

Microstructural Characteristics of Geopolymers Based on Alkali-Activated Fly Ash

M. N. Mužek,* J. Zelić, and D. Jozić

Faculty of Chemistry and Technology, University of Split,
Teslina 10/V, 21000 Split, Croatia

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Aluminosilicate geopolymers with a high silica molar ratio have been prepared by mixing Croatian coal-ash (ASTM Class F) and sodium silicate solution (water glass, technical grade). The samples were cured at 85 °C for 8 h and 24 h in different experimental conditions. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM/EDS) have been used to identify the new phases formed in geopolymeric binders, and to follow the progress of their formation. It was observed that the glassy component of fly ash used reacted with water glass. The main reaction product formed in the geopolymeric materials was amorphous alkali aluminosilicate gel that induces a shift in the T–O (T=Si or Al) asymmetric stretching band towards lower frequency (1074.58 cm^{-1}) in relation to the ones in the original fly ash. SEM/EDS detected a highly inhomogeneous glass-like matrix, constituted mainly of Na-Si-Al phases in a bulk region, together with unreacted spheres of fly ash particles.

Key words:

Geopolymers, class F fly ash, alkaline activations, XRD, FTIR, SEM/EDS

Introduction

Fly ash (FA) is a by-product of the combustion of pulverized coal in thermal power plants. Power stations, using coal as fuel, are worldwide energy sources and therefore a large amount of fly ash is generated annually. FA is mainly used as raw material in the cement and concrete industry; however, the material has favourable properties for more valuable applications, such as its conversion into alkali-activated aluminosilicate materials, or inorganic polymers referred to as “geopolymers” by Davidovits.¹ Their applications are found in construction materials that require high early-age strength, resistance to acids, stability and durability, and they can also be used for immobilisation of toxic and radioactive waste,² as an alternative to Portland cement.³

Typical geopolymer composition proposed by Davidovits¹ is generally expressed as $nM_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ (where n : 1–1.6; $x > 2$; y : 3–7; and M : Na, K) with a characteristic initial pH (alkaline) value greater than 10. Specifically, values of 2, 4 and 6 of SiO_2/Al_2O_3 molar ratios constitute three classes of geopolymers named poly(sialate), poly(sialate-siloxo) and poly(sialate-disiloxo). In a system with a high Si-concentration, the reaction of geopolymerisation starts with the formation of oligomeric silicates resulting in a rigid 3D network of polymer structures, poly(sialate-siloxo) and poly(sialate-disiloxo). Low Si-concentration results in poly(sialate) polymer structure.

The composition, structure and properties of the reaction products obtained in the alkali activation of metakaolin or fly ash are directly impacted by the specific surface and composition of the initial raw materials and the type, concentration and relative amount of alkali activator used.^{4–7} Effects of the initial SiO_2/Al_2O_3 ratios on the compressive strength and microstructure of alkali-activated aluminosilicate systems have been reported in literature.^{7–11} Typically, better properties were reported for mixtures with SiO_2/Al_2O_3 ratios in the range of 3.0–3.8 with a Na_2O/Al_2O_3 ratio of about 1. Changes in the SiO_2/Al_2O_3 ratio beyond this range have been found to result in low strength systems.^{10,11} De Silva *et al.*⁷ showed that high SiO_2/Al_2O_3 mixtures resulted in amorphous polymer containing Na-Al-Si phases (geopolymer) while low SiO_2/Al_2O_3 mixtures tended to produce grains containing Na-Al-Si phases, i.e. these grains were absent in mixtures of higher SiO_2/Al_2O_3 ratios.

The microstructures of geopolymer synthesized from FA or metakaolin with an activator containing a small concentration of soluble silica have been compared in literature. Fernández-Jiménez *et al.*¹² discovered that in a microstructure of alkali-activated Class F fly ash, a far greater level of unreacted particles was present compared to the, metakaolin-based geopolymer. Although the microstructure of a metakaolin-based geopolymer consists almost entirely of gel phases, the microstructure of FA-based geopolymer can best be described as a gel-bonded ash composite. Microstructural analysis has shown that the unreacted

*Corresponding author: M. N. Mužek – muky@ktf-split.hr

phases in FA specimens are not only the crystalline impurities but also glassy phases that are either insoluble in alkaline media due to their chemical composition or potentially soluble but have not been able to react due to their hindered mass transport.

