Mechanical and microstructural properties of alkali-activated fly ash geopolymers

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ABSTRACT

This paper investigates the properties of geopolymer obtained by alkali-activation of fly ash (FA), i.e. the influence of characteristics of the representative group of FA (class F) from Serbia, as well as that of the nature and concentration of various activators on mechanical and microstructural properties of geopolymers. Aqueous solutions of $Ca(OH)_2$, NaOH, $NaOH + Na_2CO_3$, KOH and sodium silicate (water glass) of various concentrations were used as alkali activators. It was established that the nature and concentration of the activator was the most dominant parameter in the alkali-activation process. In respect of physical characteristics of FA, the key parameter was fineness. The geopolymer based on FA with the highest content of fine particles (<43 μm), showed the highest compressive strength in all cases. Regardless of FA characteristics, nature and concentration of the activator, the alkali-activation products were mainly amorphous. The formation of crystalline phases (zeolites) occurred in some cases, depending on the reaction conditions. The highest compressive strength was obtained using sodium silicate. Together with the increase of sodium silicate SiO_2/Na_2O mass ratio, the atomic Si/Al ratio in the reaction products was also increased. Under the experimental conditions of this investigation, high strength was directly related to the high Si/Al ratio.

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1. Introduction

Thermal power plants using coal as a source of energy also produce significant amounts of fly ash (FA). It is estimated that the world production of FA in 2010 will reach 800 million tons. Until now, only a minor part of this material has been recycled (20–30%), while the rest has been disposed of in landfills, thus contributing to the pollution of soil, water and air. About 5 million tons of FA is produced annually in Serbia. The problem of FA disposal is far more complicated than disposal of majority of other industrial waste materials and requires finding the possibilities of valorisation of this material. Investigations, particularly intensive in the last decade, have indicated the possibility for development and application of geopolymers – binders based on alkali-activated FA [1–3].

FA is generally observed as a very heterogeneous material. Although there are a lot of papers on synthesis of geopolymers based on FA [4–12], the heterogeneousness of FA superimposes the need for further investigations to achieve better understanding of

the process of geopolymerization and to open the way to a wider practical application.

FA is at any rate an interesting material in respect of the sustainable development concept, since the use of FA in the alkali-activation process does not require large energy consumption, thus reducing the emission of undesirable CO_2. The use of FA in the alkali-activation process (geopolymerization) also contributes to the reduction of the exploitation of natural raw materials, and at the same time complies with the more complicated demands of the construction industry in terms of characteristics and the quality of the construction materials.

During the alkali-activation process, the vitreous phase of FA dissolves, forming aluminosilicate gel afterwards. It is not necessary to complete the dissolution of the vitreous phase for geopolymerization to proceed. This reaction depends on a whole series of parameters such as: particle size distribution, chemical composition, amount of vitreous phase in FA, nature, concentration and pH of activators [5–7,13,14]. Conditions of the reaction, i.e. the curing conditions (temperature, curing time, relative humidity), also show a great influence on the development of microstructure, and thereafter on the mechanical characteristics of alkali-activated FA [15].

Because of a large number of influential factors and complexity of the problem, it is clear that particular studies cannot provide all the answers, so there is a need for further investigations. The expan-

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sion of database in this case can strengthen trust and provide better conditions for mass production and application of alkali-activated FA.

The fundamental aim of this paper is to investigate the influence of characteristics of the representative group of fly ash (FA) from Serbia, as well as that of the nature and concentration of activators on mechanical and microstructural properties of geopolymers obtained by alkali-activation of FA. The investigated fly ashes which belong to class F (classification in accordance with ASTM C 618-03), are not only the most widely present in Serbia but, due to their characteristics and classification, possess the greatest potential for the alkali-activation process.

2. Experiment

2.1. Materials

In the course of the investigation, fly ashes from several thermal power plants (TPP) were analysed, a total of six different specimens of FA:

FA-I	TPP "Morava" – Svilajnac
FA-II	TPP "Kolubara" – Veliki Crljani
FA-III	TPP 'Kostolac B1" – Kostolac
FA-IV	TPP "Kostolac B2" – Kostolac
FA-V	TPP "Nikola Tesla A" – Obrenovac
FA-VI	TPP "Nikola Tesla B" – Obrenovac

The following activators were used: $Ca(OH)_2$ (technical "Nexe", Serbia), NaOH (p.a. 98%, "Lach-Ner", Czech Republic), Na_2CO_3 (p.a. anhydrous, "Centrohem", Serbia), KOH (p.a. 85%, "Superlab", Serbia), $Na_2O \cdot nSiO_2$ (aqueous solution of sodium silicate – water glass, modulus $n = SiO_2/Na_2O = 3.04$, $\rho = 1.36 \, g/cm^3$, 8.5% Na_2O, 25.8% SiO_2, "Centrochem", Serbia). The sodium silicate modulus was adjusted by adding NaOH.

2.2. Methods

The chemical composition of the starting FA was determined by classic chemical analysis – alkali melting. The particle size distribution was determined by sieving through a mesh.

