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MECHANICAL PROPERTIES AND HYDROLYTIC STABILITY OF GEOPOLYMERS BASED ON WHITE WASTE GLASS. INFLUENCE OF THERMAL TREATMENT

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This study explores the feasibility to produce geopolymers by alkaline activation of waste glass powder (glass cullet from white bottles) with sodium hydroxide solution. Red mud, a residue resulted in bauxite processing, was used, as addition, due to its high alkalinity and aluminum content. The values of compressive strength recorded for the mortar specimen based only on white glass powder are higher (with 20-25%) as compared with those assessed on the composition with red mud admixture. Thermal treatment at 800-900^{o}C determines swelling and, in some cases, an important volume increase, due to a foaming process specific for sodium silicate (aluminate) hydrates, the main components of these materials. The hydrolytic stability of studied materials is low; compressive strength losses (over 30%) were recorded when mortar specimens were kept immersed in water for 28 days. However, the thermal treatment at 900^{o}C increases the resistance of studied materials toward moisture/water attack.

Keywords: Waste glass, red mud, alkali activation, foam geopolymer, thermal treatment, hydrolytic stability

1. Introduction

Alkali activation of industrial wastes, such as fly ash or slag, represents today a viable way for their re-use in the production of new construction materials, called alkali activated cements or geopolymers [1-4]. Recently, was

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also reported the possibility to obtain geopolymers starting from a municipal waste i.e. powder glass obtained from glass cullet [5-11].

The main drawback of geopolymers obtained by alkali activation of glass powder is their low stability in moist conditions [5-10]. The lack of hydrolytic stability of these materials is due to their content in sodium/ potassium silicate hydrates, resulted during the activation of glass powder with sodium/potassium hydroxide solution.

Several admixtures were used in the attempt to improve the moisture resistance of these materials i.e. metakaolin, slag, fly ash [6,7] and red mud, waste resulted in bauxite processing [8-10]. The results obtained so far pointed out that a careful choice of admixtures (with respect to their nature and dosage) could increase the hydrolytic stability of geopolymers containing up to 50% glass powder. Redden and Neithalan [6] showed that for the systems based on glass powder, the doping with Ca and Al through the use of slag and metakaolin could reduce the strength loss under moisture exposure. Similar results were obtained when fly ash was added to glass system [6,7].

In our studies we've noticed also the important influence exerted on the geopolymers properties of alkali activator nature, glass powder source (cullet from glass bottles of brown and green color) [8-10] as well as of red mud used as admixture.

An interesting property of these materials is their ability to swell (important increase of volume) when subjected to thermal treatment between 600-800^{o}C [10]. This allows to produce foamed materials by thermal treatment of geopolymers resulted by the alkali activation of waste glass (cullet) with/without red mud admixture.

In this paper we present results regarding the influence of cullet glass composition (white glass) as well as red mud admixture on the compressive strength and hydrolytic stability of resulted geopolymers. We report also results regarding the influence of thermal treatment on the apparent density, porosity and hydrolytic stability of these materials.

2. Materials and methods

White waste glass (W) cullet, from a glass bottles production plant, was used as solid component for geopolymer synthesis.

The oxide composition of glass is presented in table 1. Oxide composition was determined using the methods described in Romanian standard 5771/1-11/89 [11].

The glass was milled in a ball mill up to a Blaine specific surface area of 2858 cm^2/g.

Table 1

Oxide composition of white glass powder (W)

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3
White glass (%)	71.22	1.96	0.088	10.35	2.76	13.4	0.03	0.06	0.14

The white glass thermal expansion curve was recorded with DIL 402 PC Netzsch dilatometer. The dilatometric softening point (T_D) was registered at 610°C.

Red mud sludge received from alumina plant was dewatered by filtration and the solid part was dried at 100°C up to constant mass. The dried red mud (R) was crushed in a Pulverisette mill for 5 minutes [8].