The present work explores the effect of the initial composition and reactivity of Croatian fly ash, as well as the processing conditions on the resulting geopolymer microstructure during alkali activation process in mixtures with high silica content. Previous work¹³ discussed the effect of heat curing conditions on mechanical strength development of fly ash – water glass systems, cured at 85 °C, for a period of 28 days. It has been shown that the alkali-activated fly ash (AAFA) mortars cured 24 h at 85 °C could reach the compressive strength of about 15 MPa at 28 days, which is much lower than expected. This study has been extended and the present paper is focused on investigating the influence of both: initial composition of raw materials and different curing regimes on the microstructure development of the alkali-activated fly ash, i.e., geopolymeric materials prepared.

Experimental

Materials

A type F (as defined in ASTM C618) fly ash from the Croatian power plant Plomin2 (Plomin) was used in the present study. The chemical analysis of the fly ash is given in Table 1. The amount of reactive silica and vitreous phase in the FA used were also determined.^{14,15} The specific surface area (Blaine) of the FA was 312.90 m² kg⁻¹.¹³ A technical-grade sodium silicate solution (Galenika – Magmasil, Serbia) was used as alkaline activator. It was a type S, water glass, SiO₂/Na₂O = 3.10 (Na₂O = 7.75 %, SiO₂ = 24.5 % and H₂O = 67.75 % with density 1.33 g cm⁻³).

Alkali activation of fly ash

The fly ash was activated with a sodium silicate solution to prepare paste specimens. In order to provide good workability, the “solution/ash” ratio was 0.72 and the water-to-fly ash ratio was 0.50, respectively. Solution stands for the activating solution containing the alkalis, silicate and water, and

Table 1 – Chemical composition of fly ash from Plomin, Croatia, in mass fraction, w/%

Oxide	w/%
SiO ₂	55.51
Al ₂ O ₃	23.33
Fe ₂ O ₃	9.11
CaO	3.00
MgO	1.30
Na ₂ O	0.49
TiO ₂	1.02
K ₂ O	1.01
MnO	0.01
P ₂ O ₅	0.07
ZnO	0.01
PbO	0.01
SO ₃	0.60
Total	95.47
Loss of ignition	4.94
Reactive SiO ₂	31.23
Si/O (molar ratio)	0.33
Na ₂ O/Al ₂ O ₃ (molar ratio)	0.034

the ash for FA used. Total water in system was only water from sodium silicate which itself contained $w = 67.75$ % of water. No extra water was added. The water-to-fly ash ratio of 0.50 yields a paste that is workable for several hours before it sets and hardens. The composition of the initial mixture, presented in Table 2, was calculated on the basis of mole ratios between the main oxides. After mixing, the fresh pastes were cast immediately into metallic moulds (4 x 4 x 16 cm) that were later kept in a hermetically sealed tin mould to prevent moisture evaporation. They were exposed to heat curing in a laboratory convection oven at 85 °C. Three types of curing regimes were used: the fresh pastes were precured at room temperature (about 26 °C) for 24 h and then heat cured at 85 °C for 8 h (sample C) and 24 h (sample A), respectively. In the case of sample B, the fresh pastes were heat cured at 85 °C for 24 h without precuring at room temperature.

Table 2 – Composition of the initial mixes and molar ratios between the main oxides

SiO ₂ (moles)	Al ₂ O ₃ (moles)	Na ₂ O (moles)	H ₂ O (moles)	SiO ₂ /Al ₂ O ₃ (molar ratio)	Na ₂ O/Al ₂ O ₃ (molar ratio)	Na ₂ O/SiO ₂ (molar ratio)	H ₂ O/Na ₂ O (molar ratio)
5.52	1.03	0.46	12.60	5.36	0.45	0.08	27.39

After removing from the oven, the alkali-activated fly ash (AAFA) specimens were covered with plastic to protect the samples from excessive water loss, and cured at room temperature subsequently.

