UDK 66.095.26:691:539.411
Professional article/Strokovni članek

ISSN 1580-2949
MTAEC9, 47(1)99(2013)

UTILIZATION OF GEOPOLYMERIZATION FOR OBTAINING CONSTRUCTION MATERIALS BASED ON RED MUD

UPORABA GEOPOLIMERIZACIJE ZA PRIDOBIVANJE GRADBENEGA MATERIALA NA OSNOVI RDEČEGA BLATA

Mira Vukčević[1], Danka Urović[1], Milun Krgović[1], Ivana Bošković[1], Mileta Ivanović[1], Radomir Zejak[2]

[1]University of Montenegro, Faculty of Metallurgy and Technology, 81000 Podgorica, Montenegro
[2]University of Montenegro, Faculty of Civil Engineering, Džordža Vašingtona bb, 81000 Podgorica, Montenegro
mirav@ac.me

Prejem rokopisa – received: 2012-05-08; sprejem za objavo – accepted for publication: 2012-08-29

In this study the geopolymerization process for obtaining construction materials based on red mud was used. The aim of this study was to define the most favorable conditions enabling the utilization of the geopolymerization process in the production of construction materials based on red mud as a by-product of alumina production. For this purpose, the physicochemical and mechanical properties of the obtained construction (geopolymers) materials were tested. On the basis of the results the optimal conditions for geopolymerization and the effect of the main synthesis parameters were determined with repect to the satisfactory mechanical and other properties of the obtained materials. The inorganic polymeric materials produced by the geopolymerization of red mud developed satisfactory compressive strength, which leads to the conclusion that these materials may be used in the sector of construction materials.

Keywords: geopolymerization, red mud, compressive strength, metakaolin

V tej študiji je bil uporabljen postopek geopolimerizacije za pridobivanje gradbenega materiala na osnovi rdečega blata. Namen študije je bil opredeliti najugodnejše razmere, ki bi omogočile uporabo geopolimerizacijskega postopka za pridobivanje gradbenega materiala na osnovi rdečega blata, ki je stranski proizvod pri proizvodnji aluminija. Za ta namen so bile preizkušene fizikalno-kemijske in mehanske lastnosti materiala (geopolimera). Na osnovi dobljenih rezultatov so bile določene optimalne razmere za geopolimerizacijo in učinki glavnih parametrov sinteze s stališča zadovoljivih mehanskih in drugih lastnosti. Anorganski polimerni material, izdelan z geopolimerizacijo rdečega blata, je imel zadovoljivo tlačno trdnost, kar omogoča sklep, da bi bil ta material uporaben kot gradbeni material.

Ključne besede: geopolimerizacija, rdeče blato, tlačna trdnost, metakaolin

1 INTRODUCTION

The present work investigates the possibility of using the red mud from the Bayer process for the production of construction elements made with the process of geopolymerization. The geopolymerization process is based on the heterogeneous chemical reaction that occurs between the solid, aluminosilicate-rich materials, and the highly alkaline silicate solution. The basic part of this process is the hardening of geopolymers which is based on the polycondensation reactions of the alkali precursors formed from a dissolution of active silicates and aluminosilicate solid materials in an alkali-hydroxide solution. The polymeric network as a result of the polycondensation process hardens rapidly acting as a gluing component[1]. The geopolymerization is an exothermic reaction that takes place at an atmospheric pressure and a temperature bellow 100 °C leading to a formation of compact, solid materials, typical for their three-dimensional polymer structure. Such materials are called geopolymers[2–4]. The first stage in this reaction is the formation of hydroxyl complexes of silicon and aluminum with the polymer-bond types of Si-O-Si and Si-O-Al, followed by the formation of three-dimensional aluminosilicate networks containing SiO_4 and/or AlO_4 tetrahedral, alternatively linked through a common oxygen ion. The last stage in the process is the wrapping of the insoluble solid particles in the geopolymer[5–10].