The elemental and mineralogical compositions of red mud are presented in table 2. [8-10]

Table 2

Elemental and mineralogical composition of red mud (R)

Elemental composition	Fe	Na	Al	Ti	Si	Ca	Cr	P	S	K	Other elements
Concentration (%)	37.81	25.49	17.39	5.97	5.59	2.64	0.25	0.18	0.17	0.06	4.28
Mineralogical composition	Fe_2O_3, εFe-Ti-O, $Na(AlSiO_4)$, $Si_2Al_2O_5(OH)_4$, $Na_8(Si_6Al_6O_{24})$ $H_{0.88}(CO_3)1.44(H_2O)_2$and $Ca_2Al_2Si_2O_7(OH)_2H_2O$										

The elemental composition of red mud was determined by X-ray fluorescence (XRF) spectrometry using an S8 Tiger Bruker and the mineralogical composition was assessed by X ray diffraction (XRD) using analysis using a Shimadzu XRD 6000 diffractometer. The XRD spectra were obtained using a monochromatic CuKα radiation (λ= 1.5406 Å), range 2θ from 5 to 50 degree.

White glass powder (W) or mixtures of white glass powder and red mud (25% red mud as a substitute of glass powder - WR25) were used for the preparation of geopolymers. The alkali activator was NaOH 5M aqueous solution (N5).

Two types of specimens were prepared: i) paste with liquid to solid ratio of 0.3; ii) mortars with binder to sand ratio of 0.5.

Paste specimens were prepared by mixing the solid component i.e. white glass powder (W) or mixture of white glass and 25% red mud (WR25) with NaOH solution (N5); liquid to solid ratio was (0.3) The workability of the resulting paste (W-N5 and WR25-N5) was good and the materials were cast in cubic (20x20x20mm) or rectangular (15x15x60mm) molds. The specimens were cured in the mold (covered with cling film) at 60°C the first 24 hours; after the thermal treatment the specimens were de-molded and cured in air (R.H. 65%) at 20 ±2°C.

For the preparation of mortar specimens, the solid component (W or WR25) was mixed with sand (aggregate) and alkali activator solution (N5); the liquid to solid ratio was (0.3) and solid (glass+ red mud) to sand ratio was 0.5. The resulting material was cast in rectangular molds (15x15x60mm) and vibrated for 2 minutes. The specimens were cured in the mold (covered with cling film) at 60°C the first 24 hours, then de-molded and cured at 60°C in humid air (R.H. 85%) up to 3 days. The specimens were then cured in air (R.H. 65%) at 20 ±2°C up to 28 days.

After 7 days of curing, the paste and mortar specimens were subjected to thermal treatment in an electric furnaces, at different temperatures (between 400°C to 900°C), for 1h. The heating rate was 10°C/min and the specimens were slow cooled in the oven until next day. Each thermal treatment experiment was carried out in duplicate.

The hydrolytic stability was assessed on mortar specimens using the method previously described in [7-9] and on paste specimens [12].

The first method [7-9] consists in the immersion of mortar specimens in demineralized water (water to solid ratio of 1.3) for 28 days; the immersion solutions were renewed daily, the first 4 days, and then weekly up to 28 days.

Mass and compressive strength variation of mortar specimen immersed in water for 28 days was calculated with the formula (1) and (2):

$$\Delta m = [(m_{28}-m_1)/m_1]*100\ (\%) \tag{1}$$

where m_{28} = specimen mass after 28 days of water immersions in water (g) ; m_1 = specimen mass after 1 day of immersion in water (g).

$$\Delta Cs = [(Cs_w-Cs_a)/Cs_a]\ *100\ (\%) \tag{2}$$

where Cs_w = compressive strength of specimens immersed in water for 28 days (MPa); Cs_a = compressive strength of specimens cured in air for the same time - 28days(MPa).

