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The Effects of Aggressive Environments on the Properties of Fly Ash based Geopolymers

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Abstract. This paper analyzes the effects of two different aggressive environments, concentrated ammonium nitrate solution (480 g/dm³) and sodium sulphate solution (50 g/dm³), on the structure and mechanical strength of fly ash based geopolymers. Geopolymer samples were subjected to the aggressive solutions over a period of 365 days. It was found that exposure to the NH₄NO₃ and Na₂SO₄ solutions caused small decrease in geopolymer strength (10-20 %). The most valuable insight into the structural changes caused by testing of the geopolymer samples in the aggressive solutions was provided by means of ²⁹Si MAS NMR. It was found that the immersion of geopolymer samples in the NH₄NO₃ solution caused breaking of Si-O-Al bonds in the aluminosilicate geopolymer gel structure. On the other hand, treatment of the geopolymer samples with the Na₂SO₄ solution resulted in breaking of Si-O-Si bonds in geopolymer gel structure and leaching of Si. It was concluded that the major changes in the geopolymer structure were associated with the changes in the pH values of aggressive solutions during the testing.

1. Introduction

Geopolymers are a relatively new group of binder materials that are formed by alkali activation of aluminosilicate materials such as fly ash (FA). Alkali activation reaction transforms glassy phase from starting material into the main reaction product, aluminosilicate geopolymer gel. Due to highly cross-linked three dimensional structure of the aluminosilicate geopolymer gel, geopolymers show good mechanical properties. In addition, these binders usually perform better in aggressive aqueous solutions than Portland cement [1].

Ammonium salts solutions are very aggressive to Portland cement structure [2]. NH₄NO₃ is often used as a fertilizer and concrete structures in contact with surface water from the processed agricultural soil can suffer serious damage. The concentrated NH₄NO₃ solution is frequently used for

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the accelerated decalcification test of Portland cement [2]. Decalcification process, which involves leaching of calcium from portlandite and calcium silicate hydrate, is completed after several weeks in the concentrated NH_4NO_3 solution and is accompanied by a loss of ~90 % of the initial strength of the Portland cement samples.

Sulphate ions present in groundwater or soils surrounding a concrete structure also represent a threat to long-term durability of concrete. Sulphate attack on Portland cement based concrete involves diffusion of sulphate ions into the structure and reactions with some of the phases present in the structure, thus forming new phases which can cause stress, expansion and strength loss [1, 2]. Sulphate attack on binders is most often studied in Na_2SO_4 solutions in concentrations of 44 – 50 g/dm^3 [2].

This paper investigates the effects of two aggressive solutions, concentrated NH_4NO_3 and Na_2SO_4 (50 g/dm^3) on the properties of FA based geopolymer samples.

2. Materials and methods

2.1. Materials

Two FA samples from Serbian thermal power plants were used as starting raw materials: FA Kolubara from thermal power plant (TPP) “Kolubara” and FA Svilajnac, from TPP “Morava”. In order to increase reactivity of the FA samples, fractions of the samples smaller than 63 μm were used [3, 4].

Alkaline activator was sodium silicate solution with modulus ($\text{SiO}_2/\text{Na}_2\text{O}$ mass ratio) of 3.04 (“Galenika-Magmasil”, Serbia, 8.72% Na_2O , 26.5% SiO_2 , 64.78% H_2O). Silicate modulus of the activating solution was adjusted by adding NaOH solution (“ZorkaPharm”, Serbia, p.a. 98%).

Aggressive testing solutions were prepared using NH_4NO_3 and Na_2SO_4 of 99 % purity (Superlab, Serbia).

2.2. Preparation of geopolymer samples

Sodium silicate solution with modulus of 1.5 was used as the activating solution. The activator solution/FA ratio was the same for all geopolymer samples (10 % Na_2O content with respect to the FA mass). Geopolymer mortars were prepared by adding the silicate solution to water and then mixing the solution with FA and standard sand. Different amounts of water were required in order to obtain equal workability of the mortars based on the two FA samples (mortar flow measured on a flow table was 125 ± 5 mm), so water/FA ratio was 0.76 for the mortars based on FA Kolubara and 0.56 for the mortars based on FA Svilajnac (water in water/FA ratio was calculated as water from sodium silicate solution + water added for consistency). Sand/FA ratio was 3/1. The moulds with three mortar prisms ($40 \times 40 \times 160$ mm) were placed in plastic bags to avoid moisture loss during curing.

