti 0.36 [12b].

Prema literaturnim podacima [10], formiranje tranzitne zone se odvija u nekoliko faza:

- prvo se formira film od vode na površini zrna agregata što dovodi do povećanja vodocementnog faktora;
- kasnije, kao i u cementnoj pasti, dolazi do rastvaranja kalcijum-sulfata i kalcijum-aluminata. Najveći deo zrna cementa sastavljan je od više minerala i na početku preovlađuju reakcije minerala C_3A i C_3S. U prvim momentima hemijske reakcije stvara se amorfni sloj bogat aluminijumom. Iz ovog sloja počinju da se razvijaju kristali etringita (AFt), a kada počne hidratacija tri kalcijum-silikata (C_3S), na kristalima AFt počinje rast kalcijum-siliko-hidrata (CSH) i popunjavanje praznog prostora. Na kraju ove etape formiraju se pore s prečnikom manjim od 1μm. Hidratacija se potom nastavlja rekristalizacijom AFt i formiranjem većih kristala. Uvećanje ovih kristala i kontinuiran rast CSH produkata na kraju dovodi do bolje popunjenosti prostora čvrstom materijom i smanjenjem poroznosti čime se poboljšava gustina i čvrstoća TZ [10];
- zbog većeg vodocementnog faktora u tranzitnoj zoni u odnosu na cementnu matricu, joni formiraju veće kristale i porozniju strukturu.

Proces hidratacije se takođe menja i pod uticajem superplastifikatora. Njihova uloga je da menjaju reološka svojstva svežeg betona [11] u interakciji, pre svega sa C_3A i njegovim produktima hidratacije. Oni takođe usporavaju proces hidratacije alita, a s povećanjem sadržaja C_3A, količina polimera koji se adsorbuje je veća [15].

Concrete based on LWA (LWAC) in its fresh and hard condition has qualities different from ordinary concrete. They come as the consequence of LWA properties (small apparent density, good thermo insulating properties and the ability to use absorbed water for internal curing during hardening process) [7] which makes it different from ordinary concrete. The characteristics of hardened concrete on macro level, which is used to define engineering characteristics of concrete, are seen as the characteristics of homogenous material, whereas it is considered that at mezo level there are three phases: 1) aggregate 2) cement paste (matrix) and 3) an interfacial transition zone (ITZ) which is between these two phases. The influence of ITZ to the strength and permeability of concrete is very high. Textual and mineralogical characteristics of the surface of LWA influence the formation of microstructure in this zone. Thus, it is important to study microstructure of the formed ITZ since it has been recognised that the interaction of aggregate with cement paste to a great extent modifies the characteristics of concrete when it comes to hardness, the module of elasticity and permeability to gases and liquids [2]. ITZ formed between the normal aggregate and hardened cement paste is porous (in ordinary concrete). The higher porosity is due to a "wall effect", leading to lower content of unhydrated cement grains as compared to bulk phase and consequently to an increased porosity [12a]. This means that the volume fraction of unhydrated cement grains is lower in ITZ than in cement matrix for the same water cement ratio. The reduction of water cement ratio in the bulk phase was expected to be about 0.36 compared to overall w/c of 0.4 [12b].

According to the data given in the reference [10] the formation of ITZ takes place through several stages:

- firstly, a water film is being formed on the surface of aggregate grain which leads to the increase of the water/cement ratio in the vicinity of aggregate grain;
- then, as it happens in the cement paste, in the ITZ occurs dissolving of calcium sulphate and calcium aluminate. Most cement grains are multi mineral and early reactions are dominated by C_3A and C_3S reactions. In the first moments of a chemical reaction there comes to the formation of an amorphous layer rich in aluminium. From this layer start the formation of ettringite crystals (AFt), and when the hydration C_3S starts, on crystals AFt start to grow CSH compounds and to fill porous space. At the end of this stage the diameter of the pores that are being formed is less than 1μm. Hydration then continues with recrystallization of AFt and the creation of bigger crystals. The enlargement of these crystals and the continuous growth of CSH compounds eventually bring to a better filling of space with products of hydration and decreased porosity which improve density and strength of ITZ [10];
- due to the higher water/cement ratio in ITZ than in cement matrix, the ions form large crystals and therefore porous structure appears.

The hydration process is also changing in the presence of superplastisizer. They change the rheology [11] of the fresh concrete by adsorbing preferably on the C_3A phase. They also adsorb on C_3A hydration products and retard alite hydration. With the increasing C_3A content of the cement the amount of polymer adsorbed is increasing. [15].

Tranzitna zona lakoagregatnog betona razlikuje se od TZ betona normalne težine, jer je porozan i upija vodu [16a]. Brzina upijanja vode zavisi od veličine i vrste pora, kao i od toga da li agregat formira gustu spoljašnju opnu (zatvorena poroznost) ili ne (otvorena poroznost). Laki agregat sa gustom spoljašnjom opnom formira neporoznu tranzitnu zonu. Može se zaključiti da agregat sa spoljašnjom opnom veće gustine utiče na tranzitnu zonu tako da postaje slična onoj koja se formira kod agregata normalne težine [2]. Kada opna nije velike debljine, cementna pasta može delimično da penetrira u LA kroz otvorene pore i na taj način omogući dobre mehaničke osobine između cementne matrice i agregata dok se u tranzitnoj zoni smanjuje vodocementni faktor i poroznost. Kod nekih vrsta lakih agregata s pucolanskim osobinama dolazi i do hemijske reakcije. Kada dolazi do hemijske reakcije, stvara se jaka veza između agregata i cementne matrice [13].

Procena teksturalnih svojstava tranzitne zone veoma je kompleksan proces. Scrivener K. [12a] prvi put je koristila SEM i EDS-a (u *backscatter* opciji). Drugi autori se bave isključivo analizom upijanja i otpuštanja vode zrna lakog agregata [4], a u poslednje vreme se nalaze i radovi vezani za određivanje mikrotvrdoće tranzitne zone.

Analizom teksturalnih svojstava tranzitne zone putem SEM-a, EDS-a i programa za analizu slike, mogu se dobiti informacije o promeni sastava ove zone i poroznosti. Nevolja je što je za izvođenje relevantnih zaključaka potreban veliki broj merenja, a ispitivanja zahtevaju posebnu pripremu uzorka i veoma dugo traju.

Merenjem mikrotvrdoće takođe mogu da se prate promene teksturalnih svojstava tranzitne zone u odnosu na ostatak cementne matrice [5,6]. Ovo je jedna od nekoliko metoda za direktno merenje bar nekih mehaničkih svojstava tranzitne zone. U cilju skeniranja TZ kod testa mikrotvrdoće koriste se veoma mala opterećenja s ciljem da se stvore veoma mali otisci, obično s dimenzijama od nekoliko mikrona [2]. Kvalitet informacija u pogledu poroznosti i sastava tranzitne zone pre svega zavisi od dimenzija tela koje utiskujemo u ispitivani uzorak i od kvaliteta pripreme površine u koju se izvodi utiskivanje [7], kao i od heterogenosti strukture na mikronivou. Naime, vrlo često najslabiji deo TZ nije fizička veza na površini između lakog agregata i cementne paste, već 5 do 10 μm unutar cementne paste. Na ovom rastojanju, najslabiji deo mogu biti kristali kalcijum-hidroksida određene orijentacije. Nažalost, ove stvari ponekad otežavaju pravilno tumačenje čvrstoća izmerenih na ovaj način.

U radu su dati rezultati ispitivanja sastava tranzitne zone korišćenjem SEM i EDS analize kao i merenjem mikrotvrdoće s ciljem da se ustanovi kako promena vrste veziva u betonu utiče na kvalitet TZ betona napravljenog od lakog agregata proizvedenog na bazi silikatnog, papirnog mulja i pepela.

