

The evaluation of geopolymer properties prepared by alkali activation of black coal ashes with high content of loss on ignition

Sisol Martin¹, Kolesarova Miroslava, Krinicka Ivana, Michalikova Frantiska and Prascakova Maria²

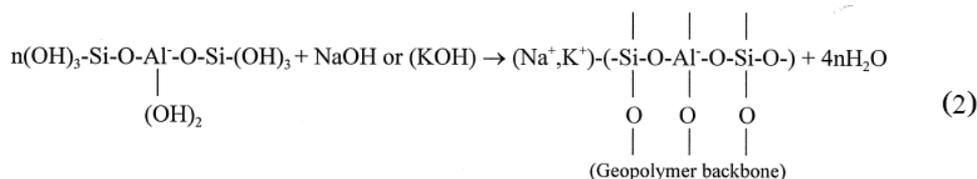
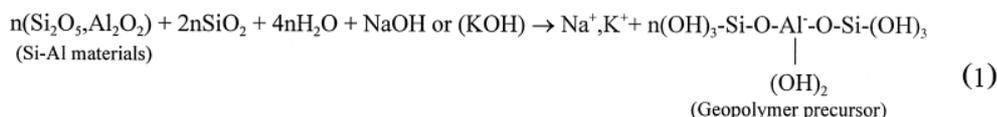
The utilization of fly ashes in Slovakia is lower than in other countries and dumping of fly ashes prevails. The dumping changes chemical and phase composition of fly ashes and so it decreases possibilities for their utilization. Fly ashes are mainly used in building industry, where the content of loss on ignition (LOI) is limited due to standards. Black coal fly ashes produced in Slovakia have a high content of loss on ignition – more than 20 % - so they straight utilization in building industry is not possible. The current possibility for their utilization is in geopolymer synthesis. Products with 28-day compression strength of 35.7 MPa and 180-day compression strength of 55.0 MPa were obtained by alkali activation of fly ashes with 23.25 % LOI with 8 wt% Na₂O and their next hardening in temperature of 80 °C during 6 hours. Products have a great frost-resistance and aggressive environments resistance (NaCl a H₂SO₄ solutions).

Key words: fly ash, geopolymer, compression strength, resistance

Introduction

Worldwide, millions of tons of fly ash are generated each year by coal-fired power plants satisfying the large demand for industrial and domestic energy. In Slovakia, a majority of fly ashes are hydraulically transported to settling basins or extracted mines and only a small amount of fly ashes is utilized. The deposited fly ashes are being exposed to exogenous and biogenous factors that change their chemical and structural composition and become harmful to the environment. Although fly ashes can be utilized in the building industry, the European standards STN EN 206-1,2 limit the content of unburned coal residues (UCR) to 2 – 5 % of loss on ignition (LOI) [1]. The tested fly ash produced in Eastern Slovakia contains a high content of LOI (more than 23 %), so it cannot be utilized in the reinforced concrete production.

A current possibility of utilizing high-carbon fly ashes is a synthesis of geopolymers. The geopolymers are alkali activated alumina-silicate binders with a three-dimensional amorphous structure and their properties are comparable with cement-base materials. The geopolymerization involves a chemical reaction between various alumina-silicate oxides with silicates under highly alkaline conditions, yielding polymeric Si-O-Al-O bonds, which can be presented schematically as follows [2]:



The above two reaction paths indicate that any Si-Al materials might become sources of geopolymerisation [3]. These include natural minerals (kaolin, feldspar, albite, stilbite) [4], treated minerals (metakaolinite) [5, 6] and waste materials (building waste, blast furnace slag, fly ash) [7, 8].

