OTPORNOST MATERIJALA NA BAZI METALURŠKOG CEMENTA NA DEJSTVO KISELINA

RESISTANCE OF CEM III/B BASED MATERIALS TO ACID ATTACK

Ksenija JANKOVIĆ
Dragan BOJOVIĆ
Marko STOJANOVIĆ
Ljiljana LONČAR

ORIGINALNI NAUČNI RAD
ORIGINAL SCIENTIFIC PAPER
UDK: 666.946:620.193.4

1 UVOD

Trajnost konstrukcija veoma je važan parametar za njihovo projektovanje i izgradnju. Kada je beton izložen dejstvu kiselina prema EN 206-1 standardu, to znači da je u XA klasi izloženosti. Prema pH vrednosti, postoje tri klase: XA1, XA2 i XA3. Hemijska agresija takođe je definisana u Nacionalnom dodatku za agresivne sredine.

Otpornost betona na kiseline zavisi od: propustljivosti, utvrđivanja u kojoj meri kiseline mogu da prodru u beton, alkalnosti i hemijskog sastava cementne paste [7].

Mineralni dodaci, kao što su leteći pepeo [2, 8], silikatna prašina i šljaka iz visokih peći [3, 9] poboljšavaju hemijsku otpornost zbog nižeg sadržaja CH, smanjenog odnosa Ca i Si u hidratima kalcijum silikata i fine strukture pora koju oni proizvode u betonu [2, 7, 10]. Mehanička aktivacija izazvala je dugoročno povećanje čvrstoće i unapredila sve performanse građevinskih kompozita smanjenjem hemijskih i mikrostrukturnih nekompatibilnosti letećeg pepela [25].

Hemijska degradacija betona posledica je reakcija između sastojaka cementnog kamena, odnosno, kalcijum silikata, kalcijum aluminata, i posebno kalcijum hidroksida,

Dr Ksenija Janković, viši naučni saradnik
Institut IMS, Bulevar vojvode Mišića 43, 11 000 Beograd, Srbija, e-mail: ksenija.jankovic@institutims.rs
Mr Dragan Bojović, dipl.inž.građ., istraživač-saradnik, Institut IMS, Bulevar vojvode Mišića 43, 11000 Beograd, dragan.bojovic @institutims.rs
Marko Stojanović, dipl.inž.građ., istraživač-pripravnik, Institut IMS, Bulevar vojvode Mišića 43, 11000 Beograd, marko.stojanovic@institutims.rs
Ljiljana Lončar, dipl.inž.građ., stručni savetnik, Institut IMS, Bulevar vojvode Mišića 43, 11000 Beograd, ljiljana.loncar@institutims.rs

1 INTRODUCTION

Durability of structures is a very important parameter for its design and building. In the standard EN 206-1 acid attack means that concrete is in the XA exposure class. According to the pH value there are three classes: XA1, XA2 and XA3. Chemical attack is also defined in National code for aggressive environment.

Acid resistance of concrete depends on: the permeability, determination of the extent to which acids can penetrate into concrete, the alkalinity and the chemical composition of the cement paste [7].

Mineral additions, such as fly ash [2, 8], silica fume and blast-furnace slag [3, 9] improve chemical resistance because of the lower CH content, reduced Ca-to-Si ratio in calcium silicate hydrates and the refined pore structure they produce in concrete [2, 7, 10]. Mechanical activation promoted long-term strength enhancement and improved over-all performances of construction composites by minimizing the chemical and micro-structural incompatibility of fly ashes [25].

Chemical degradation of concrete is the consequence of reaction between the constituents of cement stone, i.e., calcium silicates, calcium aluminates, and

Ksenija Janković , Ph.D., senior research associate
IMS Institute, Bul. vojvode Mišića 43, 11 000 Belgrade, Serbia, e-mail: ksenija.jankovic@institutims.rs
Dragan Bojović, MSc, BScCE, research assistant, Institut IMS, Bulevar vojvode Mišića 43, 11000 Beograd, dragan.bojovic @institutims.rs
Marko Stojanović, MSc, research trainee, Institut IMS, Bulevar vojvode Mišića 43, 11000 Beograd, marko.stojanovic@institutims.rs
Ljiljana Lončar, BScCE, professional adviser, Institut IMS, Bulevar vojvode Mišića 43, 11000 Beograd, ljiljana.loncar@institutims.rs

kao i drugih sastojaka, sa određenim supstancama iz vode, rastvora zemljišta, gasova, para, i tako dalje.

Razvijen je kompjuterski model za predviđanje korozije u betonu usled agresije kiselinom [1].

Otpornost na dejstvo mlečne i sirćetne kiseline od velikog je značaja, kako za podove u životinjskim objektima, tako i za silose [6]. Mlečna kiselina, koja se nalazi u otpadnim vodama silosa sa sirćetnom kiselinom ima veću agresivnost [2]. Degradacija cementnih materijala od strane organske kiseline ispitivana je i poređena sa sirćetnom kiselinom [13].

Sulfatna degradacija se primarno sastoji od uticaja sulfatnih jona na cementni kamen. Sulfatni jon je uzrok jedne od najopasnijih korozija, jer izaziva pojavu ekspanzivnih jedinjenja, od kojih je najvažnija etringita, $C_3A \cdot 3CaSO_4 \cdot 32H_2O$, u obliku prizmatičnih kristala [17]. Beton oštećen amonijum sulfatom, oštećen je ne samo ekspanzijom, već i omekšavanjem cementnog matriksa.

Hemijske reakcije između sulfata i hidratisanih cementnih komponenti daju sledeće proizvode reakcije [14]: sekundarni gips ($CaSO_4 \cdot 2H_2O$), sekundarni etringit ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), tomasit ($CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$), brucit ($Mg(OH)_2$), M–S–H ($3MgO \cdot 2SiO_2 \cdot 2H_2O$) i silika gel ($SiO_2 \cdot xH_2O$).