Interfacial transition zone of lightweight aggregate is different from the ITZ of the ordinary concrete, since lightweight aggregate is porous and absorbs water [16a]. The rate of water absorption depends on the size and the type of pores, as well as whether aggregate have a thick outer shell (closed porosity) or not (open porosity). Lightweight aggregate with a thick outer shell forms high porosity ITZ zone. It can be concluded that increased density of the outer shell of the lightweight aggregate influences ITZ so that it becomes similar to the one which forms with the aggregates of normal weight [2]. When thick outer shell is not present cement paste can partially penetrate into lightweight aggregate through the open pores and in that way a good mechanical binding between matrix and aggregate can be enabled while water/cement ratio in the ITZ would decrease as well as porosity. In some types of LWA with pozzolanic properties it comes to chemical reactions in this zone. When chemical reaction is present a strong chemical bond between aggregate and cement paste matrix may develop [13].

Evaluation of textural features of ITZ is a very complex process. Scrivener K. [12a] used SEM and EDS (in backscatter option) for the first time. Other authors only carry out analysis of absorption and release of water of LWA [16a, 16b]. Lately there are papers and work related to determination of micro hardness of ITZ.

The analysis of textural features of ITZ with SEM, EDS and a program for analyzing pictures can give information about the change of structure of this zone and porosity. The trouble is that for coming to the relevant conclusions it is necessary to carry out a number of measuring. This type of testing requires a special preparation of a sample, which takes very long time.

The changes of textural features of ITZ compared to the cement paste matrix can be followed as well as by micro hardness measurements [5,6]. This is one of several methods which is able to measure directly at least some mechanical properties of the ITZ. In order to scan across the ITZ with micro hardness tests, very small load are used, in order to create very small indentation, typically with dimensions of a few microns [2]. The quality of information when it comes to porosity and structure of ITZ in the first place depends on the geometry of indenter and upon the surface preparation [7], as well as heterogeneous structure on the interface on a micro scale. Namely, very often the weakest part of the ITZ is not at the physical interface between LWA and cement paste, but rather 5 to 10 μm inside the paste. On that distance the weakest part could be specifically oriented calcium hydroxide crystals. Unfortunately these things sometimes prevent converting micro hardness measurements into meaningful strength values.

The paper gives the results of testing structure of ITZ by using SEM and EDS analysis as well as micro hardness values with the aim of determining how the change of a concrete binder influences the quality of ITZ of concrete made of LWA based on silicate sludge, paper mud and ash.

2 MATERIJALI I METODE

Za spravljanje konstrukcijskog betona korišćene su dve vrste lakog agregata: LA na bazi otpadnih materija (Termit a.d., iz Slovenije) i komercijalni laki agregat Leca-Laterlite (Italy). Najveći udeo u odnosu na ukupnu količinu lakog agregata imao je laki agregat napravljen od silikatnog mulja, mulja iz papirne industrije i pepela [4]. Silikatni mulj je nastao prosejavanjem peska na iskopu. Pre pečenja sirovinska masa je granulisana. Temperatura pečenja je 900^{o}C.

Upijanje vode i zapreminska masa samog zrna lakog agregata određene su na osnovu procedure date u standard SRPS EN 1097-6:2007.

Čvrstoće zrna LA određene su prema proceduri datoj u literaturi [8].

Na bazi ovog agregata i peska napravljene su četiri vrste betona sa sledećim komponentnim materijalima:

Cement: CEM I 42,5R i CEM II/B-M(S-V-L)32,5R (Lafarge-BFC, Srbija), *Leteći pepeo* (Termoelektrana „Nikola Tesla B" Obrenovac), *Metakaolin* („Metamax" – SAD)

Agregat: Sitan: prirodni rečni pesak (0/4 mm) i laki agregat, Leca (2/3 mm), Italija; Krupan: laki agregat (4/8 mm), proizvođač Termit d.d, Slovenija

Hemijski dodatak: Superplastifikator Sika Viscocrete 4000BP

Voda: Gradski vodovod

Sastav betonskih mešavina, zajedno sa oznakama, dat je u Tabeli 1.

2 MATERIALS AND METHODS

Two types of LWAs were used for the preparation of structural concretes: LWA produced from waste materials and commercial one Leca-Laterlite (Italy). The main part of total amount of LWAs was prepared of silica sludge, paper mud and ash [4]. The silica sludge remains after sand screening in quarry (Termit d.d., factory from Slovenia). Before firing the batch was granulated. Firing temperature was 900^{o}C.

Water absorption and apparent density were determined according to the procedure given in standard SRPS EN 1097-6:2007.

Mechanical strength of single LWAs granules was determined according to the procedure defined in [8].

Based on this LWAs and river sand, four types of structural concretes with the following consisting materials were made:

- *Cement*: CEM I 42,5R and CEM II/B-M (S-V-L) 32,5R (Lafarge-BFC, Serbia), Fly ashe (Power plant "Nikola Tesla B" Obrenovac), Metakaolin ("Metamax"-SAD)
- *Aggregate*: small fractions: river sand (0/4mm) and lightweight aggregates:, Leca (2/3mm), Italy; large fractions : lightweight aggregate (4/8mm), produced by Termit d.d, Slovenia
- *Admixture*: Superplastificator Sika Viscocrete 4000BP
- *Water*: tap water

The composition of structural concrete mixtures is given in Table 1.

Tabela 1. Sastav betonskih mešavina, komponente su u kg/m^3
Table 1. Composition of structural concrete mixtures, kg/m3

Vrsta betona Type of concrete	LSLL-1	LSLL-2	LSLL-4	LSLL-5
CEM I 42,5R	450	-	400	244
CEM II/B-M(S-V-L)32,5R	-	450	-	-
Voda / Water	180	180	180	183
Dodatna voda / Additional water	119,5	119,5	121,2	119,5
Rečni agregat / River aggregate (0/4mm)	749	749	771	760
Leca-Laterlite / LWA Leca-Laterlite (2/3mm)	90	90	91	90
Lakoagregatni agregat - Termit / LWATermit (4/8mm)	327	327	332	327
Leteći pepeo / Fly ash	-	-	-	97,6
Metakaolin / Metakaolin	-	-	-	24,4
Sika VSC 4000BP / Sika VSC 4000BP	2,25	3,15	2,0	2,56

Da bi se sprečila absorbcija vode u većoj meri iz cementne paste, što smanjuje količinu vode koja je neophodna za hidrataciju cementa, LA se pre spravljanja betonske mešavine natapa vodom u trajanju od 30 min (dodatna voda). Količina upijene vode osigurava da LA bude „površinski zasićen" vodom.

Ukupna poroznost i raspodela veličina pora u lakom agregatu Termit proizvedenom u Sloveniji (LWA-Termit), određena je živinom porozimetrijom (MIP). Male kocke, veličine oko 1cm^3, sušene su u sušnici 24 h na 105^{o}C i analizirane u uređaju Micromeritics Autopore IV 9500 model. Uzorci su analizirani u opsegu pritisaka od 0 do 414 MPa.

Karakteristike tranzitne zone određene su putem

In order to prevent great absorption of water from the cement paste, which decreases the water amount needed for the cement hydration, LWAs were being pre-wetted with water for 30 minutes (additional water). This amount of absorbed water ensures "surface-saturated" condition prior to mixing.

Total porosity and pore size distribution of lightweight aggregate Termit, produced in Slovenia (LWA-Termit), was determined by means of mercury intrusion porosity (MIP). Small block, approximately 1cm^3 in size, were dried in an oven for 24h at 105^{o}C and analysed on a Micromeritics Autopore IV 9500 model. Samples were analysed in the range of 0 to 414 MPa.

