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EXAMINATION OF FLY ASH – RED MUD BASED GEOPOLYMERS

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Abstract: In the article, two types of geopolymer mixtures with varying red mud content (10 and 15 m/m%) were prepared and investigated: one with 0 M NaOH (replaced with H₂O) and one with 8 M NaOH in the activator solution. The tests revealed lower uniaxial compressive strength with the addition of red mud in relation to the control sample, but with different trends in case of the two mixtures. When 8 M NaOH was used, the compressive strength values started increasing after an initial decrease, while continuous decrease was observed in case of the 0 M NaOH samples. The specimen densities stagnated around the value of the control sample (at around 1.47 g/cm³) with 8 M NaOH but showed a close to linear increase with 0 M NaOH. The FT-IR spectra showed no significant difference in the samples, but the smallest peak intensities were obtained in case of the 8 M NaOH mixture with 15 m/m% red mud.

Keywords: *fly ash, geopolymer, mechanical properties NaOH concentration, red mud*

Absztrakt: A tanulmányban két különböző geopolimer keveréket vizsgáltunk változó vörösiszap-tartalommal (10 és 15 m/m%): az egyik esetében az aktiváló oldat 0 M NaOH-t (H₂O-val helyettesítve), míg a másik 8 M NaOH-t tartalmazott. A vizsgálatok során a vörösiszap-tartalmú geopolimerek alacsonyabb egytengelyű nyomószilárdsága volt megfigyelhető a kontrollmintához képest, az értékek azonban eltérő trendet követtek. 8 M NaOH használata esetén a nyomószilárdság értékek növekedése volt megfigyelhető a kezdeti csökkenés után, míg a 0 M NaOH-val készült próbatestek esetén állandó csökkenés volt tapasztalható. A testsűrűség értékek (1,47 g/cm³ körül) stagnáltak 8 M NaOH használata esetén, míg közel lineáris növekedést mutattak 0 M NaOH alkalmazásával. Az FT-IR spektrumokon nem volt megfigyelhető jelentős eltérés a minták között, azonban a legalacsonyabb csúcsintenzitást minden esetben a 8 M NaOH-val készült, 15 m/m% vörösiszap-tartalmú geopolimereknél tapasztaltunk.

Kulcsszavak: *pernye, geopolimer, mechanikai tulajdonságok, NaOH koncentráció, vörösiszap*

1. INTRODUCTION

Geopolymers are a type of inorganic binders, obtained via the reaction of a solid alumino-silicate base material and a typically alkaline solution. As a result of the geopolymerisation process, a three-dimensional amorphous to semi-crystalline aluminosilicate network is created, called a polysialate framework. Some of the advantageous properties of geopolymers include high compressive strength, acid resistance, fire resistance, low shrinkage and low thermal conductivity. Furthermore, the possible application of secondary raw materials during production makes geopolymerisation a more prosperous process. The possible raw materials of geopolymers include calcined clays, fly ashes, metallurgical slags and red mud [1, 2].

Fly ash is a pozzolanic material that consists of fine silt-sized particles, typically between 10 and 100 μm . It is generated in coal-fired power plants and separated from flue as by either electrostatic separators or fabric filters. The main oxidic compounds of fly ash are SiO_2 , Al_2O_3 , Fe_2O_3 and CaO . The highest amount of fly ash is generated in China, with an annual 600 million tons, in 2015. Red mud is a by-product of alumina extraction from bauxite via the Bayer process. The production of 1 ton of alumina results in approximately 1.5 tons of red mud discharge [3, 4, 5]. As there is a growing need for the utilisation of the already large stockpiles of these various industrial wastes and by-products, geopolymerisation has become a widespread and feasible option.

Based on previous international research, the uniaxial compressive strength of fly ash – red mud based geopolymers is comparable to conventional building materials, typically when cured at a lower ($<80\text{ }^\circ\text{C}$) temperature ranges, as well as the resistance against low and neutral pH solutions [6, 7, 8].

During the experiments, lignite fly ash – red mud based geopolymers were prepared, using NaOH with different molarities in the activator solution. The uniaxial compressive strength, specimen density and structural changes of the geopolymers were investigated.