Prema [27, 20], etringit i gips imaju ekspanzivni i destruktivni karakter, dok [22] tvrde da je doprinos gipsa ograničen, pri čemu ekspanzija etringita dominira. Formiranje tomasita dovodi do gubitka čvrstoće usled raspadanja proizvoda hidratacije koji nose čvrstoću (C–S–H) [28].

Rastvori amonijum-nitrata imaju snažan korozivni uticaj na cementne materijale [19, 23], što dovodi do raspada cementnih materijala prema sledećoj reakciji:

above all calcium hydroxide, as well as other constituents, with certain substances from water, solutions of soil, gases, vapours, etc.

A computer model for prediction of concrete corrosion by acid attack is developed in [1].

The resistance against lactic and acetic acids has major importance, both for floors in animal buildings and silos [6]. Lactic acid, which is found in silage effluents with acetic acid presents a higher aggressiveness [2]. Degradation of cementitious materials by organic acid were investigated and compared to the acetic acid [13].

Sulphate degradation primarily consists of the impact of sulphate ions toward cement stone. The sulphate ion is the cause of one of the most dangerous corrosions, i.e. the corrosion of expansion and swelling, because it initiates the occurrence of expansive compounds, the most important one - ettringite, $C_3A \cdot 3CaSO_4 \cdot 32H_2O$, in the shape of prismatic crystals [17]. The concrete damaged by ammonium sulphate, is not only damaged by expansion, but also by softening of the cement matrix.

The chemical reactions between sulphates and hydrated cement components yield the following reaction products [14]: secondary gypsum ($CaSO_4 \cdot 2H_2O$), secondary ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), thaumasite ($CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$), brucite ($Mg(OH)_2$), M–S–H ($3MgO \cdot 2SiO_2. \cdot 2H_2O$) and silica gel ($SiO_2 \cdot xH_2O$).

According to [27, 20] ettringite as well as gypsum have an expansive and destructive character, while [22] claim that the contribution of gypsum is limited while the expansion of ettringite dominates. Thaumasite formation leads to strength loss due to the decomposition of the strength-forming hydration products (C–S–H) [28].

Ammonium nitrate solutions are very corrosive to cementations materials [19, 23], which leads to dissolution of cement-based materials according to the following reaction:

$$2NH_4NO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2NH_3 + 2H_2O \qquad (1)$$

Amonijum-nitrat dekalcifikuje očvrslu cementnu pastu zbog uklanjanja kalcijum-hidroksida (Eq. (1)). Ovo dovodi do dekalcifikacije i rastvaranja drugih proizvoda iz očvrsle cementne paste, kao i do smanjenja pH vrednosti. Shodno tome, čelična armatura može brzo korodirati.

Ponašanje i trajnost cementne matrice u kiseloj sredini i njen uticaj na imobilizaciju metala u procesu stabilizacije / očvršćavanja toksičnih otpada ispitano je pomoću testa Köch-Steinegger [12,16]. Ovaj test se zasniva na evaluaciji degradacije materijala u određenom medijumu prema gubitku mehaničkih osobina, posebno otpornosti na savijanje, na koju više utiče stepen degradacije nego na čvrstoću na pritisak. Uslov za otpornost na agresivne rastvore je da zatezna čvrstoća maltera nije manja od 70% u odnosu na referentne prizme negovane u vodi.

Ispitivani su malteri s različitim tipovima mešanih i sulfatno otpornih cementa u svinjcima [15]. Otpornost betona od cementa s krečnjakom [21] i cementa s letećim pepelom [26] na dejstvo sulfata pokazuje da sulfatno otporni cementi poboljšavaju hemijsku otpornost bez povećanja troškova. Mešavine se mogu klasifikovati prema svom uticaju na povećanje otpornosti na sulfate na sledeći način: mešavine s portland cementom i

Ammonium nitrate decalcifies the hardened cement paste due to the removal of calcium hydroxide (Eq. (1)). This results in decalcification and dissolution of other products of hardened cement paste and leads to a reduction of the pH-value. Consequently, steel reinforcement corrosion may occur at an accelerated rate.

Behaviour and durability of cement matrices in acid media and its influence on metal immobilization in the stabilization/solidification process of toxic wastes was done using the Köch-Steinegger test [12,16]. This test is based on the evaluation of material degradation in a certain medium by its loss of mechanical properties, especially the flexural strength, which is more sensible to the degree of degradation in comparison with the compressive strength. Condition for resistance in aggressive solution means that flexural strength of mortar prisms is not less than 70 % of referent prisms cured in water.

Influence of pig slurry on mortar with different types of blended and sulphate-resistant cement was investigated [15]. Sulphate resistance of concrete with limestone cement [21] and fly ash cement [26] shows that sulphate-resistant cements improve the chemical resistance without cost increase. The mixtures could be krečnjakom, mešavine s metalurškim cementom, mešavine s pucolanskim cementom, mešavine s metalurškim cementom i silikatnom prašinom, i mešavine s pucolanskim cementom i silikatnom prašinom [4].

Analizirajući rezultate ispitivanja maltera i betona izloženih 10% Na_2SO_4, zaključeno je da je moguće da se dobije beton otporan na sulfatnu koroziju koristeći CEM II A-M (S-V) 42.5 N (minimalno 80% portland cementnog klinkera i do 20% dodatka zgure i silikatnog letećeg pepela). Beton s tom vrstom cementa nije otporan na rastvor amonijum-nitrata [11].

Upotreba visokog procenta zgure visokih peći (80%) smanjuje vreme nastajanja korozije uzoraka izloženih dejstvu sirćetne kiseline [18].

Značajno smanjenje degradacije betona usled kiselina zabeleženo je kod betona s metalurškim cementom [5].

Rad [24] predstavlja kritički pregled rezultata dobijenih mikroskopskim metodama.

