

## Odpadni livarski pesek kot prekurzor v procesu alkalijske aktivacije

### Waste Foundry Sand as Precursor in Alkali Activation Process

#### Izvleček

Cilj članka je predstaviti uporabnost odpadnega livarskega peska v procesu alkalne aktivacije za uporabo v gradbeništvu. S tem nizkocenovnim postopkom bi nadgradili odpadek v krožnem gospodarstvu, mu zvišali vrednost ter zmanjšali težave odlaganja odpadnega livarskega peska tako za naravo kot za industrijo.

Prekurzorji, ki so obetavni za proizvodnjo alkalijsko-aktiviranih materialov, vsebujejo amorfen  $\text{SiO}_2$  ter  $\text{Al}_2\text{O}_3$ , zato smo določili kemijsko in mineraloško sestavo livarskega peska, skladiščenega na Termitu, ter mu določili vsebnost Si in Al v kristalni ter amorfni fazi. Analizirali smo tudi obliko, velikost ter površino delcev v nepredelanem praškastem stanju.

Prizme alkalijsko aktiviranega livarskega peska smo po negi, razkalupljenju in sušenju testirali glede na tlačno in upogibno trdnost.

**Ključne besede:** alkalijska aktivacija, livarski pesek, SEM, XRF, XRD, mehanska trdnost

#### Abstract

Aim of the article is to present the usefulness of waste foundry sand in the process of alkali activation in the building industry. With this low-price process, waste would be upgraded in circular economy, its value increased, and the problem of disposal of waste foundry sand would be lowered for the industry and nature.

Precursor, that are promising for manufacture of alkali activated materials, contain amorphous  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Therefore we determined chemical and mineralogical composition of foundry sand stored in Termit's landfills and determined amounts of Si and Al in crystal and amorphous phase. Shape, size and surface of unprocessed waste foundry sand were also analyzed.

After curing, demolding and drying of alkali activated prisms from waste foundry sand, compressive and bending strength were tested.

**Key words:** alkali activation, foundry sand, SEM, XRF, XRD, mechanical strength

#### Uvod

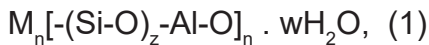
Alkalijska aktivacija odpadnih materialov predstavlja obetavno okolju prijazno ter tehnično sprejemljivo alternativo keramiki, malti in cementu, saj pri postopku

#### Introduction

Alkali activation of waste materials represents promising environment-friendly and technically acceptable alternative to ceramics, mortar and concrete, because at

ne potrebujemo naravnih surovin za prekurzorje. Prav tako sinteza poteka pri znatno nižjih temperaturah (glede na literaturo do 85 °C [1]). Za postopek lahko uporabimo različne odpadne materiale, kot so elektrofiltirski pepel, žlindra ter žgana glina, in tako s postopkom alkalijske aktivacije ne proizvedemo dodatnih odpadkov, hkrati pa tudi znižamo ogljični odtis v primerjavi z obstoječimi komercialnimi izdelki [2], kar vse poceni postopek izdelave ter spremeni odpadke v perspektiven, naravi sprejemljiv material.

Pri postopku alkalijske aktivacije odpadnih materialov je potrebno uporabiti alkalijski aktivator, kot so npr. NaOH, KOH, K- ali Na-silikati, ki aktivirajo amorfno snov v prekurzorju, raztopijo v alkaliji manj obstojne kristale ter pomagajo pri tvorbi večinoma amorfne alumo-silikatne mreže predstavljene v (1), [1]:



kjer M predstavlja alkalijski ion, n red polikondenzacije, z, n in w celo število. Mreža je sestavljena iz tetraedrov  $\text{SiO}_4$  in  $\text{AlO}_4$ , povezanih s kisikovimi mostovi. V tetraedru je  $\text{Al}^{3+}$  v koordinacijskem številu 4, zato je potrebno kompenzirati negativni naboj s pozitivnimi ioni prve in druge skupine periodnega sistema, tj. navadno se pri sintezi dodaja najcenejši  $\text{Na}^+$  v silikatu oz. hidroksidu [3].

Lastnosti alkalno aktiviranega materiala (AAM) so odvisne od:

- vrste dodanega kationa,
- razmerja prekurzor-alkalijsko-alkalijsko steklo,
- temperature med alkalijsko aktivacijo,
- časa na povišani temperaturi med sintezo, oz.
- hitrosti in postopka sušenja [1], [4], [5], [6].

its production no raw materials are needed for precursors, as well the synthesis takes places at much lower temperatures (according to the literature up to 85 °C [1]). For precursors different waste materials can be used like fly-ash, slag, metakaolin, and in this way no additional waste is produced, and at the same time carbon footprint is lowered in comparison to existing comerial products [2], which lowers the production cost and transforms waste into a promising material that is acceptable for nature.

Alkali activator is needed for alkali activation of waste material. Activators usually used are: NaOH, KOH, K- or Na-silicates, which activate amorphous part of precursor, dissolve less stable material in alkalis, and help forming mainly amorphous alumina-silicate matrix presented in formula (1), [1]:



where M represents alkali ion, n order of poly-condensation, z, n and w whole number. Matrix is built of tetrahedrons  $\text{SiO}_4$  and  $\text{AlO}_4$  that are combined by oxygen bridges. In tetrahedrons is  $\text{Al}^{3+}$  in coordination number 4, therefore the negative charge has to be compensated with positive ions of 1<sup>st</sup> and 2<sup>nd</sup> group of periodic system. Usually the cheapest  $\text{Na}^+$  in silicates and/or in hydroxide is used in the synthesis [3].

Properties of alkali activated material (AAM) depend on:

- type of added cation,
- ratio precursor-alkali-alkali glass,
- temperature during alkali activation,
- time on elevated temperature during synthesis,
- drying speed and drying procedure [1], [4], [5], [6].

Alkali activated materials are classified as polymers that already get final shape at following curing conditions:

- room temperature or elevated

Alkalijsko aktivirane materiale uvrščamo med polimere, ki dobijo končno obliko že pri sledečih pogojih nege:

- sobna temperatura oz. povišana do 30 °C za nekaj ur,
- povišana temperatura od 50 °C pa do 80 °C za nekaj minut,
- z obsevanjem z mikrovalovi za nekaj sekund [1].

V gradbeništvu predstavlja glavno merilo kakovosti materiala tlačna trdnost, ki:

- raste s staranjem alkalijsko aktiviranega materiala [6],
- je odvisna od temperature nege, tj. do določene povišane temperature znatno raste vse do platoja, kjer se rast upočasni [7] oz. trdnost zmanjšuje [8],
- je odvisna od časa nege, tj. od 2 do 5 ur v času termalne aktivacije, medtem ko postane rast tlačne trdnosti po 48 urah na povišani temperaturi zanemarljiva [4], [9].

Pričujoč članek je osredotočen na predstavitev odpadnega livarskega pesak kot enega izmed potencialnih vhodnih materialov za alkalijsko aktivacijo za namene gradbeništv. Zato smo opravili kemijsko in mineraloško analizo v Termitu pridobljenega materiala, namenjenega vgradnji v odkope kremenčevega peska, ter ga ovrednotili na podlagi rezultatov njegove mehanske trdnosti po alkalijski aktivaciji pri različnih pogojih.

## 1 Eksperimentalno delo

V Termitu, d.o.o., smo za namene raziskav na laboratorijski ravni odvzeli zadostno količino odpadnega livarskega peska (2 kg) iz njihovih odprtih odlagališč. Vzorec je bil odvzet na način, da bo reprezentativen za celoten kup odpadka na odlagališču.

temperature up to 30 °C for several hours,

- elevated temperature from 50 °C to 80 °C for few minutes,
- radiation with microwaves for few seconds [1].

Compressive strength is the main materials' property in the building industry. Compressive strength:

- grows with aging of alkali activated material [6],
- depends on curing temperature, i.e. it noticeably grows up to plateau, where growing slows down [7] or compressive strength even starts to decrease [8],
- depends on curing time, i.e. from 2 to 5 hours while thermal activation takes place, while growth of compressive strength after 48 hours on elevated temperature becomes negligible [4], [9].