Geopolymer pastes were prepared by mixing the FA with the alkaline activator solution in the same proportion as in the preparation of the geopolymer mortars. Water/FA ratio was 0.69 for the pastes prepared with FA Kolubara and 0.49 for the pastes based on FA Svilajnac. Dimensions of the paste samples were $25 \times 25 \times 30$ mm. Geopolymer mortar and paste samples were cured at 95 °C for 24 hours.

2.3. Experimental design

Testing solutions, concentrated (480 g/dm^3) NH_4NO_3 solution and 50 g/dm^3 Na_2SO_4 solution, were prepared by dissolving NH_4NO_3 and Na_2SO_4 in distilled water.

Three geopolymer mortar prisms and corresponding paste sample were immersed in plastic containers with the solutions and kept at 20 ± 2 °C for a period of up to 365 days. Geopolymer

samples were placed on plastic nettings to ensure that the entire sample surface was in contact with the aggressive solution. Solution/geopolymer mass ratio was 4/1. At the same time, reference samples were cured in the humid chamber (temperature 20 ± 2 °C, humidity ~98%).

2.4. Analytical methods

Compressive strength of the geopolymer mortars was tested using Tony Technik (Toninorm) testing machine.

Nitrogen adsorption-desorption isotherms were determined using Micrometrics ASAP 2020 instrument and powdered mortar samples.

The pH values of the aggressive solutions before and after the testing of the geopolymer samples were measured by pH-meter (pH Testr30, Eutech Instruments).

Inductively coupled plasma optical emission spectrometer (ICP-OES, SpectroGenesis EOP II, Spectro Analytical Instruments GmbH, Kleve) was used to determine the ion exchange between the geopolymers and the aggressive solutions.

Mineralogical characterization was performed by Philips PW 1710, with $\text{CuK}\alpha$ X-rays operating at 30 mA and 40 kV, with 0.02° 2θ steps, 0.5 s step^{-1} in $5 - 50^\circ$ 2θ range.

Scanning electron microscope (SEM, VEGA TS 5130 MM, Tescan) was used for morphological characterization of the samples.

^{29}Si MAS NMR were obtained using Bruker MSL 400 system, Apollo console upgraded (Tecmag) at a Larmor frequency of 79.49 MHz. Single pulse sequence was used for data acquisition with pulse width of 4 μs (corresponding to $\pi/2$ flip angle). Recycle delays were typically 20 s, the number of scans was 4,096 and the spectral width was 20,000 Hz for all recorded spectra. Chemical shifts were externally referenced to 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) standard. Prior to ^{29}Si MAS NMR analysis, iron content of the geopolymer samples was reduced by exposing the samples to a strong magnetic field.

3. Results and discussion

3.1. Effects of the aggressive solutions on mechanical properties of the geopolymer samples

Initial compressive strengths of the geopolymer mortars based on two different FA samples were significantly different (figure 1). After 24 hours of curing, geopolymer mortar based on FA Kolubara showed compressive strength of about 20 MPa, while the strength of the geopolymer mortar based on FA Svilajnac was about two times higher. Differences in the compressive strength of the geopolymer mortars based on the two FA samples were the consequences of different chemical and mineralogical composition of the FA samples and different particle size distribution [3, 4]. FA Kolubara had high quartz content [3], and significantly lower amount of fine, more reactive, FA particles compared to FA Svilajnac [4]. Due to different fine particle content in the FA samples, different quantities of water had to be added in preparation of geopolymer mortars (Section 2.2). Different water/FA ratios affected porosity of the geopolymer samples based on the two FA samples: the porosity of the geopolymer mortar based on FA Kolubara was $0.160 \text{ cm}^3/\text{g}$, while the porosity of the mortar based on FA Svilajnac was lower ($0.055 \text{ cm}^3/\text{g}$) [4].