The characteristics of ITZ were determined by SEM

SEM i EDS analize u *backscatter* modu, na uređaju JSM–6460HV, JEOL, Tokyo, Japan. Slike poliranih delova uzorka u *backscatter* modu snimljene su za različita uvećanja. Mikrohemijska analiza je bila koncentrisana na određivanja odnosa elemenata u tranzitnoj zoni kao i na odnos elemenata u lakom agregatu u blizini tranzitne zone.

Test tvrdoće po Vikersu (HV 0.3) urađen je na uređaju za određivanje mikrotvrdoće HVS-1000A, uz upotrebu opterećenja od 2.942 N (0.3 kgf) u trajanju od 15 s. Dijagonale otiska nastale aplikacijom Vikersovog dijamantskog utiskivača na površinu merene su preko optičkog uređaja sa uvećanjem od 400× i s tačnošću od ±0.1 μm. Uzorci na kojim je rađeno merenje bili su u obliku kvadratnih ploča s paralelnim površinama ukupnih dimenzija 4 cm × 4 cm × 1 cm. Pored toga, izbegnuta su merenja na bilo kakvim površinskim defektima (kao šupljine). Urađeno je najmanje pet merenja na svakom uzorku. Tvrdoća po Vikersu, HV, dobijena je prema relaciji:

and EDS analysis in backscatter mode on the instrument JSM-6460HV, JEOL, Tokyo, Japan. Back-scattered images of polished sections were obtained in diverse magnifications. Micro chemical analysis was focused on chemical composition of ITZ as well as composition of LWA close to ITZ.

Vickers hardness test (HV 0.3) was carried out with a micro-hardness tester HVS-1000A, by applying indentation load of 2.942 N (0.3 kgf) during 15 s dwell time. The indentation diagonals made by Vickers diamond pyramid indenter on the surface were measured optically under the magnification of 400× and by the precision of ±0.1 μm. The samples used for the measurements were shaped as square plates with parallel opposite sides and overall dimensions of 4 cm × 4 cm × 1 cm. Furthermore, during the measurements any large surface defects (like voids) were avoided. At least, five micro-hardness measurements were performed on every sample. The Vickers hardness values, HV, were obtained by the following relation:

$$HV = \frac{2F\sin(\frac{\alpha}{2})}{e^2} = 1.8544\frac{F}{d^2}$$

gde je F [kgf] opterećenje utiskivača, α je ugao između dijagonala dijamantskog utiskivača u obliku piramide i iznosi 136 ^{o} i d[mm] jeste aritmetička sredina dužine dve dijagonale kod otiska.

where F [kgf] is the indentation load, α is the diamond pyramid indenter diagonal angle, equal to 136^{o}, and d [mm] is the arithmetic mean of two diagonal lengths of the indentation.

3 REZULTATI I DISKUSIJA

Silikatni mulj sadrži više od 60 mas % veoma finog silikatnog peska, feldspata i gline. Papirni mulj sadrži oko 38 mas % organskih materija kao i kalcit i kaolinit. Sagorevanjem organskih materija iz papirnog mulja u prisustvu glinenih minerala formira se porozna struktura. Prisustvo papirnog mulja utiče na formiranje značajne količine otvorene poroznosti u LA-Termit. Potvrda ovoga je vrednost ukupnog upijanja vode (34 mas %) i sposobnost da se skoro celokupna količina vode upije u prvih 5 min absorpcije. Podaci za brzinu upijanja vode kao i za ukupnu količinu upijene vode dati su u Tabeli 2.

3 RESULTS AND DISCUSSION

Silica sludge contains over 60 mass% very fine silica sand, feldspar and clay. Paper mud contains about 38 mass% of organic compounds as well as calcite and kaolinite. Combustion of organic compounds from paper mud in the presence of clay minerals formed porous structure. The presence of paper mud influenced the formation of significant amount of open porosity in LWA-Termit. The indication of it was overall water absorption (34 mass%) and capability to absorb almost all amount of water in the first 5 min of absorption. Data for water absorption rate and total water absorption as well as apparent density of single grain for both LWAs are given in Table 2.

The biggest amount of water was absorbed in the first 5minutes. The water absorption of LWA after 30 minutes is: for LWA-Termit (0/4mm) and for LWA Leca (2/3mm) is respectfully 33.2% and 12.1%, Table 2.

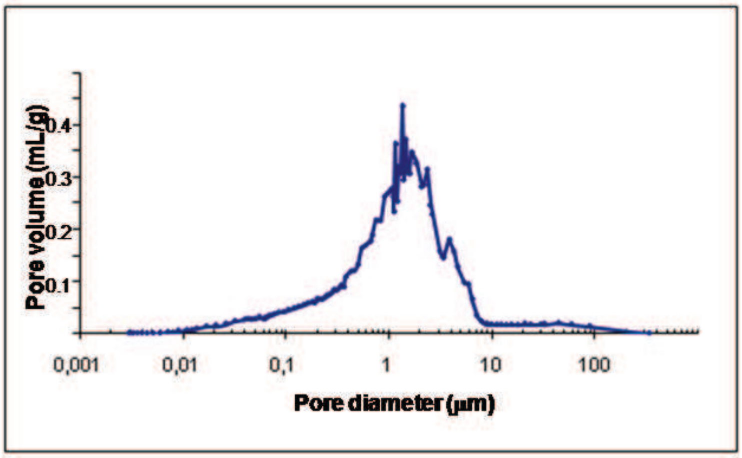
Tabela 2. Upijanje vode, zapreminska masa zrna i čvrstoća zrna
Table 2. Water absorption, apparent density and mechanical strength of LWAs grains

	5 min mas% mass%	15 min mas% mass%	30 min mas% mass%	60 min mas% mass%	120 min mas% mass%	Zap. masa Apparent density kg/m^3	Čvrstoća Strength MPa
LA -Termit (4/8mm) LWA Termit (4/8mm) mass %	32,3	32.8	33.3	33.4	33.9	1300	2.6
Leca Laterlite (2/3mm) Leca Laterlite (2/3mm) mass %	7,6	8,0	8,9	10,1	10,3	630	≥2,5

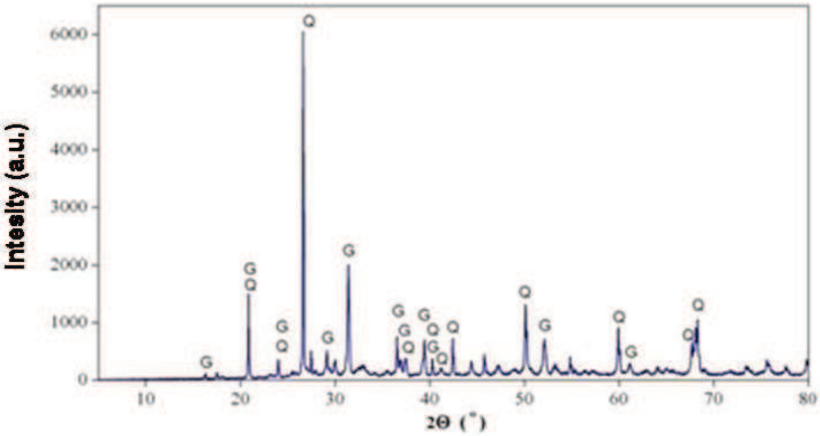
LA – Termit, slika1, ima veoma veliku otvorenu poroznost, Tabela 2. Raspodela veličina pora, slika 2, ukazuje na to da je dominantan prečnik pora oko 1µm, dok je ukupna poroznost 46.5 %. Ova veličina pora omogućava dodatnoj vodi da iz ovih i većih pora curi u TZ i učestvuje u procesu hidratacije cementne paste. Na osnovu vrednosti ukupne i otvorene poroznosti utvrđeno je da je zatvorena poroznost oko 12%.