The following article is focused on presenting waste foundry sand as one of the potentially useful precursors for alkali activation in the building industry. Therefore chemical and mineralogical analysis was performed of material collected in Termit used as filling material for excavated quartz sand mines. After alkali activation performed at different conditions the material was evaluated according to the compressive strength values.

## 1 Experimental

In Termit, d.o.o., enough sample of waste foundry sand (2 kg) was collected from Termit's open landfills for the research on laboratory level. Sample was taken in manners to be representative for the whole pile stored in the landfill.

## 1.1 Analiza odpadnega livarskega peska

Za namene rentgenske fluorescence (XRF) in rentgenske praškovne difrakcije (XRD) smo vzorec sušili v sušilniku na 70 °C 24 h, nato pa še na 105 °C v IR sušilniku do konstantne mase, da smo popolnoma odstranili vodo iz vzorca, ki smo ga nato pomleli in presejali pod 90 µm.

XRD analizo smo izvedli v območju 4° do 70° s korakom 0.0263° s pomočjo naprave Epyrean PANalytical X-Ray Diffractometer. Velikost kristalitev v odpadku smo določali s pomočjo Scherrerjeve enačbe [10], oceno amorfne faze ter mineralov pa z Rietveldovo fazno analizo [11] z zunanjim standardom (čisti kristal Al<sub>2</sub>O<sub>3</sub>) s programom X'Pert Highscore plus 4.1.

XRF analizo smo izvedli s programom OXAS na staljenih diskah, ki smo jih pripravili z mešanjem prahu Fluxana (FX-X50-2, litijev tetraborat 50 %/litijev metaborat 50 %). Podatke smo okarakterizirali s programom UniQuant 5.

XRD in XRF rezultate smo pretvorili v masne deleže po posameznih elementih v kristalni fazi in v celotnem vzorcu in določili količino amorfnega Si, Al ter količine elementov 1. in 2. skupine periodnega sistema.

Za vrstično elektronsko mikroskopijo (SEM; Jeol JSM-5500LV z volframovo katodno žičko za izvor elektronov), energijsko disperzijsko rentgensko spektroskopijo (EDXS; Oxford Instruments, Link Pentafet) pri nizkem in visokem vakuumu, ter za Brunauer-Emmett-Teller (BET; Micromeritics, ASAP 2020, Surface Area and Porosity Analyzer) analizo smo vzorec le posušili. Iz SEM mikrografov smo določili povprečne velikosti delcev, njihove oblike ter površino, iz BET analize pa specifično površino odpadnega materiala.

## 1.1. Analysis of waste foundry sand

For the purpose of X-Ray fluorescence (XRF) and X-Ray powder diffraction (XRD) sample was dried on 70 °C 24 h, after that sample was additionally dried on 105 °C in IR drier until constant mass was reached to have all water removed from the sample. The sample was milled afterwards and sieved under 90 µm.

The XRD analysis was performed in range from 4° to 70° in step 0.0263° with Epyrean PANalytical X-Ray Diffractometer. The crystallite size in the waste material was determined by means of the Scherrer formula [10], estimation of amount of amorphous phase and minerals with Rietveld refinement [11] with external standard (pure crystal of Al<sub>2</sub>O<sub>3</sub>) with program X'Pert Highscore plus 4.1.

The XRF analysis was performed with the program OXAS on melted discs, which were prepared with a mixture of Fluxana powder (FX-X50-2, lithium tetraborate 50 % / lithium methaborate 50 %). Data were characterised with program UniQuant 5.

Both the XRD and the XRF results were converted into mass percentages for elements found in the whole material and in the crystal phase, from which the amounts of amorphous Si, Al and elements of 1<sup>st</sup> and 2<sup>nd</sup> group of periodic system were determined.

For scanning electron microscopy (SEM; Jeol JSM-5500LV with tungsten cathode wire for source of electrons), energy dispersion X-Ray spectroscopy (EDXS; Oxford Instruments, Link Pentafet) at low and high vacuum, and for Brunauer-Emmett-Teller (BET; Micromeritics, ASAP 2020, Surface Area and Porosity Analyzer) the analysis sample was only dried. From the SEM micrographs average particle sizes, their shapes and surface were determined;

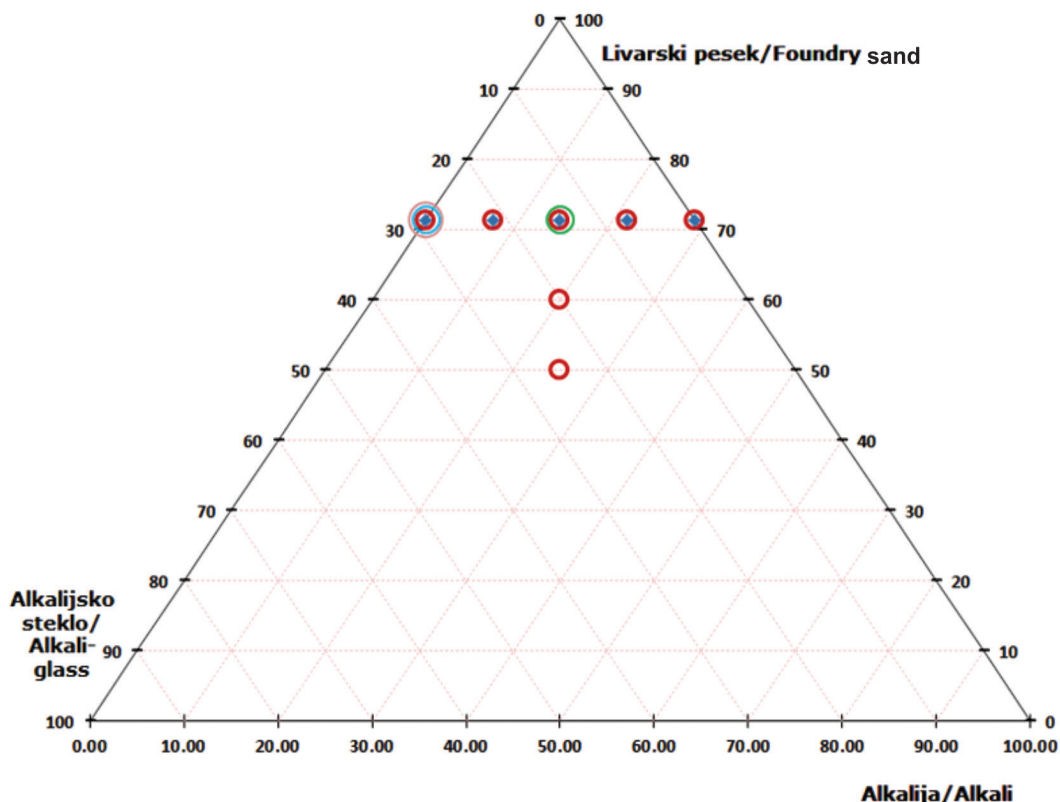
## 1.2 Priprava alkalno aktiviranega materiala

Posušenemu vzorcu smo dodali NaOH (Donau Chemie Ätznatron Schuppen, EINECS 215-785-5), KOH (Fluka, Honeywell, Cat. 30603), Na-steklo (Geosil, 344/7, Woelner), oz. K-steklo (Woellner, Betol K5020T) v različnih razmerjih. Testirali smo izdaten dodatek vode, kot tudi različne molarnosti obeh baz. Izvedeni eksperimentalni so prikazani na **Sliki 1**.

with BET analysis specific surface of waste foundry sand was measured.

## 1.2 Preparation of alkali activated material

To the dried sample NaOH (Donau Chemie Ätznatron Schuppen, EINECS 215-785-5) or KOH (Fluka, Honeywell, Cat. 30603), Na-glass (Geosil, 344/7, Woelner) or K-glass (Woellner, Betol K5020T) was added in different ratios. An extra addition of water



**Sl. 1.** Trikotni graf alkalijsko aktivirane sinteze z odpadnim livarskim peskom. Legenda: rdeč krog: 10M NaOH; modri deltoid: 10 M NaOH; zelen krog: (6, 8, 10, 12, 14) M NaOH in KOH; svetlo moder krog: dodatek enake količine vode kot je Na-stekla; vijoličen krog: Na-steklo zamenjano s K-steklom.

