

STUDY OF STRUCTURAL STABILITY, PH VARIATION IN WATER AND INFLUENCE OF CURING CONDITIONS ON MECHANICAL RESISTANCE OF MINERAL WASTES GEOPOLYMERIC ARTIFICIAL AGGREGATES (WGA) AS ALTERNATIVE MATERIALS FOR WASTEWATER TREATMENT PROCESSES

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Abstract

The aim of this preliminary study was to investigate whether artificial aggregates produced from mining wastes geopolymeric binder would be suitable to be used as alternative materials for wastewater treatment processes. Waste geopolymeric artificial aggregates (WGA) with different atomic ratios of mining waste mud/Na₂SiO (4 to 5) and Na₂SiO/NaOH (1.25 to 5) were produced using curing temperatures of 20°C and 130°C and its structural stability and pH variation after immersion in water was observed for 3 months. Results showed that WGA with mud/Na₂SiO and Na₂SiO/NaOH of 5 and 4, respectively, cured at 20°C presented good stability in water and pH decreased from 10 to 7 in 24 days. Compressive strength was determined in additional samples cured at 20°C and 80°C in dry conditions, for 13 curing ages and 15 water immersion periods (up to 14 weeks). Results of this second stage showed that increasing temperature to 80°C accelerated compressive strength gain but only during the first 3 weeks (up to 15.4 MPa). After 24 h in water compressive strength decreased to half of the initial values determined in dry conditions for all samples and, therefore, the increase of temperature did not bring benefits to WGA strength in water. Regardless of curing temperature and dry curing age comprehensive strength stabilizes between 1 MPa and 2 MPa after 4 weeks of immersion in water, which are values that makes WGA suitable to be used as bed material for wastewater treatment processes.

Streszczenie

W artykule przedstawiono wyniki wstępnej analizy, której celem było zbadanie możliwości zastosowania w oczyszczaniu ścieków sztucznego kruszywa wytwarzanego w procesie geopolimeryzacji z odpadów górniczych (WGA). Badano geopolimery mułu kopalnianego z krzemianem sodu z dodatkiem wodorotlenku sodu wytwarzane w temperaturze 20°C i 130°C pod kątem zmian strukturalnych i pH po zanurzeniu w wodzie w okresie 3 miesięcy. Wyniki wykazały, że badane WGA otrzymane w temperaturze 20°C posiadają dobrą stabilność w wodzie a pH obniżyło się z 10 do 7 w czasie 24 dni. Wykonano dodatkowe badania wytrzymałości na ściskanie dla próbek geopolimerów uzyskanych w temperaturach 20°C i 80°C w suchych warunkach i po zanurzeniu w wodzie w okresie nie przekraczającym 14 tygodni. Wyniki pokazały, że podniesienie temperatury procesu do 80°C powoduje wzrost wytrzymałość na ściskanie do 15.4 MPa ale tylko podczas pierwszych trzech tygodni. Po 24 godzinach od zanurzenia w wodzie wytrzymałość na ściskanie we wszystkich próbkach spadła do połowy wartości początkowej ustalonej w suchych warunkach. W związku z tym podniesienie tempetatury procesu do 80°C nie poprawiło wytrzymałości WGA w wodzie. Niezależnie od zastosowanej temperatury procesu i czsu twardnięcia wytrzymałość na ściskanie stabilizowała się w granicach od 1 do 2 MPa po 4 tygodniach zanurzenia w wodzie co sprawia, że WGA nadają się do zastosowania jako materiał złoża do procesów oczyszczania ścieków.

Keywords: Artificial aggregates; Compressive strength; Geopolymers; Wastewater treatment; Mining waste mud; Bed material.

1. INTRODUCTION

Reutilization of wastes is of great interest of European countries and such is the case of mining wastes. According to Eurostat [1], in year 2006 more than half of the waste generated by businesses in the European Union (EU27) was produced by industrial and construction. As industry is the main waste generating sector data was breakdown by the three main industrial sectors: mining and quarrying, manufacturing and electricity, gas and water supply. In 2006, in the EU27, approximately 55% of industrial waste was produced by mining and quarrying sector, 4.9% of which was incinerated, 43.6% recovered and 51,5% deposited. According to the same source, European countries having highest volumes of waste generated by mining and quarrying sectors, normally landfill higher volumes of wastes, like in case of Bulgaria and Romania which deposited more than 98% of waste in 2006 [2].