2. MATERIALS AND METHODS

The solid raw materials for geopolymer production were ground lignite fly ash from the Mátra Power Station and red mud (RM) from Almásfüzitő.

The raw fly ash and the RM slurry were dried at $105\text{ }^\circ\text{C}$ until constant weight, then the $>1\text{ mm}$ particles were separated from the fly ash via sieving and the dried RM was pulverised in a mortar. The chemical composition was measured with Rigaku Supermini 200 type X-ray fluorescence spectrometer, and to determine the mineral composition, a Bruker D8 Advance instrument was used. The obtained data for fly ash is summarised in *Table 1*.

The most important compounds for geopolymerisation are SiO_2 and Al_2O_3 , which make up 53.8 m/m% of the sample. Furthermore, the trace elements found in the fly ash sample include for example F ($<0.3\text{ m/m\%}$), Ba (513 ppm), Zn (280 ppm), Sr (254 ppm), Zr (101 ppm), Cr (95 ppm), Cu (95 ppm), Pb (61 ppm), etc.

Considering the mineral composition of the fly ash, the amorphous phase can be found in the highest quantity, 59.30 m/m%. Among the crystalline phases, the iron-containing minerals (maghemite and hematite) represent 9.3 m/m%, while the calcium (and magnesium) sulphates and carbonates represent 8.47 m/m%. The remaining mineral phases are various silicon and aluminium bearing mineral phases.

Table 1
Chemical and mineral composition of fly ash

Fly ash			
Chemical composition		Mineral composition	
Component	Quantity, m/m%	Phase name	Quantity, m/m%
SiO ₂	39.8	Amorphous	59.30
Al ₂ O ₃	14.0	Quartz	13.14
CaO	12.1	Maghemite	5.09
Fe ₂ O ₃	11.2	Bassanite	4.50
SO ₃	6.5	Hematite	4.21
MgO	3.41	Albite	3.54
K ₂ O	1.61	Calcite	2.64
Na ₂ O	0.54	Akermanite	2.19
TiO ₂	0.495	Cristobalite low	1.98
P ₂ O ₅	0.346	Dolomite	1.34
MnO	0.176	Illite 2M1	1.08
Σ	90.177	Mullite 3 : 2	0.96
		Microcline intermediate2	0.03
		Σ	100.00

The mechanical activation of the fly ash was carried out by grinding in a Ø305 × 305 mm ball mill for 30 minutes.

A Phenom ProX EDX scanning electron microscope was used to examine the microstructure of the ground fly ash. As it can be seen in *Figure 1*, the 30-minute grinding of fly ash in the ball mill resulted in significant fragmentation. In case of the intact, mostly spherical fly ash particles a porous structure can be observed.

The particle size data were obtained with a HORIBA LA950-V2 type laser particle size analyser, using the Mie theory to calculate the particle sizes. The characteristic particle sizes of the mechanically activated fly ash were $x_{10} = 5.47 \mu\text{m}$, $x_{50} = 18.45 \mu\text{m}$ and $x_{90} = 69.90 \mu\text{m}$. The geometric specific surface area, calculated by the particle size analyser was 2238.03 cm²/g. For RM, the values of characteristic particle sizes were: $x_{10} = 0.98 \mu\text{m}$, $x_{50} = 2.53 \mu\text{m}$, and $x_{90} = 6.07 \mu\text{m}$. The geometric specific surface area was 10,103.19 cm²/g.

For geopolymer production, first, the solid base materials and the activator solution was mixed. Then, the mixtures were poured into cylindrical moulds with 35 mm diameter and 65 mm height and compacted for 1 minute on a vibrating table. After 1 day of aging under sealed conditions, the geopolymers were demoulded and cured at 60 °C for 6 hours. After cooling, the specimens were kept under sealed conditions for 5 days.