The aim of this investigation is to define the optimal combination of the relevant parameters that would enable the use of red mud from the alumina-production process to be the dominant raw material in combination with the activator and the binder for the production of geopolymers. Geopolymerization creates favorable conditions in promoting red mud as the basis for the development of a new class of construction materials, inorganic polymers – geopolymers. The most important expectations regarding the construction materials are good physicochemical and mechanical characteristics, dimensional stability, a good fire resistance and an aggressive-environment resistance. However, the presence of hydroxyl Fe oxides in bauxite (goethite) compromises their use in the conventional construction materials because of their dehydroxylation-hydroxylation activities generating a dimensional instability. Geopolymerization lowers the level of water absorption because of the amorphous or semi-crystal structure,

lowers the micro porosity, enables higher values of the specific mass, compressive strength, etc. The final objective of this investigation was to define the influence of the relevant parameters affecting the geopolymerization. The compressive strength, the apparent density and the microstructure of polymeric materials were investigated to define the optimal conditions for a polymeric-material synthesis.

2 EXPERIMENTAL WORK

2.1 Materials

For the production of construction materials the following raw materials were used:

- red mud obtained as a byproduct of the Bayer process of obtaining alumina (Podgorica Aluminum Factory),
- sodium hydroxide of analytical grade (Merck, anhydrous pellets),
- metakaolin, which initially provides a geopolymeric system with soluble silicon and aluminum that are essential for an aluminosilicate-oligomer formation and the progress of geopolymeriztion,
- sodium-silicate solution (Merck: $m(Na_2O) : m(SiO_2) = 3.4$, $w(Na_2O) = 7.5–8.5$ %, $w(SiO_2) = 25.5–28.5$ % and $d = 1{,}347$ g cm^{-3}),
- deionized water for the synthesis of the polymeric material.

Red mud originated from the aluminum metallurgical plant in Podgorica, Montenegro, as a by-product of the alumina production known for the presence of hydroxylation Fe oxides, dried to a constant mass at a temperature of 105 °C, and then sifted through a sieve with a hole diameter of $\varphi = 1$ mm.

Metakaolin is a dehydroxylation product of the industrial mineral kaolin in the temperature range between 650 °C and 850 °C. The thermal dehydroxylation of kaolin increases its solubility in an alkaline media and it was performed at 750 °C. The basic material was mineral kaolin from the Bijele Poljane site in Montenegro. Metakaolin is a predominantly amorphous material with minor crystalline constitutes.

As an alkaline activator of the process of geopolymerization, a combination of sodium water glass and sodium hydroxide was used. The activator solution was prepared by mixing the previously mentioned components 48 h before the geopolymer production. Different concentrations of NaOH (C_{NaOH} = (3, 7 and 10) mol dm^{-3}) and a concentration of Si in Na-silica (1, 1.5 and 3.5) mol dm^{-3} were used. The levels of substitution of red mud with metakaolin in the solid phase were in mass fractions w = (4, 8 and 15) %.

2.2 Experimental procedure

The process of the sample production was performed as follows:

- mixing the solid and liquid phases (the solid-to-liquid-phase ratio was 2.5 g cm^{-3}) until a fine, thick pulp was obtained,
- mass transfer to a rectangular mould with a cover,
- setting the mould to the shaking mode for 10 min to displace the residual air,
- keeping the samples at the room temperature for 48 h and
- keeping the samples in a dryer at the temperature of 100 °C for 72 h,
- aging the samples for 14 d.

3 RESULTS AND DISCUSSION

The chemical content of red mud is shown in **Table 1**, while the chemical content of metakaolin is shown in **Table 2**. The proportion of SiO_2 in kaolin was 59.87 %, the proportion of Fe_2O_3 was 3.12 %, the proportion of Al_2O_3 was 19.45 % and the rest was water.