Finding new applications for alumino-silicate wastes is of particular interest since these types of minerals are the most abundant materials in the Earth's crust, as the Portuguese case, where an underground tungsten mine, located in Panasqueira area has been producing tonnes of wastes per day since 1980s, resulting in deposit of several millions of tonnes of alumino-silicate waste muds. Presently, Panasqueira mine produces approximately 100 tonnes of waste per day, and research in utilization of such mining wastes to produce geopolymeric binders will contribute to reduction of waste landfill site and environmental impacts [3].

As a consequence, the present research deals with a novel application of mining wastes geopolymeric binder by producing WGA aggregates as a new alternative and more durable materials for bed of wastewater treatment process, which can also bring larger perspectives for new applications of waste mining geopolymeric binder based materials.

Therefore, this work studies the influence of curing conditions (temperature and drying age) in the mechanical resistance of WGA produced with differ-

ent atomic ratios of mining waste mud/ Na_2SiO (4 to 5) and $\text{Na}_2\text{SiO}/\text{NaOH}$ (1.25 to 5) in dry conditions and after immersion in water. The pH variation after immersion was also measured. Compressive strength gain/loss was evaluated using the most stable mixture for curing temperatures of 20°C and 80°C and different dry curing ages, as well as for additional different water immersion periods.

2. MATERIALS AND METHODS

WGA was obtained using waste mud (*precursor - P*) from a local tungsten mine, after a thermal treatment for 2 hours at 800°C as suggested by [4]. The chemical composition of the waste mud was determined by energy dispersive spectrometry (EDS, Rontech, Germany) as follows: 68.54% (SiO_2), 1.14% (Na_2O), 18.27% (Al_2O_3), 5.64% (Fe_2O_3), 5.24% (K_2O) and 1.17% (TiO_2). NaOH 10M solution (H) and a Na_2SiO L60 solution (S) were used as *alkaline activators*. The specific surface of the precursor – 240 m^2/kg – was calculated through the air permeability Blaine method using an EN 196-6 equipment (Acmel Labo, France).

At first stage four mixtures of WGA having different atomic ratios of R(P/S) and R(S/H) and different molar ratios were produced as presented in Table 1. Samples of 2x3 cm size and having an approximate shape of natural aggregates were left to cure at 20°C for approximately 48 hours (16 samples per mixture). Half of samples were cured at 20°C while the other half were cured at 130°C.

Structural stability of WGA aggregates and pH alteration in water was observed for the curing period of 4 weeks, for each curing temperature.

For the age of 7, 14, 21 and 28 days of curing time, two samples of each mix, for each curing temperatures (20° and 130°C), were placed in vessels containing 1 L of tap water as shown in Fig. 1, as described in [5] resulting in a total of 32 tests, designated from A1 to D8 as presented in Table 2.

Table 1.
Mass ratios R(S/H) and R(P/S) and molar ratios of the geopolymeric mixes

Mix	R(S/H)	R(P/S)	$\text{Na}_2\text{O}/\text{SiO}_2$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}/\text{Na}_2\text{O}$
M1	1.25	4	0.102	0.102	6.97	13.556
M2	3	4	0.067	0.467	6.97	14.652
M3	4	4	0.061	0.424	6.97	14.979
M4	4	5	0.053	0.36	6.85	14.13

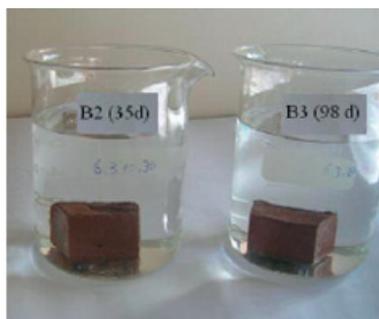


Figure 1.
Vessels containing WGA aggregates

Table 2.
Set of fed-batch experiments for different WGA

Curing time (days)	Curing temperature (°C)	1	2	3	4
7	20	A1	A3	A5	A7
	130	A2	A4	A6	A8
14	20	B1	B3	B5	B7
	130	B2	B4	B6	B8
21	20	C1	C3	C5	C7
	130	C2	C4	C6	C8
28	20	D1	D3	D5	D7
	130	D2	D4	D6	D8

— Samples disintegrated immediately

The vessels were monitored each day for several weeks until a water pH of 8 was attained or total disintegration of samples was observed. The water pH variation containing different WGA aggregates was also measured in that time. First, the pH of the tap water before adding the samples was recorded for each test, and it was found to vary from 6 to 7.5. The time of beginning of sample defragmentation was also recorded.