**Fig. 1.** Triangular graph of alkali activated synthesis of waste foundry sand. Legend: red circle: 10M NaOH; blue deltoid: 10 M NaOH; green circle: (6, 8, 10, 12, 14) M NaOH and KOH; light blue circle: addition of the same amount of water as Na-glass; purple circle: Na-glass is replaced by K-glass.

Sam postopek priprave je zahteval mešanje tekoče faze do bistrosti mešanice in šele nato vlitje v suh prekursor ob konstantnem mešanju. Zmes suhe snovi in tekoče faze smo mešali 1 minuto.

Alkalijsko aktivirane (AA) mešanice smo vlili v kalupe velikosti (80x20x20) mm<sup>3</sup>, ter jih negovali na sobni temperaturi oz. na 70 °C 24 h. Nato smo jih razkalupili ter sušili na sobni temperaturi oz. pospešeno v sušilniku ter volumetrično z mikrovalovi v mikrovalovki (Gorenje, MO 17 DW).

### 1.3 Analiza alkalno aktiviranega materiala

Alkalijsko aktivirane vzorce smo okarakterizirali z XRD (velikost kristalitev s pomočjo Scherrerjeve enačbe, da smo ocenili dogajanje med sintezo tj. rast [12] in razstapljanje kristalitev v alkalnem mediju s primerjavo rezultatov pred in po sintezi), SEM, EDXS, poroznost alkalnijsko aktiviranega materiala pa s porozimetrijo z živim srebrom (MIP).

Tlačno in upogibno trdnost smo določali s pomočjo naprave ToniTechnik ToniNORM 3 mesece po sintezi.

## 2 Rezultati in razprava

### 2.1 Analiza odpadnega livarskega peska

Z XRF analizo smo določili okside in njihove količine v prekursorju. Rezultati, kjer je masni delež ( $m_{\%\_XRF}$ ) oksida blizu oz. več kot 0,1 %, so predstavljeni v **Preglednici 1**. V isti tabeli so predstavljeni tudi rezultati XRD meritve, tj. minerali in njihovi masni deleži določeni ( $m_{\%\_XRD}$ ) z Rietveldovo fazno analizo.

was tested as well as different molarities of both alkalis. Performed experiments are shown in Figure 1.

Preparation of alkali activated material demanded mixing of liquid phase until mixture was clear. Thereafter liquid mixture was poured into dry precursor while constant stirring. Mixture of dry and liquid phase was stirred for one minute.

Alkali activated (AA) mixture was poured into molds of size (80x20x20) mm<sup>3</sup>, cured on room temperature and on 70 °C for 24 h, demolded and dried on room temperature, or in drier or with microwaves in microwave (Gorenje, MO 17 DW).

### 1.3 Analysis of Alkali Activated Material

Alkali activated samples were characterized by XRD (size of crystallites with help of the Scherrer equation to determine the activity during the synthesis, i.e. growth [12] and dissolution of crystallites in alkali media by comparing the results before and after synthesis), SEM, EDXS, porosity of alkali activated material with mercury intrusion porosimetry (MIP).

Compressive and bending strength were measured with apparatus ToniTechnik ToniNORM 3 months after synthesis.

## 2 Results and Discussion

### 2.1. Analysis of Waste Foundry Sand

With XRF analysis oxides and their amounts were determined. Results where mass percentage ( $m_{\%\_XRF}$ ) of oxide is near or more than 0,1 %, are presented on v **Table 1**. In the same table also XRD results are presented, i.e. minerals and their mass percentages determined ( $m_{\%\_XRD}$ ) by Rietveld refinement.



Oksid / Oxide	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	
m <sub>% XRF</sub> [%]	0,801	0,811	8,19	83,10	0,262	1,25	0,815	2,29	
Mineral / Mineral				kremen / quartz		kalcit / calcite			amorfn / amorphous
m <sub>% XRD</sub> [%]				65,9		0,8			38,2
Amorfn / Amorphous	Na	Mg	Al	Si	K	Ca	Ti	Fe	
m <sub>%</sub> [%]	0,594	0,489	4,34	8,08	0,217	0,573	0,489	1,60	

**Preglednica 1.** Masni delež (m<sub>% XRF</sub>) oksidov določen z XRF in masni delež (m<sub>% XRD</sub>) mineralov ter amorfn snovi določen z XRD. Amorfn snov razčlenjena glede na elemente (m<sub>%</sub>) je razlika med XRF in XRD rezultati na elementarni ravni.

**Table 1.** Mass percentage (m<sub>% XRF</sub>) of oxides determined with XRF and mass percentage (m<sub>% XRD</sub>) of minerals and amorphous phase determined with XRD. The amount of amorphous phase is broken down into elements (m<sub>%</sub>), which is the difference between XRF and XRD results for elements.

V odpadku je bil od mineralov prisoten SiO<sub>2</sub> kot kremen ter CaO kot kalcit, kar pomeni, da so vsi ostali z XRF detektirani elementi v amorfn fazi, ki predstavlja približno 40 % celotne snovi. Masni delež elemenov v amorfn snovi, ki je pomembna za alkalijsko aktivirano sintezo, smo preračunali iz razlike med XRF in XRD (**Tabela 1**). Množinsko razmerje amorfnih elementov Al:Si:Na v prekurzorju je 1:1,80:0,16, ki bi za alkalijsko aktiviran elektrofiltirski pepel naj bilo 1:1,9:1 za doseganje najvišje tlačne trdnosti glede na literaturo [13], kar uvrsti livarski pesek med potencialne prekurzorje za sintezo AAM pri dodatku zadostne količine Na,Si in tekoče faze.

## 2.2 Določitev izhodiščnega razmerja za alkalno aktivacijo

Glede na literaturno [13] optimalno razmerje Al:Si:Na (1:1,9:1) za doseg najvišje trdnosti smo določili potrebno količino dodatkov z Na<sup>+</sup>, kjer smo upoštevali, da vsi amorfni

In waste material SiO<sub>2</sub> was present as quartz and, CaO as calcite, which means that all other elements detected with XRF were in amorphous phase, which represents almost 40 % of the whole material. The mass percentage within the amorphous phase, which is important for alkali activated synthesis, was calculated from the difference between XRF and XRD (**Table 1**). Molar ratio between amorphous elements Al:Si:Na in precursor is 1:1,80:0,16, which should for alkali activated fly-ash be 1:1,9:1 to gain highest compressive strength according to the literature [13], which places waste foundry sand among potential precursors for synthesis of AAM when enough of Na,Si and liquid phase is added.

## 2.2. Determination of Baseline Ratio for Alkali Activation

According to the literature's [13] optimal ratio of Al:Si:Na (1:1,9:1) to gain the highest value of compressive strength amount of additives with Na<sup>+</sup> was determined, where all amorphous elements from 1<sup>st</sup> group were

elementi 1. skupine stopajo v kompenzacijo naboja:

- prekursor:Na-steklo:NaOH<sub>(s)</sub>=5:1:0;
- prekursor:Na-steklo:NaOH<sub>(s)</sub>=5:0:0,25 oz.
- prekursor:Na-steklo:10M NaOH<sub>(aq)</sub>=5:0:0,5.

V reakcijo tvorbe mreže ni nujno, da vstopi ves Al in vsi amorfni elementi 1. skupine, vsebovani v prekursorju. Vsak Al, ki pa vstopi v reakcijo tvorbe alumosilikatne mreže, pa potrebuje kompenzacijo naboja z elementom iz 1. skupine, oz. 2 Al, ki sta blizu, si lahko kompenzirata negativni naboj z elementom iz 2. skupine, ne glede na vir. Ker ne moremo zagotoviti, da bo vsak Al, četudi ne vstopi ves v tvorbo mreže, imel ob sebi kompenzacijski element, če jih dodamo minimalno potrebno, je bilo naše izhodiščno razmerje prekursor:Na-steklo:10M NaOH<sub>(aq)</sub>=5:1:1 ob predpostavki, da je viskoznost take mešanice dovolj majhna, da onemogočamo mehaniko kontinuov na veliki skali, ter sledimo tlačni trdnosti, nastanku kristalov in eflorescenci. Razmerje tekoče alkalne faze in prekursorja smo ohranjali konstantno.