Table 1: Chemical content of the red mud from the Podgorica Aluminum Factory in mass fractions
Tabela 1: Kemijska sestava rdečega blata iz Tovarne aluminija Podgorica v masnih deležih

oxide	*w*/%
Fe_2O_3	40.78
Al_2O_3	17.91
SiO_2	11.28
TiO_2	10.20
Na_2O	6.9

Table 2: Chemical content of metakaolin in mass fractions
Tabela 2: Kemijska sestava metakaolina v masnih deležih

oxide	*w*/%
SiO_2	52.26
Al_2O_3	42.83
Fe_2O_3	1.01
CaO	0.02
MgO	0.09
Na_2O	0.02
K_2O	1.56
TiO_2	0.13
ZnO	<0.01

The XRD analysis of red mud (**Figure 1**) shows the presence of hematite Fe_2O_3, gibbsite $Al(OH)_3$, akdalaite $4Al_2O_3 \cdot H_2O$, lapidocrocte FeO(OH) and calcite $CaCO_3$.

The value of the specific mass of red mud was ρ_{CM} = 2.7773 g cm^{-3}, and for metakaolin this value was ρ_{MK} = 2.4738 g cm^{-3}.

The investigation of the chemical composition, mineralogical content and thermal characteristics was performed on several geopolymeric samples obtained under different synthesis conditions (**Table 3**).

According to the X-ray diffraction analysis, the geopolymer samples (specimens under numbers 1 and 8 from **Table 3**) showed that the dominating minerals are

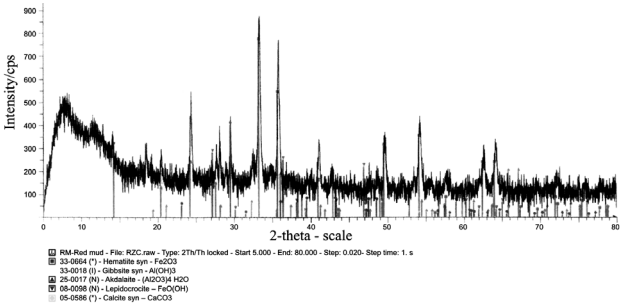

Figure 1: X-ray diffractogram of red mud
Slika 1: Rentgenski difraktogram rdečega blata

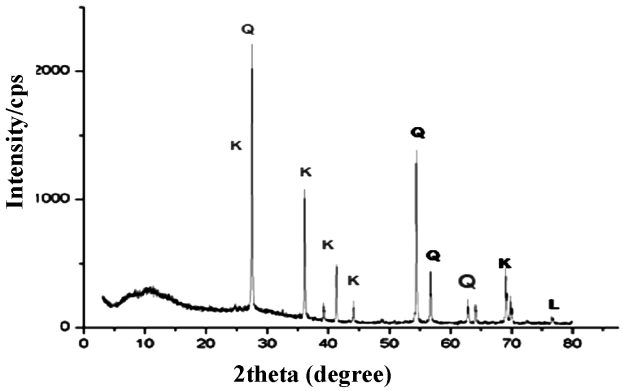

Figure 2: X-ray diffractogram of sample 1
Slika 2: Rentgenski difraktogram vzorca 1

Table 3: Geopolymer samples under different synthesis conditions
Tabela 3: Vzorci geopolimerov iz različnih razmer pri sintezi

Number of sample	C_{NaOH}/ (mol dm^{-3})	C_{Si}/ (mol dm^{-3})	Content of metakaolin (w/%)
1	3	1	2
2	7	1	2
3	10	1	2
4	3	1.5	2
5	7	1.5	2
6	10	1.5	2
7	3	3.5	2
8	7	3.5	2
9	10	3.5	2
10	3	1	8
11	7	1	8
12	10	1	8
13	3	1.5	8
14	7	1.5	8
15	10	1.5	8
16	3	3.5	8
17	3	3.5	8
18	10	3.5	8
19	3	1	15
20	7	1	15
21	10	1	15
22	3	1.5	15
23	7	1.5	15
24	10	1.5	15
25	3	3.5	15
26	7	3.5	15
27	10	3.5	15