Statistical analysis was performed using the SPSS program (SPSS Inc., USA; Version 17.0). The data was analyzed by means of Scheffé test (study of the influence of mixture composition in time to achieve $\text{pH} \leq 8$) for statistical significance of differences ($p < 0.05$).

A second stage, the mixture with more stable behaviour was selected for testing compressive strength in dry and wet conditions. Samples of the dimension $40 \times 40 \times 40 \text{ cm}^3$ were produced in a total of 352 cubes. The samples were first submitted for an initial dry curing period of 7 days at 20°C and approximately 40% relative humidity and afterwards 144 units were kept at 20°C while the other 208 units were cured at

80°C followed by different periods of immersion in water. In Phase I, 144 samples (cured at 20°C) were immersed in water after 35, 42, 49, 56, 63, 70, 77, 84 and 91 days dry curing ages (9 Series of experiments, each one including 16 samples for testing). In Phase II, 208 samples cured at 20°C (for an initial period of 7 days in moulds) and 80°C (after removal from moulds) were immersed in water for the same dry curing ages (13 Series of experiments, each one including 16 samples for testing).

After each dry curing age, a set of 15 samples of each Series in each Phase was selected for water immersion in separate vessels containing approximately 1 L of water for 24 hours, 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77, 84, 91 and 98 days (*i.e.* from 1 to 14 weeks of immersion period). During the immersion period water in the vessels was changed every two days. A dry sample of each Series was tested to evaluate the compressive strength in dry conditions. After each immersion period, samples were removed and submitted to compressive strength (*i.e.* compressive strength was carried out for dry conditions and for 24 hours, 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77, 84, 91 and 98 days after immersion in water in each Series of both Phases). Compressive strength was determined according to ASTM C 109 for testing hardened concrete.

3. RESULTS AND DISCUSSION

It was verified for 32 experiments that initial pH values varied from 9.3 (for test D6) to 12.6 (as found in test A1), decreasing along time.

According to the Portuguese Law 236/98 (Water quality) the pH of treated wastewater at the discharge point should not be higher than 9. Thus, the number of days needed to obtain pH value lower than this value was recorded for all WGA aggregate samples (pH = 8 was adopted, instead of 9 to increase reliance of results in this study).

The WGA more properly for wastewater treatment processes are the ones which allow to lower pH quickly to the values below 8 and which maintains the structural stability in water.

The number of days to obtain pH value lower than 8 for each sample is presented in Table 3. It was found that average time necessary to get that pH value varied between 17 days (for M4) and 42 days (for M3).

The results also show that mixes 1, 2 and 3 present both higher initial and final pH water values and the number of days to obtain pH lower than 8 was also

Table 3.
Number of days necessary to obtain pH value lower than 8

Mix	Fed-batch test label	Initial pH	Days to obtain pH ≤ 8	Average days ($\mu \pm \sigma$)
M1	A2	12.6	49	39 \pm 9a
	B2	10.5	42	
	C2	10.8	35	
	D2	10.2	28	
M2	A4	10.5	49	39 \pm 8a
	B4	11.0	42	
	C4	9.7	42	
	D3	10.6	28	
M3	A6	10.6	49	42 \pm 7a
	B6	10.4	49	
	C6	9.7	42	
	D5	9.5	35	
M4	D6	9.3	35	17 \pm 4b
	A7	10	21	
	B7	10	14	
	B8	10	21	
	C7	9.5	14	
	C8	10	14	
	D7	10	14	
	D8	10	21	

μ : average; σ : standard deviation

higher for those mixes when compared with M4. This circumstance is probably related to the mass ratio percentage of sodium silicate and sodium hydroxide solutions with precursor, which was higher for these three mixes, indicating that part of Na^+ cations that did not combine in the chemical reaction of geopolymerization were dissolved in water, increasing water pH. This effect was not so evident for M4 where the mass percentage of alkaline activators with precursor was reduced.