U ovom radu je predstavljena otpornost maltera i betona s metalurškim cementom CEM III/B na koroziju uzrokovanu sulfatnom, nitratnom, ureom, mlečnom i sirćetnom kiselinom. Skenirajuća elektronska mikroskopija (SEM) korišćena je da se ispita efekat agresivnih rastvora na mikrostrukturu i mehaničke osobine maltera. Za ocenu, korišćen je metod Köch-Steinegger.

2 EKSPERIMENTALNI RAD

Prikazano je ispitivanje na malteru i betonu usled uticaja pet agresivnih sredina - sulfatna, nitratna, urea, mlečna i sirćetna kiselina. Hemijska otpornost je ispitana u skladu s postupkom Koch-Steinegger.

Uzorci su napravljeni korišćenjem cementa CEM III/B 32.5 N - LH/SR (20-34% portland cementni klinker i 66-80% dodatka zgure).

Hemijski sastav cementa prikazan je u Tabeli 1.

classified in order of increasing sulfate resistance as follows: mixtures with Portland limestone cement, mixtures with blast furnace slag cement, mixtures with pozzolanic cement, mixtures with BFC plus SF, and mixtures with pozzolanic cement plus SF [4].

Analysing testing results of mortar and concrete exposed to 10% Na_2SO_4 it was concluded that it is possible to get concrete resistant to sulphate corrosion using CEM II A-M (S-V) 42.5 N (minimum 80% Portland cement clinker and up to 20% addition of slag and silicate fly ash). Concrete with that cement type is not resistant to ammonium nitrate solution [11].

The use of high percentage of blast-furnace slag (80%) decreases the time to initiate the corrosion for specimen subjected to acetic acid attack [18].

A significant reduction of acid deterioration was recorded for blast-furnace slag concrete [5].

Paper presents critical review of results obtained with microscopic methods [24].

The resistance to corrosion caused by sulphate, nitrate, carbamide, lactic and acetic acid on mortar and concrete with CEM III/B was presented. Optical and scanning electron microscopy (SEM) was used to examine the effect of aggressive solutions on the microstructure and mechanical properties of mortar. The results of the durability using the Köch-Steinegger method have been presented in this paper.

2 EXPERIMENTAL WORK

Testing the influence of five aggressive solutions - sulphate, nitrate, carbamide, lactic and acetic acid on mortar and concrete were presented. The chemical resistance was tested according to the Koch-Steinegger method.

The specimens were made by using cement CEM III/B 32.5 N - LH/SR (20 - 34 % Portland cement clinker and 66-80% additions of slag). The chemical composition of cement is shown in Table 1.

Tabela 1. Hemijski sastav cementa
Table 1. Chemical composition of cement

SiO_2 (%)	31.82
Al_2O_3 (%)	7.36
Fe_2O_3 (%)	1.32
CaO (%)	44.21
MgO (%)	7.88
SO_3 (%)	2.92
S^{2-} (%)	0.42
Na_2O (%)	0.40
K_2O (%)	0.57
MnO	0.736
Gubitak žarenjem (%) Loss on ignition (%)	2.21
Cl- (%)	0.014

Prizme od maltera 10x10x60 mm sastoje se od: 450 g cementa, 1350 g standardnog peska u skladu sa EN 196-1 i 200 g vode. Referentne prizme su čuvane u destilovanoj vodi. Njihova čvrstoća pri pritisku i pri savijanju data je u Tabeli 2. Pre nego što su prizme bile

Mortar prisms 10x10x60 mm consist of: 450 g cement, 1350g standard sand according to EN 196-1 and 200g water. Referent prisms were stored in distilled water. Its compressive and flexural strength is given in the Table 2. Before the prisms were exposed to izložene agresivnim rastvorima, negovane su jedan dan u kalupu i 27 dana u vodi. Testiran je uticaj 10% rastvora Na_2SO_4, 2% rastvora NH_4NO_3, 10% uree, 5% rastvora mlečne kiseline i 2% rastvora sirćetne kiseline na malter. Čvrstoća pri pritisku i čvrstoća pri savijanju određena je posle 28 i 56 dana čuvanja u agresivnim rastvorima.

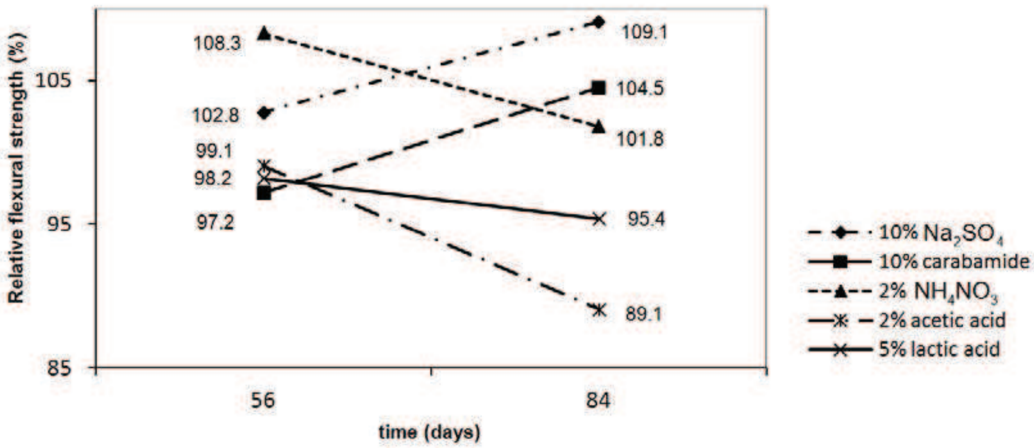
Na Slici 1-2, prikazani su rezultati ispitivanja kao prosečna vrednost od tri ispitana uzorka.

aggressive solutions, they were cured 1 day in the mould and 27 days in water. The influence of the 10 % Na_2SO_4 solution, 2 % NH_4NO_3 solution, 10% carbamide, 5% lactic acid solution and 2% acetic acid solution were tested. Compressive and flexural strength were determined after 28 and 56 days of storage in the aggressive solution.