Glede na literaturo [13] bi bilo potrebno prekursorju dodati tudi Si v razmerju prekursor:Na-steklo:NaOH<sub>(s)</sub>=5:0,2:0, če se seveda kremen niti deloma ne razstaplja v alkalnem mediju, čemur smo sledili v 3.3.4.

### 2.3 Analiza alkalijsko aktiviranega materiala

Alkalno aktiviran livarski pesek se pri alkalni aktivaciji ni penil, kar ustreza podatkom iz literature za elektrofiltrski pepel [13] glede na množinsko razmerje Al:Si, ki je večje kot 1:1,4 ne glede na dodatke (noben dodatek ni vseboval Al).

taken into account for compensation of the charge:

- precursor:Na-glass:NaOH<sub>(s)</sub>=5:1:0;
- precursor:Na-glass:NaOH<sub>(s)</sub>=5:0:0,25 or
- precursor:Na-glass:10M NaOH<sub>(aq)</sub>=5:0:0,5.

It is not necessary that all amorphous Al and the elements from the 1<sup>st</sup> group in the precursor participate in the formation of aluminosilicate matrix. But every Al that steps into reaction of the matrix formation needs compensation of its charge with element from 1<sup>st</sup> group, or 2 Al, that are close in the matrix, can compensate negative charge with element from the 2<sup>nd</sup> group, regardless to its source. Because it is impossible to provide that every Al, even if whole Al does not enter into matrix formation reaction, will have near the charge compensation element, if minimal needed amount is added, the starting ratio precursor:Na-glass:10M NaOH<sub>(aq)</sub>=5:1:1 where the assumption was that viscosity of such mixture is low enough to avoid mechanics of continuum on large scale, following compressive strength, crystal formation and efflorescence. Ratio liquid alkali phase and precursor was kept constant.

According to the literature [13] addition of Si to the precursor is needed in ration precursor:Na-glass:NaOH<sub>(s)</sub>=5:0,2:0, if quartz does not dissolve in alkali media, which was followed in 3.3.4.

### 2.3 Analysis of Alkali Activated Material

Alkali activated foundry sand did not foam during alkali activation, which corresponds data from literature for fly-ash [13] according to the molar mass Al:Si which is bigger than 1:1,4 regardless of additives (no additive contained Al).



### 2.3.1 Alkalijsko aktiviran material – tlačna trdnost

Rezultati tlačne trdnosti, v gradbeni industriji ene izmed najpomembnejših lastnosti, so predstavljeni v **Preglednici 2**, skupaj z upogibno trdnostjo.

Iz meritev predstavljenih v Tabela 2 lahko zaključimo, da:

### 2.3.1 Alkali Activated Material – Compressive Strength

Results of compressive strength, which is in building industry one of the most important properties, are presented on **Tabel 2**, along with bending strength.

From measurements presented on Tabel 2 it can be concluded that:

Razmerje l.pesek:alkalijsko steklo:voda / Ratio f.sand:alkali:a.glass:water	Alkalijska / Alkali	Alkalijsko steklo / Alkali glass	Nega / Curing	Sušenje / Drying	Upogibna trdnost / Bending strength [N/mm]	Tlačna trdnost / Compressive strength [N/mm]
5:1:1:0	6 M NaOH	Na-steklo / Na-glass	70 °C 24 h	RC	4,1	17,6
	8 M NaOH				4,1	15,4
	10 M NaOH		RC	/	/	
			110 °C 24 h	4,1	10,5	
			microwave 2,33 min	1,9	12,9	
				0,02	12,4	
	12 M NaOH			2,7	21,8	
	14 M NaOH			3	21,4	
	6 M KOH			2,3	13,8	
	8 M KOH			2,5	18,8	
10 M KOH		2,9	19,5			
12 M KOH		1,6	18,9			
14 M KOH		2,8	19,4			
5:2:0:0	10 M NaOH	Na-steklo / Na-glass	70 °C 24 h	RC	2,6	5,2
5:1,5:0,5:0					1,7	9
5:0,5:1,5:0			4,5	18,6		
5:2:0:0			2,5	6,9		
5:1,5:0,5:0	10 M KOH			4,1	13,1	
5:0,5:1,5:0			3,9	18		
3:1:1:0			3,9	10,5		
2:1:1:0	10 M NaOH			/	/	
				6,6	27,7	
5:0:2:0	/		K-steklo / K-glass			2,7
5:0:2:2		Na-steklo / Na-glass			0,1	1,5

**Preglednica 2.** Mehanske lastnosti alkalijsko aktiviranega odpadnega livarskega peska. Sobni pogoji so označeni z RC.

**Table 2.** Mechanical properties of alkali activated waste foundry sand. Room conditions are labelled with RC

- preveč tekoče faze (ko je viskoznost merljiva) drastično zmanjša upogibno in tlačno trdnost;
- manj kot je tekoče faze (vode), višja je trdnost, tako v primeru NaOH, kot KOH;
- upogibne in tlačne trdnosti pri uporabi več oz. do iste količine NaOH in KOH, kot smo dodali Na-vodnega stekla, so višje pri dodatku KOH;
- upogibne in tlačne trdnosti ob dodatku večje količine Na-stekla, kot pa je alkalije, so neodvisne od dodane alkalije (NaOH oz. KOH);
- najvišja dosežena tako upogibna kot tlačna trdnost je v primeru, ko uporabimo le Na-vodno steklo brez dodatka alkalije (upogibna trdnost 6,6 MPa in tlačna trdnost 27,7 MPa);
- odvisnost upogibne in tlačne trdnosti od molarnosti alkalije je manj očitna, tj. za kompenzacijo negativnega naboja v mreži potrebujemo le toliko Na, kolikor Al vstopa v tvorbo mreže, sicer se odvečni Na porabi pri nastanku kristalov v mreži, ali pa povzroča eflorescenco (glej **3.3.4** in **3.3.5**). Potrebna pa je ustrezna porazdelitev Na po mešanici, da je Na dovolj blizu Al, ki vstopi v reakcijo tvorbe mreže. Prav tako je potrebno imeti dovolj tekoče faze, da se omogoči lokalna difuzija Na do Al, ne pa tudi difuzija na veliki skali, ki bi omogočila porušitev enakomerne porazdelitve snovi v odpadnem materialu z mehaniko kontinuov. Zelo pomembna je enakomerna porazdelitev snovi pred sintezo po celotnem volumnu;
- z uporabo Na-stekla dobimo dvakratne vrednosti upogibne in tlačne trdnosti v primerjavi z uporabo K-stekla;
- nega ob alkalni aktivaciji na temperaturi 70 °C je dala pozitivne rezultate glede na nego pri le sobnih pogojih;
- tlačna trdnost se merljivo poveča pri sušenju na povišani temperaturi (110
- too much liquid phase (when viscosity is measurable) drastically lowers bending and compressive strength;
- if there is less liquid phase (water), than strength is higher, both in the case of NaOH, as well as KOH;
- when more or same amount of NaOH and KOH comparing to the amount of Na-glass is added, bending and compressive strength are higher in case of KOH addition;
- bending and compressive strength, when bigger amount of Na-glass is added than alkali, do not depend on the added alkali (NaOH or KOH);
- maximal gained bending and compressive strength is reached when Na-glass without addition of alkali is used (bending strength is 6,6 MPa, compressive strength 27,7 MPa);
- dependence of bending and compressive strength on molarity of alkali is less obvious, i.e. for compensation of negative charge in the matrix it is needed only as much Na as Al that enters into reaction of formation of matrix, otherwise excessive Na is used for crystal growth in the matrix, or it causes efflorescence (look 3.3.4 in 3.3.5). However, an appropriate distribution of Na in the mixture is needed, so that Na is in the proximity of Al, that enters into matrix formation. It is also necessary to have enough liquid phase to allow local diffusion of Na to Al, but not also the diffusion on large scale that would result in collapse of the uniform distribution of ingredients in the waste foundry sand with mechanics of continuum. Uniform distribution of all ingredients throughout the volume before synthesis is very important;
- AAM prepared with Na-glass has bending and compressive strengths 2-times higher comparing to AAM

°C), kot tudi pri sušenju z mikrovalovi, a hkrati se upogibna trdnost zelo poslabša glede na alkalijsko aktiviran material, sušen pri sobnih pogojih.