Finally, the study of AAFA microstructure and development of the new phases formed in the AAFA samples, as well as the progress of their formation, were performed for aging times of 3, 7, and 28 days.

Characterization of AAFA pastes

The mineralogical and microstructural characteristics of AAFA pastes were studied by X-ray Diffraction, Fourier Transform Infrared Spectroscopy, and Scanning Electron Microscopy-Energy Dispersive Spectroscopy. X-ray powder diffraction analysis was recorded on a PANalytical X'Pert Pro, the PW spectrometer 3040/60 model with Xray tube PW3373/00 Cu LFF DK119707 at current of 40 mA and voltage of 40 kV and goniometer PW 3050/60 with a scanning rate of 2° min^{-1} in the range of $4^\circ < 2\theta < 64^\circ$. The FTIR spectrum was made on KBr pastille on a Perkin Elmer Spectrum One in the range from 4000 to 400 cm^{-1} . Microstructural studies utilised a SEM equipped with EDS analyser (a Scanning SEM/EDS Tescan VEGA Electron Microscope Oxford INCA EDS, PA, USA). The fracture surface of geopolymer samples was carbon-coated. Generated products were identified through determining the degree of reaction (α) by attacking the hardened AAFA samples with a 1:20 HCl solution at the respective reaction times (3, 7 and 28 days). This procedure separates the reaction products (sodium aluminosilicate gel and zeolites) dissolved in the acid from the unreacted ash, which remains in the insoluble residue.¹⁵

Results and discussion

The chemical composition of FA used in the present study is given in Table 1. It contained mainly SiO_2 , Al_2O_3 , Fe_2O_3 and the oxides of Ca, Mg, alkalis (Na and K), Ti etc. The analysis also showed that FA contained $w = 31.23 \%$ of "reactive silica", as the part of FA that reacts with alumina and the alkalis giving place to a cementitious material. The vitreous (soluble) and crystalline (insoluble residue) phases, quantified by the acid treatment with 1 % HF, were $w = 77.25 \%$, and $w = 22.75 \%$ respectively.

The composition of the initial mixture, given in Table 2, indicates total mole ratios of the main oxides of interest. The general formula obtained for initial composition of mixtures prepared was: $0.46 \text{ Na}_2\text{O} \cdot 1.03 \text{ Al}_2\text{O}_3 \cdot 5.52 \text{ SiO}_2 \cdot 12.60 \text{ H}_2\text{O}$. The method applied in this study was based on a ratio

between main oxides ($\text{SiO}_2/\text{Al}_2\text{O}_3$) in a reacting mixture; it makes understanding the structure formation process related to the features of microstructure synthesized easier. Most of the studies support preparation of geopolymeric materials from aluminosilicate and sodium silicate solutions using restricted $\text{SiO}_2/\text{Al}_2\text{O}_3$ composition range. Khale and Chaundhary¹⁶ suggested that there exist certain synthesis limits in the formation of geopolymeric products. $\text{Na}_2\text{O}/\text{SiO}_2$, $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratios lay in the range of 0.2–0.48, 3.3–4.5, 10–25 and 0.8–1.6 respectively. As seen from Table 2, both $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratios (5.36 and 0.45, respectively) differ from the favourable limits (3.3–4.5 and 0.8–1.6, respectively). These deviations may result in incomplete dissolution of FA used (due to its relatively poor dissolution characteristics even under high alkaline conditions, $\text{pH} = 13.4$), which consequently reflects on the structure and condensation process of geopolymers.¹⁷

Fig. 1 shows the variation in degree of reaction with aging time (3, 7 and 28 days) and also with a heat curing conditions for all the AAFA systems analysed (A, B, C samples). The degree of reaction, estimated from the remaining (unreacted) content of FA in the AAFA samples after the acid treatment with a 1:20 HCl, showed that only $w = 21.26\text{--}32.86 \%$ of the FA was converted in reaction during 28 days. However, in all samples studied the degree of reaction increases with aging time. A possible reason for this is that in systems with a high silica content, more silicate species are available for condensation and reaction between silicate species resulting in oligomeric silicate. Further condensation between oligomeric silicates and aluminates results in a 3D rigid polymeric structure.⁷