LWA-Termit, Figure 1, has a very high open porosity, Table 2. Pore size distribution, Figure 2, indicates that dominant pore diameter is 1 µm, while total porosity is 46.5%. This size of the pores enables additional water from these and bigger pores to take part in the process of hydration of cement paste. Based on the values of total and open porosity it was determined that the closed porosity is around 12%.

Slika 1. Laki agregat-Termit
Figure 1. Llightweight aggregate-Termit



Slika 2. Raspodela veličina pora u LA-Termit
Figure 2. Pore size distribution in LWA-Termit



Slika 3. Rendgeno-strukturna analiza LA-Termit (Q- kvarc, G-gelenit)
Figure 3. XRD analysis of LWA-Termit (Q- quartz, G-gehlenite)

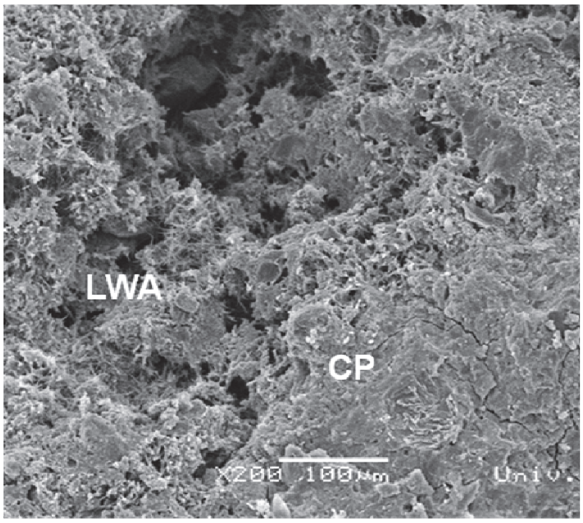
Mineraloški sastav LA-Termit (slika 3) ukazuje na prisustvo dva dobro iskristalisana minerala: gelenit i kvarc.

Na slici 4a predstavljeno je zrno LWA-Termit u betonu LSLL1, starosti 14 dana. Zapaža se da ne postoji oštra granica između zrna LA-Termit i cementne paste. Mikrostruktura poprečnog preseka LA-Termit, slika 4a, ukazuje na prisustvo šupljina i pukotina nastalih u toku procesa proizvodnje. Odsustvo guste spoljašnje opne, koja kontroliše absorpciju/desorpciju vode, trebalo bi da omogući dotok vode u cementnu pastu tokom hidratacije u slučaju desorpcije. Na ovaj način, slojevi cementne paste bliži površini LA postaju gušći za kraće vreme. U unutrašnjosti zrna LWA mogu se videti kristalne forme

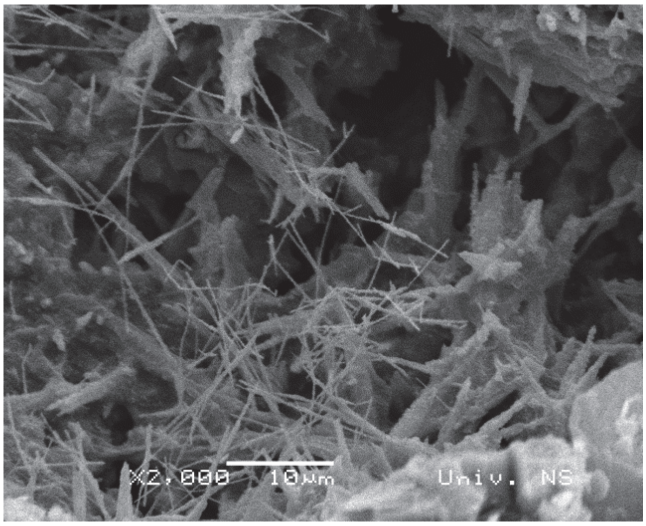
Mineralogical composition of LWA-Termit, (Figure 3) shows the presence of two well crystallized minerals: gehlenite and quartz.

Figure 4a shows a grain of LWA-Termit in concrete LSLL1, 14 days old. It is evident that there is no distinct difference between the LWA grain and the cement paste. The microstructure of the LWA-Termit grain cross section, Figure 4a, indicates the presence of voids and fissures formed during the manufacturing process. The lack of outer shell, which controls absorption/ desorption of water, should facilitate supply of cement paste with water in the case of desorption. In that way near-surface layer of the cement paste becomes denser in a shorter period of time. Inside of the LWA grain nano sized nanoveličine, slika 4b, koje podsećaju na etringit čija identifikacija u ovoj veličini nije laka. Nastale su najverovatnije nakon absorbcije vode u LWA, ali ovu pojavu treba dodatno istražiti.

crystal forms can be seen, Figure 4b. They remind of the structure of the ettringite (AFt) whose identification is difficult due to a size effect. The crystal forms were probably made after the absorption of water in LWA. However, this occurrence needs further investigation.



Slika 4a.SEM LA-Termit u betonu LSLL1, starost 14 dana (x200)
LWA-lak agregat, CP- cementna pasta
Figure 4a. SEM of LWA-Termit in LSLL 1 concrete,14 days old (x200),
LWA-lightweight aggregate, CP-cement paste



Slika 4b.SEM LA-Termit u betonu LSLL1, starost 14 dana (x200)

Figure 4b. SEM of LWA-Termitin LSLL 1 concrete,14 days old, (x2000)

Iako na poprečnom preseku LA-Termit nije utvrđeno da postoji gusta spoljašnja opna, razlike u sastavu površine i unutrašnjeg dela zrna jesu moguće. Po rastvaranju neizreagovanih zrna cementa, javlja se koncentracioni gradijent koji može dovesti do difuzije jona iz cementne paste do TZ i unutrašnjih delova LA. Najpokretljiviji joni u portland cementu su Na+, K+, Al(OH)4, Ca2+ [13].

Na osnovu EDS ispitivanja sadržaja elemenata u tranzitnoj zoni u opsegu od -10 µm (počinje u zrnu lakog agregata) do ≈ 90 µm (završava se u cementnoj pasti), i kriterijuma datih u radu [14], određuje se odnos atoma (Ca, Si, Al, Fe, S) i tip hidradisanog produkta prema sledećim formulama:

Although the shell structure is not seen in the cross section of LWA grain the differences in oxide composition of surface and inner part of the LWA are possible. After the dissolution of cement anhydrous grains, the appearance of concentrations gradient could induce a transport of ions by diffusion from cement paste to ITZ and inner part of LWA. The most mobile ions are Na^+, K^+, $Al(OH)_4^-$, Ca^{2+} in ordinary portland cement [13].

EDS examinations of element composition in ITZ ranged between -10 µm (starts in the grain of LWA) to ≈ 90 µm (finished in cement paste), and the criteria given in paper [14] determines the ratio of atoms (Ca,Si,Al,Fe,S) and type of hydrated products according to the following formulas:

C-S-H:	$0.8 \leq Ca/Si \leq 2.5$,	$(Al+Fe)/Ca \leq 0.2$
CH:	$Ca/Si \geq 10$,	$(Al+Fe)/Ca \leq 0.4$, $S/Ca \leq 0.04$
AFm[1]:	$Ca/Si \geq 4.0$,	$(Al+Fe)/Ca > 0.4$, $S/Ca > 0.15$

Na osnovu datih kriterijuma utvrđuje se koja jedinjenja preovlađuju u hidratnim formama (CSH, CH, AFm). Ako rezultati pokažu sastav koji je između ovih granica, smatra se da su formirane hidratne forme mešavina oksida. Ideja je bila da se napravi razlika između hidratnih oblika bogatih C-S-H jedinjenjima, jedinjenjima kalcijum-hidroksida (CH) i monosulfata (AFm) ili etringita (AFt). Primer proračuna je dat u tabelama 3-7 za različite betone starosti sedam dana.