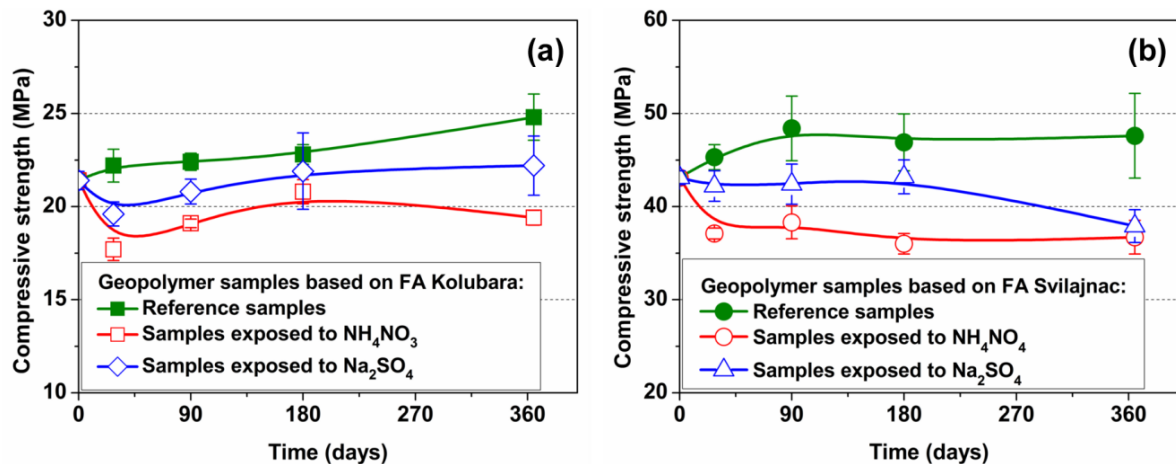


Figure 1. Compressive strength of the geopolymer samples: (a) FA Kolubara geopolymers, (b) FA Svilajnac geopolymers.

Compressive strength of both groups of geopolymer samples (based on FA Kolubara and FA Svilajnac) decreased due to the exposure to the aggressive solutions (figure 1). The strength decrease was more pronounced in the samples exposed to the effects of the NH_4NO_3 solution. The greatest decrease in strength ($\sim 20\%$) was observed after the first 28 days in the NH_4NO_3 solution (figure 1).

After the first 28 days in the Na_2SO_4 solution, compressive strength of the geopolymer samples based on FA Kolubara decreased about 10%. After the initial decrease in strength, the subsequent investigation showed there was a strength increase (figure 1a). Compressive strength of the geopolymer samples based on FA Svilajnac immersed into the Na_2SO_4 solution did not change significantly during the first 180 days of testing. A more noticeable decrease in strength of these samples was noticed only after 365 days in the Na_2SO_4 solution (figure 1b). Differences in strength change of the geopolymer samples based on FA Kolubara and FA Svilajnac exposed to the effects of the Na_2SO_4 solution were probably due to differences in the starting compressive strength (figure 1) and porosity of the samples [4].

It must be noted that testing of Portland cement samples in the same aggressive solutions usually results in much higher decrease in mechanical properties [1, 2].

3.2. Analyses of the aggressive solutions

The initial pH value of the NH_4NO_3 solution was ~ 4 while the initial pH value of the Na_2SO_4 solution was ~ 6 (Table 1). During the testing of the geopolymer samples, pH values of both solutions increased due to the leaching of pore solution alkalis [3, 4]. While the pH value of the NH_4NO_3 was lower than 9.25 throughout the whole testing period [3], the pH value of the Na_2SO_4 solution reached the value of ~ 12 already after the first 28 days of testing.

Table 1. pH values of the aggressive solutions.