As the activation solution, a highly alkaline solution of sodium or potassium silicate and sodium or potassium hydroxide is used [2, 5, 6]. A major part of fly ash consists of amorphous alumina-silicates (approx. 80 %), so that fly ashes are suitable material for geopolymers production, having an important

¹ Ing. Sisol Martin, PhD., Ing. Kolesarova Miroslava, PhD., Ing.; Krinicka Ivana, PhD., doc. Ing. Michalikova Frantiska, CSc., Institute of Montaneous Sciences and Environmental Protection, Faculty of Mining, Ecology, Process Control and Geotechnologies, TU Kosice, Park Komenskeho 19, 043 84 Kosice Slovak Republic, martin.sisol@tuke.sk

² Ing. Prascakova Maria, Institute of Geotechnics, SAV Kosice, Slovak Republic

economical and ecological benefit. The content of UCR is an important factor for its influence on mechanical properties and the ability of geopolymer matrix to fix heavy metals. The heavy metal immobilization in geopolymer structures is not thought to be caused by physical encapsulation alone, but also through adsorption of the metal ions onto the geopolymer structure and possibly even bonding of the metal ions into the structure [9]. According to Jaarsveld et al. [3, 7], the higher content of UCR causes the lower compressive strength and higher porosity of the final geopolymer.

Geopolymeric materials are attractive because of the excellent mechanical properties, durability and the thermal stability [10]. Furthermore, due to a much lower Ca content, geopolymer-based materials are much more resistant to the acid attack than the Portland cement based ones [11].

Material and methods

Fly ash originating from black coal-fired melting boilers in a district heating plant in Kosice, Slovakia at the temperature of 1400 – 1600°C was used as a basic material in the geopolymer synthesis. The content of UCR was 23.25 % LOI. The samples of fly ash were collected from an upper layer of the coal ash settling basin. The homogenized material was dried to achieve the 0.5 wt. % water content and sieved on a sieve with 1 mm openings to remove coarse impurities. The grain size analysis shows that approx. 80 % of fly ash particles were less than 45 µm. The partial chemical composition of used fly ash is in Table 1. The mineralogical composition was determined by the XRD analysis using the URD-6 (Rich. Seifert-FPM, SRN) diffractometer (CoK α /Ni filter, 35 mA) (Tab. 2).

Tab. 1. Chemical composition of fly ash.

wt. %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	LOI	SiO ₂ /Al ₂ O ₃
Fly ash	46.77	15.69	8.34	3.93	1.21	23.25	2.98

Tab. 2. Mineralogical composition of fly ash.

wt. %	Amorphous phase	Hematite	Silica	Mullite
Fly ash	83.56±2.04	1.57±0.93	6.42±0.96	8.46±1.83

The activation solution was prepared by mixing of solid NaOH pellets with Na-water glass (Na₂SiO₃) and water in the ratio requested, always a day before the process. Water glass from Kittfort Prague Co. with the density of 1.328 – 1.378 g.cm⁻³ contains 36 – 38 % Na₂SiO₃. The molar ratio SiO₂-to-Na₂O was from 3.2 to 3.5. The solid NaOH was obtained from different producers but they all have a similar chemical composition and physical properties, containing at least 98 % of NaOH and up to 1 % of Na₂CO₃, the density was 2.13 g.cm⁻³.

The SiO₂-to-Na₂O ratio (M_s modulus) in the alkali activation solution was adjusted by adding NaOH into the water glass (M_s of water glass was 3.2) to range from 0.75 to 1.65. The activation solution with M_s=0 contains only sodium hydroxide and M_s=3.2 only Na-water glass. The content of Na₂O ranges from 6 to 9 wt. % of the weight of basic material. The water content w was set constant at 0.3.

The preparation of geopolymers consists in the mixing of fly ash with the activation solution for 15 minutes. The homogenous mixture was poured into 40x40x160 mm forms, compacted on the vibration table VSB-40 for 10 minutes at the frequency 50 Hz and cured in a hot-air drying chamber for 6 or 12 hours at the temperature of 21, 40, 60, 80 and 100 °C. After that, the samples were removed from forms, marked and stored in a laboratory conditions until their next usage.

The compressive strength of hardened samples was determined after the elapse of 1, 7, 28, 90 and 180 days using the hydraulic machine Form+Test MEGA 100-200-10D. The measurements were realized on 3 samples and the final value is the average value.