Based on the given criteria, it is determined which compounds are dominant in hydration forms (CSH, CH, AFm). If the results show structure which is between these values then it is considered that the produced hydration forms are mixtures of oxides. The idea was to make difference between hydrates rich in C-S-H compounds, compositions reach in calcium hydroxide (CH) and monosulphate (AFm) or etringite (AF_t). The examples of calculations are given in Tables 3-7.

[1] AFm su u hidratisanom cementu produkti hidratacije C_3A (monosulfat i monokarbonat).

[1] Afm phases in hydrated cements are products of C_3A hydration (monosulfate and monocarbonate)

Na osnovu datih kriterijuma utvrđuje se koja jedinjenja preovlađuju u hidratnim formama (CSH, CH, AFm). Ako rezultati pokažu sastav koji je između ovih granica, smatra se da su formirane hidratne forme mešavina oksida. Ideja je bila da se napravi razlika između hidratnih oblika bogatih C-S-H jedinjenjima, jedinjenjima kalcijum-hidroksida (CH) i monosulfata (AFm) ili etringita (AFt). Primer proračuna je dat u tabelama 3-7 za različite betone starosti sedam dana. U Tabeli 3 je predstavljen hemijski sastav spoljašnje opne zrna LA-Termit. pre ugrađivanje u beton. Struktura LA-Termit u blizini TZ prikazuju tačke 1-3 u Tabeli 4, tačke 3 i 4 u Tabeli 5 i 6, tačke 4-6 u Tabeli 7. Ostale tačke pokazuju sastav tranzitne zone.

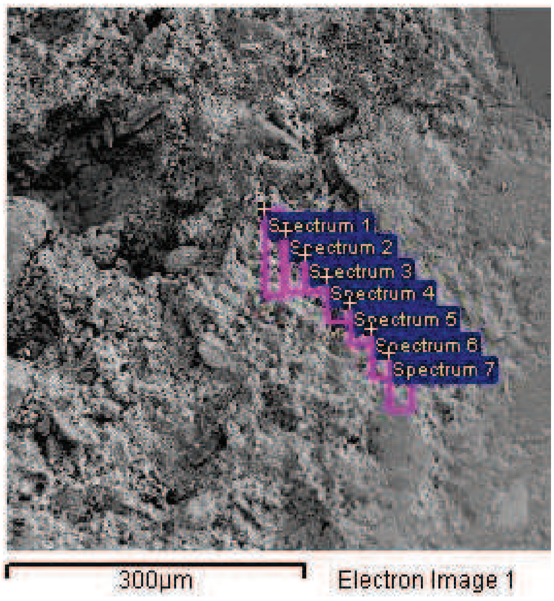
Based on the given criteria, it is determined which compounds are dominant in hydration forms (CSH, CH, AFm). If the results show structure which is between these values then it is considered that the produced hydration forms are mixtures of oxides. The idea was to make difference between hydrates rich in C-S-H compounds, compositions reach in calcium hydroxide (CH) and monosulphate (AFm) or etringite (AF_t). The examples of calculations are given in Tables 3-7. Chemical composition of the LWA-Termit grain outer shell before concrete preparation is presented in Table 3; in Table 4 points 1-3 show structure of the grain of LWA-Termit, in Tables 5, 6 these points are 3 and 4 while in Table 7 are 4-6. The rest of the points show the composition of ITZ.

Tabela 3. Rezultati EDS analiza spoljašnje opne zrna LA-Termit, mas%
Table 3. The results of EDS analysis of LWA -Termit grain outer shell, mass%

Spec.	C	O	Mg	Al	Si	K	Ca	Ti	Fe	Ca/Si	(Al+Fe)/Ca	S/Ca	
Range	24.6-45	47.9-50	0.57-0.86	4.43-12.9	0-18	0-0.4	11.2-30.2	0-0.3	0.46-0.74				
Aver.	23.2	32.6	0.68	8.45	9.4	0.2	21.2	0.1	0.61	**2.25**	**0.43**	-	mix

Analizom sastava tačaka 1 i 2 (spektri 1 i 2), Tabela 4, koje se nalaze u zrnu LA-Termit vidi se povećanje koncentracije kalijuma i gvožđa u odnosu na vrednosti u Tabeli 3. Odnos Ca/Si raste od tačke 1 do 3. Rast odnosa atoma Ca/Si upućuje na postojanje difuzije jona. Zbog velikih razlika u sastavu zrna LA-Termit, Tabela 3, teško je reći u kom smeru se dominantno odvija difuzija (od cementne paste ka zrnu LA ili obrnuto, ili u oba pravca).

By analyzing the composition of points 1 and 2 (spectrum 1 and 2), Table 4, which are in the LWA-Termit grain, a certain increase of the concentration of potassium and iron can be seen in comparison to values in Table 3. The increase of Ca/Si ratio indicates the diffusion of ions between cementous paste and LWA-Termit grain. Due to the large differences in the composition of LWA-Termit grain, Table 3, it is difficult to say in which direction the diffusion dominantly takes place (from cement paste to the LWA grain or vice versa, or that it maybe goes in both directions) [16b].



Slika 5. Mesta na kojim je urađena EDS analiza 7 dana starog betona LSLL-1
Figure 5. Spots on which EDS analysis was carried out for 7-day old concrete LSLL-1

Tabela 4. Rezultati EDS analize betona LSLL-1 starog 7 dana
Table 4. The results of EDS analysis of 7-day old concrete LSLL-1

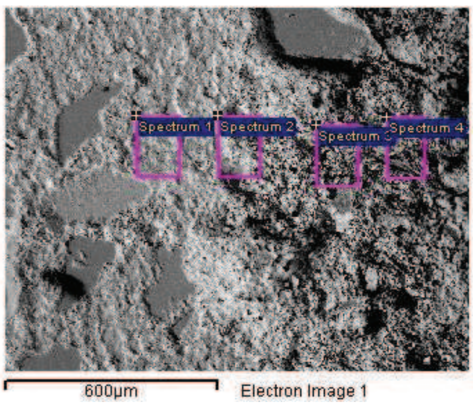
Spec	C	O	Mg	Al	Si	K	Ca	Ti	Fe	Ca/Si	Al+Fe/Ca	
Tačke u LA-Termit Points in LWA-Termit												
Spec 1	0.00	49.40	0.87	6.17	15.29	1.46	25.61		1.21	**1.67**	**0.29**	mix
Spec 2	13.81	43.07	0.78	5.44	9.89	0.64	25.22		1.15	**2.55**	**0.26**	mix
Spec 3	0.00	50.29	1.37	6.38	9.29	0.57	30.66	0.25	1.20	**3.00**	**0.25**	mix
Tačke u TZ Points in ITZ												
Spec 4	25.39	42.75	0.49	3.29	5.43	0.84	21.27		0.55	**3.91**	**0.18**	mix
Spec 5	16.78	47.54	0.77	2.43	5.07	1.20	25.92		0.29	**5.11**	**0.10**	mix
Spec 6	13.39	44.52	0.89	4.77	7.69	1.22	26.66		0.86	**3.47**	**0.21**	mix
Spec 7	14.65	45.36	0.43	4.46	13.79	0.79	19.79		0.73	**1.44**	**0.26**	mix

U betonu gde je kao vezivo korišćen CEM I 42,5R (LSLL1), na mestima 1 i 2, koja se nalaze u zrnu LWA-Termit, odnosi Ca/Si i (Al+Fe)/Ca bliski su vrednostima za CSH jedinjenja, Tabela 4. Moguće je da zidovi pora LWA služe kao termodinamički najpovoljnija mesta za formiranje CSH (heterogena nukleacija). U tačkama gde treba da se nalazi TZ (tačke 4-7, Tabela 4) dobijeno je povećanje vrednosti Ca/Si (tačke 4 i 5), a potom smanjenje (tačke 6 i 7). Ovi rezultati su u skladu s pretpostavljenom strukturom sloja TZ najbližeg zrnu agregata, jer ukazuju na povećanje koncentracije portlandita. Naime ovaj deo ITZ trebalo bi da bude u većoj meri sastavljen od kristala portlandita, a potom i od CSH, AFm i Aft jedinjenja.

