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The influence of the amorphous SiO_2 content on the characteristics of red-mud based geopolymers

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Abstract— Curing conditions as well as type and content of silica in raw mixture seem to be very important in both producing quality as well as stability of red-mud-based geopolymers. The influence of amorphous SiO_2 along with the other components of raw mixture was studied in this paper. The presence of amorphous silica turned to be a very important factor influencing the strength of red-mud-based geopolymers. The results confirm that the compressive strength of geopolymers increases (up to 41MPa) with the presence of amorphous silica in raw mixture up to the certain point (50 wt %). Excessive content of amorphous silica causes sharp decrease in strength. Microstructure analysis confirms the existence of homogenous structure. The presence of gluing geopolymer phase is also detectable by various techniques.

Keywords— compressive strength, geopolymers, red mud, volcanic tuff

I. *Introduction*

Aluminosilicates can be transformed into aluminosilicate polymer-like structure through the process alkali activated chemical polymerization [1-9]. The result of the polymerization of aluminosilicate monomers in alkaline solution is a reaction pathway which involves polycondensation of hypothetical monomers i.e. sialate ions. As the result of these reactions, stable material similar to zeolite is formed [10, 11].

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These materials consist of SiO_4 and AlO_4 tetrahedra linked alternatively by sharing oxThe type of final structure is significantly influenced by Si/Al ratio in the raw mixture. When this ratio is close to one, polycondensation is dominantly performed between aluminates and silicate components, resulting in the development of poly-sialate polymeric structure [3].

With increased Si/Al ratio, polymer structures are obtained as the consequence of hydrolysis of SiO_2 [4]. As a result, oligomeric silicates are formed. Silicates condensate with $Al(OH)_4^-$ ions, forming rigid polysialate-syloxo and polysialate-disyloxo structure [5].

Wide spectrum of raw aluminosilicate materials can be used for geopolymerization: fly ash, slag as well as red mud as the by-product in aluminum industry [6,7].

Compared to widely used materials such as cements, geopolymers perform better chemical stability, resistance to aggressive environments, resistance to corrosion, resistance to extreme temperatures. All these characteristics make geopolymers long-lasting durability [8,9]. Geopolymers are also considered as eco-friendly materials, without significant CO_2 emissions [9,12].

The purpose of this study is to improve the properties of red-mud-based geopolymers by optimizing the curing conditions and raw mixture content. Recent results [5,9] have demonstrated the influence of some curing parameters like solid-liquid ratio, Si/Al ratio, concentration of alkaline solution, curing regime on the performances of geopolymers. Red mud is one of the most present aluminosilicate materials and a huge environmental problem at the same time. As the carrier of aluminosilicates it can be used for the preparation of geopolymers although with less level of compressive strength. The purpose of this

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investigation is to combine already known influencing factors with the presence of amorphous silica with the aim to

optimize the performances of obtained material.

II. *Experimental*

Geopolymers were synthesized using following raw materials:

- red mud obtained as a by-product of the Bayer process of obtaining alumina.(Aluminum Factory, Podgorica),
- sodium hydroxide of analytical grade (Merck, anhydrous pellets),
- metakaolin, which provides initially the geopolymeric system with soluble silicon and aluminum that are essential for alumo-silicate oligomers formation and progress of the geopolymerization,
-volcanic tuff "Jugoštica"
- volcanic tuff "Strmoš"
-sodium-silicate solution (Merck Na_2O: SiO_2= 3,25 Na_2O 7.5-8.5 %, SiO_2 25.5-28.5 % and
d =1,347 g cm^{-3})
-deionized water for the synthesis of polymeric material.

The chemical composition of red mud is shown in **Table I**, while the chemical composition of metakaolin is shown in **Table II**.

TABLE I. Chemical composition of red mud from the Alumina factory KAP Podgorica

Oxides	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	Na_2O	CaO
wt/%	11.28	40.78	17.91	10.20	6.9	1.5

TABLE II. Chemical composition of metakaolin

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2
wt/%	52.26	42.83	1.01	0.02	0.09	0.02	1.56	0.13

Chemical analysis of volcanic tuff "Strmoš" (**Table III.**) shows the high content of SiO_2 (90.47 wt %) as well as low content of Al_2O_3 (2.91 wt %), in respect with volcanic tuff "Jugoštica" (68.76 wt % SiO_2 and 14.59 wt % Al_2O_3) (**Table IV.**)

TABLE III Chemical composition of tuff "Strmoš"