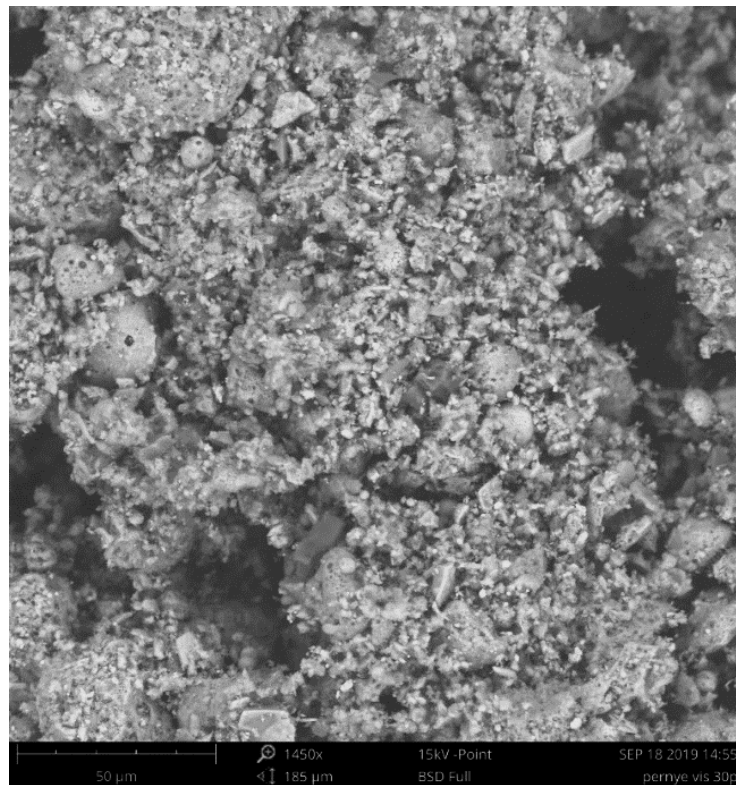


Figure 1
SEM image of ground fly ash, $M = 1450\times$

The uniaxial compressive strength of the geopolymers was measured with a SZF-1 type hydraulic testing machine with 25 kN maximal load.

For the structural analyses, a JASCO FT-IR 4200 type FTIR Spectrometer was used. The spectra were collected in the absorbance range from 7,800.65 to 349.053 cm^{-1} , at a resolution of 4 cm^{-1} . All spectra were baseline corrected.

3. RESULTS

After the 7-day aging, the uniaxial compressive strength tests and specimen density measurements of the geopolymers were performed. The results are summarised in Table 2.

Table 2
Uniaxial compressive strength, relative standard deviation and
specimen density values

RM content, m/m%	NaOH molarity, mol/L	Uniaxial compressive strength, MPa	Relative standard deviation, –	Specimen density, g/cm ³
0	8	13.78	0.15	1.47
10	8	10.42	0.25	1.45
15	8	10.85	0.52	1.48
10	0	9.08	0.56	1.57
15	0	8.32	0.20	1.58

The obtained strength and density values of the RM containing specimens were compared to a base specimen without RM addition for mixtures with both 8 M NaOH (Figure 2) and 0 M NaOH (Figure 3).

In case of the RM geopolymer specimens prepared with 8 M NaOH in the activator solution (Figure 2), the comparison of the compressive strength values reveals that the changes can be described with a second-degree polynomial equation, with $R^2 = 1$. With 10 m/m% RM, the compressive strength decreased from 13.78 MPa to 10.42 MPa, but the addition of further 5 m/m% RM resulted in a slight increase, to 10.85 MPa. However, the standard deviation of the compressive strength values rose from 0.15 to 0.52 with higher RM quantity in the specimens. The specimen density of the specimens was scarcely impacted by RM addition, the values changed between 1.45–1.48 g/cm³.