Sušenje na sobnih pogojih poteka počasneje v primerjavi s površinskim sušenjem na 110 °C (24 h), še počasneje pa v primerjavi z volumetričnim sušenjem z mikrovalovi (2,33 min), saj je bilo potrebnih nekaj tednov do enako velikega skrčka kot v primeru sušenja z mikrovalovi. S hitrostjo sušenja se napake v strukturi večajo, saj povečujemo pritisk znotraj strukture z dvigom temperature in prisilimo vodo k utiranju novih poti iz alkalijsko aktiviranega materiala. Posledica razpok je zmanjšanje upogibne trdnosti na 50 % pri sušenju na 110 °C oz. na 5 ‰ pri volumetrim sušenju.

### 2.3.2 XRD rezultati pred in po sintezi

XRD rezultati odpadnega livarskega peska ter alkalijsko aktiviranega materiala, pripravljenega z različnimi dodatki, so predstavljeni v **Preglednici 3**. Sledili smo razstapljanju in rasti kristalinitov s pomočjo Scherrerjeve enačbe, ki je v programu X'Pert Highscore uporabna le za kristalite do velikosti 150 nm, kot tudi masnemu deležu mineralov in amorfne snovi z Rietveldovo fazno analizo.

Odpadni livarski pesek vsebuje 65 % kremenca, kalcit v sledovih, amorfne snovi več kot 30 %. Med alkalijsko aktivacijo se kristaliti kremenca raztapljajo, tj. velikost kristalinitov se je zmanjšala z 130 nm na 110 nm, tj. masa kremenca, ki je postala dostopna za tvorbo mreže, se je zmanjšala za 20 % do 40 %.

Z alkalijsko aktivacijo se tvori amorfna alumosilikatna mreža, kot posledica odvečnega Na in/ali K pa pride do nukleacije in kristalizacije. Kadar je bilo za alkalijsko aktivacijo za tekočo fazo

prepared with K-glass;

- curing on 70 °C gave positive results with regard to curing on room temperature;
- compressive strength increases measurably when drying on elevated temperature (110 °C), as well as when drying with microwaves. At the same time bending strength decreases drastically with respect to AAM dried at room conditions.

Drying at room conditions is slower compared to surface drying at 110 °C (24 h), and even more slowly compared to volumetric drying with microwaves (2,33 min), because it took several weeks to get the same shrinkage as when AAM was dried with microwaves. With the drying rate defects in the structure get bigger as pressure in the structure is increased due to the elevated temperature with which water is forced to find path out from alkali activated material. Result of the cracks is lowering of the bending strength by 50 % when drying at 110 °C, and to 5 ‰ at volumetric drying.

### 2.3.2 XRD Results Before and After synthesis

XRD results of waste foundry sand and alkali activated material prepared with various additives are presented on **Tabel 3**. Dissolution of crystals as well as crystal growth were followed with Scherrer equation, that can be used in X'Pert Highscore only for crystallites smaller than 150 nm. As to mass percentage of minerals and amorphous phase was followed with Rietveld Refinement.

Waste foundry sand contains 65 % of quartz, calcite in traces, amorphous phase more than 30 %. During alkali activation quartz crystals dissolve, i.e. size of crystallites decreases from 130 nm to 110 nm, i.e. mass of quartz, that became

Mineral / Mineral	Kremen / Quartz	Kalcit / Calcite	Termonatrit / Thermonatrite	Kalicinit / Kalicinite	Trona	Sodalit / Sodalite	Amorfno / Amorphous
Kemjska formula / Chemical formula	SiO <sub>2</sub>	CaCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> · H <sub>2</sub> O	CHKO <sub>3</sub>	C <sub>2</sub> H <sub>3</sub> Na <sub>3</sub> O <sub>8</sub>	Al <sub>3</sub> Na <sub>3</sub> O <sub>24</sub> Si <sub>6</sub>	/
Mohsova lestvica trdnosti [M] / Mohs hardness scale [M]	7	3	1-1,5	1-2	2,5	5,5-6	
Velikost kristalitev [nm] / Size of crystallites [nm]	130	x					
Masni delež [%] / Mass percentage [%]	65,9	0,8					33,2
Velikost kristalitev [nm] / Size of crystallites [nm]	110	x	60				
Masni delež [%] / Mass percentage [%]	36,4	0,3	11,4				51,9
Velikost kristalitev [nm] / Size of crystallites [nm]	100	x			40		
Masni delež [%] / Mass percentage [%]	40,3	0,4			4,4		54,9
Velikost kristalitev [nm] / Size of crystallites [nm]	140	x			45		
Masni delež [%] / Mass percentage [%]	40,6	0,1			4,5		54,8
Velikost kristalitev [nm] / Size of crystallites [nm]	120	x	x		x		
Masni delež [%] / Mass percentage [%]	37,5	0,4	1,0		1,9		59,2
Prekursor / Precursor [P]							
P : 10M NaOH : Na-steklo/glass = 5 : 1 : 1							
P : 10M NaOH : Na-steklo/glass = 5 : 1 : 1 Sušenje na 110 °C / Drying on 110 °C							
P : 10M NaOH : Na-steklo/glass = 5 : 1 : 1 Sušenje z mikrovvalovi / Drying with microwaves							
P : 10M NaOH : Na-steklo/glass = 5 : 0 : 2							

P : 10M NaOH : K-steklo/glass = 5 : 0 : 2	Velikost kristalitov [nm] / Size of crystallites [nm]	110	x			x			
	Masni delež [%] / Mass percentage [%]	39,3	0,4			1,1			59,2
P : 10M NaOH : Na-steklo/glass : H2O = 5 : 0 : 2 : 2	Velikost kristalitov [nm] / Size of crystallites [nm]	110	x				x		
	Masni delež [%] / Mass percentage [%]	37,7	0,4				1,0		60,9
P : 10M NaOH : Na-steklo/glass = 5 : 2 : 0	Velikost kristalitov [nm] / Size of crystallites [nm]	120	x				45	x	
	Masni delež [%] / Mass percentage [%]	40,4	0,1				6,9	1,3	51,3
P : 10M KOH : Na-steklo/glass = 5 : 2 : 0	Velikost kristalitov [nm] / Size of crystallites [nm]	120	x			25			
	Masni delež [%] / Mass percentage [%]	38,4	0,5			3,4			57,6
P : 10M KOH : Na-steklo/glass = 5 : 1 : 1	Velikost kristalitov [nm] / Size of crystallites [nm]	100	x				40		
	Masni delež [%] / Mass percentage [%]	36,8	0,2				4,7		58,3

**Preglednica 3.** Minerali prisotni v odpadnem livarskem pesku ter v alkaljsko aktiviranemu materialu, negovanem na 70 °C 24 h in sušenem pri sobnih pogojih, če ni napisano drugače. Velikosti kristalitov so dobljene s Scherrerjevo enačbo, masne deleže kristalov in amorfnosti pa z Rietveldovo fazno analizo. x označuje kristalite večje od 150 nm.

**Table 3.** Minerals present in waste foundry sand and alkalai activated material cured at 70 °C 24 h and dried at room conditions, if not stated otherwise. Crystallite sizes are obtained with Scherrer formula, mass percentage of crystals and amorphous phase with Rietvel refinement. x stands for crystallites bigger from 150 nm.

uporabljeno le alkalijsko steklo, so bili kristaliti večji (preveliki za določevanje s Scherrerjevo enačbo), hkrati pa je bil masni delež novo nastalih mineralov manjši, kot v primeru dodatka alkalije oz. v primeru le uporabe alkalije. To pomeni, da v primeru alkalijskega stekla rastejo posamezni kristaliti, sama nukleacija pa je otežena, v primeru 10 M alkalije, kjer je pri isti masi alkalijskega stekla več Na oz. K, pa je nukleacija prevladujoča, zato zmanjka snovi za rast kristalitov.