Oxides	SiO_2	Fe_2O_3	Al_2O_3	MgO	Na_2O	CaO	K_2O	SO_3
wt/%	90.47	in trace	2.91	0.75	0.29	2.40	0.08	0.54

The rest in wt% is lost of ignition

TABLE IV. Chemical composition of tuff "Jugoštica"

Oxides	SiO_2	Fe_2O_3	Al_2O_3	MgO	Na_2O	CaO	K_2O	SO_3
wt/%	68.76	2.50	14.59	1.11	2.52	2.95	2.53	0.29

The rest in wt% is lost of ignition

Red mud has been dried to constant mass at the temperature of 105˚C and then sifted through a 250μm sieve.

Metakaolin is the dehydroxylation product of the industrial mineral kaolin obtained during the thermal treatment in the temperature range 650˚C-850˚C. The thermal dehydroxylation of kaolin increases its solubility in alkaline media. It has been performed at 750˚C. Metakaolin is dominantly amorphous material with minor crystalline constitutes.

As an alkaline activator of the geopolymerization process, a combination of sodium water glass and sodiumhydroxide was used. The activator solution was prepared by mixing the previously mentioned components 48 hours before the geopolymer production. Metakaolin was used as a binder in both cases.

Two different raw mixtures (solid part) were used in this research:

- red mud (50 wt%, 60 wt% , 70 wt%, 80 wt %) and volcanic tuff "Jugoštica"
- red mud (50 wt%, 60 wt% , 70 wt%, 80 wt %) and volcanic tuff "Strmoš"

Other relevant process parameters (concentration of liquid-phase components) were as follows: C_{NaOH}= 10 mol dm^{-3},C_{Si}= 6 mol dm^{-3}, Na_2SiO_3/NaOH=2 and Na_2SiO_3/NaOH=2,5.

A. *Curing procedure*

The samples have passed the following path:

- sieving of raw-mixture components through 250 μm sieve,

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- homogenization of pulp by mixing of the solid and liquid components of raw mixture,
- molding into plastic cylindrical containers with dimensions as follows: d=8.6 cm, H= 9 cm,
- drying of the specimens at 70°C in duration of 48 h,
- air aging of the specimens in duration of 21 days.

B. *Chemical, microstructural and phase analysis of geopolymers*

The chemical analysis of red mud, metakaolin, volcanic tuff "Strmoš" and volcanic tuff "Jugoštica" was done on the instrument IPC 6000-THERMO SCIENTIFIC.

The X-ray diffraction (XRD) was carried out on powdered samples to identify remaining crystalline and potentially newly formed phases of amorphous character on the PHILIPS PW 1050 with scan rate 2°/min (35 kV, 20 mA) which is formed by monochromator MR-ADVANCE METALS RESEARCH CORPORATION. XRD analysis of "Strmoš" tuff was carried out on PHILIPS PW 1010 instrument with CuK_{α} radiation (38kV, 18 mA). The XRD patterns were measured from 2° to 6° at a scan rate of 1°/min. Diffraction analysis of "Jugoštica" tuff was done on the PHILIPS PW 1717 instrument.

Compressive strength of geopolymers was done on the laboratory press HPN 400.

SEM analysis was performed on TESLA SEM instrument with OXFORD EDX system and digital activation of signals. The samples were pre-coated with gold under vacuum.

FTIR Perkin Elmer 16C Spectrometer was used for the investigation of amorphous phase formation.

III. *Results and discussion*

The XRD analysis of red mud from KAP (**Fig. 1.**) shows the presence of hematite- Fe_2O_3, gibbsite -$Al(OH)_3$, akdalaite -$Al_2O_3{\cdot}H_2O$, lepidocrocite- FeO(OH) and calcite- $CaCO_3$. Based on mineralogical and chemical content of red mud (**Fig. 1.** and **Table I.**), it can be seen that this material is a significant alumosilicates carrier and accordingly suitable material for geopolymerization.

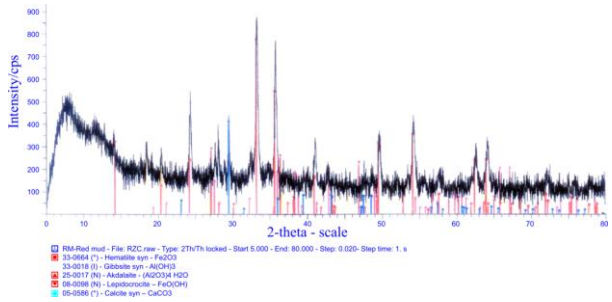

Figure 1. X-ray diffractogram of red mud from KAP

Based on the intensity and positions of the peaks on diffractogram (**Fig. 2**.) it can be concluded that the "Jugoštica" tuff is the carrier of dominantly crystalline SiO_2.