The second method, applied for paste specimens, before and after thermal treatment, was used by Vancea and Lazau [12] for the assessment of hydrolytic stability of glass foams; the method is described in ISO 719-1985 [13]. This method determines the hydrolytic resistance of glass grains in hot water and consists in keeping 2 g of material, for 60 min in 50 ml de-ionized water at 98°C. A volume of 25 ml of the obtained solution is titrated with 0.01 M HCl solution. The volume of HCl needed for neutralization is recorded in order to calculate the equivalent Na_2O extracted.

The increase of volume of paste specimens thermally treated at 800°C and 900°C was calculated with the formula:

$$\Delta V = [(V_t-V_b)/V_b]*100\ (\%) \tag{3}$$

where V_t = specimen volume after thermal treatment at temperature "t"(cm^3);
V_b = specimen volume before thermal treatment (cm^3).

Apparent density and open porosity of pastes, before and after thermal treatment at 900°C, were measured using the liquid saturation method under vacuum [14]; as working liquid was used xylene (C_8H_{10}, ρ=0.866 g/ml).

3. Results and discussions

3.1 Compressive strength

The geopolymer based on white glass (W-N5) achieves after 1 day of curing at 60°C a good compressive strength (23.8 MPa) – fig. 1; the decrease of the curing temperature at 20°C (after the first day) determines a small reduction of compressive strengths but the values remains around 20 MPa.

The substitution of white glass with 25% red mud (WR25-N5) determines a certain reduction of compressive strength, with reference to the compressive strength assessed on W-N5 mortars, i.e. 20-35% in correlation with the curing time.

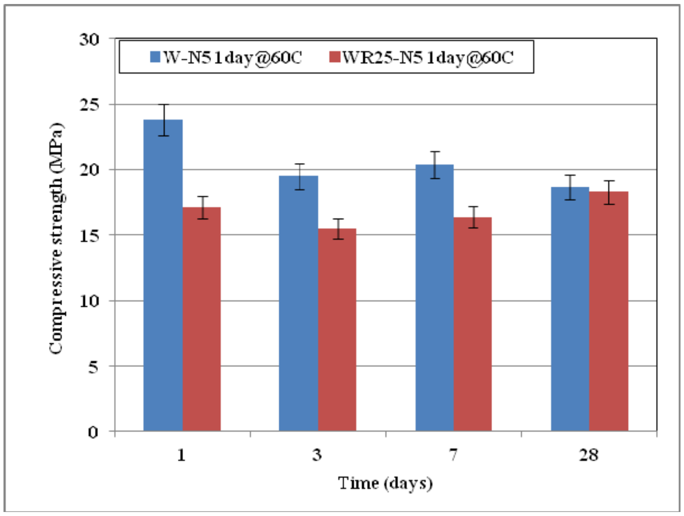

Fig. 1. The compressive strength developed by the compositions based on white glass powder (W) and glass powder with 25% red mud (WR25), activated with NaOH 5M, cured the first day at 60°C

Fig. 2 shows the influence of the increase of initial curing time at 60°C, from 1 day to 3 days; the increase of curing time at 60ºC do not exerts an important influence on the compressive strengths values of W-N5 and WR25-N5 mortars i.e. the values remains around 20MPa for W-N5 and around 15 MPa for WR25-N5 (see also fig.1).

The values of compressive strength recorded for the specimen with red mud (WR25-N5) continues to be lower, as compared with those recorded for the mortar based only on white glass powder (W-N5), even when the curing time at 60ºC increases from 1 to 3 days. These lower values are explained by the substitution of reactive glass powder with the red mud; this waste contains crystalline compounds (see §2) and has a lower reactivity vs. alkali solution as compared with glass powder; similar results were obtained in previous studies made on different types of glasses [8,9].