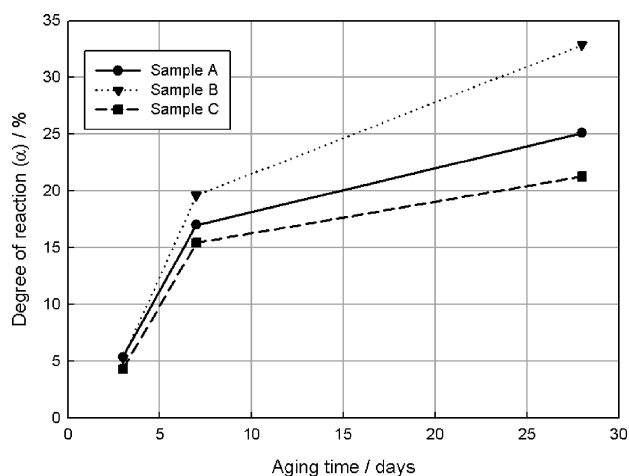


Fig. 1 – Degree of reaction (α) vs. aging time for the AAFA systems (A, B, C samples): A – cured 24 h at 85°C after 24 h precuring at room temperature, B – cured 8 h at 85°C without precuring; C – cured 8 h at 85°C after 24 h precuring at room temperature

Fig. 1 also indicates that the B samples cured 24 h at 85 °C had better conversion than the ones precured at room temperature for 24 h before heat treatment (A and C samples), suggesting that precuring at room temperature had no beneficial effect on reaction progress.

These observations are consistent with the compressive strength development as previously reported,¹³ where the B samples reached higher values, at about 15 MPa at 28 days. It is obvious that the presence of soluble silicate alone is not sufficient to fully dissolve the aluminium ions, which leave unreacted FA in the sample⁸ resulting in the decrease of compressive strengths.

XRD analysis of AAFA pastes

The XRD analysis was used to confirm the crystalline character of the phases formed during the alkali activation. Fig. 2 shows the XRD patterns of the original FA and AAFA systems after seven days, respectively. Comparing the XRD pattern of the original fly ash with those of the geopolymeric materials, it can be seen that the crystalline phases originally existent in the FA (quartz, mullite and hematite) have not been transformed by the activation reaction. This relatively large amount of fly ash still present in the hardened samples is an indicator of incomplete geopolymerisation reaction. Results also suggest that the structure of these geopolymers is typically glass-like.

The broad “hump” in the XRD diffractogram (Fig. 2b) corresponding to the glassy phase is convoluted with that of the original fly ash. In addition, the broad amorphous background feature in the region $2\theta = 16\text{--}34^\circ$, present in all samples after thermal treatment, suggests that the main reaction prod-