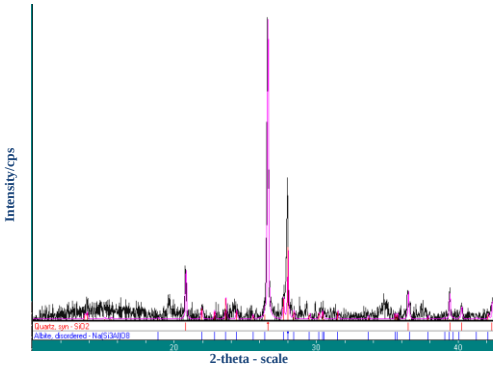

Figure. 2. X-ray diffractogram of volcanic tuff ″Jugoštica″

X-ray analysis of volcanic tuff ″Strmoš″ (**Fig. 3**.) shows the presence of dominantly amorphous SiO_2 with the traces of crystalline SiO_2 (quartz and tridimite) as well as the presence of amorphous or crypto-crystalline carbonates.

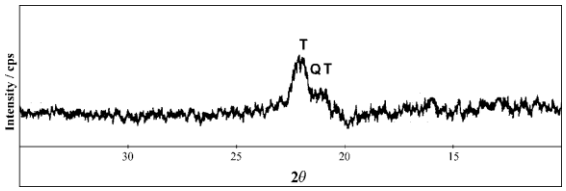

Figure 3. X-ray diffractogram of volcanic tuff ″Strmoš″

One of the components of raw mixture with the significant influence on the geopolymerization process is

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alkaline activator (Na_2SiO_3 and NaOH). The process of geopolymerization can be effectuated in the highly alkaline environment . If the hydroxide concentration is less then 5 mol dm^{-3} , pH of the system is adequately low to enable the dissolution of $Ca(OH)_2$. This reaction provides enough calcium for the forming of hydroxy-calcium-silicate phases (CHS). Low value of pH disables dissolution of primary material and leaves the whole system without enough dissolved Al ions to form alkali alumosilicates [13]. The greater concentration of NaOH (beyond 10 mol dm^{-3}), because of the potential entrapping of the excessive NaOH in geopolymer mass causing decreased compressive strength.

The increased Na_2SiO_3/ NaOH ratio (2 to 2.5) goes along with the increased compressive strength (**Fig. 4-a**). The reason is increased content of soluble silicon needed for the creation of geopolymer bonds. Si/Al ratio is very important because aluminum affects dynamics of the bonding while silicon affects strength. The presence of amorphous SiO_2 influences the increasing compressive strength, which can be concluded by comparison with previously obtained results with the raw materials without amorphous SiO_2 [14].

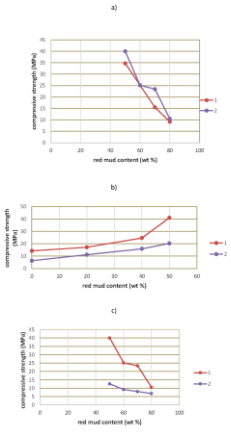

Figure 4. Compressive strength as a function of red mud content: a)(C_{NaOH}=10 mol dm^{-3}, curve 1-Na_2SiO_3/NaOH=2; curve 2-Na_2SiO_3/NaOH=2,5 , 8 wt % metakaolin, volcanic tuff ″Strmoš″); b)(C_{NaOH}=10 mol dm^{-3}, Na_2SiO_3/ NaOH=2,5; curve 1- 8 wt % of metakaolin, curve 2 -4 wt % of metakaolin, volcanic tuff ″Strmoš″);(C_{NaOH}=10 mol dm^{-3}, curve 1-Na_2SiO_3/NaOH=2; curve 2-Na_2SiO_3/NaOH=2,5 , 8 wt % metakaolin, volcanic tuff ″Strmoš″); c) (C_{NaOH}=10 mol dm^{-3}, Na_2SiO_3/ NaOH=2,5 , 8 wt % metakaolin; curve 1-volcanic tuff ″Strmoš″, curve 2-volcanic tuff ″Jugoštica″)

Compressive strength values of the specimen with the different content of metakaolin (4 wt % and 8 wt %) show increasing trend up to the metakaolin content of 8 wt% (**Fig. 4 -b**.).The wt percentage of metakaolin in raw mixture in the range of 4 wt % and 8 wt % was established upon the preliminary research results of the metakaolin's influence on the geopolymer's performances [15].