Pozzolanic characteristics (pozzolanic class) of FA were determined according to Serbian standard SRPS B.C.018/01. Mortar was prepared using calcium hydroxide (hydrated lime) as an activator, fly ash, standard sand and water in a mass ratio of 1:2:9:1.8, respectively. When calcium hydroxide and FA are taken as a binder, the sand/binder ratio is 3:1. The sand/binder (FA) ratio = 3:1 was also used in the investigation of alkali-activated FA. The mortar specimens (40 mm × 40 mm × 160 mm) within the moulds were placed

into plastic bags, and cured at room temperature of $20 \pm 2 \,°C$ during the first 24 h. For the next 6 days, the mortar specimens were cured at an elevated temperature of $55 \pm 2 \,°C$. After curing, the specimens were taken out of the moulds and cooled down to the room temperature.

Strength testing of alkali-activated FA mortars was carried out according to SRPS EN 196-1, which is in compliance with European EN 196-1 standard. The strength of the alkali-activated FA was determined using mortar prisms (40 mm × 40 mm × 160 mm).

Regardless of the type of the activator used, the mortars were prepared first by adding the activator into water, and then by mixing the solution with FA and the standard sand. The concentration of the activator was expressed as a percentage of an appropriate oxide in relation to the mass of FA (Table 2). Although some authors have reported the strength loss after 3 days of heat curing [5], in order to determine the relativity of the existing standard SRPS B.C.018/01 in relation to the investigated geopolymers, the same geopolymer curing conditions were kept as for the standard test.

Since different kinds of FA require different amounts of water, the water was added in the amount necessary to obtain equal consistency, i.e. flow of mortars (the mortar flow, measured on a flow table, was 125 ± 5 mm).

The temperature and the nature of an activator are the factors that have significant influence on the mechanical characteristics of the alkali-activated FA [2]. The efficiency (activation potential) of different activators on the alkali-activation process can be determined if the curing conditions remain constant. During these investigations the curing conditions (temperature and time) were constant in all cases. The mortar prisms were protected by a plastic foil to prevent undesirable water loss during curing at the elevated temperature.

Mineralogical and microstructural characterization of FA was carried out on pastes. The pastes were prepared first by adding the appropriate activator into water, and then by mixing the solution with FA. After the period of curing (1 day at $20 \pm 2 \,°C$ and 6 days at $55 \pm 2 \,°C$), the reaction was stopped by soaking and grinding the specimens in isopropyl alcohol, and the specimens were dried to constant mass at $50 \,°C$.

The mineralogical characterization was carried out by PHILLIPS PW 1710 powder diffractometer under the following conditions: Cu $K\alpha = 1.54178 \,Å$, $U = 40 \, kV$, $I = 30 \, mA$, 5–50° 2θ, with a step of 0.02° and holding time of 0.5 s for each step.

The morphological characterization of the starting and activated FA was determined by Tescan VEGA TS 5130 MM scanning electron microscope (SEM). Energy dispersive X-ray analysis (EDS) was carried out by INCAPentaFET-x3 device (Oxford Instruments). The

Table 1
Chemical composition (%) and particle size distribution of FA.

Investigated properties	FA					
	I	II	III	IV	V	VI
SiO_2	51.74	60.29	44.09	44.71	48.12	53.96
Al_2O_3	21.36	17.53	21.74	22.43	23.99	24.83
Fe_2O_3	8.80	9.61	14.49	15.04	7.90	6.75
MnO	0.04	0.03	0.03	0.04	0.03	0.02
CaO	11.34	6.21	10.96	10.27	11.03	7.93
MgO	1.56	1.20	1.19	1.09	1.30	1.24
SO_3	1.27	0.66	1.77	1.56	2.25	0.90
Na_2O	0.64	0.58	0.52	0.40	0.46	0.48
K_2O	1.35	1.04	0.76	0.81	1.31	1.31
LOI at 1000 °C	1.60	2.83	4.40	3.59	3.61	2.31
Sum of oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$)	81.90	87.43	80.32	82.18	80.01	85.54
Classification acc. to ASTM C 618	F	F	F	F	F	F
SiO_2/Al_2O_3	2.42	3.44	2.03	1.99	2.01	2.17
Particle content > 63 μm (%)	23.30	42.65	56.50	30.35	30.66	55.70
Particle content 43–63 μm (%)	8.05	5.30	6.00	8.45	7.33	8.25
Particle content < 43 μm (%)	68.65	52.05	37.50	61.20	62.01	36.05

Table 2
Strength (N/mm^2) and water/FA ratio of alkali-activated FA mortar after 7 days (1 day at $20 \pm 2\,^\circ$C and 6 days at $55 \pm 2\,^\circ$C).