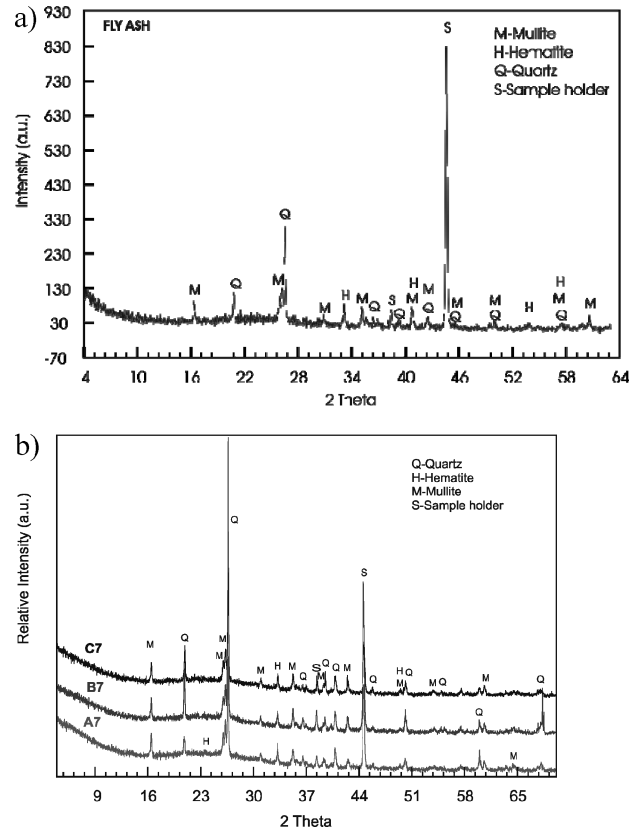


Fig. 2 – XRD patterns for the original FA (a), and the AAFA systems (b)

uct formed is “alkaline aluminosilicate gel” with low-ordered crystalline structure.^{18,19}

FTIR analysis of AAFA pastes

The FTIR spectra for all the AAFA systems, as well as the spectrum for the original FA, are plotted in Fig. 3. These spectra reveal the differences be-

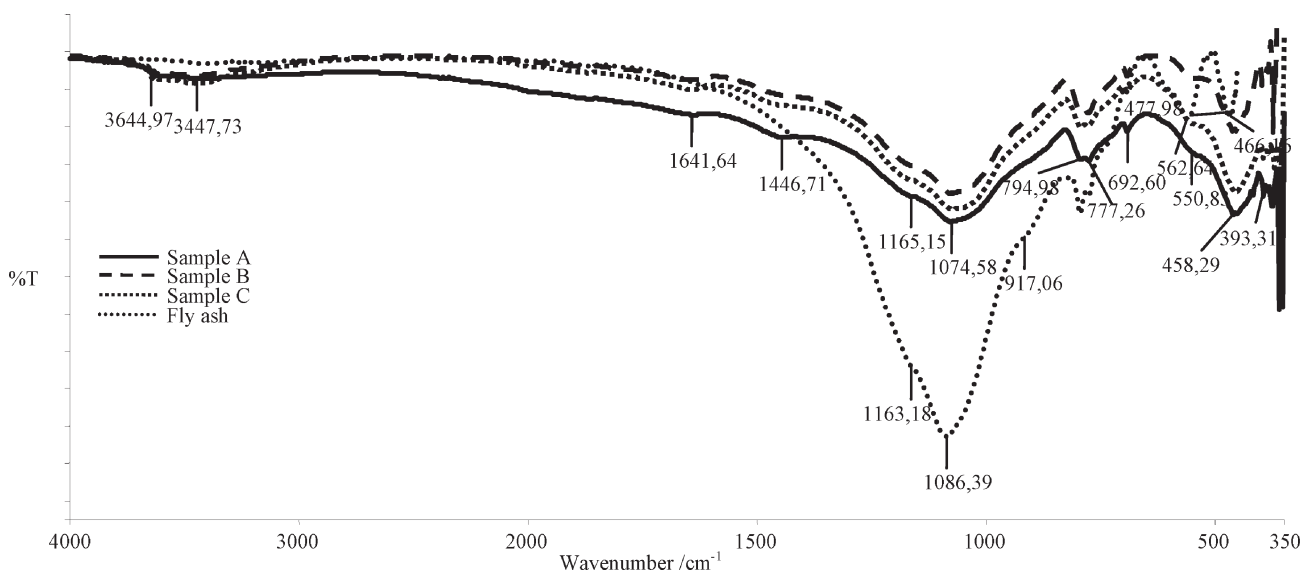


Fig. 3 – FTIR spectra for the original FA and AAFA systems. Wave numbers of interest are indicated. Letters A, B and C indicate samples.

tween the original FA and geopolymeric materials formed. The main broad band at 1086.39 cm^{-1} in the original FA, corresponding to asymmetric stretching vibrations of Si–O–Si and Al–O–Si^{20,21} becomes sharper and shifts toward lower frequencies ($\sim 1074\text{ cm}^{-1}$) as a result of the formation of new reaction products associated with ongoing alkali activation. The formation of this new amorphous aluminosilicate gel phase suggests depolymerisation and structural reorganisation of the amorphous phases in the AAFA materials. The bands located at 794.98 cm^{-1} and 466.16 cm^{-1} are ascribed to bending vibrations of Si–O–Si and O–Si–O bonds, implying the presence of quartz that is hardly affected by alkaline activation of FA.^{22,23} The bands located at 692.60 cm^{-1} and 550.83 cm^{-1} indicate the presence of mullite. XRD analysis also confirmed the presence of these phases.