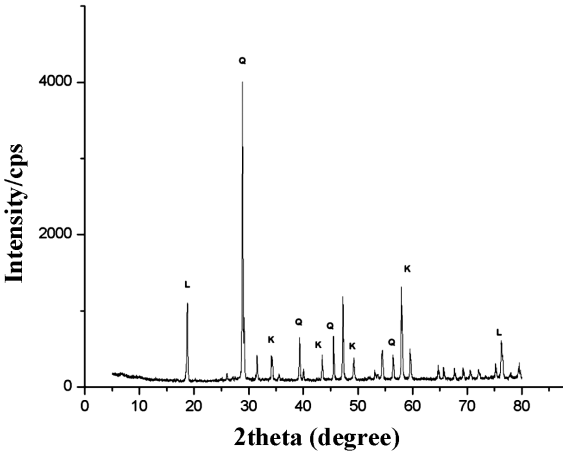

Figure 3: X-ray diffractogram of sample 8
Slika 3: Rentgenski difraktogram vzorca 8

quartz (Q) and kaolinite (K) as shown in **Figures 2** and **3**. The feldspar appears in trace amounts. The X-ray diagrams indicate that the treatment is characterized by dissolution of the starting material and a formation of amorphous and crystalline aluminosilicate phases as well as the stable phases of leucite and kalsilite. The existence of non-dissolved solid particles of red mud is also indicated. The unidentified peaks in XRD diagrams represent the residual unreacted kaolinite or sodium-aluminosilicate phase. The selected diagrams show the existence of an amorphous phase in the system (baseline noise) of the aluminosilicate material. It is also clear that

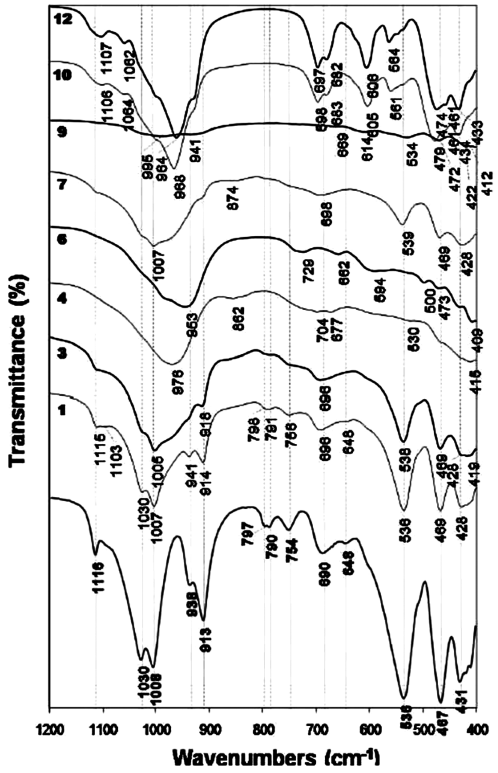

Figure 4: Infrared spectroscopy of geopolymer samples
Slika 4: Infrardeča spektroskopija vzorca geopolimera

increasing concentrations of NaOH as well as an increasing participation of the binder in the solid phase lead to a formation of a more pronounced peak of the new phase, i.e., sodium aluminosilicate.

The FTIR spectroscopy was used to determine the changes in the structure during the treatment of the starting material using the concentrated solution of NaOH and Na-silica (**Figure 4**).

The characteristic wavenumbers for kaolinite are:

OH- at (3700, 3650, 3620) cm^{-1};

Al–OH at 913 cm^{-1};

Si–O at (1032, 1008, 469) cm^{-1};

Si–O–Al at 538 cm^{-1}.

The absence of the Al-O-H bands at 913 cm^{-1} as well as the band duplication at 3700 cm^{-1} and 3620 cm^{-1} are evident. The absence of the bands at 539 cm^{-1} and 913 cm^{-1} and the presence of the new bands at 800 cm^{-1} can be explained with the transformation of the octahedral structure of Al^{3+} into a tetrahedral one under the influence of the agents. The bands at 1100 cm^{-1} and 1200 cm^{-1} are related to the amorphous SiO_2. The characteristic peaks of metakaolin were reduced under the influence of the agents, but they did not disappear after introducing 1 mol dm^{-3} NaOH solution. When using 7 mol dm^{-3} NaOH solution, these peaks almost disappear and create a new band within the wavenumber range of 1200–850 cm^{-1}.