The tests of water absorbance were done on the 28-days old samples dried before the test at the temperature of 105 – 110 °C to the constant temperature. Dried samples were plunged to the water with the temperature of 20 °C, 2 cm under the surface. The water absorbance was measured in 10, 40, 90, 360 and 1440 minute intervals according to the Standard STN 73 1316.

The geopolymer samples were also subjected to alternating freezing and defrosting cycles according to the Slovak Standard STN 73 1325. The tests of cold resistance were done on the 28-days old samples. One cycle consists of 4 hours of freezing and 2 hours of defrosting. After 25 or 50 cycles, the samples were dried at the temperature of 105 – 110 °C to the constant temperature and than the compressive strength was measured. The obtained values of the compressive strength were compared with the values of reference samples of the same age but not exposed to the freezing and defrosting cycles.

The resistance of geopolymer samples to the aggressive solutions of NaCl and Na₂SO₄ or H₂SO₄ was detected on 28-days old samples for the period of 150 days. The concentrations of these solutions were in

agreement with the regulations given in the respective standard (STN EN 206-1) valid for the concrete testing: Na_2SO_4 $44 \text{ g}\cdot\text{dm}^{-3}$ and NaCl $164 \text{ g}\cdot\text{dm}^{-3}$. The solution of 1 % HCl was used. The solutions were replaced once a month and the samples were weighed to find out a possible variation in their mass. Mechanical properties of the samples were determined after the period of 150 days after their drying. The obtained values of the compressive strength were compared with the values of the reference samples of the same age but not exposed to aggressive solutions.

Results and discussion

Effect of the Na_2O -to-fly ash ratio

The untreated fly ash with the content of 23.25 wt. % LOI was mixed with the activation solution, providing the total amount of Na_2O in the solution to be 6, 7, 8 and 9 % of the fly ash mass ($\text{Na}_2\text{O}/\text{BM}\times 100$). The samples were cured 6 hours at 80°C . As shown in Fig. 1, the increase of Na_2O amount results in an increase of the 180-day compressive strength of the hardening geopolymers from 30,4 MPa to 55,5 MPa for 6 and 9 % Na_2O , respectively.

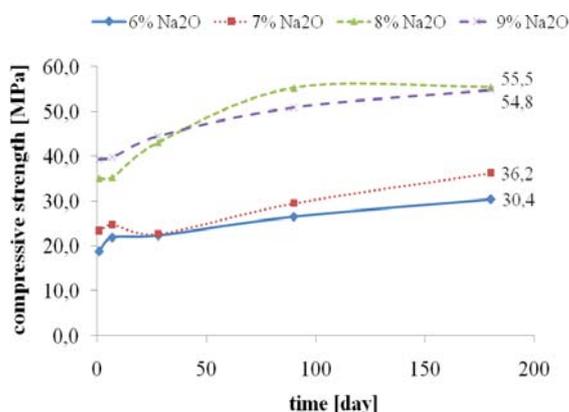


Fig. 1. Compressive strength development of fly ash-based geopolymers with a different amount of Na_2O related to the fly ash. Cured 6 hours at 80°C , $M_s=1.25$ and $w=0.3$

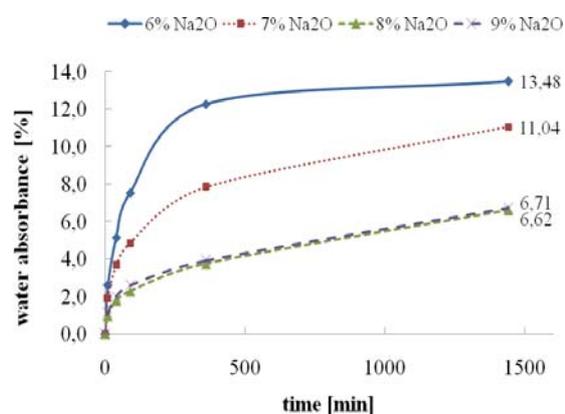


Fig. 2. Water absorbance of geopolymers with a different amount of Na_2O related to the fly ash. Cured 6 hours at 80°C , $M_s=1.25$ and $w=0.3$

The significant increase (34 %) was noticed between the sample of 7 % Na_2O (36.2) and the sample 8 % Na_2O (54.8). The compressive strength of the sample with 8 % Na_2O stayed after 90 days constant and achieved the value of 55 MPa.