The role of metakaolin is to be the main carrier of soluble silicon and aluminum thus fostering the reaction of polycondensation. Increased content of metakaolin can create surface nonpermeable membrans which entrapped the water from the liquid phase. This process can compromise the mechanical characteristics of geopolymers [5,15].Compressive strength values for the specimens with the tuff "Strmoš" (**Fig. 4-c**.) show increased values relative to those for the specimens with tuff "Jugoštica". According to the X-ray analysis (**Fig. 3**.), volcanic tuff "Strmoš" contains dominantly amorphous SiO_2, while volcanic tuff "Jugoštica" contains crystalline SiO_2 (**Fig. 2**.). The presence of amorphous SiO_2 in raw mixture enables fostering of polycondensation, because of better reactivity of amorphous SiO_2.The result is the product with enhanced characteristics. Presence of crystalline SiO_2 results in heterogenous materials without stronger cohesion. FTIR analysis of geopolymer with tuff "Strmoš" is presented in **Fig. 5.**

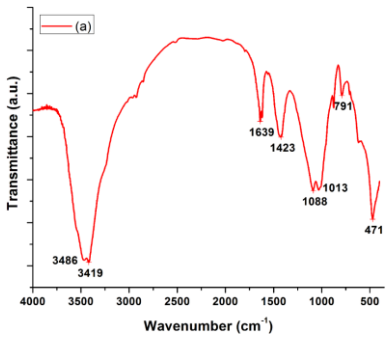

Figure 5. FTIR analysis of geopolymer (50 wt % red mud, volcanic tuff „Strmoš", 8 wt % metakaolin)

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According to FTIR results, it is visible that the typical bonds Al-O-H at 913 cm^{-1} are missing after the geopolymerization. Relaxing or absence of the bond at 539 cm^{-1} as well as 913 cm^{-1} can be dedicated to the transformation of octahedral Al^{3+} structure in tetrahedral which is the base for the polycondensation. Bonds in the range 1100 cm^{-1} reffer to the amorphous silicon dioxide. The presence of the class of bands in the range of 1420 cm^{-1} indicates the formation of amorphous phase.

SEM analysis (**Fig. 6.**) shows the certain level of compact, with the pore size up to few microns (marked as B) , clearly visible amorphous phase (marked as C) and unreacted structure (marked as A). Granular internal structure after geopolymerization partially remained, while the particles are dominantly conglomerated by the new amorphous phase.

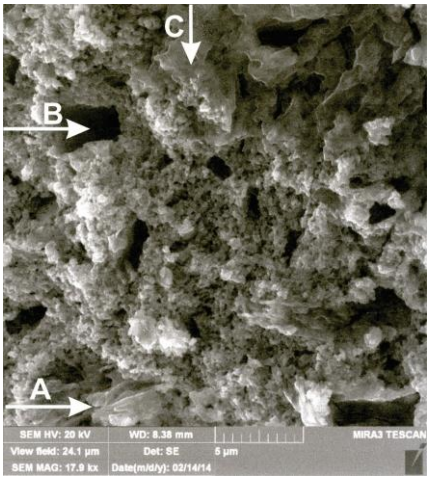

Figure 6. Microstructure of geopolymer (50 wt % red mud, volcanic tuff „Strmoš“, 8 wt % metakaolin, magn. 5800 X)

IV. *Conclusions*

Based on the overall research results and analysis the following conclusions can be reached:

- Volcanic tuff with dominantly amorphous SiO_2 can be utilized as the part of the raw mixture in the process of geopolymerization.
- The presence of SiO_2 and the level of its crystallinity is of almost importance for the progress of geopolymerization. The higher compressive strength values are obtained with the amorphous SiO_2.
- There is the clear limit of the content of amorphous SiO_2 in the raw mixture (50 wt%) which affects the compressive strength in positive manner (up to 41.02 MPa).
- Increasing content of metakaolinite (from 4 wt% to 8 wt%) induces the increasing values of compressive strength. The important role for the process of geopolymerization has the Na_2SiO_3/NaOH ratio. Higher values of compressive strength can be obtained by increasing of this value from 2 to 2.5.

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