In all geopolymeric materials, new bands appeared in the regions of 1600 cm^{-1} and 3450 cm^{-1}

that were attributed to bending vibrations (H–O–H) and stretching vibrations (–OH, H–O–H). Water is needed for the process of geopolymerisation as it implicates the destruction of solid particles and hydrolysis of dissolved Al^{3+} and Si^{4+} ions. The bond at 1446.71 cm^{-1} assigned to the stretching vibrations of O–C–O bond occurred in all AAFA samples, suggesting the presence of sodium bicarbonate.

This observation of changes in the FTIR spectra of the AAFA materials indicate that the geopolymerisation reaction occurred leading to the formation of the main reaction product, an amorphous aluminosilicate gel in all samples examined.

SEM analysis of AAFA pastes

SEM images with EDS analysis (Figs. 4 and 5) show the morphology changes that occurred in the hardened AAFA samples. In all samples studied, the sodium silicate gel was observed as the majority

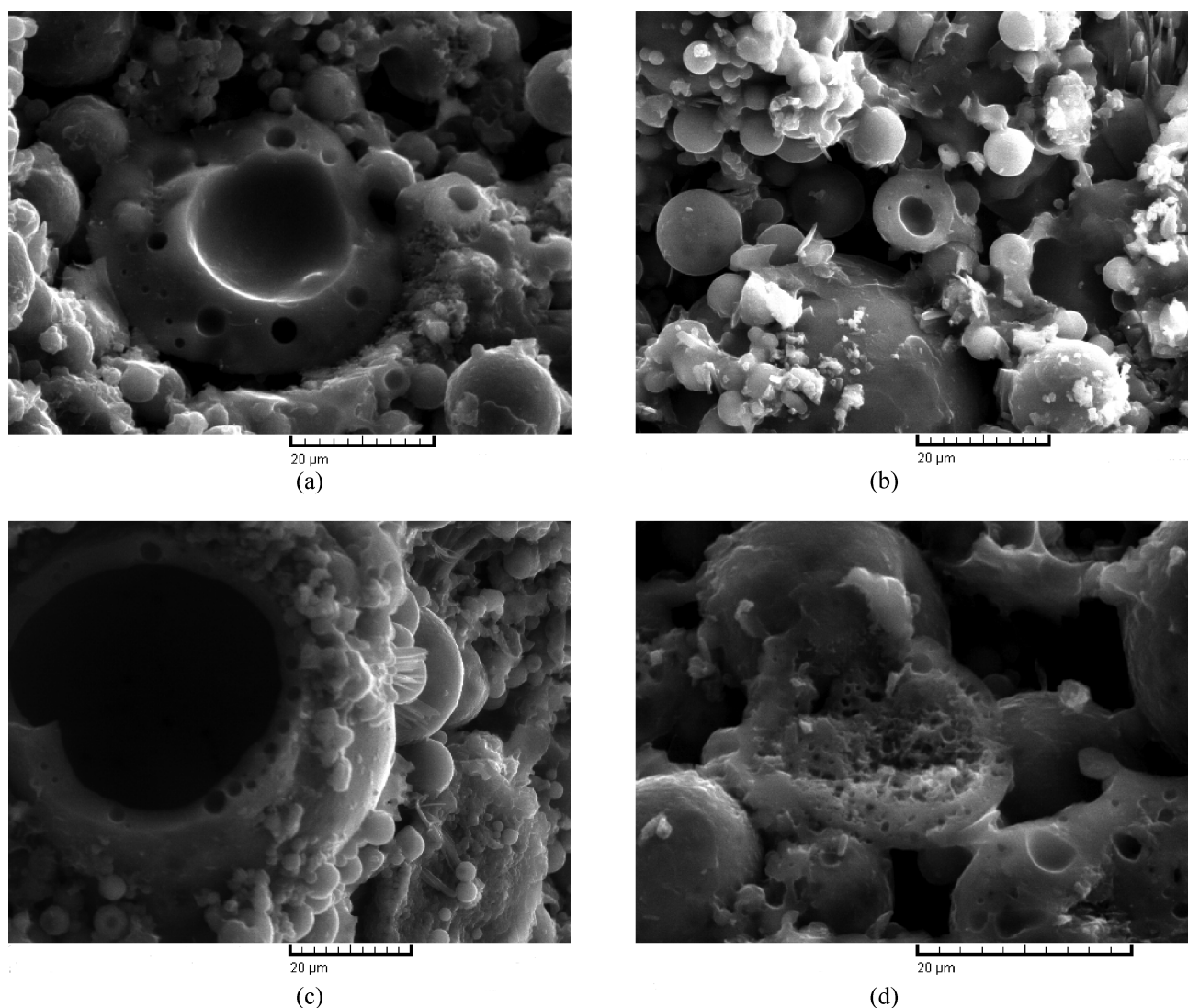


Fig. 4 – SEM micrographs of the hardened AAFA samples

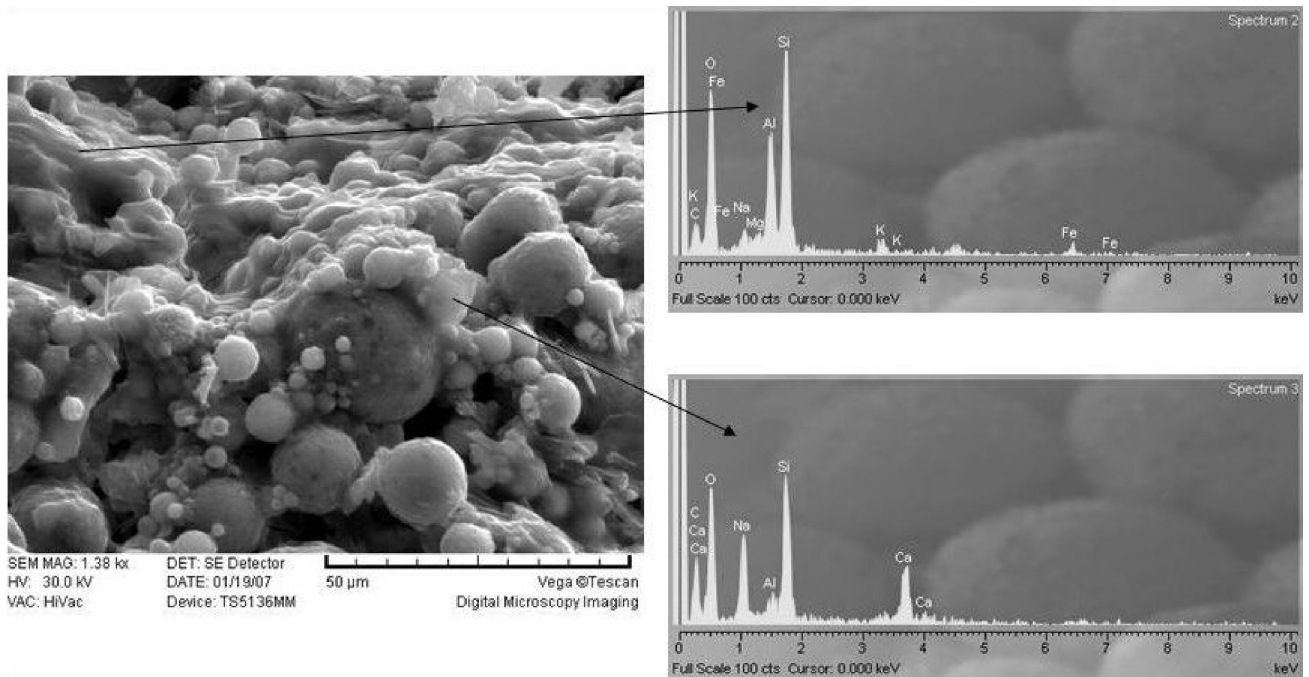


Fig. 5 – SEM micrographs and EDS analysis of the hardened AAFA samples

product, along with the unreacted FA particles, during the aging time up to 28 days. The microstructure was highly inhomogeneous and the matrix was full of loosely structured FA grains of different sizes. Numerous circular cavities belonging to FA particles are evident in the gel. Cavities surroundings consist of tubular vitreous network (Figs. 4a-c). The considerable amount of unreacted spheres, as well as the presence of pores in the geopolymer matrix (Fig. 4d) indicate an incomplete reaction in the system and could explain why the AAFA samples show a lower degree of reaction. Fig. 5 clearly shows inhomogeneous glass-like matrix of the amorphous aluminosilicate gel. The unreacted spheres of FA indicate an incomplete reaction in the systems investigated. The low degree of reaction (up to 32.86 % after 28 days), Fig. 1, associated with low reactivity of FA used also confirms this finding. If the silica content increases, the degree of reaction taking place in a geopolymer forming paste decreases according to observations of Provis and van Deventer.²⁴