The water absorbance of the geopolymer samples decreases with the higher amount of Na_2O in the mixture (Fig. 2). Geopolymers with 8 % and 9 % of Na_2O achieved the value of the water absorbance 6.7 and 6.6 %, respectively. On the other hand, the value of the water absorbance of geopolymer with the content of 6 % Na_2O was 13.5 %.

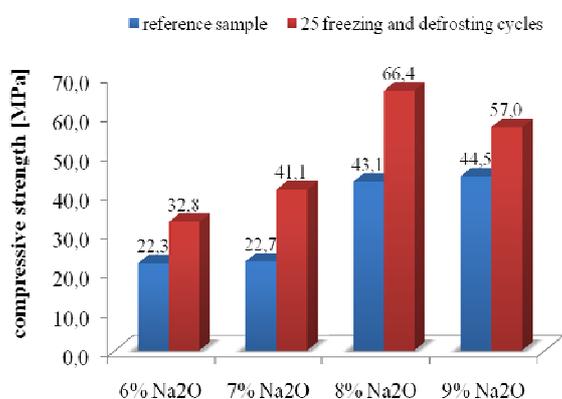


Fig. 3. The compressive strength of 28-days old geopolymer samples after the cold resistance test (25 freezing and defrosting cycles) (left) and reference sample (right).

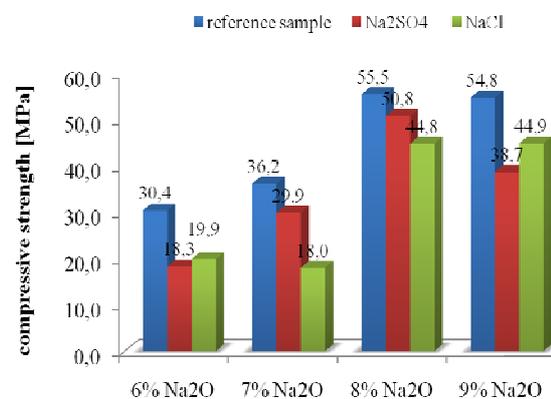


Fig. 4. The comparison of compressive strengths of geopolymers with the different amount of Na_2O related to the fly ash of after 150 days of aggressive solutions treatment Na_2SO_4 and NaCl and reference samples (left).

The cold resistance of fly ash-based geopolymers was higher in the samples with the higher $\text{Na}_2\text{O}/\text{BM}$ ratio. The significant increase (from 43.1 MPa to 66.4 MPa) of the compressive strength in comparison to 28-day old non-treated samples was noticed in the geopolymer with 8 % of Na_2O in the activation solution related to the fly ash mass. The compressive strength of geopolymer samples after 150-day aggressive solution treatment in the solution of Na_2SO_4 and NaCl decreased from 8 % and 19 %, respectively in comparison with the reference sample (non-treated).

The increasing of Na_2O content in the activation solution caused the decreasing of the water absorbance of geopolymers and simultaneously increases their compressive strength. The compressive strength of fly ash-based geopolymers produced with the content of 8 % of Na_2O in the activation solution related to fly ash mass was after 25 cycles of the cold test 66.4 MPa, which is the value comparable with the compressive strength of high-grades cement concretes.

Effect of the SiO_2 -to- Na_2O ratio (M_s modulus)

The compressive strength development of fly ash-based geopolymers with a different M_s (SiO_2 -to- Na_2O ratio), cured for 6 hours at 80°C is shown in the Fig. 1. The alkali activator had M_s in the range 0 to 3.2 and the total amount of Na_2O was set at 8 wt. %.