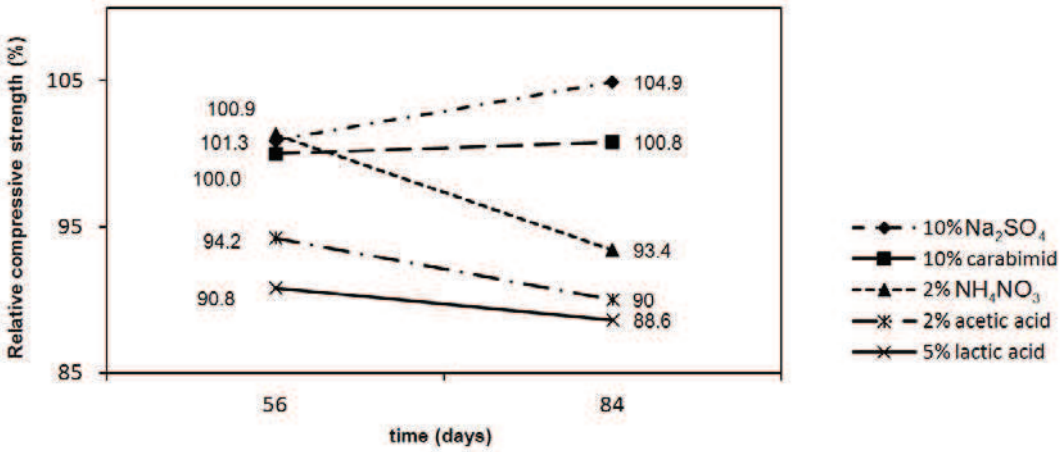
The results, as an average value of three specimens, are given in the Figures 1-2.

Tabela 2. Pritisna i savojna čvrstoća referentnog maltera
Table 2. Compressive and flexural strength of referent mortar

Vreme (dani) Time (days)	28	56	84
Čvrstoća pri pritisku (MPa) Compressive strength (MPa)	38.4	44.5	47.2
Čvrstoća pri savijanju (MPa) Flexural strength (MPa)	10.8	10.9	11



Slika 1. Relativna čvrstoća pri savijanju maltera u odnosu na vreme odležavanja u agresivnom rastvoru
Figure 1. Relative flexural strength of mortar vs. time in aggressive solution

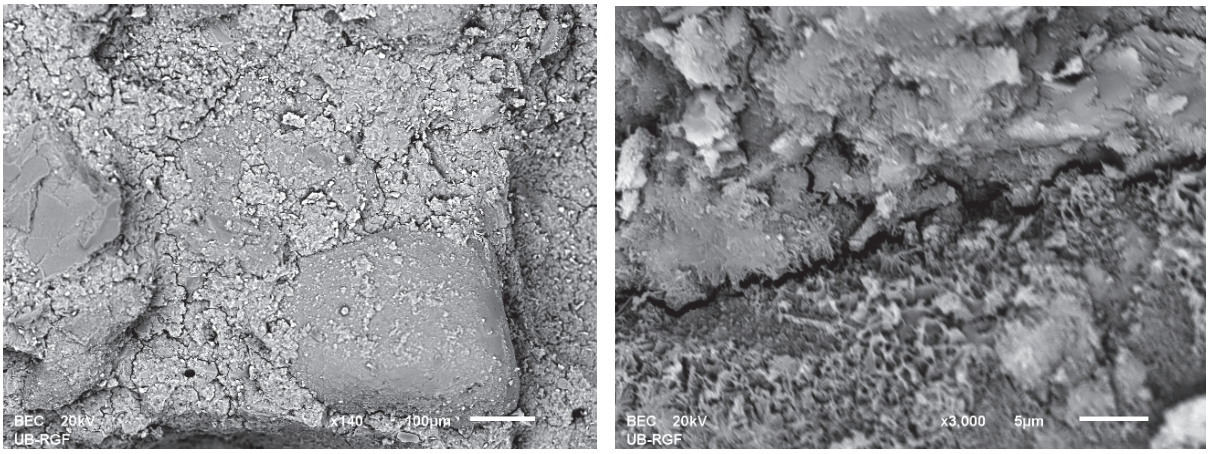


Slika 2. Relativna čvrstoća pri pritisku maltera u odnosu na vreme čuvanja u agresivnom rastvoru
Figure 2. Relative compressive strength of mortar vs. time in aggressive solution

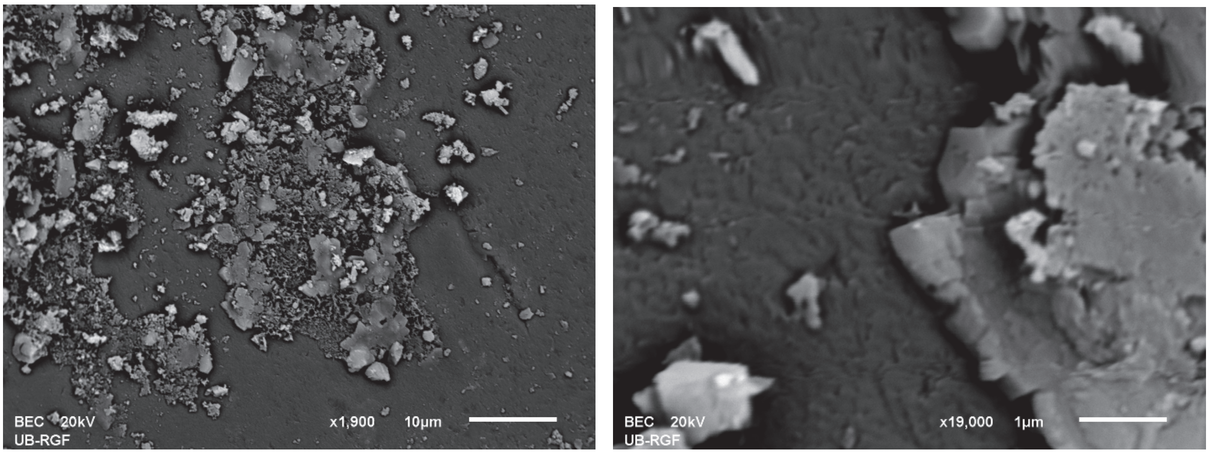
Smanjena čvrstoća pri savijanju uočena je kod uzoraka koji su čuvani u mlečnoj i sirćetnoj kiselini. Skenirajuća elektronska mikroskopija (SEM) korišćena je da se ispita efekat agresivnih rastvora na mikrostrukturu i mehaničke osobine maltera.Tranzitna zona kvarcnog