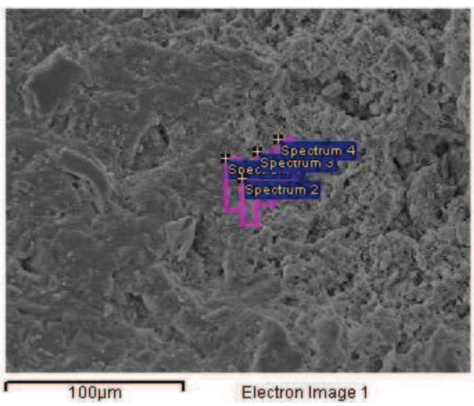
Poređenjem vrednosti udela elemenata, pre svega Ca i Si u betonu LSLL1, sa betonom napravljenim od manje količine istog cementa i većim vodocementnim faktorom (LSLL4-CEM I 42,5R), Tabele 4 i 6, uočava se povećanje koncentracije pomenutih, ali i drugih elemenata (kao Al i Fe) kod betona LSLL 4 (tacke 1 i 2- TZ zona). Prema navodima datim u literaturi [12b] vodocementni faktor ima mali uticaj na mikrostrukturu tranzitne zone. U uslovima povećanog vodocementnog faktora odvija se kontinualno rastvaranje i interakcija vode sa CSH. Posebno su visoke koncentracije elementa Si,

In concrete where CEM I 42,5R (LSLL1) was used as a binder, in points 1 and 2 (Table 4 spectrum 1 and 2), which are in LWA-Termit grain, the ratios Ca/Si and (Al+Fe)/Ca are close to the values for CSH compounds. It is possible that the walls of the LWA pores are used as thermodynamically most favourable places for the formation of CSH (heterogeneous nucleation). In points where there should be ITZ (points 4 - 7), there was an increase in value of Ca/Si (points 4 and 5), and then a decrease (points 6 and 7). These results are in accordance with the assumed structure of the layer closest to the grain of the LWA-Termit indicating the increase of mineral portlandit. Namely, this part of ITZ should be mostly composed of the portlandit crystals and CSH, AFm and Aft phases as well.

When comparing the values of the ratio of elements, first of all Ca and Si in concrete LSLL1, with concrete made from a less amount of cement and greater water cement ratio (LSLL4-CEM I 42,5R), Tables 4 and 6, it can be found that the concentration of the mentioned and other elements (Al and Fe) has increased in concrete LSLL4 (spectrum 1 and 2-ITZ zone). According to reference [12b] water to cement content have a minor influence on the microstructure of the ITZ. In the conditions of the increased water/cement ratio (LSLL 4)



Slika 6. Mesta na kojim je urađena EDS analiza za beton LSLL-2 starosti 7 dana
Figure 6. Spots on which EDS analysis was carried out for 7-day old LSLL-2



Slika 7. Mesta na kojim je urađena EDS analiza za beton LSLL-4 starosti 7 dana
Figure 7. Spots on which EDS analysis was carried out for 7-day old concrete LSLL-4

što može da se odrazi na povećanje mikrotvrdoće [9].

a continuous dissolution and an interaction of water with CSH happens. The Si content is especially high which could increase micro hardness values [9].

Tabela 5. Rezultati EDS analize betona LSLL-2 starog 7 dana
Table 5. The results of EDS analysis of 7-day old concrete LSLL-2

Spec	O	Mg	Al	Si	K	Ca	Fe	Ca/Si	Al+Fe/Ca	S/Ca	
Tačke u TZ Points in ITZ											
Spec 1	41.52	1.64	2.73	10.53	0.45	42.07	1.06	**4.00**	**0.09**	**-**	**mix.**
Spec 2	43.95	0.75	3.05	16.62	0.72	33.59	1.32	**2.02**	**0.13**	**-**	**CSH**
Tačke u LA-Termit Points in LWA-Termit											
Spec 3	40.58	0.94	4.95	16.70	0.94	33.78	2.12	**2.02**	**0.209**	**-**	**≈CSH**
Spec 4	40.53	0.64	4.13	28.42	1.89	22.48	1.91	**0.79**	**0.267**	**-**	**mix.**

Kod betona gde se kao vezivo koristio cement CEM II/B-M(S-V-L)32,5R, Tabela 5, odnosi elemenata upućuju da se u tranzitnoj zoni (tačka 2) kao i u zrnu LWA-Termit formiraju CSH strukture (Spektar 4, Tabela 5, Slika 6). Kalcijum-karbonat koji je kao dodatak prisutan u cementu, može da bude veoma efikasan kao nukleus za CSH strukture.

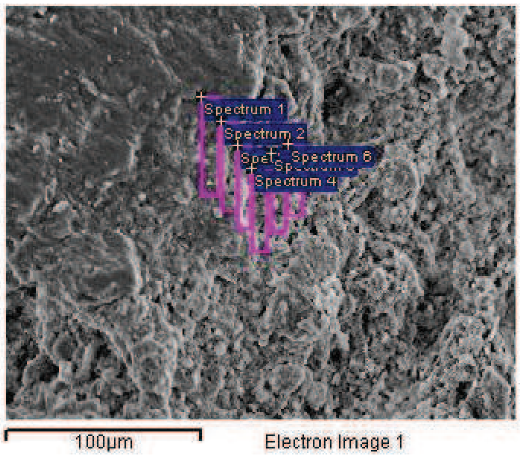
Kod betona LSLL 5 gde je u svojstvu dodatka dodan i metakaolin, dobijeni odnosi su slični rezultatima za prethodno navedene betone. Mnogo veću pažnju privlači smanjenje koncentracije aluminijuma, iako s metakaolinom treba da se poveća sadržaj elementa aluminijuma. U ovom slučaju bi na odvijanje procesa hidratacije mogao veću ulogu da odigra *polycarboxylate-based superplastificator* Sika VSC 4000BP. Absorbcija superplastifikatora na površini C_3A dovodi do usporavanja procesa hidratacije i povećavanja koncentracije elemenata Si i Ca, Tabela 7.

In concrete where cement CEM II/B-M (S-V-L) 32,5R was used as a binder, Table 5, the ratio of elements indicates that in ITZ (spectrum 2), as well as in the LWA-Termit grain, CSH structures are formed (Spectrum 4, Table 5, Figure 6). Calcium carbonate from cement is itself quite effective as a nucleus for C-S-H.

In concrete LSLL5 where metakaolin was used as an addition, the obtained ratios are similar to the results for the previously mentioned concretes. A much greater attention is brought to the decrease in concentration of aluminium, even though with metakaolin the presence of aluminium should be increased. In this case the development of the process of hydration could be influenced much more by polycarboxylate-based superplastificator Sika VSC 4000BP. With the absorption on the surface of C_3A compounds the process of the hydration is slower and the concentration of Si and Ca is increased, Table 7.