Analysing the results presented in Table 3 it can be seen that the minimum number of days to achieve pH lower than 8 is found in M4. It was verified that M4 is the one that shows the shortest times to achieve pH ≤ 8 and they are significantly different ($p < 0.05$) for mixes 1, 2 and 3. However, the mixture that presents a minor variation interval is M4 as it can be observed in Table 3.

However, for M4, there are samples cured at 20°C (B7, C7 and D7) which maintained stability for 3 months. From the economic point of view, WGA cured at 20°C is more advantageous since it presents low energy consumption. Additionally, the use of WGA promotes the recycling of mining wastes and contributes to minimization of environmental impacts.

Mixes may be divided into two groups. The group with mixes 1, 2 and 3 that present high initial water pH and higher mean time to achieve pH ≤ 8 and mix 4 showing lower both initial pH and mean time to reach pH ≤ 8 .

In first group, WGA aggregates of mixes 1, 2 and 3, cured at 20°C and immersed in water for 1, 2 and 3 weeks started to disintegrate immediately (all samples) (Table 2, Fig. 2). In some cases disintegration process started on first days of immersion and in others it started after two to four days. In this group of mixes the immersion tests ended after four to five

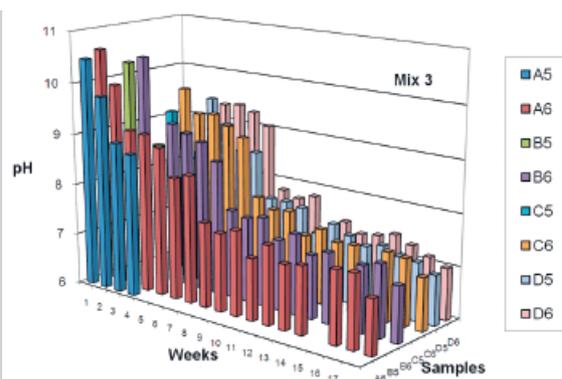


Figure 2.
Variation of water pH versus immersion time of WGA aggregates of M3

weeks. WGA aggregates of all mixes cured for different periods (7, 14, 21 and 28 days) at 130°C and mixes cured for 28 days at 20°C remained structurally stable for 18 weeks of the immersion test as it can be seen in Fig. 2.

In the second group, mix M4 presents 7 samples (3 cured at 20°C, 4 cured at 130°C) which maintained the stability for 18 weeks of immersion test and did not disintegrate during immersion times with the exception of mix cured in 7 days at 20°C (see Fig. 3).

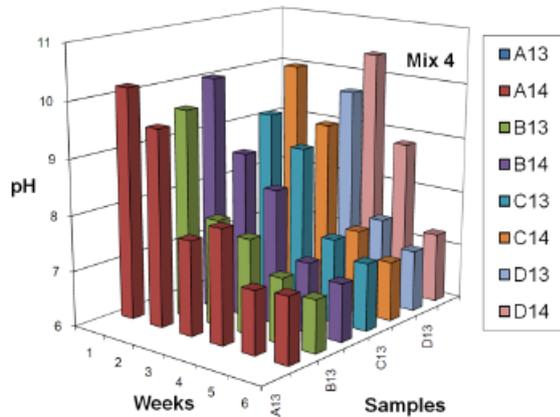


Figure 3. Variation of water pH versus immersion time of WGA aggregates of M4

Previous studies [5] have shown that a minimal of 35 days was required for total activation of WGA at 20°C. Therefore, mixture M4 cured in 35 days at 20°C was selected for the second stage of experiments. As presented in Fig. 4, WGA showed different tendency (gain or loss) in evolution of strength for both curing temperatures. Samples cured at 20°C in dry conditions presented higher compressive strength at early curing ages (9.1 MPa for 42 and 49 days) that decreased and became more instable for curing ages over 56 days. The average compressive strength between 42 and 91 days of curing time was 7.3 MPa. Results observed at 20°C are in agreement with the ones observed by Torgal *et al.* [6] for NaOH 24M but three times lower, which reflects the effect of activator concentration in the strengthening of WGA.