Pri uporabi NaOH z oz. brez Na-stekla je ~10 % manj amorfne snovi, kar je posledica največjega prebitka Na v vhodni tekoči fazi med vsemi eksperimenti. Odvečen Na zraste v minerale, ki pa so po Mohsovi lestvici trdnosti mehki in zato ne pripomorejo k trdnosti alkalijsko aktiviranega materiala.

Pri sušenju alkalijsko aktiviranega materiala na 110 °C se je velikost kristalitov kremenca zmanjšala z 110 nm na 100 nm, tj. masa posameznega kristalita se je zmanjšala za skoraj 25 %, a masni delež vsega kremenca se je pa povečal za 4 %, kar pomeni, da se je večina Si za tvorbo dodatnega kremenca črpala predvsem iz aluminosilikatne mreže, deloma pa tudi iz površine kremenca iz prekursorja. Kalcita je bilo pred in po sušenju na 110 °C enako, medtem ko se je termonatrit razgradil v amorfno snov oz. v po Mohsovi skali bolj trd kristal trona, kar je povečalo tlačno trdnost iz 10,5 MPa na 12,9 MPa.

Z volumetričnim sušenjem ravno tako povečamo masni delež vsega kremenca v alkalijsko aktiviranem materialu za 4 %, a z razliko od sušenja na 100 °C kristaliti kremenca zrastejo z 110 nm na 140 nm, kar je povečanje volumna posameznega kristalita kremenca za več kot 100 %. To pomeni, da se je Si za tvorbo novega kremenca oz. za rast obstoječega kremenca črpal le iz aluminosilikatne mreže. Ker se kristalna modifikacija kremenca ni

available for matrix formation, lowered from 20 % to 40 %.

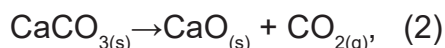
With alkali activation amorphous aluminosilicate matrix is formed, due to abundant Na and/or K nucleation and crystallization occur. When only alkali glass was used for the liquid phase, crystallites were bigger (too big to be able to determine their size with Scherrer equation), at the same time mass percentage of newly formed minerals was lower than when alkali was added or when only alkali was used. This means that when alkali glass is used, individual crystallites grow while nucleation is hindered, in case of 10 M alkali, where at the same mass as the alkali glass there is more Na/K, nucleation is dominant, therefore there is no material left for crystal growth.

When NaOH with or without Na-glass is used, there is ca. 10 % less amorphous material, which is the consequence of largest amount of abundant Na in liquid phase among all experiments. Excessive Na grows into minerals that are on Mohs hardness scale soft and therefore do not contribute to the strength of the alkali activated material.

When drying alkali activated material at 110 °C, the size of quartz crystallites decreases from 110 nm to 100 nm, i.e. mass of individual crystallite lowered for almost 25 %, but mass percentage of whole quartz increased for 4 %. This means that the majority of Si used for quartz formation is from Aluminosilicate matrix, partially also from surface of quartz in the precursor. Amount of calcite was same before and after drying on 110 °C, while termonatrite transformed into amorphous substance, or into crystal trona that has a higher hardness according to Mohs hardness scale, which increased compressive strength from 10,5 MPa to 12,9 MPa.



spremenila, je pritisk znotraj strukture med obsevanjem z mikrovalovi, glede na fazni diagram kristalnega SiO<sub>2</sub> na Slika 1 v [14] in temperaturo, ki se jo dosega z mikrovalovi (čez 1000 °C) [15], med 2 in 3 GPa. Struktura sicer prenese ta pritisk, a glede na zmanjšano upogibno trdnost, s poškodbami. Masni odstotek kalcita se je po mikrovalovnem sušenju zmanjšal zaradi visoke temperature med volumetričnim sušenjem, katere posledica je kaclinacija (2), ki poteka že pri 750 °C [16]:



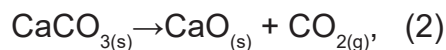
Enako kot pri površinskem se je tudi pri volumetričnem sušenju termonatrit deloma razgradil v amorfno snov in deloma v kristal trona. Tako kot so kristaliti kremena v primeru sušenja z mikrovalovi večji, tako so tudi kristaliti trone večji, a le za 5 nm. Tlačna trdnost po volumetričnem sušenju je 12,5 MPa, kar je bolje kot pri sušenju pri sobnih pogojih zaradi nastanka po Mohsovi skali trših kristalov in primerljivo s površinskim sušenjem.

### 2.3.3 SEM ter EDXS analiza pred in po sintezi

Povprečne vrednosti delcev v odpadnem livarskem pesku, ki so predstavljene v **Preglednici 4**, smo določili pri različnih povečavah elektronskega vrstičnega mikroskopa. Velikostni razpon je od pod 1,5 μm pa čez 300 μm. Specifična površina dobljena z BET analizo posušenega, a sicer neobdelanega odpadnega livarskega peska, je 15,9734 m<sup>2</sup>/g.

Odpadni livarski pesek je predstavljen na **Sliki 2** pri 35-kratni in 600-kratni povečavi. Delci so naključnih oblik z zaobljenimi robovi. Beli delčki, vidni na SEM slikah, predstavljajo elementarno Fe, kar smo potrdili z EDXS analizo, ki je

By means of volumetric drying mass percentage of quartz was also increased in alkali activated material for 4 %, but unlike drying at 100 °C, quartz crystallites grow from 110 nm to 140 nm, which increased individual quartz crystallite volume for more than 100 %. This means that Si used in formation of new quartz or growth of existing quartz came only from an aluminosilicate matrix. Because crystal modification of quartz did not change, there is pressure inside the structure during radiation with microwaves, according to both, the phase diagram of crystalline SiO<sub>2</sub> on Figure 1 in [14], and the temperature reached with microwaves (over 1000 °C) [15], between 2 and 3 GPa. structure does survive this pressure, but with a damage according to the lowered bending strength. The mass percentage of calcite was reduced after drying with microwaves due to high temperature during volumetric drying, resulting in calcination (2), which already takes place at 750 °C [16]:



As with surface drying, also with volumetric drying thermonatrite partially transformed into amorphous phase and partially into crystal trona. Just like the quartz crystals, which are in the case of drying with microwaves bigger, also the trona crystals are bigger, but just for five nm. The compressive strength after volumetric drying is 12,5 MPa, which is better comparing to the drying at room conditions due to the formation of crystals that have higher hardness on Mohs scale, and is comparable to the compressive strength results obtained with surface drying of alkali activated material.

SEM povečava / SEM magnification	Povprečna velikost delcev [ $\mu\text{m}$ ] / Average particle size [ $\mu\text{m}$ ]	Največji in najmanjši opaženi delec [ $\mu\text{m}$ ] / Largest and smallest observed particle [ $\mu\text{m}$ ]
35x	185	> 300
370x	35	
1700x	3	< 1,5

**Preglednica 4.** SEM statistika premera velikosti delcev aproksimiranih s sfero v odpadnem livarskem pesku

**Table 4.** SEM statistics of diameter of waste foundry sand particles' sizes approximated by sphere

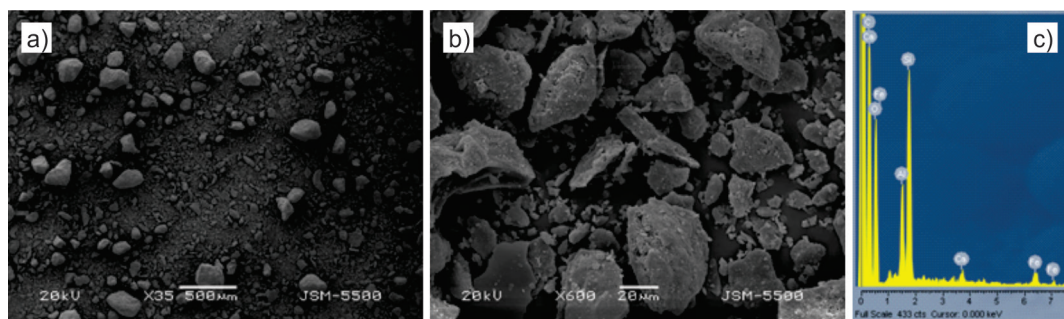
predstavljena na Sliki 2 c. Fe ni nastopalo kot večji samostojni delci, ki bi jih lahko odstranili iz snovi z magneti. Oba elementa, najbolj pomembna pri tvorbi mreže v alkalijsko aktiviranem materialu, Si in Al, sta glede na EDXS prisotna v večjih deležih. Edini element, ki bi lahko kompenziral negativni naboj glede na EDXS, je Ca, ki ga je tudi največ med elementi 1. in 2. skupine glede na XRF, vendar kljub vsemu premalo glede na razpoložljiv Al.