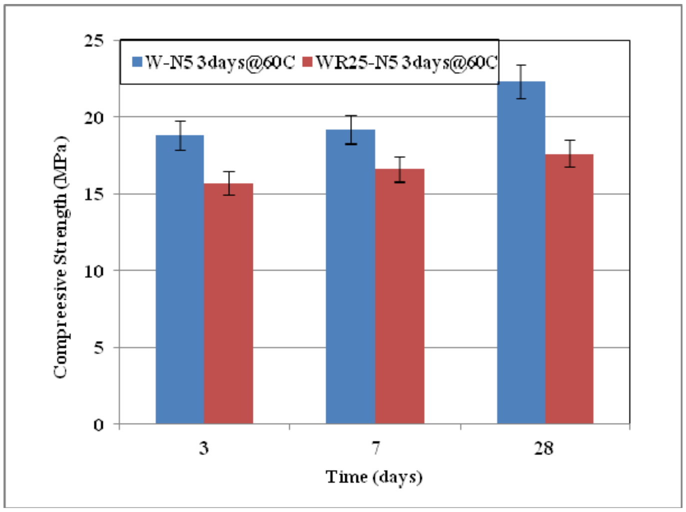

Fig. 2. The compressive strength developed by the compositions based on white glass powder (W) and glass powder with 25% red mud (WR25), activated with NaOH 5M, cured the first 3 days at 60°C

Due to the reduced influence exerted by the increase of curing time at 60°C (from 1 to 3 days) on the compressive strength values of studied compositions, the following properties were assessed only on specimens cured for 1 day at 60°C.

3.2. Influence of thermal treatment

Previous results [10] showed that thermal treatment of geopolymers obtained by the alkali activation of brown glass (with/without red mud addition), at temperatures comprised between 600-800°C, determines an important volume increase; this is due to a foaming process specific for sodium silicate (aluminate) hydrates, the main components of these materials.

In order to check the influence of glass composition and red mud addition on the behavior geopolymers at high temperatures, the pastes based on white glass, were subjected to a similar thermal treatment.

The visual aspect of W-N5 paste specimens after the thermal treatment at temperatures comprised between 200-800°C is presented in fig. 3. It can be noticed the shape deformation and cracking of specimens cured at 200°C, 600°C and 700°C. The specimens thermally treated at 700°C and 800°C exhibit swelling and foaming on small areas (at the surface and edges of the specimens); this is due to a foaming process, also noticed for geopolymers based on brown glass [10]. When the thermal treatment temperature increases at 900°C (fig.4) a certain contraction of W-N5 specimen occurs, most probably due to a sintering effect.

For the specimens with 25% red mud (WR25-N5), an important swelling effect is noticed even from 800°C and increases with the increase of temperature at 900°C (Fig. 4). It is interesting to notice the white spots on the surface of WR25-N5 specimens (Fig.4); this suggests that white glass grains did not react completely with the sodium hydroxide solution.

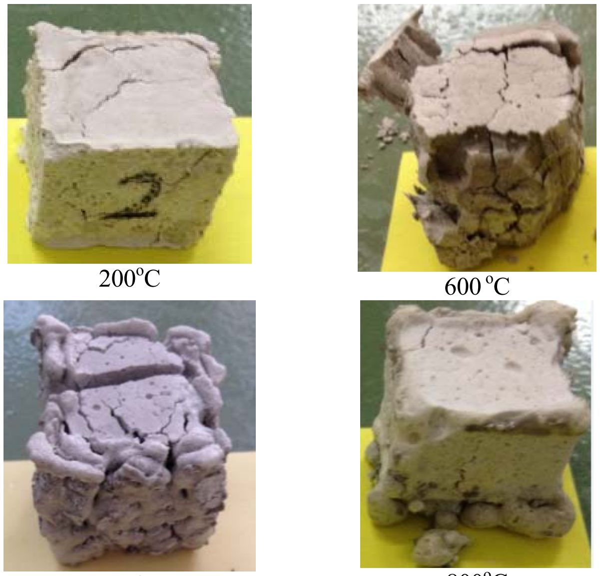
200°C
600 °C
700°C
800°C

Fig. 3. Visual aspect of W-N5 pastes thermally treatment for 1 h at different temperatures

The modification of the specimen's form (from cube to prism – Fig. 4) and the increase of the surface exposed to high temperature, did not affect the processes that take place when the temperature increases and the specimen's visual aspect.