In samples cured at 80°C compressive strength was higher than observed in samples cured at 20°C except for older curing ages, reaching a maximum value of 15.4 MPa for 21 days. Higher curing temperature for more than 21 days does not seem to have positive effect on the compressive strength (values ranged from 11 MPa and 13.6 MPa between 21 and 63 curing

ages) and curing for more than 63 days decreased the strength rapidly. Strength decline may be explained by prolonged curing period at high temperature that breaks down the gelular structure of the geopolymer synthesis mixture, resulting in dehydration and excessive shrinkage as observed by [7]. WGA has shown high strength when cured at 80°C even at early dry curing ages confirming the extreme reactivity of mine waste mud when activated with a highly alkaline solution. Similar results were observed by [8] that reported strength increase with curing temperature for alkali-activated fly ash. Therefore, the reason for gain and loss of strength could be explained by the occurrence of two parallel processes: further geopolymerisation of unreacted waste mud and/or sintering process (strength increase); breakdown of the geopolymer structure due to exposition to prolonged high temperature (strength decrease). These two opposing processes may have occurred simultaneously in the WGA cured at 80°C and whether the strength increases or decreases is dependent on the dominant process.

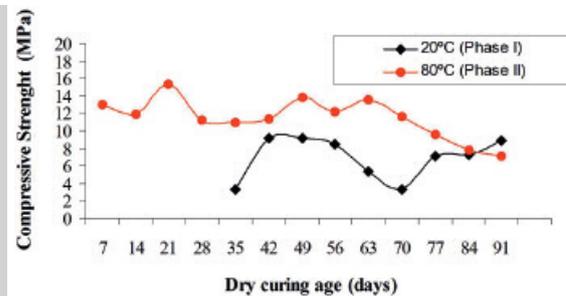


Figure 4. Compressive strength variation over dry curing ages for 20°C and 80°C curing temperatures (mixture M4)

Regardless of the curing temperature and curing age, compressive strength reduced to approximately half of initial values (dry conditions) after 24 hours of water immersion (Fig. 5 and 6). The decrease in strength continued for first 4 weeks of immersion, stabilizing most of samples after that time between 1 MPa and 2 MPa. In samples cured at 20°C for longer dry curing ages (91 days) the values stabilized between 2 MPa and 3 MPa after 6 weeks of immersion. These results show that water curing leads to a strength decrease of WGA as also observed by [9] for alkali-activated metakaolin. Water in excess seems to have affected the hydrolysis species and, therefore, hinders polycondensation kinetics, leading to molecular destabilization of the geopolymer matrix.

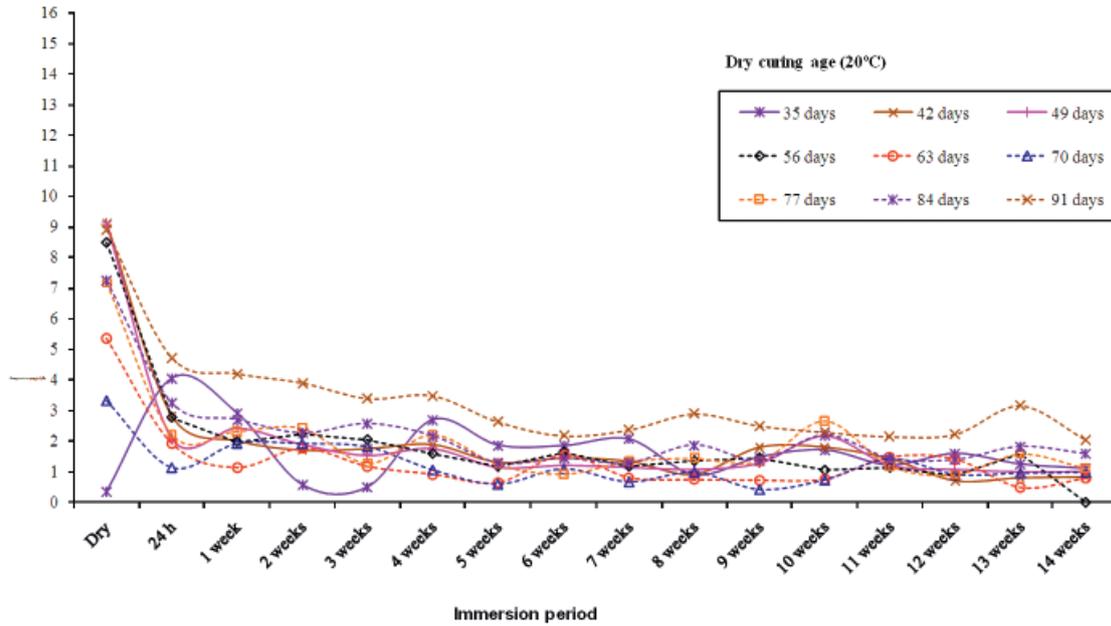


Figure 5. Compressive strength over water immersion period for curing temperature of 20°C (Mixture M4 – Phase I)