FA	Ca(OH)$_2$ (standard test)[a] 25% CaO[b]	NaOH 10% Na$_2$O	15% Na$_2$O	NaOH + Na$_2$CO$_3$ Mass ratio = 2/1 10% Na$_2$O	KOH 10% K$_2$O	Na$_2$O·nSiO$_2$ n = 0.5 10% Na$_2$O	n = 1.0 10% Na$_2$O	n = 1.5 8% Na$_2$O	10% Na$_2$O	n = 2.0 10% Na$_2$O
I	12.42[c] (0.90)[d]	12.87 (0.54)	16.25 (0.50)	2.96 (0.63)	2.46 (0.57)	9.53 (0.64)	34.72 (0.57)	29.24 (0.60)	43.21 (0.54)	41.40 (0.58)
II	9.22 (0.90)	2.15 (0.68)	4.53 (0.63)	1.84 (0.75)	0.00 –	–	–	9.48 (0.71)	19.45 (0.70)	–
III	9.37 (0.90)	0.26 (0.79)	–	–	–	–	–	–	–	–
IV	11.16 (0.90)	3.36 (0.66)	16.04 (0.55)	0.00 (0.64)	0.00	–	–	16.71 (0.62)	23.08 (0.62)	–
V	11.30 (0.90)	1.56 (0.87)	–	–	–	–	–	–	–	–
VI	6.50 (0.90)	0.00 (0.81)	–	–	–	–	–	–	–	–

[a] According to SRPS B.C1.018/01 standard.
[b] Activator/FA mass ratio (activator concentration was given as a percentage of appropriate oxide).
[c] Strength.
[d] Water/FA mass ratio (in brackets).

specimens were coated with a mixture of Au and Pd prior to the analysis.

3. Results and discussions

3.1. Characterization of fly ashes

The chemical composition and particle size distribution of FA are given in Table 1. Based on the chemical composition and according to ASTM C 618 criteria, the fly ashes investigated can be classified as class F. The fly ashes marked as I, IV and V contained the highest rate of particles smaller than 43 μm (over 60%). In spite of the differences among the analysed FA, in most cases the basic mineral composition was as usual: minor amounts of crystalline phases were present in the form of quartz, mullite, feldspar, magnetite, anhydrite and calcite [16].

3.2. Strength of alkali-activated fly ash mortars

The strength of mortars based on FA activated by different types and concentrations of activators, under the same curing conditions, is shown in Table 2.

The investigation of the pozzolanic class (Table 2, the test with Ca(OH)$_2$) indicated that there were small differences in respect of the compressive strength amongst FA. Significantly lower strength was noticed only at FA-VI. According to SRPS B.C1.018/01 standard, the fly ashes investigated can be classified into two classes: FA-II, -III and -VI satisfy requirements for pozzolanic class 5 (minimum strength of 5 N/mm^2), while FA-I, -IV and -V satisfy requirements for pozzolanic class 10 (minimum strength of 10 N/mm^2). No FA satisfied requirements for pozzolanic class 15 (minimum strength of 15 N/mm^2).

FA activated by NaOH (10% Na$_2$O) showed very low strength after 7 days (Table 2). The exception was FA-I, the strength of which was comparable with the previous test.

Compared to the other activators, the highest compressive strength was obtained using the aqueous solution of sodium silicate. Thus, it can be concluded that the type, i.e. nature of activator, is the most dominant parameter in the reaction of alkali activation.

Activation potential of the activators investigated (taking into account equal concentrations) can be represented by the following pattern:

$$KOH < NaOH + Na_2CO_3 < NaOH < Na_2O \cdot nSiO_2 \tag{1}$$
$$\text{min} \rightarrow \text{activation potential} \rightarrow \text{max}$$
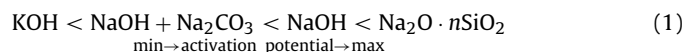
KOH, as well as the combination of NaOH + Na$_2$CO$_3$, showed a very low activation potential. This noticeably lower potential of KOH compared to NaOH was probably due to the difference in ionic diameter between sodium and potassium [2]. The presence of Na$_2$CO$_3$ obviously had a negative effect on the activation potential of NaOH, probably as a result of a decrease in pH of the solution, followed by a slower dissolution of FA and low strength values. Ca(OH)$_2$ showed a considerable activation potential, in most cases higher than NaOH. However, it must be taken into account that the concentration of CaO was higher compared to that of the other activators.

Concentration of activator can also considerably influence the mechanical characteristics of mortars based on alkali-activated FA. The increase of activator concentration led to the compressive strength increase.

The determination of the pozzolanic class (standard test, Table 2), even as a standardized method, cannot be authoritative for assessing the potential reactivity of FA in the alkali-activation process. Since standards are meant to enable innovation, there is an obvious need for developing and standardizing a specific methodology for the potential reactivity assessment of FA in the alkali-activation process [1].

Complex composition, fineness of the particles, variable morphology and characteristics of FA cause serious problems during their characterization, specification and application. The chemical composition and physical characteristics are commonly used for specification and industrial application of FA. This classification has appeared to be insufficient for reliable determination of possibilities of using FA, since the prevalence and the way the elements emerge (minerals and phases) also plays an important role [17].