The TG-analysis was performed within the temperature range of 20–1200 °C.

The TGA results (**Figures 5** and **6** refer to the specimens under the numbers 1 and 8 in **Table 3**, respectively) show that the mass loss occurs in two steps. In the first step, at a temperature below 150 °C, the absorbed water is released into the pores and on the surface. In the temperature range of 150–600 °C, the weight loss is associated with the pre-dehydration process, where there is a reorganization of the octahedral lattice. In the second step, the dehydroxylation of the starting material occurs within the temperature range of 350–800 °C.

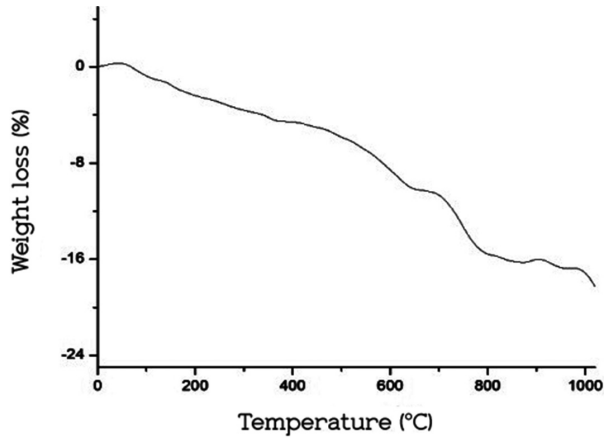

Figure 5: TG analysis of geopolymer, sample 1
Slika 5: TG-analiza geopolimera, vzorec 1

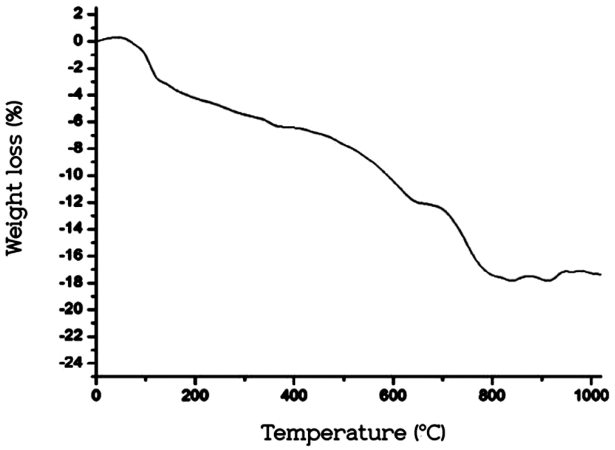

Figure 6: TG analysis of geopolymer, sample 8
Slika 6: TG-analiza geopolimera, vzorec 8

Table 4: Values of the sample density
Tabela 4: Gostota vzorcev

Number of sample	C_{NaOH}/ (mol dm^{-3})	C_{Si}/ (mol dm^{-3})	Content of metakaolin (*w*/%)	Density (g cm^{-3})
1	3	1	2	2.2743
2	7	1	2	2.2760
3	10	1	2	2.2750
4	3	1.5	2	2.2791
5	7	1.5	2	2.2808
6	10	1.5	2	2.2820
7	3	3.5	2	2.2747
8	7	3.5	2	2.2806
9	10	3.5	2	2.2816
10	3	1	8	2.2673
11	7	1	8	2.2705
12	10	1	8	2.2710
13	3	1.5	8	2.2650
14	7	1.5	8	2.2670
15	10	1.5	8	2.2690
16	3	3.5	8	2.2655
17	3	3.5	8	2.2659
18	10	3.5	8	2.2690
19	3	1	15	2.2520
20	7	1	15	2.2530
21	10	1	15	2.2550
22	3	1.5	15	2.2443
23	7	1.5	15	2.2480
24	10	1.5	15	2.2550
25	3	3.5	15	2.2510
26	7	3.5	15	2.2520
27	10	3.5	15	2.2540