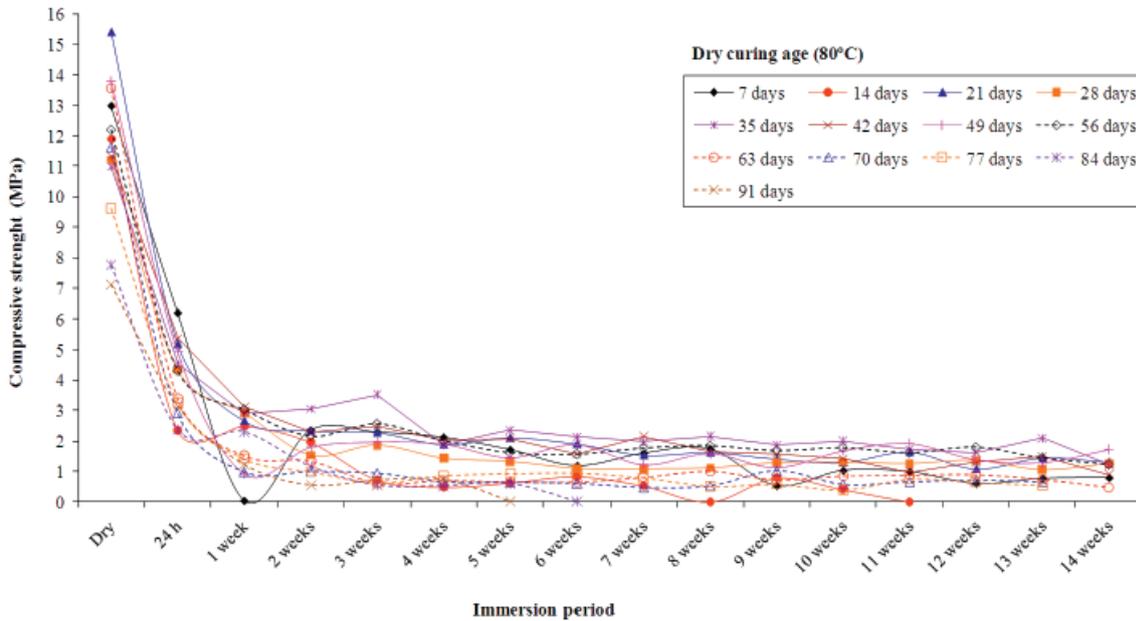


Figure 6. Compressive strength over water immersion period for curing temperature of 80°C (Mixture M4 – Phase II)

Additionally, alkali ions have leached out from surfaces of geopolymers leading to pH rising, which may have contributed to a slow compressive strength development.

Regardless of the ratios of P/S and S/H, all samples cured at 20°C during less than 35 days disintegrated

or dissolved in water between 1 day and 2 weeks. This behaviour might be related to the stage of geopolymer activation and mixture composition, which may have changed after contact with water. It is believed that increasing R(P/S) might result in higher Si and Al dissolution resulting in better geopolymerisation and consequently a stronger geopolymer structure.

According to [4], the final $\text{SiO}_2/\text{Al}_2\text{O}_3$ atomic ratio in the hardened binder depends mainly on the reactivity of Al-Si because not all the silica and alumina are reactive. Admitting that Al and Si have synchro-dissolution behaviour in alkaline solution they could be dissolved from the mineral in some linked form and, therefore, the Si/Al ratio was not the same in the final hydration product.