Although there is a certain synergism of physical, chemical and mineralogical characteristics of FA in the alkali-activation process, the physical characteristics of FA constitute a very important parameter, the influence of which can be analysed independently. The compressive strength results (Fig. 1) show that, independent of the activator type, the compressive strength was predominantly affected by the content of FA fine particles (smaller than 43 μm). Accordingly, the highest compressive strength in all cases was shown by mortars made of FA-I which had the highest content
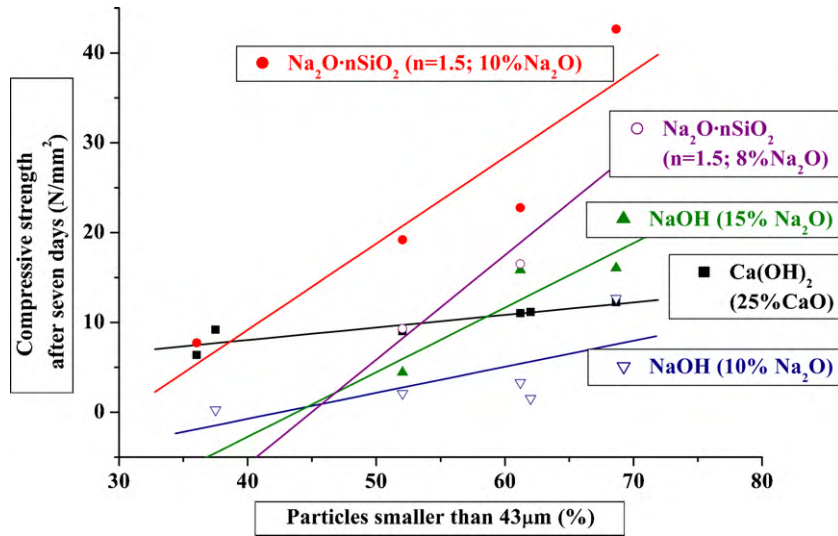
Fig. 1. Compressive strength of alkali-activated FA mortar as a function of the content of FA fine particles (smaller than 43 μm).

of fine particles. This conclusively indicates that coarse particles (larger than 43 μm) were less active in the alkali-activation process. The fineness or particle size distribution was the key parameter in terms of physical characteristics of FA [6].

Physico-mechanical characteristics of alkali-activated FA were also closely related to the presence of sodium and silicon dissolved in the system. It has already been stated that the increase in sodium concentration led to the increased strength. When the concentration of sodium was maintained constant, as it had been the case with most experiments with sodium silicate (10% Na$_2$O in relation to FA mass), the concentration of silicon became the key factor in determining the strength of alkali-activated FA. Thus, the presence of dissolved silicon in the aqueous solution of sodium silicate obviously contributed to the increase of reaction velocity, and therefore led to the increased compressive strength.

The higher the concentration of dissolved silicon in the system, the higher the strength obtained [2,3,10]. However, by increasing the concentration of silicon, i.e. modulus of a sodium silicate solution, compressive strength was increased, but only up to a certain value (Table 2). The further increase in concentration of silicon led to a decrease in compressive strength. Therefore, the optimal value of sodium silicate modulus was about 1.5. In alkali silicate solutions with a high SiO$_2$/Na$_2$O ratio, silicon is present in a broad spectrum of structurally different polymeric forms (oligomers), as well as in the form of a monomer [18]. Types of oligomers and their presence affect the structure formation, and consequently the strength as well.
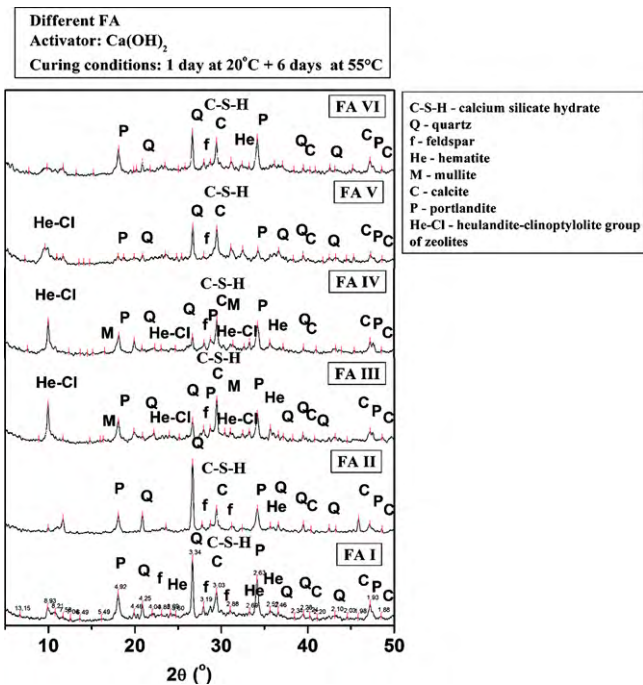

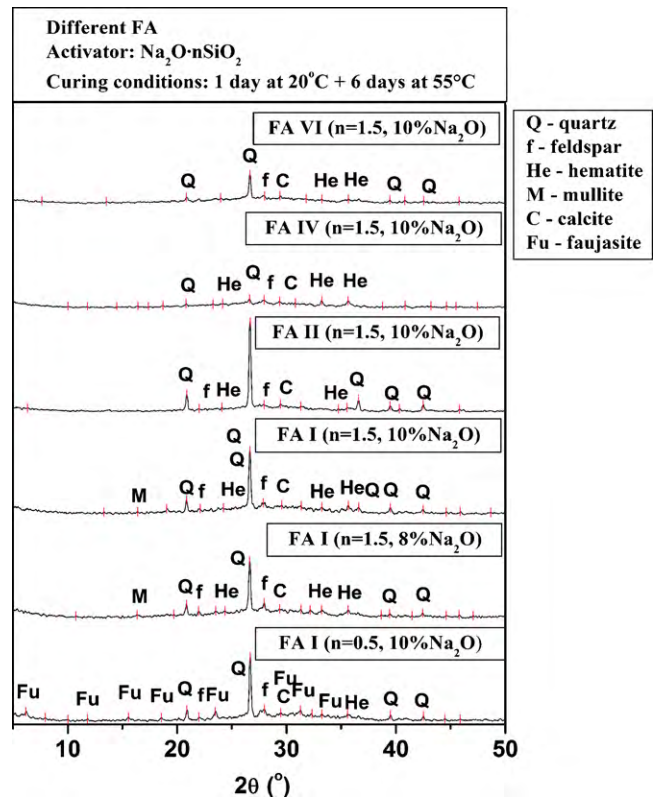**Fig. 2.** Diffractograms of different FA activated by calcium hydroxide.