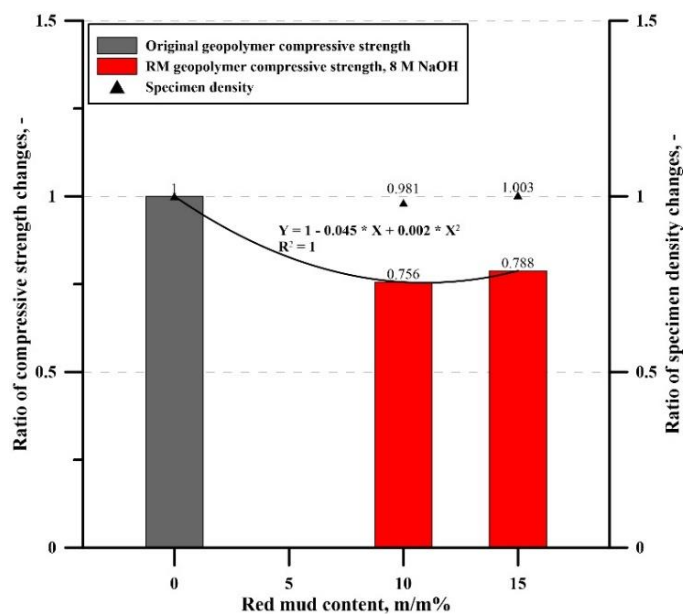


Figure 2

Effect of RM on the uniaxial compressive strength and specimen density, using 8 M NaOH

The application of 0 M NaOH (replaced with H₂O) affected the compressive strength and specimen density more than with 8 M NaOH. The initial 13.78 MPa compressive strength decreased to 9.08 MPa with 10 m/m%, and to 8.32 MPa with 15 m/m% RM in the mixtures. As it is illustrated in *Figure 3*, the compressive strength data showed an exponential decrease with RM addition, that can be described with $R^2 = 0.996$. The standard deviations showed no clear trend, as the values increased from 0.15 to 0.56 with 10 m/m% RM, then decreased to 0.20 with 15 m/m% RM. On the other hand, the specimen density values had a clear increasing trend, which rose from the 1.47 g/cm³ of the base specimen to 1.57 g/cm³ and 1.58 g/cm³ as the RM content became higher in the specimens.