Tabela 6. Rezultati EDS analize betona LSLL-4 starog 7 dana
Table 6. The results of EDS analysis of 7-day old concrete LSLL-4

Spec	C	O	Mg	Al	Si	K	Ca	Ti	Fe	Ca/Si	(Al+Fe)/Ca	S/Ca	
Tačke u TZ Points in ITZ													
Spec 1		35.13	0.91	7.55	18.92	0.98	34.45		2.05	**1.82**	**0.279**		**≈CSH**
Spec 2		28.89		7.89	13.27	1.55	46.01		2.40	**3.47**	**0.224**		**mix.**
Tačke u LA-Termit Points in LWA-Termit													
Spec 3	0.00	31.46		3.58	7.85	0.61	49.39	3.53	3.59	**6.3**	**0.145**		**mix.**
Spec 4	11.67	35.09	0.62	4.14	14.27	0.48	32.17		1.55	**2.25**	**0.177**		**CSH**



Slika 8. Mesta na kojim je urađena EDS analiza za beton LSLL-5 starosti 7 dana
Figure 8. Spots on which EDS analysis was carried out for 7-day old concrete LSLL-5

Rezultati EDS analize ukazuju:

- da se udeo mešanih produkata hidratacije povećava dok prisustvo kalcijum- hidroksida nije veliko. Njegovo odsustvo kod betona gde se kao vezivo pored cementa koriste dodaci s pucolanskom aktivnošću (zgura, elektrofilterski pepeo, metakaolin) jeste očekivano (betoni LSLL2 i LSLL5) [5]. Međutim, njegovo odsustvo u drugim uzorcima nije očekivano. Takođe je interesantno da nema etringita, s obzirom na to što prisustvo sumpora nije registrovano. Objašnjenje za ovu pojavu može biti interakcija superplastifikatora s rastvornim sulfatnim jonima [15].

The results of EDS analysis show

- the presence of mixed products of hydration, whereas the crystals of calcium hydroxide are not registered in greater amount. The absence/small amount of calcium hydroxide in the samples of concrete where one of the components were pozzolanic materials was expected (concretes LSLL2 and LSLL5) [5]. However, its absence in other samples was unexpected. It is also interesting that there are no AFt considering that the presence of sulphur was not found. The explanation for this could be found in possible interaction of superplastificatros with soluble sulphate ions [15].

Tabela 7. Rezultati EDS analize betona LSLL-5 starog 7 dana
Table 7. The results of EDS analysis of 7-day old concrete LSLL-5

Spec	O	Mg	Al	Si	K	Ca	Ti	Fe	Ca/Si	Al+Fe/Ca	S/Ca	
Tačke u TZ Points in ITZ												
Spec 1	38.95	1.01	3.24	10.19	2.41	42.28		1.92	**4.15**	**0.12**	**-**	**mix.**
Spec 2	37.34		3.55	10.05	2.84	44.68		1.54	**4.45**	**0.11**	**-**	**mix.**
Spec 3	35.41		3.54	15.27	2.82	41.07		1.88	**2.69**	**0.13**	**-**	**≈CSH**
Tačke u LA-Termit Points in LWA-Termit												
Spec 4	45.44		3.46	9.16	2.57	37.75		1.62	**4.12**	**0.135**	**-**	**mix.**
Spec 5	43.21	1.27	5.15	11.63	1.37	35.74		1.62	**3.07**	**0.189**	**-**	**mix.**
Spec 6	44.26		4.70	13.59	1.28	33.80	0.77	1.60	**2.48**	**0.186**	**-**	**mix.**

- Visoke vrednosti za odnos atoma Ca/Si u TZ za betone LSLL 1 i LSLL5 upućuju na slabo prisustvo kalcijum-siliko-hidrata.
- Promene atomskih odnosa u zrnu LA-Termit u zonama koje su blizu TZ u odnosu na sastav pre ugrađivanja ukazuje na to da postoji difuzija jona između zrna i cementne paste. Osim toga, velika hrapavost površine zrna LWA-Termit olakšava proces kristalizacije produkata hidratacije. Ova pojava je prisutna kod svih analiziranih betona. U zrnu LA-Termit vrednosti odnosa Ca/Si manje su u odnosu na TZ: 1.67 (LSLL-1) i 1.82

- High Ca/Si ratio in ITZ for LSLL-1 and LSLL-5 signifies that the ITZ is relatively poor in calcium silicate hydrates.
- The changes of atomic ratios in the LWA-Termit grain in zones close to ITZ comparing to the composition before the insertion, indicates that there is a diffusion of ions between the grain and the cement paste. Besides, a great roughness of the surface of the LWA-Termit grain makes the process of crystallization of hydration products easier. This occurrence is present in all the analyzed concretes. In LWA-Termit grain the values of

(LSLL-4) što ukazuje na formiranje CSH strukture veće gustine.

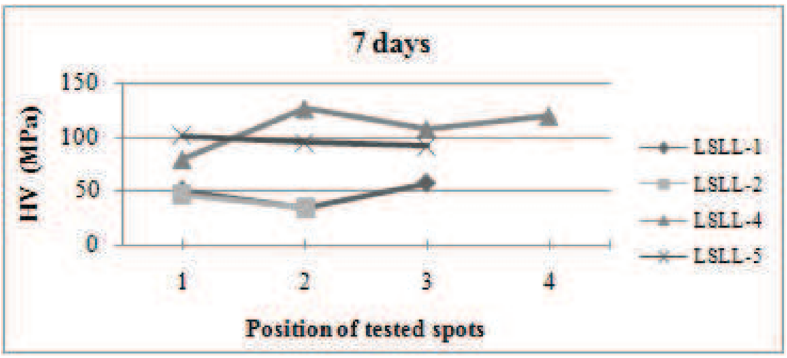
• Visoka vrednost odnosa atoma Ca/Si u TZ kod betona LSLL-1 i LSLL-5 upućuje na relativno mali sadržaj kalcijum-siliko-hidrata.

Na vrednosti mikrotvrdoće tranzitne zone utiče poroznost, vrsta i veličina kristala produkata hidratacije. Srednje vrednosti mikrotvrdoća izmerene u TZ za svaku vrstu betona predstavljene su u odnosu na udaljenost od površine agregata kao tačke 1, 2, 3 i 4. U uslovima merenja čiji rezultati su prikazani u ovom radu, može se smatrati da će vrednosti tvrdoće biti u najvećoj meri rezultat formirane poroznosti (naročito u početnom periodu hidratacije), veličine i vrste zrna kristala produkata hidratacije i veličine čestica neizreagovanog veziva. U tom smislu su interesantna poređenja prikazana na slikama 9 i 10 za sve četiri vrste betona. Na apscisi su sa 1-4 predstavljena ispitna mesta, pri čemu je sa 1 označeno ispitno mesto najbliže zrnu LA-Termit. Ako se uzmu u obzir dimenzije otiska (30-50 μm) i dimenzije TZ (max 100 μm), dâ se zaključiti da su tačke 3 i 4 već u cementnom kamenu dok na vrednost tvrdoće prve tačke utiče i blizina zrna agregata. Nakon sedam dana, tvrdoća TZ trebalo bi da bude najmanja za betone na bazi Portland cementa (LSLL1 i LSLL4), jer je pakovanje čestica cementa otežano zbog efekta zida. Čestice elektrofilterskog pepela u CEM II (beton LSLL-2) i metakaolina u betonu LSSL5 daleko lakše popunjavaju prostor u TZ što bi trebalo da poveća vrednosti mikrotvrdoće u odnosu na betone na bazi Portland cementa [1]. Međutim, od ovog pretpostavljenog trenda odstupaju vrednosti dobijene za beton LSLL4 (vezivo je bilo čist Portland cement – umanjena količina). Nije moguće dati pouzdano objašnjenje za ove pojave, ali je interesantan podatak da je koncentracija atoma silicijuma u TZ, nakon sedam dana, najveća kod LSLL4 i LSLL5 (tabele 6 i 7, slike 9 i 10). Istovremeno su vrednosti mikrotvrdoće najveće za ove vrste betona stare sedam dana (slike 9 i 10). U drugoj tački vrednosti se mnogo manje razlikuju za različite vrste betona za starost od 28 dana u odnosu na vrednosti dobijene nakon sedam dana. Ovaj podatak ukazuje na to da nestaju početne prednosti u boljem pakovanju čestica veziva u tranzitnoj zoni s procesom hidratacije.