EDS analysis of gel showed that gel mostly consists of the phases containing Na-Si-Al in the bulk region suggesting the formation of silicate-activated gel by polymerization throughout the inter particles volume.^{7,25} This correlates with the published works of Lee and Deventer²³ meaning that, in a medium with a high concentration of dissolved silica, the species dissolved from the surface of FA particles migrate from the surface into the bulk solution.

In addition to Na, Si and Al, a small amount of Fe, Ca, K and Mg was also observed in the gel by EDS analysis (Fig. 5). These remnants (Fe, Ca, K, Mg) obviously represent the FA phases, which for various reasons, did not dissolve during alkali activation. Lloyd *et al.*²⁶ suggested that during alkaline activation these remnants may even disperse through the gel. According to the authors, different solubility of phases in the aluminosilicate gel formed determines the distance of these remnants from the surface of FA particle. It appears that Mg does not disperse in the gel to the same extent as Ca (Fig. 5).

The properties of resulting geopolymer systems depend on not only the composition and reactivity of the fly ash used, but also on the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the mixture, which is evident from the experimental data presented here and the discussion above. Pre-processing (e.g. fine grinding etc.) and/or use of a combination of raw materials of different reactivity, as well as selection of an activator in a geopolymer system are required to achieve the desired product properties.

Conclusions