Time (days)	NH ₄ NO ₃ solution Geopolymer samples		Na ₂ SO ₄ solution Geopolymer samples	
	FA Kolubara	FA Svilajnac	FA Kolubara	FA Svilajnac
0	4.17	4.17	5.64	5.90
28	8.27	8.31	11.90	11.90
90	8.32	8.40	12.11	12.13
180	8.34	8.44	11.86	12.06
365	7.98	8.47	11.68	11.67

ICP-OES analysis of the NH₄NO₃ solutions showed that alkali (Na, K) and alkaline earth (Ca, Mg) elements were leached from the geopolymers (data shown elsewhere [3]). The main elements of the geopolymer structure (Si and Al) were not detected. Analyses of the Na₂SO₄ solutions indicated that exposure of the geopolymer samples to the effects of the sulphate solution caused leaching of Si (Table 2). The maximum concentrations of Si in the Na₂SO₄ solutions were detected after the same testing periods, in which the maximum strength decrease of the geopolymer mortars was observed (figure1), thus suggesting that Si was probably leached from the aluminosilicate geopolymer gel.

Table 2. Concentrations of Si in the Na₂SO₄ solutions (mg/dm³).

Time (days)	Geopolymer samples	
	FA Kolubara	FA Svilajnac
0	0	0
28	157.6	44.88
365	154.3	163.5

3.3. Effects of the aggressive solutions on the structure of the geopolymer samples

XRD analysis of the geopolymer samples did not indicate formation of any new crystalline phases formed due to a reaction with the aggressive testing solutions (figures 2 and 3). Besides the phases typical for FA [3], only two new phases were observed: calcite, formed as a result of carbonation of the samples, and NH₄NO₃ in the samples that were exposed to the NH₄NO₃ solution.

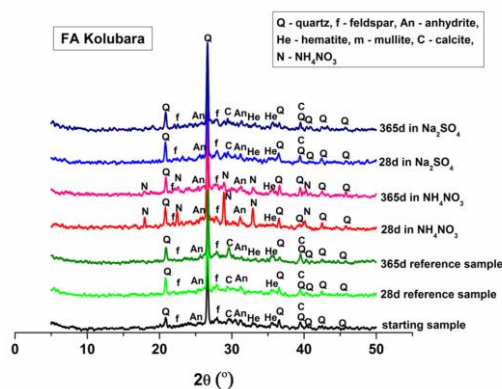


Figure 2. XRD patterns of the FA Kolubara geopolymer samples.

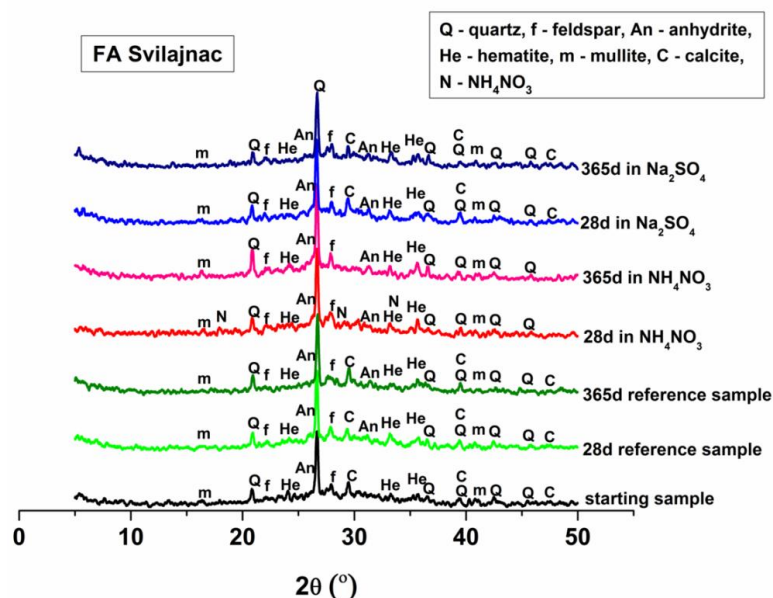


Figure 3. XRD patterns of the FA Svilajnac geopolymer samples.

No significant changes in the structure of the geopolymer samples exposed to the aggressive solutions were detected by SEM analysis of the samples (figures 4 and 5). Both reference and geopolymer samples treated with the NH_4NO_3 and Na_2SO_4 solutions showed microstructure typical for FA based geopolymers, with remnant FA particles embedded in matrix (aluminosilicate geopolymer gel).