Alkalno aktiviran odpadni livarski pesek je optično izgledal po celotnem volumnu enako, prikazano na SEM sliki na Sliki 3 a, kar pomeni, da je razpršenost različnih snovi v odpadnem livarskem pesku enakomerno

### 2.3.3 SEM and EDXS Analysis Before and After Synthesis

Average particle values in waste foundry sand, presented in **Table 4**, were determined at different magnitudes of scanning electron microscope. Size range is from under 1,5  $\mu\text{m}$  to over 300  $\mu\text{m}$ . BET specific surface of dried otherwise untreated waste foundry sand is 15,9734  $\text{m}^2/\text{g}$ .

Waste foundry sand is presented in Figure 2 at 35-times and 600-times magnification. Particles are of random shape with rounded edges. White particles visible on SEM micrographs present elemental Fe, which was confirmed by EDXS analysis, which is presented in Figure 2 c. Fe was not in form of large independent particles that could be removed from the material by magnets. Both elements, most crucial for matrix formation in alkali activated material, Si and Al, were according to EDXS present in larger amounts. Only the element detected by EDXS that would be able to compensate the negative charge is Ca, which, according to XRF, is among elements of 1st and 2nd group in the waste foundry sand in largest quantity. However, the whole amount of Ca in the precursor is not enough for available Al.

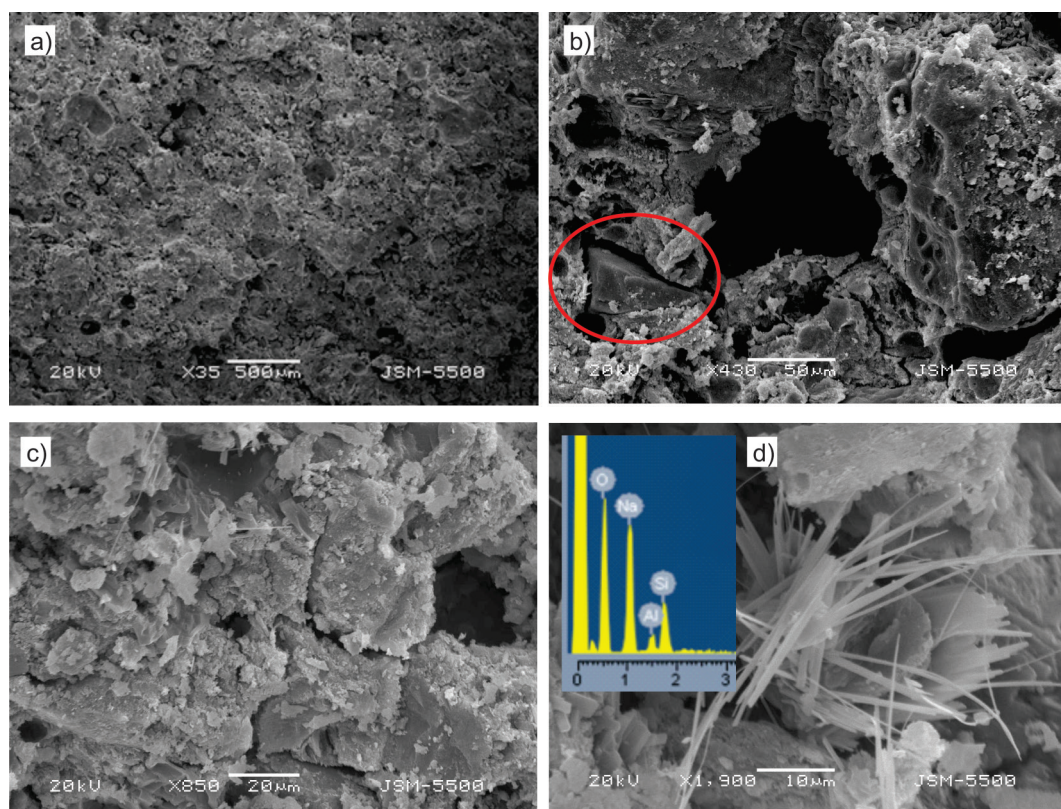


**Sl. 2.** SEM slika odpadnega livarskega peska pri povečavi a) 35 in b) 600. c) EDXS spekter praškastega vzorca

**Fig. 2.** SEM micrograph of waste foundry sand at magnification a) 35 and b) 600. C) EDXS spectrum of powder sample

porazdeljena, kot tudi, da je viskoznost pri sintezi bila dovolj velika, da ni omogočala več kot le tvorbe mreže ter lokalnih reakcij. Posledica le-teh so tudi enakomerno porazdeljene pore po celotnem volumnu različnih dimenzij. Nekatere od teh por so se sicer združile, a večina majhnih por je ostala ujetih v mreži, saj je bila očitno viskoznost dovolj visoka in strjevanje med nego dovolj hitro, da so bile migracije mehurčkov močno

Alkali activated waste foundry sand visually looked uniform throughout the whole volume, shown on SEM micrograph in Figure 3 a, which means that distribution of different substances in waste foundry sand is uniform, as well as that viscosity during synthesis was high enough to allow only formation of aluminosilikate matrix and local reactions. The result of local reactions is also pores of different dimensions



**Sl. 3.** SEM slike alkalijsko aktiviranega odpadnega livarskega peska, pripravljenega v razmerju livarski pesek : 8 M NaOH : Na-steklo : H<sub>2</sub>O = 5 : 1 : 1 : 0, negovanega na 70 °C 24 h, ter sušenega pri sobnih pogojih pri povečavi a) 35, b) 430, c) 850 in d) 1900. Vstavljena slika prikazuje EDXS igličastih struktur ter okolico, ki jo zajame detektor.

**Fig. 3.** SEM micrographs of alkali activated waste foundry sand prepared in ratio foundry sand: 8 M NaOH : Na-glass : H<sub>2</sub>O = 5 : 1 : 1 : 0, cured at 70 °C 24 h, dried at room conditions at magnification a) 35, b) 430, c) 850 and d) 1900. The inset represent EDXS needle-like structures with surrounding captured by detector.



ovirane (Slika 3 a). V strukturo je ujet tudi kremen (Slika 3 b v rdečem krogu) iz odpadnega livarskega peska, ki ni zreagiral z alkalijo in je le kot polnilo v alumosilikatni mreži. Alumosilikatna mreža je v obliki 2D kosmičev, če ni bilo dovolj reagentov v okolici, sicer pa je zrasla v 3D strukturo omejeno z okolico (kalup oz. nezreagiran kremen), prikazano na Sliki 3 c.

Igličaste strukture (Slika 3 d), neopažene s prostim očesom, so bile opažene pod SEM po več kot 6 mesecih od sinteze. Glede na EDXS, vstavljen na Sliki 3 d, so igličaste strukture zgrajene predvsem iz Na, tj. so posledica eflorescence soli iz prebitnega Na v sintezi, ki se ni vgradil v alumosilikatno mrežo ali pa bil uporabljen pri rasti novih kristalov med alkalno aktivacijo (novonastali minerali so predstavljeni v Tabeli 3).

### 3 Sklep

Med alkalijsko aktivacijo se kremen deloma raztaplja in vstopa v tvorbo mreže oz. sodeluje pri nastanku novih mineralov, ki polnijo mrežo. Prebitni Na v alkalno aktivirani sintezi, ki ni bil uporabljen za kompenzacijo negativnega naboja zaradi neustreznega koordinacijskega števila Al v alumosilikatni mreži, se uporabi med reakcijo pri tvorbi novih kristalov, preostanek pa se izloča v obliki soli skozi daljše časovno obdobje.