Decrease of flexural strength was seen on specimens' immersion in lactic and acetic acid solutions. Optical and scanning electron microscopy (SEM) was used to show the effect of those aggressive solutions on the microstructure and mechanical properties of peska i C-S-H faze kod referentnog maltera prikazana je na Slici 3. Uzorci izloženi 2% rastvoru sirćetne kiseline prikazani su na Slici 4. Uzorci izloženi 5% rastvoru mlečne kiseline prikazani su na Slici 5.

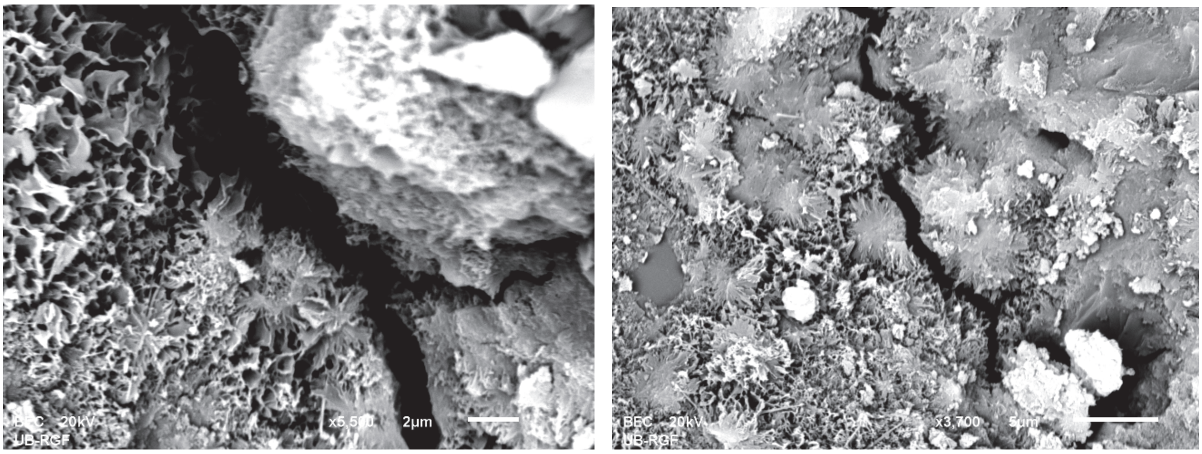
mortar. Transition zone between quartz grain and C-S-H phase on referent mortar is shown on Figure 3. Specimens exposed to 2% acetic acid solution are shown on Figures 4. Specimens exposed to 5 % lactic acid solution are shown on Figures 5.



Slika 3. SEM slika – Tranzitna zona kvarcnog peska i C-S-H faze
Figure 3. SEM image - Transition zone between quartz grain and C-S-H phase



Slika 4. SEM slika – Uzorci izloženi 2% rastvoru sirćetne kiseline
Figure 4. SEM image - Specimens exposed to 2% acetic acid solution



Slika 5. SEM slika - Uzorci izloženi 5% rastvoru mlečne kiseline
Figure 5. SEM image - Specimens exposed to 5 % lactic acid solution

U drugoj fazi ispitivane su dve vrste betona. Uzorci su napravljeni sa istim cementom kao malter - CEM III / B 32,5 N - LH / SR, prirodni agregat (D_{max} = 16 mm) iz reke Morave u Srbiji, superplastifikator (0,8%) i voda. Informacije o sastavu betona prikazane su u Tabeli 3. Količine komponentnih materijala usvojene su za dobijanje betona iste konzistencije.

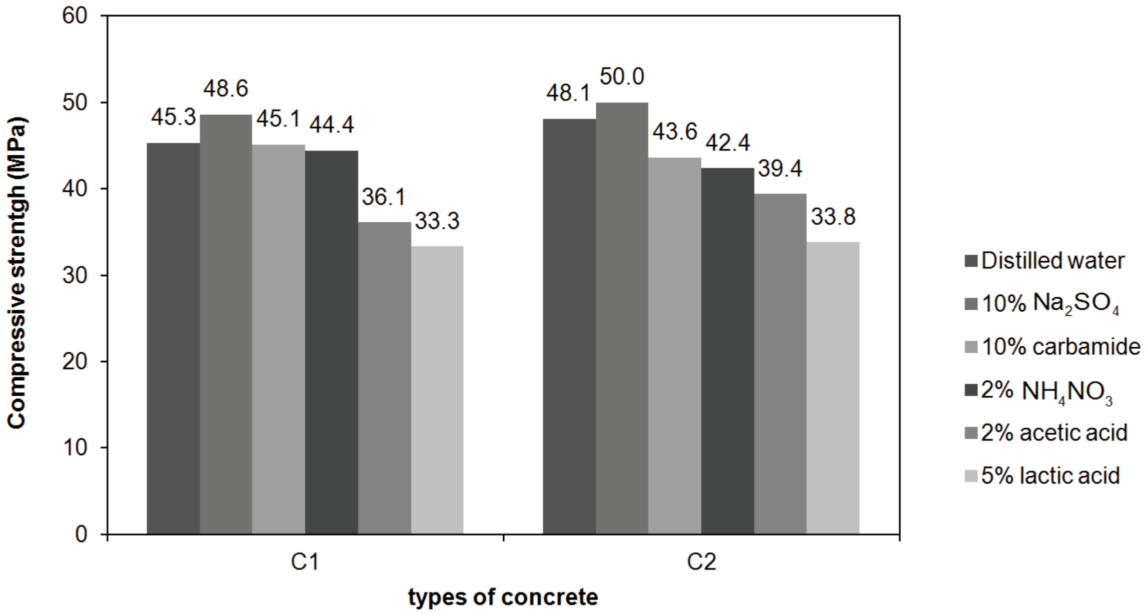
In the second phase two types of concrete were tested. The specimens were made with the same cement as mortar – CEM III/B 32.5 N – LH/SR, natural aggregate (D_{max}=16 mm) from river Morava, Serbia, super plasticizer (0.8%) and water. Information about composition of concrete is shown in Table 3. Amounts of component materials were adopted to obtain concrete with the same consistency.