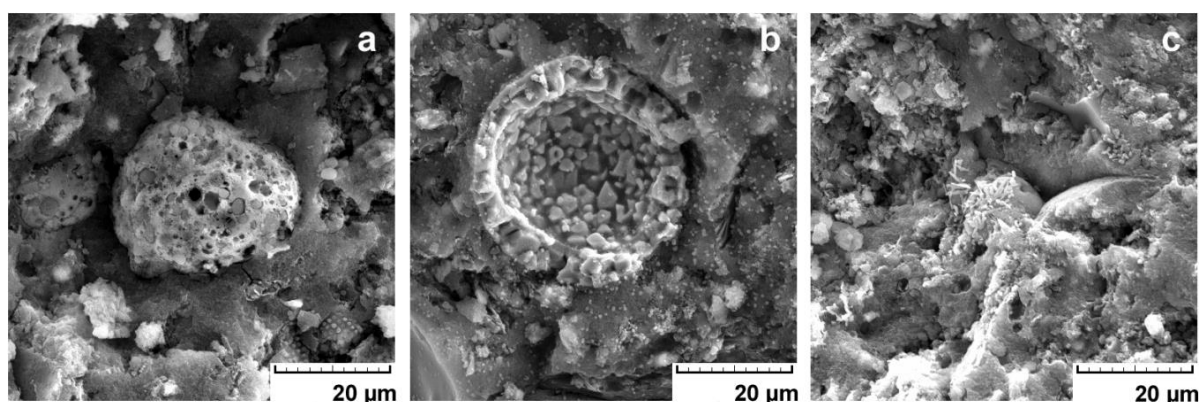


Figure 4. Microstructure of the FA Kolubara geopolymer samples: (a) 365 days reference sample, (b) 365 days in NH_4NO_3 , (c) 365 days in Na_2SO_4 .

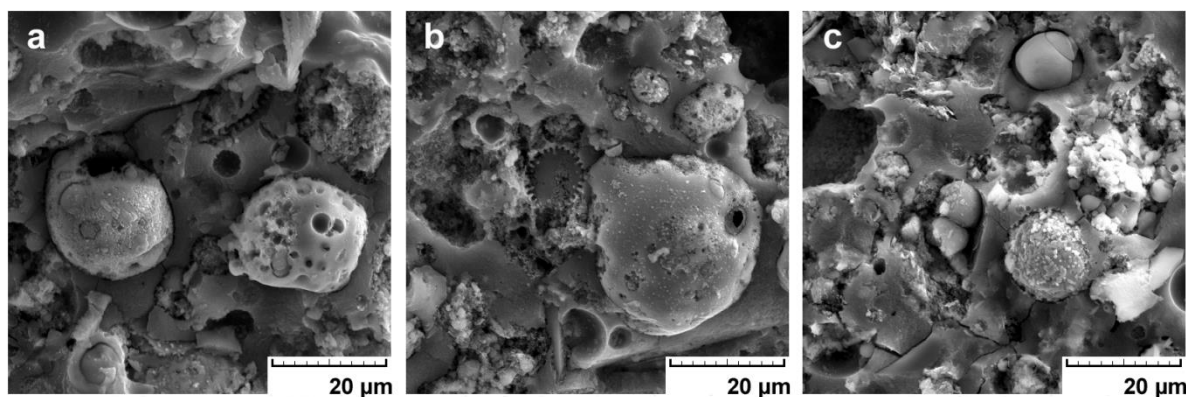


Figure 5. Microstructure of the FA Svilajnac geopolymer samples: (a) 365 days reference sample, (b) 365 days in NH_4NO_3 , (c) 365 days in Na_2SO_4 .

^{29}Si MAS NMR analysis of the geopolymer samples based on FA Kolubara and FA Svilajnac showed broad resonances, centred at -90 to -100 ppm, typical for geopolymers (figures 6 and 7) [3, 4]. Broad ^{29}Si MAS NMR spectra indicate that silicon is surrounded by a wide range of environments. A ^{29}Si MAS NMR spectrum of FA based geopolymer consists of overlapping resonances attributed to silicon sites in different silicate and aluminosilicate phases present in the material: aluminosilicate geopolymer gel, un-reacted glassy and crystalline phases (such as quartz and mullite) from the starting FA [3].