Najvišjo tlačno in upogibno trdnost, 27,7 MPa in 6,6 MPa, smo dosegli ob uporabi le Na-stekla s prekursorjem, s čimer smo se dovolj dobro približali ustreznim vrednostim dodatka Na za kompenzacijo naboja, hkrati ohranili reakcijo v bolj viskozni mešanici, alkalijsko aktiviran material pa je imel le manjši delež novih mineralov in ~60 % amorfne snovi.

Nega in sušenje po negi vplivata na rezultate tlačne in upogibne trdnosti. V primeru nege in sušenja pri sobnih pogojih,

throughout the whole volume. Some of these pores merged, but majority stayed trapped in the matrix, as viscosity was apparently high enough and solidification during curing fast enough that migration of bubbles was severely hindered (Figure 3 a). Also quartz, which was found in the waste foundry sand, was trapped in the alkali activated structure (Figure 3 b in red circle). Quartz obviously did not react with alkali and was present in aluminosilicate matrix only as filler. Aluminosilicate matrix is in form of 2D flakes, if there were not enough reagents in the surrounding area, otherwise it grew into 3D structure limited with boundary conditions (mold or not reacted quartz), shown in Figure 3 c.

Needle-like structures (Figure 3 d), not visible with naked eye, were observed under SEM after more than 6 months from the synthesis. According to the EDXS (inset in Figure 3 d) there are composed mainly from Na, i.e. they are consequence of the efflorescence of salt from excessive Na in the synthesis, which is not incorporated in the aluminosilicate matrix nor was used in crystal growth during alkali activation (newly grown minerals are presented in Table 3).

### 3 Conclusion

Quartz partially dissolved during alkali activation and was used either in matrix formation, or in formation of new minerals that are filling the matrix. Excessive Na in alkali activated synthesis, which was not used for compensation of negative charge due to the inadequate coordination number of Al in aluminosilicate matrix, is used during reaction for formation of new crystals, remaining Na goes out from the alkali activated material as salt with efflorescence over a long period of time.

je eksperiment neuspešen, v primeru nege na 70 °C, pa je rezultat trdnosti odvisen še od preostalih parametrov. Sušenje na 100 °C in z mikrovalovi izboljšata tlačno trdnost alkalijsko aktiviranemu odpadnemu livarskemu pesku, a izredno poslabšata upogibno trdnost.

Ugotovili smo, da z ustrezno izbiro vhodnih parametrov lahko predelamo odpadni livarski pesek v alkalijsko aktiviran material perspektiven za nadaljnjo uporabo v gradbeništvu. Za dokončno potrditev bodo potrebne še analize trajnosti tovrstnega materiala.

#### 4 Zahvala

Projekt št. C3330-17-529032 „Raziskovalci-2.0-ZAG-529032“ je odobrila Republika Slovenija, Ministrstvo za izobraževanje, znanost in šport. Naložbo sofinancirata Evropska unija iz Evropskega sklada za regionalni razvoj in Republika Slovenija.

Za uporabo XRF gre zahvala Uradu RS za meroslovje (MIRS).

Za pomoč pri delu se zahvaljujemo sodelavcem iz Laboratorija za cemente, malte in keramiko.

#### 5 Viri / Reference

- [1] J. Davidovits, Geopolymers - Inorganic Polymeric New Materials, J. Therm. Anal., 37 (1991) 1633-56
- [2] J. L. Provis, S. J. van Denventer, Alkali Activated Materials, State-of-the-Art Report, Springer, Netherlands 2014
- [3] F. Škvara, Alkali activated material - geopolymer, [http://www.geopolymery.eu/aitom/upload/documents/publikace/2007/2007\\_praha\\_skvara.pdf](http://www.geopolymery.eu/aitom/upload/documents/publikace/2007/2007_praha_skvara.pdf), 20. 12. 2017
- [4] J. C. Petermann, A. Saeed, M. I.

Highest compressive and bending strength, 27,7 MPa and 6,6 MPa, was achieved using only Na-glass with precursor, which was good enough approximation to appropriate value of addition of Na for charge compensation, at the same time reaction in more viscose mixture was retained, alkali activated material only had a smaller percentage of new minerals and ~60 % of amorphous phase.

Curing and drying after curing influences the results of compressive and bending strength. When curing and drying were performed at room conditions, the experiment was not successful, but when curing is performed at 70 °C, the strength's value depends also on other parameters. Drying on 100 °C and with microwaves improve compressive strength of alkali activated waste foundry sand, but at the same time drastically decreases the value of bending strength.

It was found, that with appropriate choice of input parameters waste foundry sand can be processed into alkali activated material promising for further use in building industry. For final approval, analysis of durability tests of alkali activated waste foundry sand have to be performed.

#### 4 Acknowledgement

Project No. C3330-17-529032 “Raziskovalci-2.0-ZAG-529032” was granted by Ministry of Education, Science and Sport of Republic of Slovenia. The investment is co-financed by the Republic of Slovenia, Ministry of Education, Science and Sport and the European Regional Development Fund.

The Metrology Institute of the Republic of Slovenia is acknowledged for the use of XRF. Contribution of coworkers of Laboratorz of Cements, Mortar and Ceramics is greatly acknowledged.

- Hammons, Alkali activated geopolymers: a literature review, Air force research laboratory, materials and manufacturing directorate, 2010
- [5] S. Cho, Geopolymer composites and their application in stress wave mitigation, dissertation, University of Illinois at Urbana-Champaign, 2015
- [6] P. Duxson, A. Fernández-Jiménez, J. L. Provis, G. C. Lukey, A. Palomo, J. Van Deventer, Geopolymer Technology: The Current State of the Art, *J. Mater. Sci.*, 42 (2007) 2917-33, doi: 10.1007/s10853-006-0637-z
- [7] B. V. Rangan, Fly Ash-Based Geopolymer Concrete, Research Report GC4, Curtin University of Technology, Perth, Australia, 2008
- [8] D. M. J. Sumajouw, D. Hardjito, S. E. Wallah, B. V. Rangan, Fly ash-based geopolymer concrete: study of slender reinforced columns, *J. Mater. Sci.*, 42 (2007) 3124, doi: 10.1007/s10853-006-0523-8
- [9] D. Khale, R. Chaudhary, Mechanism of geopolymerization and factors influencing its development: a review, *J. Mater. Sci.*, 42 (2007) 729, doi: 10.1007/s10853-006-0401-4
- [10] B. Ingham, M. F. Toney, X-ray diffraction for characterizing metallic films, *Structure, Processing and Properties*, (2014) 3-38, doi: 10.1533/9780857096296.1.3
- [11] H. M. Rietveld, A profile refinement method for nuclear and magnetic structures, *Journal of Applied Crystallography*, 2 (1969), 65-71, doi: 10.1107/s0021889869006558
- [12] B. Horvat, A. Rečnik, G. Dražič, The growth of anatase bipyramidal crystals during hydrothermal synthesis, *Journal of Crystal Growth*, 347 (2012) 19-24, doi: 10.1016/j.jcrysgro.2012.03.027
- [13] Peter Duxson, John L. Provis, Grant C. Lukey, Seth W. Mallicoat, Waltraud M. Kriven, Jannie S. J. van Deventer, Understanding the relationship between geopolymer composition microstructure and mechanical properties, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 269 (2005) 47-58, doi: 10.1016/j.colsurfa.2005.06.060
- [14] A. C. Akhavan, The Silica Group, Overview of Silica Polymorphs, [http://www.quartzpage.de/gen\\_mod.html](http://www.quartzpage.de/gen_mod.html), last accessed: 07. 12. 2018
- [15] K. H. Brosnan, G. L. Mesing, D. K. Agrawal, Microwave Sintering of Alumina at 2.45 GHz, *Journal of the American Ceramics Society*, 86 (2003) 1307-1312, doi: 10.1111/j.1151-2916.2003.tb03467.x
- [16] C. Rodriguez-Navarro, E. Ruiz-Agudo, A. Luque, A. B. Rodriguez-Navarro, M. Ortega-Huerta, Thermal decomposition of calcite: Mechanisms of formation and textural evolution of CaO nanocrystals, *American Mineralogist*, 94 (2009) 578-593, doi: 10.2138/am.2009.3021