Fig. 3. Diffractograms of different FA activated by sodium silicate of various moduli (*n*) and concentrations.
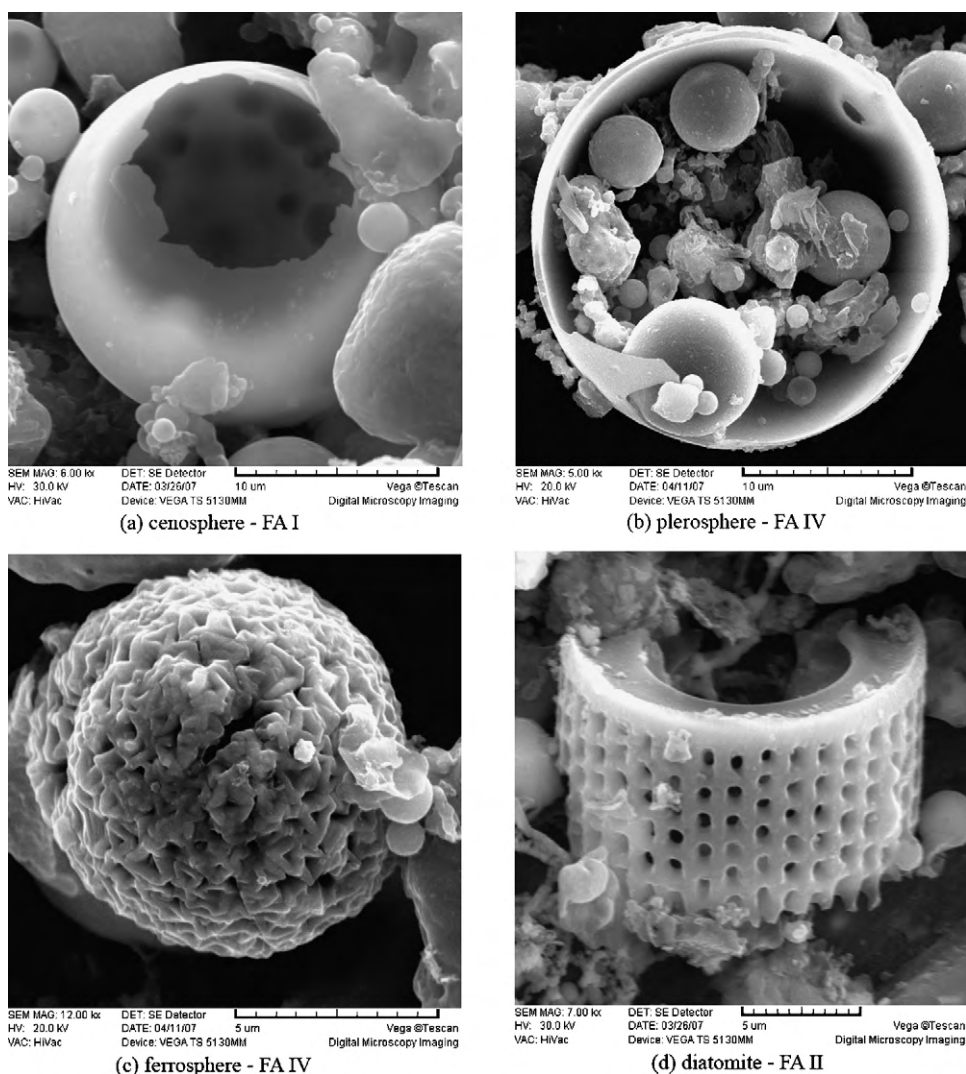
Fig. 4. Morphology of FA.

When the dependence between strength and water/FA ratio is analysed, it can be seen that, in the case of sodium hydroxide as an activator, the strength increases with the decrease of water/FA ratio. This phenomenon was also noticed by other authors [19]. The highest strength corresponds to lowest water/FA ratio (0.54 in the case of 10%Na_2O and 0.50 in the case of 15%Na_2O), which is the case with FA I. It is followed by FA-IV (0.66 and 0.55 respectively) and FA-II (0.68 and 0.63). In other FAs a relatively high water/FA ratio is present in the case of 10% Na_2O (about 0.8 and higher), and, consequently, very low strength. When sodium silicate is used as an activator, with the change of the modulus (SiO_2/Na_2O) from 0.5 to 2.0 the strength also changes in accordance with water/FA ratio.

However, the fact that water/FA ratio is not a dominating criterion is explicitly indicated when KOH is used as an activator. Here, the water/FA ratio is very low (0.57), but the strength is also very low. So, water/FA ratio has limited importance. Therefore, geopolymer strength does not only depend on characteristics of FA or water/FA ratio, but also on characteristics of activator.