The alkaline activation of Class F fly ash used with water glass solution, cured at 85 °C, produces an alkaline aluminosilicate gel as the major reaction product regardless of the experimental conditions (duration of thermal treatment and aging time). Precuring at room temperature had no beneficial ef-

fect on the reaction progress. The low degree of reaction in systems with high silica content ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 5.36) suggests that these pastes solidify before the dissolution of FA reaches its completion.

The T-O (T=Si or Al) asymmetric stretching band (as evident from the FTIR) shifts toward lower wave-number in reference to the ones of the original fly ash suggesting depolymerisation and structural reorganization of the amorphous phases in the AAFA materials.

The presence of glass-like matrix of the amorphous aluminosilicate gel is observed in all AAFA systems investigated. It mostly consists of amorphous gel containing Na, Si, Al (as evident from EDS) mixed together with the unreacted spheres of fly ash (as evident from the SEM).

The microstructure of the AAFA systems with high silica content was highly inhomogeneous (as evident from the SEM) and correlates with the synthesis parameters studied (initial composition of mixtures and reactivity of FA used). The low degree of reaction (up to 32.86 % after 28 days) associated with low reactivity of FA used, as well as low compressive strengths presented in earlier work also confirm this finding.

The results presented here show that Croatian fly ash could be used as a valuable raw material instead of being disposed in landfills as a waste material, which could be increasingly expensive causing an environmental problem.

Results also show the importance of the proper selection of raw materials as the key to gaining a high-performance geopolymer, and are therefore very useful in opening up a way to synthesize new geopolymeric binders using Croatian fly ash the properties of which will have to be investigated.

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