Tabela 3. Količine komponentnih materijala betona
Table 3. Quantities of component materials of concrete

Vrsta betona Type of concrete	C1	C2
Cement (kg/m^3) Cement (kg/m^3)	390	420
Agregat (kg/m^3) Aggregate (kg/m^3)	1830	1813
Voda (kg/m^3) Water (kg/m^3)	147	147
Dodatak (kg/m^3) Admixture (kg/m^3)	3,1	3,4

Pre nego što su kocke 7×7×7 cm (minimalna dimenzija uzoraka veća od 4 x D_{max}) bile izložene agresivnim rastvorima, negovane su jedan dan u kalupu i 27 dana u vodi. Čvrstoća uzoraka pri pritisku ispitivana je nakon 28 i 84 dana (56 dana odležavanja u agresivnim rastvorima i referentnog betona u vodi). Na Slici 6 prikazani su rezultati ispitivanja kao prosečne vrednosti od tri uzorka.

Before the cubes 7×7×7 cm (minimum specimen dimension greater than 4·D_{max}) were exposed to aggressive solutions, they were cured 1 day in the mould and 27 days in water. Compressive strength of specimens was tested after 28, and 84 days (56 days of storage in the aggressive solutions and referent concrete in water). The results, as an average value of three specimens, are given in the Figure 6.



Slika 6. Čvrstoća betona pri pritisku nakon 84 dana
Figure 6. Compressive strength of concrete after 84 days

Relativna čvrstoća pri pritisku prikazana je u Tabeli 4.

Relative compressive strength is shown in the Table 4.

Tabela 4. Relativna čvrstoća betona pri pritisku posle 56 dana u agresivnom rastvoru
Table 4. Relative compressive strength of concrete after 56 days in aggressive solution

Relativna čvrstoća pri pritisku (%) Relative compressive strength (%)	10% Na_2SO_4	2% NH_4NO_3	10% karbamid - urea 10% carbamide	5% rastvora mlečne kiseline 5% lactic acid solution	2% sirćetne kiseline 2% acetic acid
C1	107.3	98.0	99.6	73.5	79.7
C2	104.0	88.1	90.6	70.3	81.9

3 DISKUSIJA I ZAKLJUČAK

Posle 56 dana odležavanja prizmi od maltera u 10% rastvoru Na_2SO_4, čvrstoća pri savijanju prizmi je bila 9,1% veća nego kod kontrolnih uzoraka, dok je čvrstoća prizmi pri pritisku dostigla 104,9% vrednosti referentnih uzoraka negovanih u vodi. Posle 56 dana u 10% rastvoru uree, čvrstoća prizmi od maltera pri savijanju bila je 4,5% veća, ali je čvrstoća pri pritisku bila ista kao i kod kontrolnih uzoraka. Treći agresivan rastvor - 2% NH_4NO_3 veoma je korozivan za cementne materijale, ali je čvrstoća pri savijanju uzoraka koji su negovani 56 dana u njoj bila 1,8% veća nego kod referentnih uzoraka. Čvrstoća pri pritisku smanjena je za 6,6%. Sledeći agresivan rastvor - 2% sirćetne kiseline takođe je veoma korozivan za cementne materijale. Čvrstoća pri savijanju uzoraka koji su odležali 56 dana u tom rastvoru bila je manja za 10,9%. Čvrstoća pri pritisku dostigla je 90,0% vrednosti kontrolnih uzoraka. Rezultati ispitivanja uzoraka koji su odležali u 5% rastvoru mlečne kiseline su sledeći: nakon 56 dana u agresivnom rastvoru imali su smanjenu čvrstoću pri savijanju za 4,6%, a čvrstoća pri pritisku bila je 88,6% referentnog maltera.

Analizirajući rezultate čvrstoće pri savijanju prizmi napravljenih od maltera koje su izložene agresivnim rastvorima i kontrolnih uzoraka koji su negovani u vodi, može se zaključiti da je CEM III / B 32,5 N - LH / SR otporan na uticaj svih rastvora kojima su tretirani, jer je po Koch-Steinegger metodi uslov za otpornost na agresivne rastvore taj da čvrstoća pri savijanju prizmi od maltera treba da bude manja od 70% vrednosti za referentne prizme negovane u vodi.

Upoređujući rezultate čvrstoće pri pritisku betona napravljenih sa istim cementom, može se uočiti da uzorci, nakon 56 dana potapanja u rastvor sulfata, nitrata, uree, mlečne i sirćetne kiseline, imaju čvrstoću pri pritisku veću od 70% vrednosti referentnih uzoraka koji su negovani u vodi. Pokazano je da su mlečna i sirćetna kiselina veoma agresivni rastvori. Čvrstoća pri pritisku betona C1 izloženog 5% rastvoru mlečne kiseline dostigao je 73,5% vrednosti referentnog betona, dok je beton C2 negovan u istom rastvoru imao 70,3% čvrstoće uzoraka negovanih u vodi. Čvrstoća pri pritisku betona koji je odležao 56 dana u 2% rastvoru sirćetne kiseline smanjen je za oko 20% u odnosu na kontrolne uzorke betona negovanih u vodi.