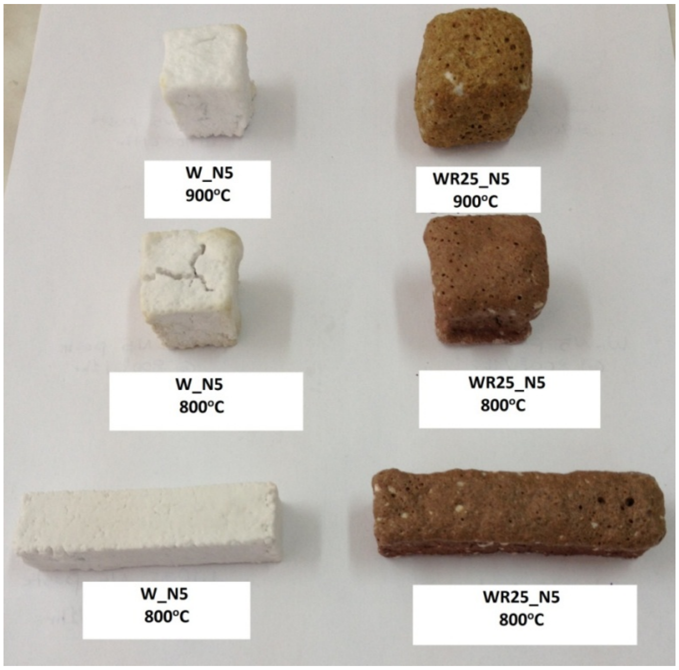

Fig. 4. Visual aspect of W-N5 and WR25-N5 pastes thermally treatment for 1 h at 800°C and 900°C

The volume changes recorded for the paste specimens thermally treated at 800°C and 900°C calculated with formula (3) are presented in fig. 5. These data confirms the contraction phenomenon visually noticed for the W-N5 composition thermally treated at 900°C (as compared with the same specimen thermally treated at 800°C) and the important volume increase noticed for the specimens with red mud addition (WR25-N5).

The values of apparent density and open porosity measured by liquid saturation method are presented in figs. 6 and 7.

The specimen WR25-N5 thermally treated at 900°C floated on xylene, therefore we assume that this material has a value of apparent density below 0.866 g/cm^3

Thermal treatment of geopolymers (W-N5 and WR25-N5) decreases the values of apparent density; this can be explained both by the decrease of specimen's weight [10] and also by the increase of volume (especially for WR25-N5).

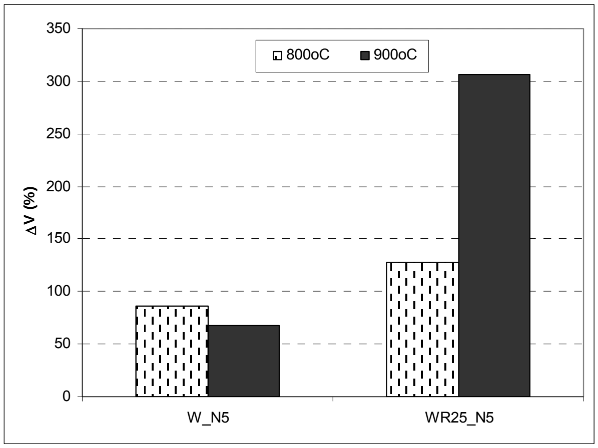

Fig. 5. Volume increases of cubic paste specimens after thermal treatment (with reference to the paste specimen before thermal treatment)