The density values of the obtained samples are shown in **Table 4**. The density values for the geopolymer samples are in the range between 2.2443 g cm^{-3} and 2.2816 g cm^{-3}.The highest density values were obtained with the lowest percentage of metakaolin as a binder in the raw mixture. The explanation for this can be found in the fact that the participation of red mud as a very dense component in the raw mixture is the highest in the samples with the lowest percentage of the added binder. The results also show that an important parameter is the

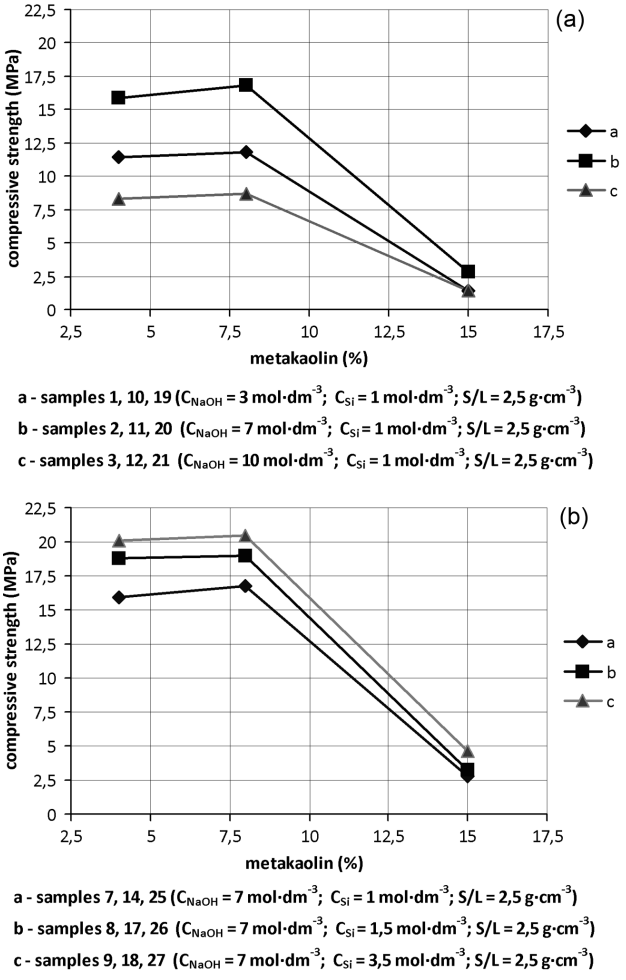

Figure 7: Values of compressive strength of geopolymer samples: a) influence of NaOH concentration on compressive strength as a function of binder percentage; b) influence of Si concentration on compressive strength as a function of binder percentage

Slika 7: Vrednosti tlačne trdnosti vzorcev geopolimera: a) vpliv koncentracije NaOH na tlačno trdnost v odvisnosti od deleža veziva; b) vpliv koncentracije Si na tlačno trdnost v odvisnosti od deleža veziva