Analizirajući rezultate ispitivanja maltera i betona izloženih sledećim rastvorima: 10% Na_2SO_4, 2% NH_4NO_3, 10% uree, 5% mlečne kiseline i 2% sirćetne

3 DISCUSSION AND CONCLUSION

After the 56 days in the 10 % Na_2SO_4 solution flexural strength of mortar prisms was 9.1 % greater than control specimens while compressive strength had 104.9 % value of referent specimens cured in water. After 56 days in 10% carbamide solution, flexural strength of mortar prisms was 4.5 % greater but compressive strength was at the same level as for control specimens. The third aggressive solution – 2 % NH_4NO_3 is very corrosive to cementations materials but flexural strength of the specimens cured 56 days in it was 1.8 % greater than referent. The compressive strength was reduced 6.6 %. The next aggressive solution – 2% acetic acid is also very corrosive to cementations materials. Flexural strength of the specimens cured 56 days in that solution was reduced 10.9%. Compressive strength reached 90.0 % of control specimens. Results of testing specimens' immersion in 5% lactic acid solution were: after 56 days in aggressive solution the flexural strength decreased 4.6 % and compressive strength was 88.6 % of referent mortar.

Analyzing flexural strength of mortar prisms exposed to aggressive solutions and control specimens stored in water, it can be concluded that CEM III/B 32.5 N – LH/SR is resistant to the influence of all treated solutions because the condition for resistance in aggressive solution is that the flexural strength of mortar prisms should be no less than 70 % of referent prisms cured in water according to Köch-Steinegger method.

When comparing the results of the compressive strength of concrete made with the same cement it can be seen that specimens, after 56 days immersion in sulphate, nitrate, carbamide, lactic and acetic acid, have more than 70% value of referent specimens cured in water. It was shown that lactic acid and acetic acid are very aggressive solutions. The compressive strength of concrete C1 exposed to 5% lactic acid solution reached 73.5 % of referent concrete, while concrete C2 cured in the same solution had 70.3 % of strength of the specimens cured in water. The compressive strength of concrete immersed 56 days in 2% acetic acid solution decreased about 20 % compared to control concrete cured in water.

Analysing the testing results of mortar and concrete exposed to 10% Na_2SO_4, 2% NH_4NO_3, 10% carbamide, 5% lactic acid and 2% acetic acid solution, it can be concluded that it is possible to get concrete resistant to that type of chemical corrosion using CEM III/B 32.5 N –

kiseline, može se zaključiti da je moguće dobiti beton otporan na taj tip hemijske korozije koristeći CEM III / B 32,5 N - LH / SR. Ovi rezultati se podudaraju sa istraživanjima uticaja zgure iz visoke peći na otpornost betona na organske kiseline ili dejstva sulfata [5].

ZAHVALNOST

U radu je prikazan deo istraživanja koje je pomoglo Ministarstvo za nauku i tehnološki razvoj 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”.

LH/SR. These results match with research of the influence of blast-furnance slag on the resistance of concrete against organic acid or sulphate attack [5].

ACKNOWLEDGMENTS

The 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 for Science and Technology, Republic of Serbia. This support is gratefully acknowledged.

4 LITERATURA
REFERENCE

[1] Beddoe, R. E., Dorner, H. W., Modelling acid attack on concrete: Part I. The essential mechanisms, Cement and Concrete Research, 35, (2005), 2333–2339

[2] Bertron, A., Duchesne, J., Escadeillas, G., Attack of cement pastes exposed to organic acids in manure, Cement and Concrete Composites, 27, (2005), 898–909

[3] Bertron, A., Escadeillas, G., Duchesne, J., Cement pastes alteration by liquid manure organic acids: chemical and mineralogical characterization, Cement and Concrete Research, 34, (2004), 1823–1835

[4] Girardi, F., Vaona, W., Di Maggio, R., Resistance of different types of concretes to cyclic sulfuric acid and sodium sulfate attack, Cement & Concrete Composites, 32, (2010), 595–602

[5] Gruyaert, E., Van den Heede, P., Maes, M., De Belie, N., Investigation of the influence of blast-furnace slag on the resistance of concrete against organic acid or sulphate attack by means of accelerated degradation tests Cement and Concrete Research, 42, (2012), 173–185

[6] De Belie N., Lenehan, J. J., Braam, C. R., Svennerstedt, B., Richardson, M., Sonck, B., Durability of Building Materials and Components in the Agricultural Environment, Part III: Concrete Structures, Journal of Agricultural Engineering Research, 76, (2000), 3–16

[7] De Belie, N., De Coster¸ V., Van Nieuwenburg, D., Use of fly ash or silica fume to increase the resistance of concrete to feed acids, Magazine of Concrete Research, 49, (1997), 337–344

[8] De Belie, N., Debruyckere, M., Van Nieuwenburg, D., De Blaere, B., Attack of concrete floors in pig houses by feed acids: influence of fly ash addition and cement-bound surface layers, Journal of Agricultural Engineering Research, 68, (1997), 101–108

[9] De Belie, N., Verschoore, R., Van Nieuwenburg, D., Resistance of concrete with limestone sand or polymer additions to feed acids, Transactions of the ASAE, 41, (1998), 227–233

[10] Janković, K., Bojović, D., Nikolić, D., Lončar, Lj., Some Properties of Ultra High Strength Concrete”, Građevinski materijali i konstrukcije, Vol. 53, No. 1, Beograd, (2010), 43–51

[11] Janković, K., Miličić Lj., Stanković, S. and Šušić, N., Investigation of the mortar and concrete resistance in aggressive solutions, Technical Gazette, Vol. 21, No.1, (2014), 173–176

[12] Koch, A., Steinegger, H., Ein Schnellprufverfahren fur Zement auf ihr Verhalten bei Sulfatangriff _A rapid test method for cement behaviour under sulphate attack, Zement-Kalk-Gips, 7, (1960), 317–324.