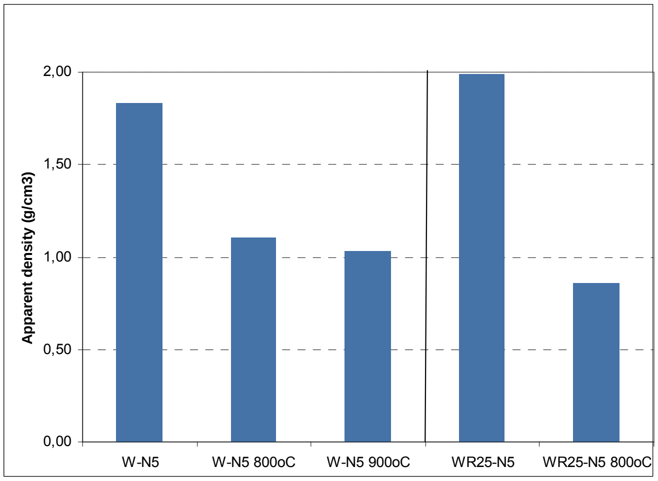

Fig. 6. Apparent density of geopolymers before and after thermal treatment

The evolution of open porosity is different for the studied materials:

- for W-N5 the open porosity decreases when the thermal treatment is performed at 900^{o}C, most probably due to a sintering phenomenon;
- for WR25-N5, the open porosity increases with the increase of thermal treatment temperature, due to softening (partial melting) and foaming processes.

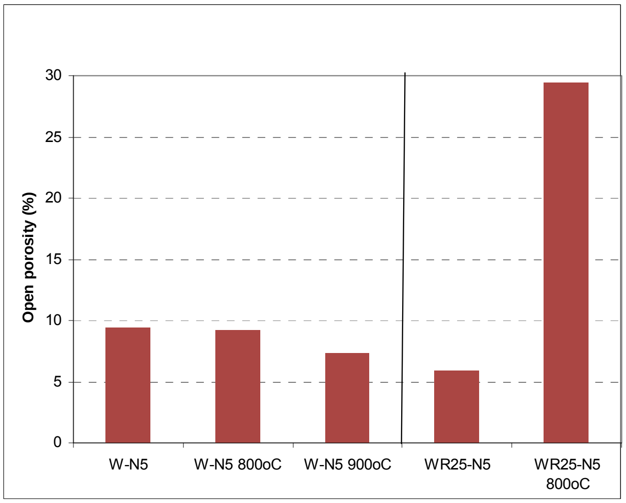

Fig. 7. Open porosity of geopolymers before and after thermal treatment

3.3. Hydrolytic stability

Previous results obtained on geopolymers synthesized by alkali activation, with NaOH solution, of green or brown glasses, with/without red mud addition, showed a high sensitivity to moisture [8, 9].

For the geopolymers based on white glass with/without red mud, the values of mass and compressive strength losses, after 28 days of immersion in water, calculated with formulas (1) and (2), are presented in fig. 8. Important strength losses (over 30%) were recorded for both compositions; these values correlated with the mass losses, confirm the dissolution process of the main phases present in these materials i.e. sodium silicate (aluminate) hydrates [5-9].

In order to assess the influence of thermal treatment on the hydrolytic stability of studied geopolymers the method presented in ISO 719-1985 [13] was also used. The amount of Na_2O equivalent, extracted per 1g of material (geopolymer), before and after thermal treatment at 900^{o}C, is presented in fig. 9. It can be seen that thermal treatment increases the resistance of studied materials toward hot water attack i.e. reduces the amount of solubilized Na_2O. This can be explained by the compositional changes determined by the processes that take place during the thermal treatment and illustrated by XRD patterns presented in fig. 10 and 11.