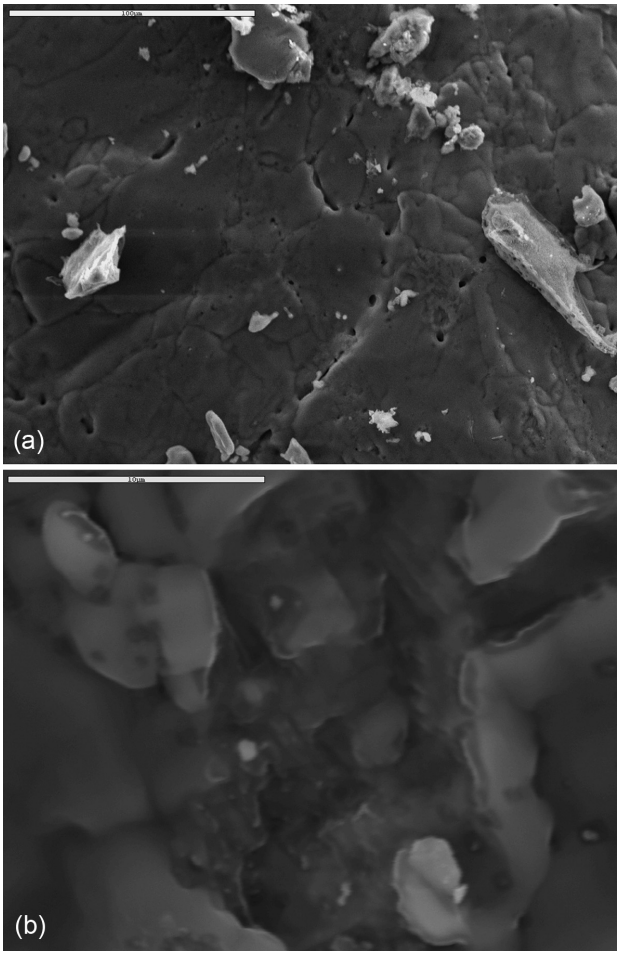

Figure 8: SEM microphotographs of inorganic polymer materials: a) sample (C_{NaOH} = 7 mol dm^{-3}; C_{Si} = 1.5 mol dm^{-3}; *S/L* = 2.5 g cm^{-3}), magnification 500-times; b) sample (C_{NaOH} = 7 mol dm^{-3}; C_{Si} = 1.5 mol dm^{-3}; *S/L* = 2.5 g cm^{-3}), magnification 5000-times

Slika 8: SEM-posnetek anorganskega polimera: a) vzorec (C_{NaOH} = 7 mol dm^{-3}; C_{Si} = 1,5 mol dm^{-3}; *S/L* = 2,5 g cm^{-3}), povečava 500-kratna; b) vzorec (C_{NaOH} = 7 mol dm^{-3}; C_{Si} = 1,5 mol dm^{-3}; *S/L* = 2,5 g cm^{-3}), povečava 5000-kratna

ratio of the components in an alkaline activator, so the combination of a high hydroxide concentration and a low silicate concentration generates lower density values. The explanation can be found in the fact that a high NaOH concentration influences the deficit of the silicon needed for the reaction of geopolymerization.[2,4]

The values of compressive strength of geopolymer in dependence of the concentration of the activator (NaOH -Na-silicate) and the presence of a binder are shown in **Figures 7a** and **b**, respectively.

The factors affecting an increase in compressive strength are different concentrations of alkaline activators. The results show that with the increasing concentrations of NaOH (3, 7, 10) mol dm^{-3} the compressive strength increases up to a NaOH concentration of 7 mol dm^{-3}. Higher NaOH concentrations (10 mol dm^{-3}) cause a reduction in the compressive-strength value. The explanation for this lies in the fact that the initial increase in the NaOH concentration leads to an increase in the silicon and aluminum dissolution from the solid phase[2]. The increased Si and Al contents in the aqueous phase are essential for initiating the oligomer formation and polycondensation. The decrease in the values that occurs under higher NaOH concentrations is the consequence of the fact that dissolved silicon and aluminum remain almost constant while the free NaOH increases, resulting in a lower SiO_2/Na_2O ratio in the aqueous phase. Therefore, the monosilicates and oligomeric species are predominantly in favor of polymer and consequently the polycondensation is slower[2].

Change in the silicon concentration in Na-silicate (1, 1.5, 3.5) mol dm^{-3} causes an increase in the compressive strength of the geopolymer samples. With the increasing concentration of the alkaline activator, the amount of dissolved silicon in the reaction mixture increases as well. Silica originating from sodium silicate has an

important role because it starts the reaction of geopolymerization by allowing a faster and more complete dissolution from the raw material[2]. A higher silicon concentration leads to the formation of silicate species with a complex polymeric structure, thus allowing the three-dimensional polymeric framework to rise. Soluble silica fosters the polycondensation. Under the higher initial silica concentrations, the surface cracks were noticed. This might be because of the entrapped free water of the aqueous phase (the water for the Na-silicate dissolution).

The level of substitution of red mud with metakaolin w = (4, 8 and 15) % causes an increase in the compressive-strength value up to w = 15 %. The lower level of the compressive strength with 15 % of metakaolin, or higher, can be explained with a lack of NaOH for dissolving such a quantity of metakaolin, or with the fact that a high level of polycondensation (because of an excessive amount of metakaolin) can create a surface non-permeable membrane entrapping water from the liquid phase (water for the dissolution of Na-silicate)[4].