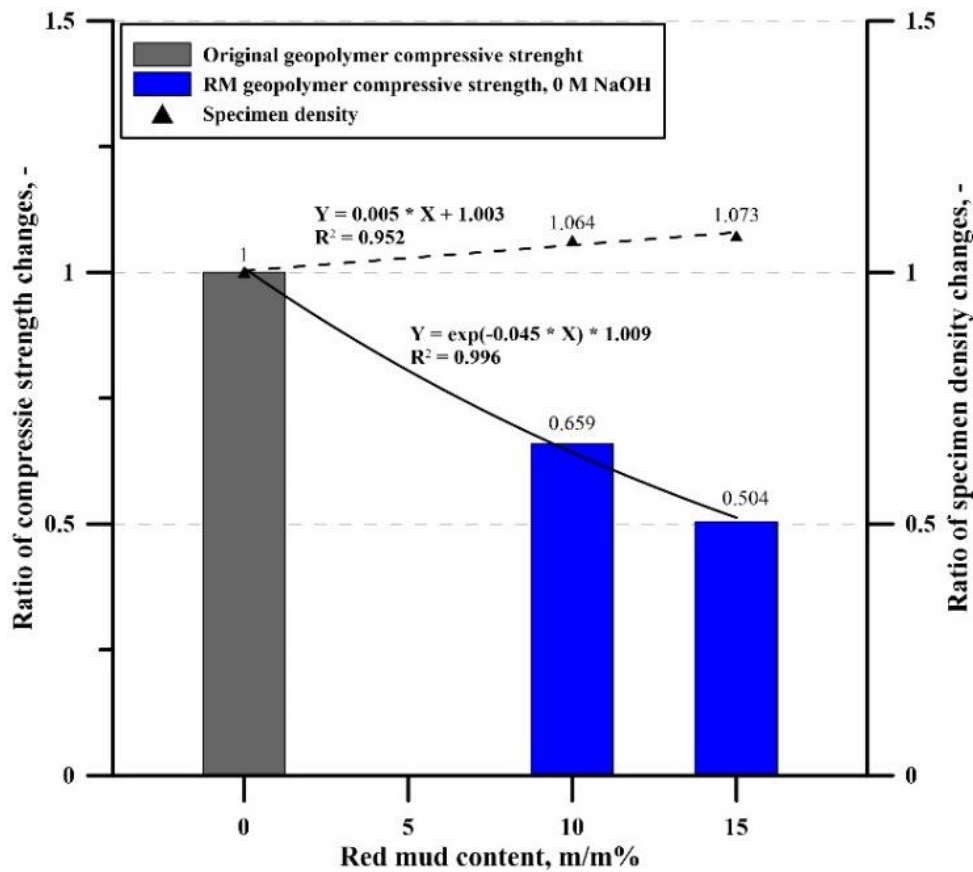


Figure 3
Effect of RM on the uniaxial compressive strength and specimen density, using 0 M NaOH

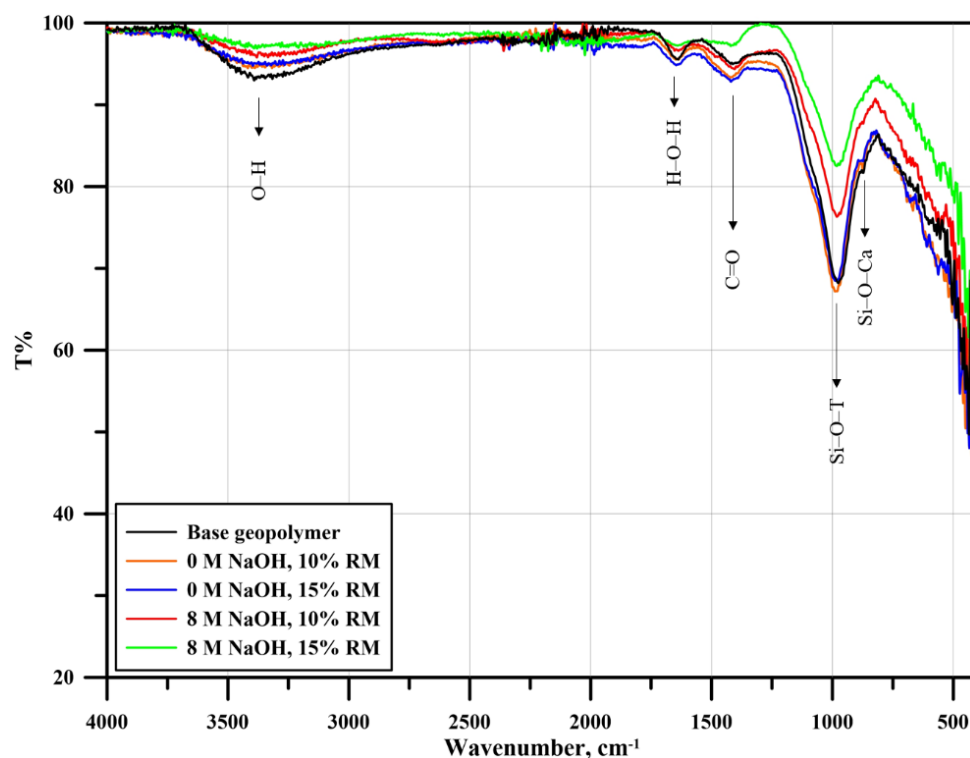


Figure 4
FT-IR spectra of geopolymers

The FT-IR spectra with the main bands are summarised in *Figure 4*. The bands centred at $\sim 3,300\text{ cm}^{-1}$ and $\sim 1,650$ are associated with the stretching vibration of O–H bonds and the H–O–H bending vibrations. These are the result of structural and surface water in the geopolymer matrix. The peak at $1,450\text{ cm}^{-1}$ is related to the asymmetric stretching of C = O bond (CO_3^{2-} ions) which may indicate the presence and possibility of atmospheric carbonation. The asymmetric stretching vibrations of the Si–O–T (T: Al or Si) band are represented just below $1,000\text{ cm}^{-1}$ wavenumber, signifying the result of geopolymerisation taking place in the systems. At $\sim 900\text{ cm}^{-1}$, the Si–O–Ca vibration bond can be seen, which is typically a result of calcium addition to the system [9, 10]. However, the high Ca content of the fly ash may contribute to appearance this peak.