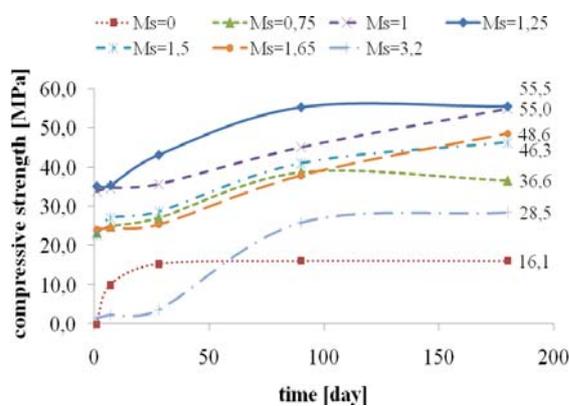


Fig. 5. Compressive strength development of fly ash-based geopolymers with a different M_s ($\text{SiO}_2/\text{Na}_2\text{O}$), cured for 6 hours at 80°C , $\text{Na}_2\text{O}/\text{BM} \times 100 = 8\%$, $w = 30\%$.

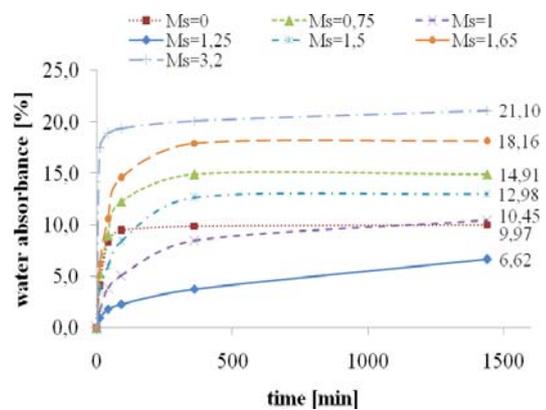


Fig. 6. Water absorbance of fly ash-based geopolymers with a different M_s ($\text{SiO}_2/\text{Al}_2\text{O}_3$), cured for 6 hours at 80°C , $\text{Na}_2\text{O}/\text{BM} \times 100 = 8\%$, $w = 30\%$.

Higher compressive strengths were achieved with the activation solution consisted of the mixture of water glass and hydroxide. The lowest value of compressive strength (16.1 MPa after 180 days of hardening) were achieved in the sample with $M_s = 0$ (the solution consisted of sodium hydroxide). The compressive strength of that sample was after 28 days of hardening 15.4 MPa and it did not change much during the next period of time, so after 28 days the geopolymerization finished.

The increase of water glass in the activation solution caused the increase in compressive strength of geopolymer samples. The maximum value was achieved with $M_s = 1.25$ and the compressive strength was 55.5 MPa after 180 days of hardening. The next addition of water glass caused the decrease in compressive strength. The compressive strength of the sample with $M_s = 3.2$ (the solution consisted of water glass) was 28.5 MPa after 180 days of hardening.

The water absorbance of 6.62 % was measured in the sample with $M_s = 1.25$ what was the lowest value, but the dependency of water absorbance on M_s modulus was not found.

The geopolymers had an excellent resistance against freezing and defrosting cycles in all samples with a different M_s modulus except $M_s = 3.2$ (Fig. 7). The compressive strength of the sample with $M_s = 3.2$ was decrease about 70 % in comparison to the reference sample. The best result of compressive strength was achieved in the sample with $M_s = 1$, which had after 50 cycles of cold resistance test the same value as the reference sample (non-treated) (45.1 MPa).

The compressive strengths of samples after aggressive solutions (H_2SO_4 and NaCl) resistance were lower than in the reference samples (Fig. 8). The highest decrease in the compressive strength was determined in the sample with $M_s = 3.2$, where the decrease of the samples after H_2SO_4 and NaCl treatment were 90.5 and 81 %, respectively.

According to the results, the use of water glass as the activation solution causes a lower compressive strength and a higher water absorbance of the final product and has a bad cold resistance and resistance to aggressive solutions. It is not suitable to use only the solution of sodium hydroxide for the alkali activation due to low values of the compressive strength (only 16.1 MPa after 180 days of hardening). The most suitable activation solution consists of NaOH and water glass with the ratio (M_s modulus) of 1 or 1.25.