The microstructure of the synthesized inorganic polymer material was investigated by scanning electron microscopy and it is shown in **Figure 8**.

SEM microphotographs show that the obtained materials are compact, with no discontinuity, which is confirmed by the mechanical properties. The isolated pores noticed inside the material are in the range of up to 200 μm. The presence of a new amorphous phase can be seen in **Figure 8a**. In **Figure 8b** a gelatinous phase around the particles of the starting material is identified under high magnification.

4 CONCLUSION

This investigation shows that the red mud obtained as a by-product of the Bayer process for obtaining aluminum in the Podgorica Aluminum Factory is, according to its physicochemical and mechanical properties, a good-quality aluminum-silicate material appropriate for geopolymer formation. Under the optimum synthesis conditions (the S/L ratio of 2.5 g cm^{-3}, the NaOH concentration of 7 mol dm^{-3}, the metakaolin percentage of 10 %), the red-mud/metakaolin-based polymeric materials develop satisfactory compressive strength. These mechanical properties were attributed to the formation of the amorphous phase that bonded the non-dissolved particles of the raw solid materials in a good manner. The presence of this phase was also revealed by the XRD, TG and FTIR analyses as well as SEM analysis.

The results of the investigations of the basic properties of the developed geopolymer show that it can be used in civil engineering (as a substitute for brick products and road foundations). Depending on the purpose of a product, an additional research is required (resistance to different external effects, durability in exploitation conditions, etc.) as well as an analysis of the economic feasibility.

Apart from that, the described process of geopolymerization can contribute significantly to environmental preservation, since there is a possibility of conserving large quantities of industrial waste.

5 REFERENCES

[1] J. Davidovits, Geopolymer, green chemistry and sustainable development: The poly (sialate) terminology: a very usefull and simple model for the promotion and understanding of green chemistry, Proceedings of the world congress Geopolymer 2005; Ed.: J. Davidovits, Published by Institut Geopolymer, 2005, 9–17

[2] I. Giannopoulou, D. Dimas, I. Maragkos, D.Panias, Utilization of Metallurgical solid by-products for the development of inorganic polymeric construction materials, Global NEST Journal, 11 (**2009**), 127–136

[3] J. C. Swanepoel, C. A. Strydom, Utilization of fly ash in a geopolymeric material, Applied Geochemistry, 17 (**2002**) 8, 1143–1148

[4] D. Dimas, I. Giannopolu, D. Panias, Utilization of aluminia red mud for synthesys of inorganic polymeric materials, Mineral processing and extractive metallurgy review, 30 (**2009**) 3, 211–239

[5] M. Izquierdo, X. Querol, C. Phillipart, D. Antenucci, World of coal ash (WOAC) Conference, Lexington, KY, USA, 2008

[6] B. V. Rangan, Fly ash-based geopolymer concrete, Research report GC 4, Engineering Faculty, Curtin University of Technology, Perth, Australia, 2008

[7] P. De Silva, K. Sagoe-Crenstil, V. Sirivivatnanon, Kinetics of geopolymerisation: Role of Al_2O_3 and SiO_2, Cement and Concrete Research, 37 (**2007**), 512–518

[8] K. Sagoe-Crenstil, L. Wang, Dissolution processes, hydrolysis and condensation reaction during geopolymer synthesis: Part 2. High Si/Al ratio systems, Journal of Materials Science, 42 (**2007**), 3007–3014

[9] J. S. J. van Deventer, J. L. Provis, P. Duxon, G. C. Lukey, Reaction mechanisms in the geopolymeric conversion of inorganic waste to usefull products, Journal of hazardous materials, A139 (**2007**), 506–513

[10] J. L. Provis, J. S. J. van Deventer, Geopolimerysation kinetics. 2. Reaction kinetic modelling, Chemical Engineering Science, 62 (**2007**), 2318–2329