The base sample had the highest intensity of the O–H bond, indicating the RM addition reduced the interlayer adsorbed H_2O in the geopolymer matrix. In general, the same intensity can be observed in case of the two mixtures prepared with 0 M NaOH at each peak on the spectra. At the Si–O–T band, these mixtures demonstrated the highest intensity, along with the original geopolymer. The lowest peak intensities were displayed by the geopolymers with 8 M NaOH and 15 m/m% RM.

4. CONCLUSIONS

The uniaxial compressive strength, specimen density and structural changes were examined for fly ash – RM based geopolymers, with different NaOH molar concentrations. Decrease in the compressive strength values was observed with the replacement of fly ash with RM with both NaOH concentrations. The specimen density values barely changed when 8 M NaOH was used. However, the application of 0 M NaOH in the activator solution led to increased specimen densities. The FT-IR measurements showed lower intensities for all peaks with 8 M NaOH, especially with 15 m/m% RM.

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REFERENCES

- [1] PROVIS, John L. – VAN DEVENTER, Jannie S. J. (eds.): *Geopolymers – Structure, processing, properties and industrial applications*. Woodhead Publishing Limited, Cambridge, 2009.
- [2] KOSHY, Nevin – DONDROB, Kunga – HU, Liming – WEN, Quingbo – MEEGODA, Jay N.: Synthesis and characterization of geopolymers derived from coal gangue, fly ash and red mud. *Construction and Building Materials*, 2019, 206, pp. 287–296.
- [3] MA, Shu-Hua – XU, Min-Di – QIQIGE-WANG, Xiao-Hui – ZHOU, Xiao: Challenges and Developments in the Utilization of Fly Ash in China. *International Journal of Environmental Science and Development*, 2017, 8 (11), pp. 781–785.
- [4] American Coal Ash Association: *Coal Ash Recycling Reaches Record 64 Percent Amid Shifting Production and Use Patterns*. [Online] Available at: <https://www.acaa-usa.org/Portals/9/Files/PDFs/Coal-Ash-Production-and-Use-2017.pdf>. Accessed: 08. 06. 2020.
- [5] WANG, Li – SUN, Ning – TANG, Honghu – SUN, Wei: A Review on Comprehensive Utilization of Red Mud and Prospect Analysis. *Minerals*, 2019, 9, pp. 362–381.

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- [6] YANG, Zhaotong – MOCADLO, Ryan – ZHAO, Mengxuan – SISSON, Richard D. – TAO, Mingjiang – LIANG, Jianyu: Preparation of a geopolymer from red mud slurry and class F fly ash and its behavior at elevated temperatures. *Construction and Building Materials*, 2019, 221, pp. 308–317.
 - [7] ZHANG, Mo. – ZHAO, Mengxuan – ZHANG, Guoping – SIETINS, Jennifer M. – GRANADOS-FOCIL, Sergio – PEPI, Marc S. – XU, Yan – TAO Mingjiang: Reaction kinetics of red mud-fly ash based geopolymers: Effects of curing temperature on chemical bonding, porosity, and mechanical strength. *Cement and Concrete Composites*, 2018, 93, pp. 175–185.
 - [8] ZHANG, Mo – ZHAO, Mengxuan – ZHANG, Guoping – MANN, Derrick – LUMSDEN, Kevon – TAO, Mingjiang: Durability of red mud-fly ash based geopolymer and leaching behavior of heavy metals in sulfuric acid solutions and deionized water. *Construction and Building Materials*, 2016, 124, pp. 373–382.
 - [9] NATH, S. K. – KUMAR, Sanjay: Role of particle fineness on engineering properties and microstructure of fly ash derived geopolymer. *Construction and Building Materials*, 2020, 233, p. 117294.
 - [10] PEYNE, Julie – GAUTRON, Jérôme – DOUDEAU, Julie – JOUSSEIN, Emmanuel – ROSSIGNOL, Sylvie: Influence of calcium addition on calcined brick clay based geopolymers: A thermal and FTIR spectroscopy study. *Construction and Building Materials*, 2017, 152, pp. 794–803.

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