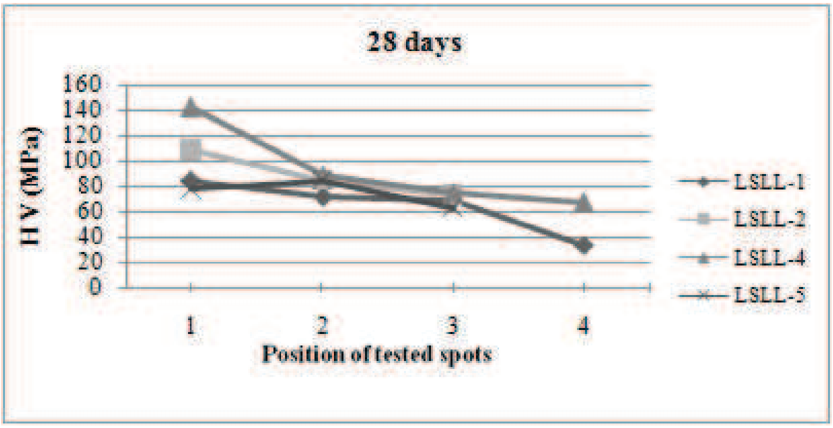
the ratio Ca/Si are smaller in comparison to ITZ: 1.67 (LSLL-1) and 1.82 (LSLL-4), which points to the formation of CSH structures with a greater density.

• High Ca/Si ratio is present in ITZ for LSLL-1 and LSLL-5 signifying that the ITZ is relatively poor in calcium silicate hydrates.

Porosity, type and size of crystals as products of hydration influenced the values of micro hardness of ITZ. The average micro hardness distribution measured in the ITZ of each concrete was plotted versus the distance from aggregate surface presented as points 1,2 ,3 and 4. In the conditions of measuring that gave results from this paper, it can be considered that the values of hardness would be mostly a result of the porosity formed (especially at the beginning of hydration), the size and type of crystal grain produced from hydration and the size of the unhydrated binder particles. Thus, the comparison given in Figures 9 and 10, for all 4 types of concrete is interesting. The *x* asics shows on tested spots 1-4, where 1 represents tested spot closest to the grain of aggregate. Considering the dimensions of the depth of penetration of indenter (30-50 μm) and dimensions of ITZ (max 100 μm), it brings to the conclusion that points 3 and 4 are already in the cement paste, whereas the value of hardness of the first point is influenced by the closeness of the aggregate grain as well. After 7 days, the hardness of ITZ, as predicted, turned out to be the lowest for the concrete based on Portland cement (LSLL1 and LSLL4), since the packing of particles is harder due to the wall effect. In the same time the particles of fly ashes in CEM II (concrete LSLL-2) and metakaolin in concrete LSLL-5 are far easier to fill in the space in ITZ, which should increase the values of micro hardness in comparison with concrete based on Portland cement [1]. However, this supposed tendency disagrees with the values obtained for concrete LSLL4 (binder was ordinary Portland cement-in a smaller amount than in LSLL1). It is impossible to give a reliable explanation for these occurrences. However, there is an interesting data which shows that the concentration of the atoms of silicon in ITZ, after 7 days, is the highest in LSLL4 and LSLL5, tables 6 and 7. At the same time their micro hardness values are greatest for 7 day old concrete Figures 9 and 10. At the second point the values differ much less for different types of concrete after 28 days, when compared to the values obtained after 7 days. This data implies that initial advantages disappear with the progress of hydration.



Slika 9. Mikrotvrdoća nakon 7 dana
Figure 9. Micro hardness values after 7 days



Slika 10. Mikrotvrdoća nakon 28 dana
Figure 10. Micro hardness values after 28 days

4 ZAKLJUČAK

Istraživanja teksturalnih i mikrostrukturnih promena tranzitne zone korišćenjem SEM i EDS metoda, kao i određivanje mikrotvrdoće, mogu da doprinesu boljem razumevanju veze između vrste formiranih produkata hidratacije i jačine veze između agregata i cementnog kamena. Međutim, uspostavljanje direktne veze između ovih vrednosti i makroosobina betona zahteva i dodatne načine karakterizacije osobina tranzitne zone. Rezultati EDS analize upućuju na to da:

- postoji razmena jona difuzijom između zrna lakog agregata Termit i cementne paste. Osim toga, veliki stepen hrapavosti površine zidova pora pomaže procesu heterogene kristalizacije produkata hidratacije i stvaranja CSH jedinjenja veće gustine;
- vrednosti odnosa Ca/Si velike su za tranzitnu zonu za sve tipove betona, ali su posebno velike za betone LSLL-1 i LSLL-5, što ukazuje na to da je TZ relativno siromašna kalcijum-siliko-hidratima;
- nije moguće dati pouzdanu vezu između sastava tranzitne zone i vrednosti mikrotvrdoće za različite betone.

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”.

4 CONCLUSION

The research of textural and micro structural changes of interfacial transition zone, with the use of SEM and EDS methods as well as determination of micro hardness values, can contribute better understanding of relation between the type of hydration products formed and the strength of the connection between the aggregate and the hardened cement paste. However, in order to make a direct connection between these values and the macro characteristics of the concrete additional ways of characterization of ITZ qualities are needed. The results of EDS analysis indicate that:

- There is an exchange of ions through diffusion between the grain of lightweight aggregate Termit and cement paste. Beside that a high level of the roughness of pore walls aids to the process of heterogeneous crystallization of the products of hydration and formation of CSH compounds with a greater density.
- Values of Ca/Si ratio are high interfacial transition zone for all types of concrete, but especially high for LSLL-1 and LSLL-5, signifying that the interfacial transition zone is relatively poor in calcium silicate hydrates
- It is impossible to make a reliable connection between the composition of the interfacial transition zone and the micro hardness values for different concretes.

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REZIME

KARAKTERISTIKE TRANZITNE ZONE BETONA NA BAZI LAKOG AGREGATA

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U radu je prikazana karakterizacija tranzitne zone između zrna lakog agregata proizvedenih na bazi otpadnih materijala i vezivnog kamena pomoću metoda SEM, EDS i određivanjem Vikersove tvrdoće. Na bazi SEM i EDS analize, kao i kriterijuma za odnose atoma elemenata koji ulaze u sastav nekih produkata hidratacije, može se dobiti uvid u preovlađujući sastav tranzitne zone. Vrednosti Vikersove tvrdoće za četiri vrste ispitanih betona se nakon sedam dana hidratacije nije moguće povezati sa gustinom pakovanja čestica veziva u tranzitnoj zoni sa velikom sigurnošću, a nakon dvadeset osam dana razlike u vrednostima nisu značajne.

Ključne reči: laki agregat, otpadni materijal, tranzitna zona

SUMMARY

CHARACTERISTICS OF LIGHTWEIGHT AGGREGATE CONCRETE INTERFACIAL TRANSITION ZONE

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The paper presents the characteristics of the interfacial zone between the lightweight aggregate produced on the basis of waste materials and binder matrix with the application of the methods SEM, EDS and the Vickers micro hardness test. On the basis of the SEM and EDS analysis, as well as the criteria for the atomic ratio of elements which compose some products of hydration, we can gain insight into the dominant composition of the interfacial zone. The values of the Vickers micro hardness test for four kinds of tested concrete after seven days of hydration is impossible to correlate with the composition of the interfacial zone in reliable way, whereas after twenty eight days the differences in values are insignificant.

Key words: lightweight aggregate, waste material, interfacial zone.