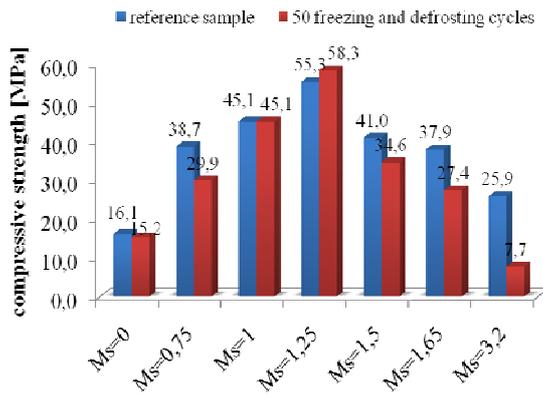


Fig. 7 The comparison of compressive strengths of fly ash-based geopolymer samples with different M_s modulus in the activation solution after the cold resistance test (50 freezing and defrosting cycles) (left) and reference samples (right)

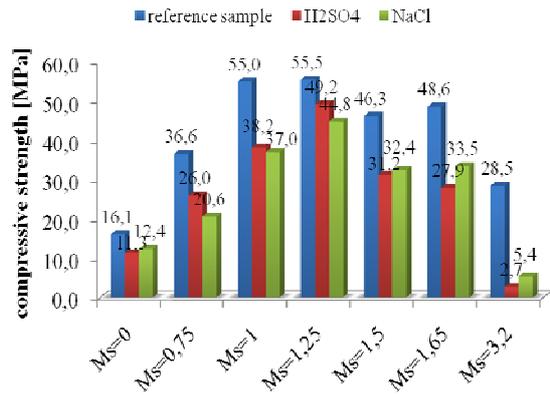


Fig. 8 The comparison of compressive strengths of fly ash-based geopolymer samples with different M_s modulus in the activation solution after 150-days long aggressive solution (H_2SO_4 a NaCl) treatment and reference samples (left)

Effect of the curing temperature

Fig. 9 displays a compressive strength development of geopolymer samples prepared from fly ash with the content of UCR 23.25 wt. % LOI by alkali activation using the activation solution with $M_s=1.25$, $Na_2O/BM \times 100=8\%$, $w=0.3$ and cured for 12 hours at different temperatures. The temperature was set to 21, 40, 60, 80 and 100 °C.

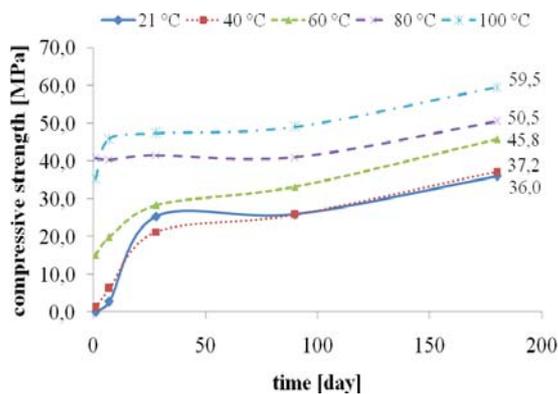


Fig. 9. Compressive strength development of fly ash-based geopolymers cured at a different temperature for 12 hours, $M_s=1.25$, $Na_2O/BM \times 100=8\%$ and $w=0.3$.

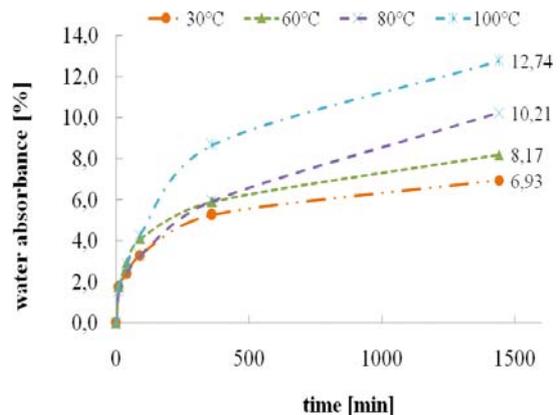


Fig. 10. Water absorbance of fly ash-based geopolymers cured at a different temperature for 12 hours, $M_s=1.25$, $Na_2O/BM \times 100=8\%$ and $w=0.3$.