[13] Larreur-Cayol S., Bertron, A., Escadeillas, G., Degradation of cement-based materials by various organic acids in agro-industrial waste-waters, Cement and Concrete Research, 41 (2011), 882–892

[14] Liu, Z. Study of the basic mechanisms of sulfate attack on cementitious materials, PhD, University of Ghent and Central South University, (2010)

[15] Massana, J., Guerrero, A., Anto´n, R., Garcimartı´n a, M.A., Sa´nchez E., The aggressiveness of pig slurry to cement mortars, Biosystems Engineering, 114, (2013), 124-134

[16] Macías, A., Goñi, S., Madrid, J., Limitations of Köch-Steinegger test to evaluate the durability of cement pastes in acid medium, Cement and Concrete Research, 29, (1999), 2005–2009

[17] Miletic, S., Ilic, M., Ranogajec, J., Marinovic-Neducin, R., Djuric, M., Portland ash cement degradation in ammonium-sulfate solution, Cement and Concrete Research, 28, (1998), 713–725

[18] Oueslati, O., Duchesne, J., The effect of SCMs on the corrosion of rebar embedded in mortars subjected to an acetic acid attack, Cement and Concrete Research, 42, (2012) 467–475

[19] Pavllk, V., Corrosion of hardened cement paste by acetic and nitric acids, Part II: Formation and chemical composition of the corrosion products layer, Cement and Concrete Research, 24, (1994), 1495–1508

[20] Santhanam, M., Cohen, M. D., Olek, J., Effects of gypsumformation on the performance of cement mortars during external sulfate attack, Cement and Concrete Research, 33, (2003), 325–332

[21] Sotiriadis K., Nikolopoulou, E., Tsivilis, S., Sulfate resistance of limestone cement concrete exposed to combined chloride and sulfate environment at low temperature, Cement & Concrete Composites, 34 (2012), 903–910

[22] Schmidt, T., Lotenbach, B., Romer, M., Neuenschwander, J., Scrivener, K.L., Physical and microstructural aspects of sulfate attack on ordinary and limestone blended Portland cements, Cement and Concrete Research, 39, (2009), 1111–1121

[23] Schneider, U., Chen, S.W., Deterioration of high-performance concrete subjected to attack by the combination of ammonium nitrate solution and flexure stress, Cement and Concrete Research, 35, (2005), 1705–1713

[24] Terzić, A., Pavlović, Lj., Radojević, Z., Primena mikroskopskih metoda u analizi mikrostrukture različitih tipova betona sa recikliranim agregatom, Građevinski materijali i konstrukcije, Vol. 52, No 1, (2009), 34–39

[25] Terzić, A., Pavlović, Lj., Miličić Lj., Radojević Z., Aćimović-Pavlović Z., Svojstva vatrostalnog veziva na bazi otpadnog materijala, Građevinski materijali i konstrukcije, Vol. 55, No 2, (2012), 47–57

[26] Torgal, F. P., Jalali, S., Sulphuric acid resistance of plain, polymer modified, and fly ash cement concretes, Construction and Building Materials, 23, (2009), 3485–3491

[27] El-Hachem, R., Rozière, E., Grondin, F., Loukili, A., Influence of sulphate solution concentration on the performance of cementitious materials during external sulphate attack; Concrete in Aggressive Aqueous Environments, Performance, Testing and modeling, RILEM publications SARL, Toulouse, France, (2009)

[28] Crammond, N., The occurence of thaumasite in modern construction – a review, Cement and Concrete Composites, 24, (2002), 393–402

REZIME

OTPORNOST MATERIJALA NA BAZI METALURŠKOG CEMENTA NA DEJSTVO KISELINA

Ksenija JANKOVIĆ
Dragan BOJOVIĆ
Marko STOJANOVIĆ
Ljiljana LONČAR

Cementni materijali u poljoprivrednim i drugim industrijskim objektima izloženi su dejstvu kiselina. Zbog toga vek konstrukcija zavisi od trajnosti maltera ili betonskih elemenata u agresivnoj sredini. U radu je predstavljena otpornost na koroziju koja je uzrokovana sulfatnom, nitratnom, ureom, mlečnom i sirćetnom kiselinom. Skenirajuća elektronska mikroskopija (SEM) korišćena je da se ispita efekat agresivnih rastvora na mikrostrukturu i mehaničke osobine maltera. Hemijska otpornost prizmi od maltera i dve vrste betona testirana je prema metodi Koch-Steinegger. Kako je uslov za otpornost na agresivne rastvore taj da zatezna čvrstoća maltera nije manja od 70% u odnosu na referentne prizme negovane u vodi, može se zaključiti da su malter i beton, napravljeni sa CEM III/B, u ovom istraživanju otporni na sve kiseline kojima su tretirani.

Ključne reči: hemijska agresija, metalurški cement, Koch-Steinegger metod, trajnost

SUMMARY

RESISTANCE OF CEM III/B BASED MATERIALS TO ACID ATTACK

Ksenija JANKOVIĆ
Dragan BOJOVIĆ
Marko STOJANOVIĆ
Ljiljana LONČAR

Cement based materials in the agricultural and other industrial structures are exposed to acid attack. That is the reason why the service life of structure depends on the durability of mortar or concrete elements in aggressive environment. Resistance to corrosion caused by sulphate, nitrate, carbamide, lactic acid and acetic acid was presented. Optical and scanning electron microscopy (SEM) was used to examine the effect of aggressive solutions on the microstructure and mechanical properties of mortar. The chemical resistance of mortar prisms and two types of concrete were tested according to the Koch-Steinegger method. As the condition for resistance in aggressive solution is that flexural strength of mortar prisms is no less than 70 % compared to referent prisms cured in water it can be concluded that mortar and concrete made with CEM III/B in this investigation are resistant to all treated acids.

Keywords: chemical aggression, CEM III/B, Koch-Steinegger method, durability