For Si/Al of 1.9 [4] good results in strength were obtained with Al/Na equal to 1 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ equal to 11. It was also found that Na^+ cation play a role in order to balance the deficit of electrical charges of the aluminium atom, and so the ratio Na/Al should be close to 1 for all bonds Si-O-Al to be established. However, the increased resistance is not only due to the strength of connections but also to the improvement of the microstructure. The molar ratios of the WGA used in this study were as follows: $\text{Na}_2\text{O}/\text{SiO}_2 = 0.053$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.36$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6.852$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 14.129$ (Table 1). The $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios are too low and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is too high when compared with [10] results, namely $4.86 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 5.9$, $0.31 < \text{Na}_2\text{O}/\text{SiO}_2 < 0.41$ and $1.50 < \text{Na}_2\text{O}/\text{Al}_2\text{O}_3 < 2.42$. On the other hand, the ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ is also too high when compared with [10] results and could have lead to lower compressive resistance values, as found by [4].

The compressive strength after immersion stabilized around 1-2 MPa similar to the values presented by LECA (1.7 MPa), which needs high temperatures to be produced, but lower than the ones presented by granite gravel (up to 120 MPa), which is extracted from earth. The advantage of this WGA over that two materials is that it is produced from a hazardous material (*i.e.* promotes the reuse and encapsulation of waste mud from mine activities) at 20°C , presents good stability in water, does not change significantly the characteristics of water, is durable and, therefore, may have the same effectiveness of other materials for pollutant removal from wastewaters.

4. CONCLUSIONS

Mix M4 was found to be structurally stabled in water for a period of 6 months and having pH stabilization around 8 in the shortest period of time (24 days). Results obtained on mixture M4 for different curing conditions showed that compressive strength increased with curing temperature but not with curing age. Regardless of the curing temperature and curing age, compressive strength reduced to approximately half of initial values (dry conditions) after 24 hours of water immersion, stabilizing between 1 MPa and 2 MPa after 4 weeks immersion. As compressive strength after longer periods of water immersion was equivalent in samples cured at 20°C and 80°C , WGA cured at room temperatures presents both environmental and economical production advantages. Therefore, WGA produced for ratios $R(\text{P}/\text{S}) = 5$ and $R(\text{S}/\text{H}) = 4$, cured at 20°C and with a minimal curing age of 35 days, it appears as a potential bed material to be used in WWTP.

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REFERENCES

- [1] Pacheco-Torgal F., Castro-Gomes J.P., Jalali S.; Properties of tungsten mine waste geopolymeric binder, *Construction and Building Materials*, Volume 22, Issue 6, June 2008; p.1201-1211
- [2] Eurostat, Theme 8 Environment and Energy. Generation and treatment of waste. Data 2006, 2009
- [3] Pacheco-Torgal F., Jalali S., Castro-Gomes J.P.; Utilization of mining wastes to produce geopolymeric binders, in *Geopolymer: structure, processing, properties and industrial applications*, Edited by John Provis and Jannie van Deventer, CRC press, Woodhead Publishing Limited, June 2008
- [4] Pacheco-Torgal F.; Development of alkali-activated binders using waste mud from Panasqueira mine, PhD thesis, University of Beira Interior, 2007 (in Portuguese)
- [5] Silva I., Castro-Gomes J., Albuquerque A.; Mineral wastes geopolymeric artificial (WGA) aggregates as alternative materials for wastewater treatment processes – study of structural stability and pH variation in water, *Proc. of the International Conference on Sustainable Building Affordable to All (SB10)*, Vila Moura, Portugal, 10, March 2010; p.17-19

- [6] *Pacheco-Torgal F., Castro-Gomes J., Jalali S.*; Investigations on mix design of tungsten mine waste geopolymeric binder, *Construction and Building Materials*, 9, 2008; p.1939-1949
- [7] *Jaarsveld J., Deventer J., Lukey G.*; The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers. *Chem. Eng. J.*, 89, 2002; p.63-73
- [8] *Katz A.*; Microscopic study of alkali-activation fly ash, *Cem. Concr. Res.*, 28, 1998; p.197-208
- [9] *Kirschner A., Harmuth H.*; Investigation of geopolymer binders with respect to their application for building materials. *Ceram. Silic.*, 48, 2004; p.117-120
- [10] *Duxson P., Provis J., Lukey G., Mallicoat S., Kriven W., Deventer J.*; Understanding the relationship between geopolymer composition microstructure and mechanical properties, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 269, 2005; p.47-58