In the end, the fact that the reaction of geopolymerization is a chemical reaction between dissolved silicates and aluminates in the presence of a very alkaline medium should be underlined. The water is a transporting medium for dissolved substances, but it does not take part in the chemical reaction, as in the case of portland cement. Nevertheless, if there are appropriate conditions for the reaction of geopolymerization, then the amount of water present in the system becomes an important factor for mortar workability and consequently for mortar strength [5].

3.3. X-ray diffraction analysis

X-ray diffraction analysis of the alkali-activated FA samples indicated that the products of the reaction were mostly amorphous, which was confirmed by a wide and diffusive reflection in an interval from 25° to 35° 2θ (Figs. 2 and 3). Distinguished reflections as for quartz, mullite, hematite, magnetite, anhydrite and feldspar referred to crystalline phases originating from the starting FA.

When $Ca(OH)_2$ was used as an activator (Fig. 2), besides calcite and unreacted portlandite, the presence of calcium silicate hydrate (C–S–H) was recorded in all activated FA samples. Also, in particular cases (FA-III, FA-IV and FA-V) the presence of zeolites of heulandite–clinoptylolite type was noticed.

Fig. 3 shows the diffractograms of different FA activated by the sodium silicate solutions of various moduli and concentrations. The presence of the zeolite phases (faujasite) was noticed in the case when the modulus of the sodium silicate solution was 0.5. However, this type of zeolite was not found when the same FA had been activated by the sodium silicate solution with a modulus of 1.5
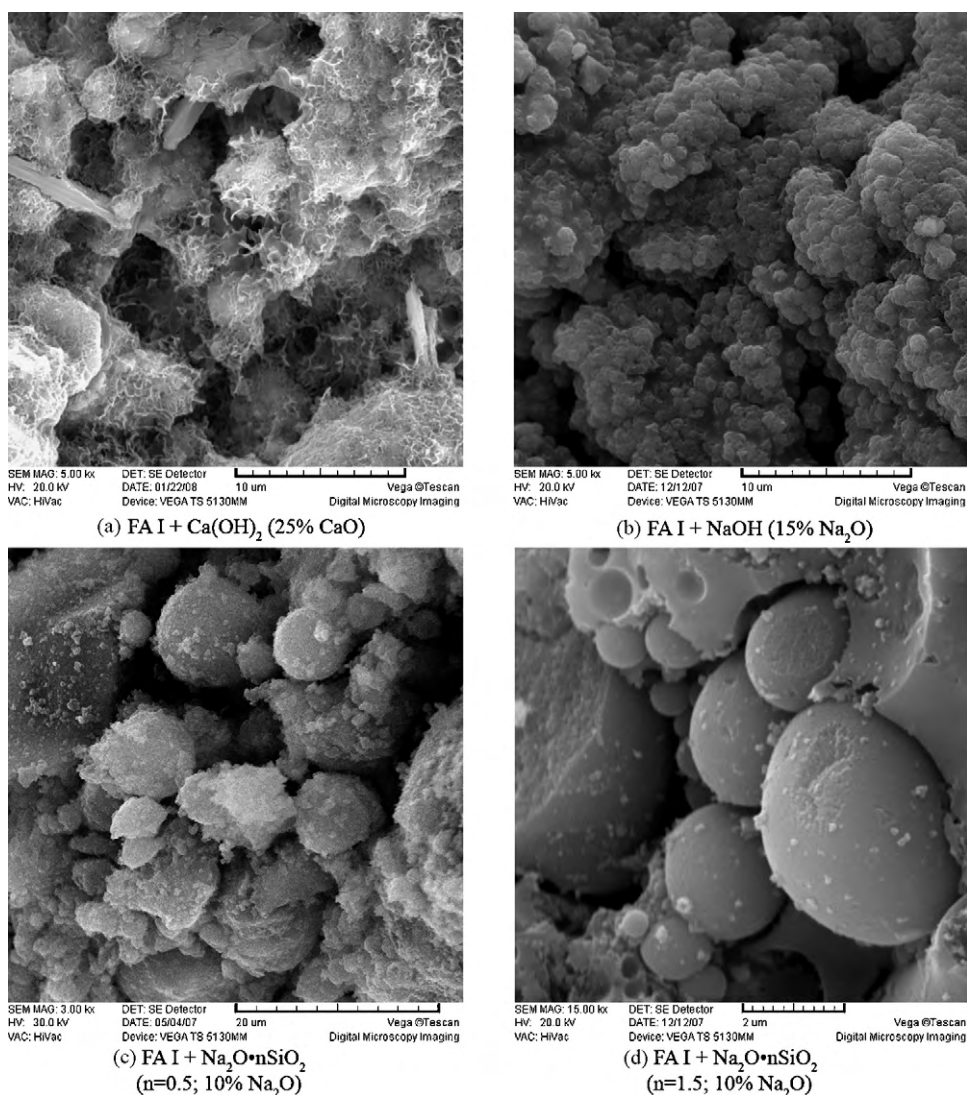
Fig. 5. Morphology of alkali-activated FA-I.

and cured under the same conditions, independent of the activator concentration.