The temperature of curing had an important influence on the compressive strength development. The increase in temperature caused an increase in the compressive strength. The increase in temperature accelerates the geopolymerization reaction and leads to the higher initial (immediately after the release from forms) compressive strengths. It is visible that the samples cured at lower temperatures (21, 40 and 60 °C) manifest a step-like development of strength with time. For all curing temperatures, after the initial increase within 28 days of hardening, an easy increasing of compressive strength is observable for the next period between 28 and 180 days. The temperature has an influence on the water absorbance, too (Fig. 10). The water absorbance was increasing with temperature from 6.9 % to 12.7 % for the samples cured at temperature of 30 °C and 100 °C, respectively.

Conclusion

The article presents the results of laboratory tests with a view to confirm the suitability of use the solid waste – fly ash – from combustion of black coal in melting boilers. Geopolymer materials, formed from the tested fly ash with the content of unburned coal residues of 23.25 wt. % LOI, have mechanical properties comparable with the cement concrete. The experiments confirmed the positive effect of the amount of Na_2O in the activation solution and the higher temperature to the compressive strength development. The rising of the compressive strength and decreasing of the water absorbance of geopolymers was observed with

the increasing amount of Na₂O in the activation solution. Increased temperature has a positive effect to the rate and intensity of geopolymerization. The cold resistance tests confirmed the resistance of geopolymer samples against freezing and defrosting cycles. In some cases, the compressive strength was increased after the cold resistance test. Materials produced by alkali activation of fly ashes with a high content of loss on ignition were resistant against solutions of NaCl and Na₂SO₄ or H₂SO₄.

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References

- [1] Michalikova, F., Florekova, L., Benkova, M.: Vlastnosti energetického odpadu – popula. *Využitie technológií pre environmentálne nakladanie. Košice 2003. 228 pp. ISBN 80-8073-054-7.*
- [2] Xu, H., Van Deventer, J.S.J.: The geopolymerisation of alumina-silicate materials. *In: Int. J. Miner. Process, vol. 59, 2000, p. 257-266.*
- [3] Van Jaarsveld, J.G.S., Van Deventer, J.S.J., Lorenzen, L.: The potential use of geopolymeric materials to immobilise toxic metals: Part I. Theory and applications. *In: Minerals Engineering, 1997, vol. 10, no. 7, p. 659-669.*
- [4] Xu, H., Van Deventer, J.S.J.: Geopolymerisation of multiple minerals. *In: Miner. Eng., 2002, vol. 15, p. 1131-1139.*
- [5] Davidovits, J.: Geopolymers: Inorganic Polymeric new materials. *In: Journal of thermal analysis, vol. 37, 1991, pp. 1633-1656.*
- [6] Palomo, A., Grutzeck, M.W., Blanco-Varela, M.T.: Alkali-activated fly ashes. A cement for the future. *In: Cement and Concrete Research, vol. 29, 1999, pp. 1323-1329.*
- [7] Van Jaarsveld, J.G.S., Van Deventer, J.S.J., Schwartzman, A.: The potential use of geopolymeric materials to immobilise toxic metals: Part II. Material and leaching characteristics. *In: Miner. Eng, vol. 12, no. 1, 1999, pp. 75-91.*
- [8] Bakharev, T.: Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperature curing. *In: Cement and Concrete Research, vol. 36, 2006, pp. 1134-1147.*
- [9] Van Jaarsveld, J.G.S., Van Deventer, J.S.J., Lorenzen, L.: Factors affecting the immobilization of metals in geopolymerised fly ash. *In: Research Report, Department of Chemical Engineering, University of Stellenbosch, South Africa, 1995.*
- [10] Andini, S., Cioffi, R., Colangelo, F., Grieco, T., Montagnaro, F., Santoro, L.: Coal fly ash as raw material for the manufacture of geopolymer-based products. *In: Waste Management, vol. 28, 2008, p. 416-423.*
- [11] Bakharev, T.: Resistance of geopolymer materials to acid attack. *In: Cement and Concrete Research, vol. 35, 2005, pp. 658-670.*