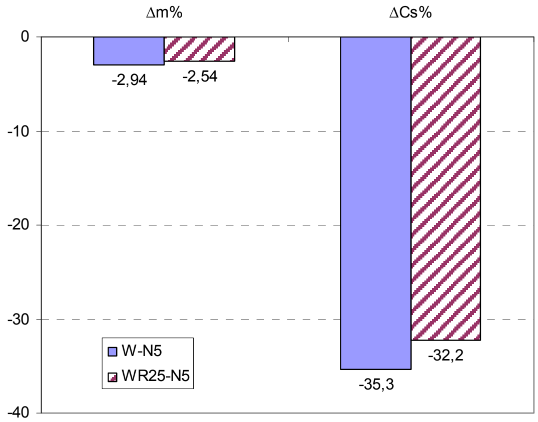

Fig. 8 Mass loss (Δm) and compressive strength loss (ΔCs) of mortar specimens immersed in water for 28 days

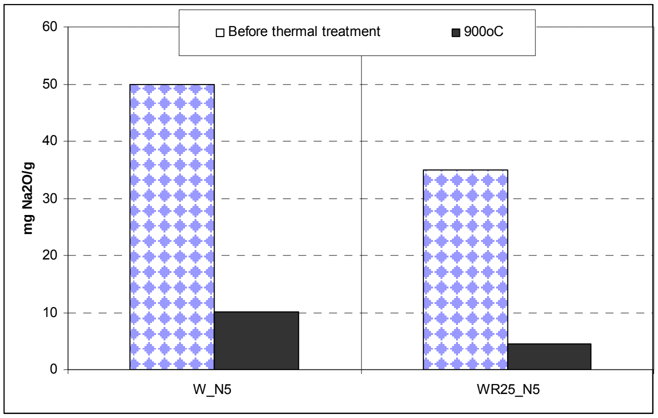

Fig.9. Amount of Na_2O equivalent extracted in water (at 98°C) per unit mass of W-N5 and WR25-N5, before and after thermal treatment at 900°C

The wide halo from $2\theta=20\text{-}35^{o}$ present on the XRD patterns of white glass activated with NaOH 5M solution (fig.9) suggests a preponderant amorphous structure of this material.

The thermal treatment of this material, for 1 hour at 900°C, followed by slow cooling in the furnace for 24 hours, determines the formation of several crystalline phases such as: sodium disilicate (Na_2SiO_5 – PDF 19-1237, 22-1397), SiO_2 (PDF- 83-1294, 83-1828) and devitrite $Na_2Ca_3Si_6O_{16}$ (PDF-77-0410). The presence of devitrite and SiO_2 can be explained by a partial crystallization of the glass grains [15,16] as well as to the decomposition of sodium silicates hydrates with the formation of sodium disilicate and SiO_2 [17]. Similar data were obtained when alkali-activated brown glass was thermally treated at 600-800°C [10].

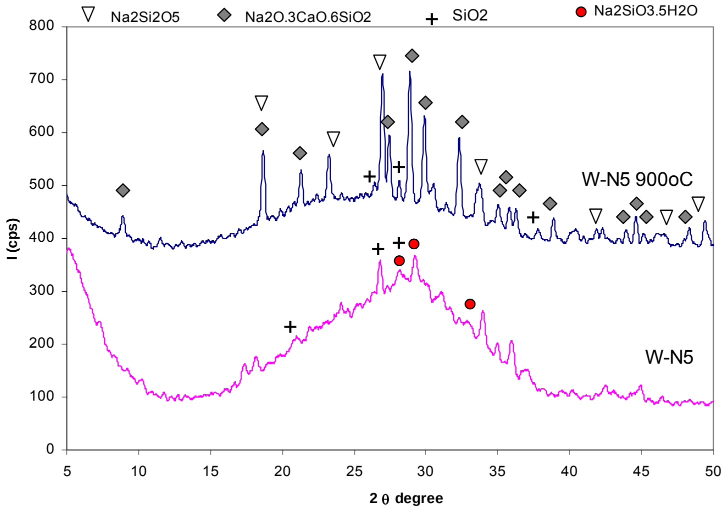

Fig. 10. XRD patterns of alkali activated white glass before (W-N5) and after thermal treatment (W-N5 900°C)