The fundamental difference between the synthesis of zeolites and alkali-activation of FA lies in different reaction conditions [3]. The alkali-activation of FA implies the use of very concentrated alkali solutions, as well as a rather low solid/liquid ratio, whereas

Table 3
The average content of different elements (atomic %) and their ratios in the products of the reaction FA-I + $Na_2O \cdot nSiO_2$ (10% Na_2O).

Elements and ratios	SiO_2/Na_2O	
	0.5	1.5
Si	10.25	17.40
Al	3.95	5.91
Na	11.66	4.41
Ca	2.32	2.62
Fe	0.87	0.98
Si/Al	2.64	3.16
Na/Si	1.98	0.26
Na/Al	4.47	0.86

The results presented in Table 3 are the average values from 40 to 50 individual EDS analyses.

the nuclei of zeolites are formed as the products of the reaction. However, the growth of the zeolite crystals is very slow, so the amorphous binding matrix (aluminosilicate gel, "zeolite precursor" or "prezeolite") was initially stabilized. Aluminosilicate gel has a three-dimensional structure of a poor zeolitic organization [8]. The presence of small amounts of zeolite crystals indicates in which direction the system could evolve if being able to reach the thermodynamic balance.

The crystallization of zeolites was slowed down with a greater participation of dissolved silicon in the solution (Fig. 3: FA-I, $n = 0.5$ and 1.5, 10% Na_2O). With the increase of SiO_2/Na_2O ratio in the solution, the alkali-activation process was accelerated, while the probability of the formation of zeolites was reduced, and the amorphous phases became the only reaction products [20]. The absence of crystalline products was closely related to higher compressive strength (Fig. 3 and Table 2).

In general, regardless of the FA characteristics, nature and concentration of an activator, the alkali-activation products were mostly amorphous. In particular cases, as secondary products of the reaction, the crystalline phases, similar to some types of zeolites (faujasite), were formed. However, it was the exception rather than the rule.

3.4. Scanning electron microscopy

Scanning electron microscopy (SEM) indicated that FA represents a heterogeneous material comprising particles of different dimensions and shapes (regular and irregular). Some of the particles present in FA are shown in Fig. 4. The irregularly shaped particles consisted mainly of quartz, agglomerates and unburned particles of coal, while the regularly shaped particles were mostly spheres (cenospheres, plerospheres, and ferrospheres).

Since the alkali-activated FA-I in all cases showed the highest compressive strength, the morphological investigation was limited to these samples. The alkali-activation products also represented a heterogeneous material, containing both the compact matrix (completely reacted FA particles) and partially reacted or unreacted FA particles (Fig. 5a–d).

Depending on the type and concentration of the activator, a change in the morphology and porosity of alkali-activated FA-I was noticed. The network of fibrous products – calcium silicate hydrates and noticeably present porosity can be seen in Fig. 5a. FA-I activated by NaOH showed cluster-like morphology of the reaction products, and with similar porosity as the previous ones (Fig. 5b). The products of a lower crystallinity arose in a system with sodium silicate compared to sodium hydroxide, as a result of fast nucleation of solid products that immediately surround the FA particles [21]. The difference in morphology and porosity of FA-I activated by sodium silicate of different moduli was also visible. In Fig. 5d (FA-I activated by sodium silicate, $n = 1.5$) although unreacted spherical FA particles were visibly present, a very compact structure was noticed, i.e. a surface continuity of the reaction products resembling an instantly frozen viscous fluid, implying high mechanical characteristics [10].

Morphological heterogeneity was mostly the result of the heterogeneity of starting FA. On the other hand, the type and concentration of the activator also had a certain influence on the microstructural development and morphology of the reaction products. There is no doubt that the curing conditions can influence the microstructural development as well as the morphology of the reaction products, but their influence was not investigated in this study.

3.5. Energy dispersive spectroscopy (EDS) analysis

The results of EDS analysis of FA-I activated by an aqueous solution of sodium silicate are shown in Table 3 and Fig. 6. The results presented in Table 3 are the average values from 40 to 50 individual EDS analyses.

With the increase of the sodium silicate SiO_2/Na_2O mass ratio, primarily there was an increase in the content of silicon in the products of the reaction, followed by an increase in aluminium, while the content of calcium and iron was slightly changed (Table 3). In bridge, the content of sodium decreased rapidly. Also, with the increase of the SiO_2/Na_2O ratio, the Si/Al atomic ratio increased, while Na/Si and Na/Al decreased.