The chemical shift at which maximum peak intensity of the ^{29}Si MAS NMR spectrum occurs depends on the Si/Al atomic ratio of the material [5]. By comparing the ^{29}Si MAS NMR spectra of the reference samples and the geopolymer samples exposed to the aggressive environments, it is clear that the treatment of the geopolymer samples with the NH_4NO_3 and Na_2SO_4 solutions caused changes in the Si/Al atomic ratio of the samples, i.e. changes in the structure of the aluminosilicate geopolymer gel.

The ^{29}Si MAS NMR spectra of the starting geopolymer sample based on FA Kolubara and the reference sample after 28 days of curing were centred at -94 ppm (figure 6). After curing of the reference sample in the humid chamber for 365 days, the maximum peak intensity was centred at -93 ppm. The maximum peak intensity of the starting geopolymer sample based on FA Svilajnac and the reference samples cured for 28 and 365 days was centred at -93 ppm (figure 7).

Shifting of the maximum peak intensities of the geopolymer samples treated with the NH_4NO_3 solution to more negative chemical shifts (figures 6 and 7) indicated that the structure of these samples consisted of species richer in silicon. Since none of the main elements of the aluminosilicate geopolymer gel structure (Si and Al) were detected by the ICP-OES analysis of the solution, it is more likely that exposure of the geopolymer samples led to breaking of -Si-O-Al- bonds in the aluminosilicate gel structure. Breaking of -Si-O-Al- bonds caused the strength decrease of the samples (figure 1) and changed the local environment of the silicon in the aluminosilicate structure, as indicated by the ^{29}Si MAS NMR analysis. The observed degradation mechanism represents the first step of the dealumination reaction, the process that is usually observed in the case of acid attack on geopolymer binder [1, 3].

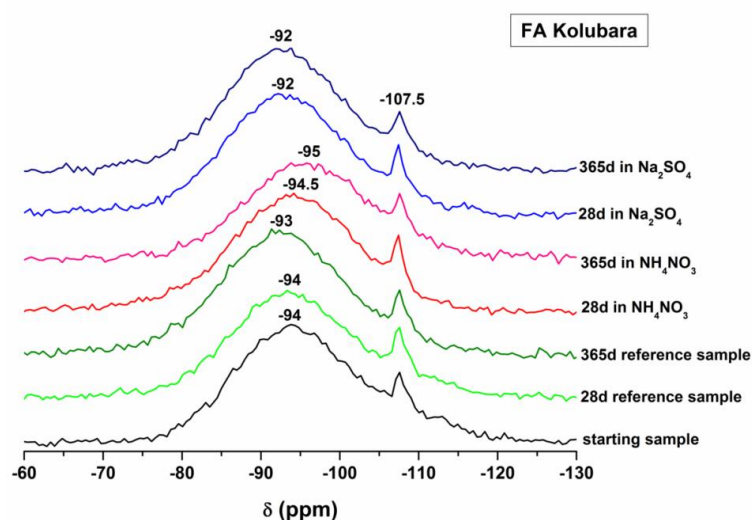


Figure 6. ^{29}Si MAS NMR spectra of the FA Kolubara geopolymer samples.

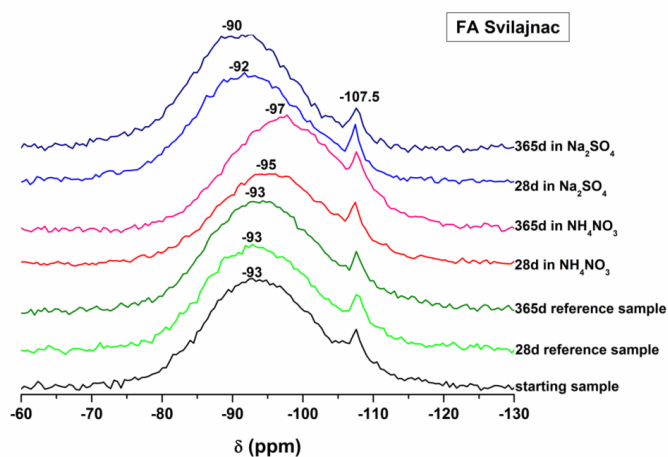


Figure 7. ^{29}Si MAS NMR spectra of the FA Svilajnac geopolymer samples.