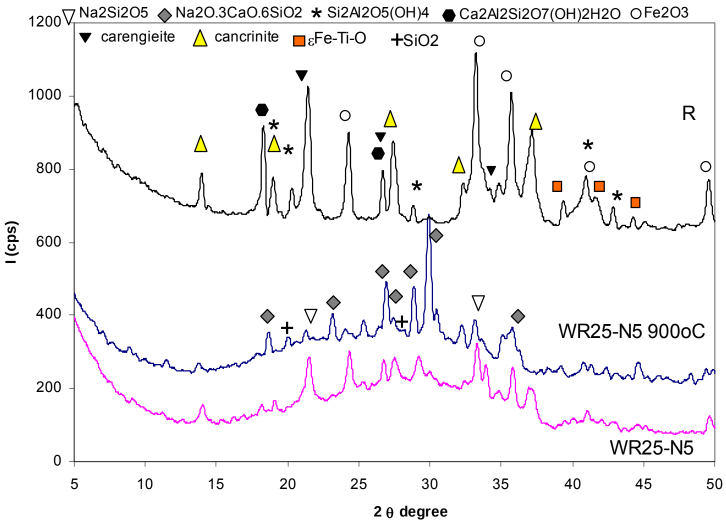

Fig.11. XRD patterns of red mud (R) and alkali activated white glass+25% red mud before (WR25-N5) and after thermal treatment (WR25-N5 900°C)

Thermal treatment at 900°C of the material resulted by the alkali-activation of white glass and red mud mixture (WR25-N5) determines also the formation of crystalline phases i.e. sodium disilicate, devitrite and SiO_2 (fig.11); as expected, the XRD patterns of these compositions (WR25-N5, before and after thermal treatment) exhibit also XRD peaks specific for the crystalline compounds present in the red mud (R) – fig. 11.

The conversion of sodium silicate (aluminate) hydrates gels in crystalline phases (with lower solubility in water), in the specimens thermally treated at 900°C explains the increase of hydrolytic stability.

This finding is important, if the projected utilization for these materials is as light, thermal and acoustic insulations; thermal treatment determines beside the foaming process and porosity increase, the increase of this material's durability in humid environment and can extent it's life cycle.

4. Conclusions

Waste glass with/without red mud can be used as solid component for the synthesis of geopolymers, by alkaline activation with NaOH solution and thermal treatment at 60°C. The values of compressive strength recorded for the mortar specimen based only on white glass powder are higher (with 20-25%) as compared with those assessed on the composition with red mud admixture. The increases of curing time at 60°C, from 1 to 3 days, do not exert an important influence on the compressive strengths values of W-N5 and WR25-N5 mortars.

Thermal treatment at temperatures comprised between 200°C-800°C of paste specimens based on white glass (W-N5), determines cracking, shape deformation and for higher temperatures (700-800°C) swelling and foaming on small areas. For the geopolymers with red mud addition (WR25-N5), a swelling effect is noticed when thermal treatement is performed at 800°C and 900°C. This important volume increase is due to a foaming process specific for sodium silicate (aluminate) hydrates, the main components of these materials.Thermal treatment of W-N5 and WR25-N5 pastes decreases the values of apparent density; this can be explained both by the decrease of specimen's weight and increase of volume (especially for WR25-N5). For WR25-N5 paste the open porosity increases with the increase of thermal treatment temperature (from 800°C to 900°C).

The hydrolytic stability of studied materials is low; compressive strength losses (over 30%) were recorded when mortar specimens were kept immersed in water for 28 days. However, the thermal treatment at 900°C increases the resistance of studied materials toward moisture/water attack. This finding is important, if the projected utilization for these materials is as light, thermal and acoustic insulations

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