In alkali silicate solutions with a high SiO_2/Na_2O ratio, silicon is present in a broad spectrum of structurally different polymeric forms (oligomers), as well as in a form of monomer [18]. In these solutions there is also an insufficient amount of sodium hydroxide to fully neutralize weak hydrogen ions, thus enabling only 15% of oxygen sites to be charged [22]. The presence of these charges is the main cause of mutual repulsions of small oligomers and coagulation prevention. This system responds to changes in alkali content by changing its degree of polymerization inversely, i.e. the higher the content of alkali (compared to silicon), the lower the degree of polymerization and vice versa.
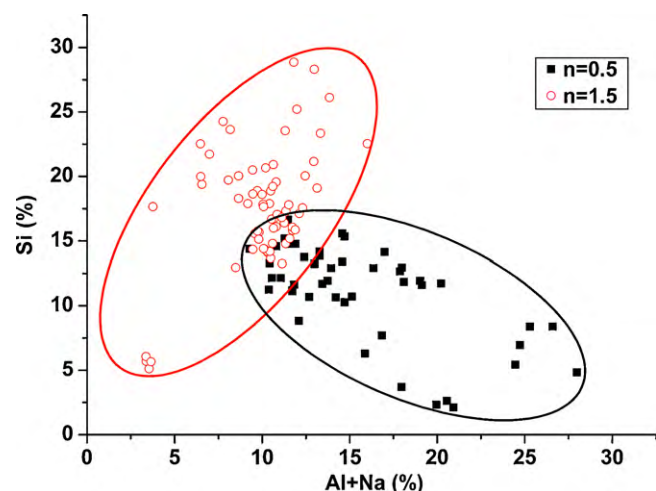

Fig. 6. Ratios of major elements in the products of the reaction. FA-I + Na$_2$O·nSiO$_2$ (10% Na$_2$O)

The alkali-activated systems require highly alkaline solutions to prompt dissolving of solid aluminosilicates. High initial pH values hinder coagulation and precipitation of dissolved silicates present in the aqueous solution of sodium silicate. As the pH value of sodium silicate solution begins to decrease from its initial value of about 14 to lower values, due to dissolving of solid aluminosilicates from FA, the polycondensation starts to take place rapidly. The polycondensation includes both dissolved silicates present in an activator and dissolved substances from FA. As a result, the whole series of processes starts to happen, such as coagulation, formation of colloids, gel formation as well as gel restructuration, while the reaction products are being formed – an amorphous aluminosilicate matrix which is incorporated with immiscible particles of FA of different composition and size (Fig. 5). The greater presence of oligomers in the system, together with a higher SiO_2/Na_2O ratio, and their participation in the reaction could ultimately result in the increase of Si/Al ratio in the reaction products, which was proved by the EDS analysis (Table 3).

As the compressive strength was significantly higher after 7 days in the case of $SiO_2/Na_2O = 1.5$, compared to $SiO_2/Na_2O = 0.5$ (Table 2), it means that higher strength values were directly related to higher Si/Al ratio; the higher the Si/Al ratio in the products of the reaction, the higher the strength [23]. This practically means that depending on the SiO_2/Na_2O ratio in the sodium silicate two diversely organized geopolymer structures were identified (Fig. 6), and the pattern of geopolymer structure organization was responsible for the strength differences.

On the other hand, in a solution with a lower SiO_2/Na_2O ratio (0.5), a greater amount of silicate monomers was present, as well as a significant amount of sodium hydroxide, resulting in almost complete neutralization of weak hydrogen ions. A greater incorporation of monomers into the products of the reaction, plus significant participation of sodium could lead to a decrease of the Si/Al ratio in the products, as well as a significant increase of the Na/Si and Na/Al ratios. This was confirmed by the EDS analysis (Table 3). Moreover, an increased content of sodium when SiO_2/Na_2O is 0.5 is probably linked with the formation of zeolites and precipitation of unreacted sodium silicate as well.

4. Conclusions

In this paper, the properties of geopolymer obtained by alkali-activation of fly ash (FA) have been investigated, i.e. the influence of characteristics of the representative group of FA (class F) from

Serbia, as well as that of the nature and concentration of various activators on mechanical and microstructural properties of geopolymers.

In respect of the physical characteristic of FA, the fineness, or particle size distribution was the key parameter. The compressive strength of geopolymers predominantly depended on the content of FA fine particles (smaller than 43 μm). In all cases, the highest mortar compressive strength showed the FA which had the highest amount of fine particles.

The nature and the concentration of the activators were the most dominant factors in the reaction of alkali activation. The highest compressive strength was obtained using an aqueous solution of sodium silicate as an activator ($n = 1.5$; 10% Na_2O). The greatest activation potential of sodium silicate lies in the fact that, compared to the other activators, it contains dissolved and partially polymerized silicon which reacts easily, incorporates into the reaction products and significantly contributes to improving the mortar characteristics.

The investigation of the pozzolanic class (the standard test with calcium hydroxide) cannot be authoritative for assessing the potential reactivity of FA in the alkali-activation process. It is necessary to develop and standardize a specific methodology for the potential reactivity assessment of FA in the alkali-activation process.

Regardless of FA characteristics, nature and concentration of the activator, the alkali-activation products were mainly amorphous. The formation of crystalline phases (zeolites) as secondary products occurred in some cases, depending on the reaction conditions. The probability of the emergence of zeolites decreased with the increase of silicon ions in the solution. The absence of crystalline products (zeolites) was closely related to the high compressive strength.

The alkali-activation products represented a heterogeneous material, containing both the compact matrix (completely reacted FA particles) and the partially reacted or unreacted FA particles.

With the increase of the SiO_2/Na_2O mass ratio of sodium silicate, the content of silicon in the reaction products was significantly increased, followed by the increase of aluminium, while the content of sodium was significantly decreased. The atomic Si/Al ratio was also increased. Under the experimental conditions of this investigation, the high strength was directly related to the high Si/Al ratio; the greater the Si/Al ratio in the reaction products, the higher the strength.

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