^{29}Si MAS NMR analysis of the geopolymer samples treated with the Na_2SO_4 solution indicated a decrease in the Si/Al atomic ratio of these samples, i.e. confirmed leaching of Si (Table 2). Decrease in the Si/Al atomic ratio of the samples exposed to the Na_2SO_4 solution was indicated by shifting of the maximum peak intensities of the ^{29}Si MAS NMR spectra to less negative chemical shifts (figures 6 and 7). The observed small decrease in strength of the geopolymer samples treated with the Na_2SO_4 solution was caused by breaking of the $-\text{Si}-\text{O}-\text{Si}-$ bonds and leaching of Si. This type of degradation mechanism has already been observed in geopolymer samples exposed to moderately alkaline solutions [1]. Subsequent increase in strength of the geopolymer samples based on FA Kolubara

(figure 1) was most probably due to continuing of the alkali activation reaction [1, 4]. Conditions to which the geopolymer samples were subjected throughout the testing in the Na_2SO_4 solution, high concentration of Na in the solution and high pH values of the solution (Table 1) were favourable for continuing the alkali activation reaction [1].

4. Conclusions

In this paper, effects of two different aggressive environments, NH_4NO_3 solution (480 g/dm^3) and Na_2SO_4 solution (50 g/dm^3), on mechanical strength and structure of FA based geopolymers were investigated over a period of 365 days. It was found that testing of the geopolymer samples in the aggressive solutions caused small decrease in compressive strength (10-20 %). No new phases were formed in the geopolymer structure due to a reaction with either of the aggressive solutions. Based on the ^{29}Si MAS NMR analyses, it was found that the exposure of the geopolymer samples to the aggressive solutions caused alterations in the aluminosilicate gel. Small strength decrease of the geopolymer samples exposed to the NH_4NO_3 solution was due to breaking of -Si-O-Al- bonds in the aluminosilicate geopolymer gel structure. On the other hand, exposure of the geopolymer samples to the Na_2SO_4 solution caused breaking of the -Si-O-Si- bonds and leaching of Si.

The observed degradation mechanisms can be associated with changes in pH values of the aggressive solutions. It was found that leaching of pore solution alkalis caused increase in pH values of both testing solutions. The pH value of the initially acidic (pH = ~4) NH_4NO_3 solution increased to ~8.3, while the pH value of the Na_2SO_4 solution increased from the starting ~6 to ~12 after the first 28 days of testing. Changes in the geopolymer structure observed after the treatment with the NH_4NO_3 solution represent the first step of the degradation mechanism observed in the case of acid attack on geopolymers. Conversely, high pH value of the Na_2SO_4 solution caused breaking of the -Si-O-Si- bonds and leaching of Si, degradation process usually observed when geopolymer samples are exposed to moderately alkaline conditions.

The results obtained in this work suggest that, compared to traditional Portland cement, FA based geopolymers show better resistance to some types of aggressive environments.

5. References

- [1] Baščarević Z 2015 The resistance of alkali-activated cement-based binders to chemical attack *Handbook of Alkali-activated Cements, Mortars and Concretes* ed F Pacheco-Torgal, J Labrincha, C Leonelli, A Palomo and P Chindaprasit (Cambridge, UK: Woodhead Publishing) chapter 14 pp 373 – 396
- [2] Alexander M, Bertron A and De Belie N (ed) 2013 *Performance of Cement-Based Materials in Aggressive Aqueous Environment* (Berlin: Springer)
- [3] Baščarević Z, Komljenović M, Miladinović Z, Nikolić V, Marjanović N, Žujović Z and Petrović R 2013 *Constr. Build. Mater.* **41** 570 – 579
- [4] Baščarević Z, Komljenović M, Miladinović Z, Nikolić V, Marjanović N and Petrović R 2015 *Mater. Struct.* **48** 683 – 697
- [5] Engelhardt G and Michel D 1987 *High resolution solid state NMR of silicates and zeolites* (New York: John Wiley & Sons)

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