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Optimization of activator solution and heat treatment of ground lignite type fly ash geopolymers

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Abstract. Geopolymers are inorganic polymers which can be produced by the reaction between silico aluminate oxides and alkali silicates in alkaline medium. Materialscontaining silica and alumina compounds are suitable for geopolymer production. These can beprimary materials or industrial wastes, i. e. fly ash, metallurgical slag and red mud.

In this paper, the results of the systematic experimental series are presented which were carried out in order to optimize the geopolymer preparation process. Fly ash was ground for different residence time (0, 5, 10, 30, 60 min) in order to investigate the optimal specific surface area. NaOH activator solution concentration also varied (6, 8, 10, 12, 14 M). Furthermore, sodium silicate was added to NaOH as a network builder solution. In this last serie different heat curing temperatures (30, 60, 90°C) were also applied. After seven days of ageing the physical properties of the geopolymer(compressive strength and specimen density)were measured. Chemical leaching tests on the rawmaterial and the geopolymers were carried out to determine the elements which can be mobilized by different leaching solutions. It was found that the above mentioned parameters (fly ash fineness, molar concentration and composition of activator solution, heat curing) has great effect on the physical and chemical properties of geopolymer specimens. Optimal conditions were as follows: specific surface area of the fly ash above 2000 cm^2/g, 10 M NaOH, 30°C heat curing temperature which resulted in 21 MPa compressive strength geopolymer.

1. Introduction

Geopolymers can be produced by the reactions between alumina silicate oxides and alkali silicates, aluminates in high alkaline conditions. A possible way is to use fly ashmixed with NaOH solution. The reaction products might have different mechanical properties based on the type of fly ash (class C and F), the origin of the coal used and the applied combustion technologies, since they resulted difference in the raw material properties(composition, amount of glassy phases etc…) and the fly ash reactivity is also different. Activation state of fly ash can be enhanced by mechanical and/or chemical activation. The mechanical activation can be carried out by grinding in conventional ball mills or in high energy density mills (vibratory, stirred media mills).

Kumar et al.[1] activated the fly ash in attrition and vibratory mill. They stated that better mechanical properties of geopolymer reached by mechanical activation. Other authors investigated the effect of mechanical activation of fly ash on geopolymer properties in various mills [3-6]. Kumar et al.

[1] and Álvarez-Ayuso et al.[2] investigated the effect of NaOH molar concentration. They concluded that increasing of NaOH solution concentration better mechanical properties can be reached with different types of fly ash.

Álvárez-Ayuso et al.[7] use different heat curing temperature and curing time. The increasing curing time and curing temperature has positive effect on mechanical properties on the resulted products.

Leaching characteristics are very important from the point of view of practical applications of fly ash based geopolymers due to its environmental effect. According to Provis et al. [7] many elements from periodic table can bounded in geopolymer framework. The following elements bound with limited success or increase its availability by geopolymerisation: Mo, Ni, As, Se. Izquierdo et al. [8] investigated leaching properties of fly ash based geopolymers. They concluded that geopolymers suitable for immobilization of many hazardous elements from fly ash like Be, Bi, Cd, Co, Cr, Cu, Nb, Ni, Pb, Sn, Th, U, Y, Zr and rare earth elements, but more elements was mobilized like As, B, Se, V, W due to oxianionic mobilizing in high alkaline conditions. This confirmed the fact that an optimal dosage of the compounds, the synthesis and the curing conditions are crucial for the environmental properties of the final product.

2. Materials and methods

The fresh fly ash used as main component of geopolymers originated from Mátra power plant, Hungary has the following physical and chemical properties. Moisture content was 0.27 m/m%. The bulk density of the raw fly ash was 0.73 g/cm^3, particle density was 1.93 g/cm^3. Particle size distribution and specific surface area measured by Horiba LA950 V2 type laser particle size analyzer; the characteristic particle size values were x_{10}=10.77 μm; x_{50}=52.04 μm; x_{80}=119.32 μm, specific surface area: 1152.07 cm^2/g.Based on XRF analysis the chemical composition of the fly ash is given in Table 1. From the analysis the SiO_2/Al_2O_3 ratio was found to be 3.34 and the sum of SiO_2, Al_2O_3 and Fe_2O_3 content of the fly ash was 73.49 wt.%.

Table 1. Chemical composition of the lignite type fly ash (Visonta)

Component	Visonta fly ash, Mass concentration, wt.%
SiO_2	48.1
Al_2O_3	14.42
Fe_2O_3	10.97
Na_2O	0.37
K_2O	1.66
CaO	11.76
MgO	3.34
TiO2	0.492
P_2O_5	0.264
MnO	0.171

For geopolymer production NaOH solution in various concentrations was used as activator and Na-K-silicate (Betol SB) was used as network builder additive. Its chemical composition was as follows: K_2O=2.7%; Na_2O=13.7%; SiO_2=25.3%.

Fly ash was ground in tumbling mill for 5, 10, 30 and 60 minutes in order to mechanically activate the raw material (improving its reactivity), with e=80% of critical revolution number and φ=110 % mill filling ratio.

Geopolymer specimens made by mixing of raw and ball milled fly ash and alkaline activator in the ratio of 40 m/m % (L/S=0.67) and 45 m/m % (L/S=0.82) to fly ash. The higher sludge concentration was necessary in order to increase the workability of the geopolymer paste. Mixture was placed into pre-oiled moulds and compacted by vibration. The compacted mixture was kept in moulds for 24 hours insulated at ambient temperature. Then heat curedfor 6 hours. After heat curing the specimens were cooled down to ambient temperature. The compressive strength tests were carried out usinga Compression Testing Machine at the age of 7 days.The fly ash fineness, the NaOH concentration of activator solution (6, 8, 10, 12, 14 M), the amount of waterglass mass ratio in activator solution (25, 50, 75, 100 m/m%) and the heat curing temperature (30, 60, 90°C) were optimized.

In addition, FTIR analysisin transmission mode (KBr pellet) was performed in the case of various alkali concentration geopolymers to monitor the structural rearrangements during geopolymerisation reactions.

Chemical leaching tests have been done on both: the raw ground ash and the produced geopolymers. The mobilisation of the elements by distilled water and different strength acids (1 M acetic acid, 2 M nitric acid) were determined.

3. Results and discussion

In this part the research results are presented focusing on the optimization of the characteristic particles size and specific surface area of fly ash due to grinding, alkaline activator composition and curing temperature. The Figure 1. shows the effect of mechanical activation on fly ash fineness.

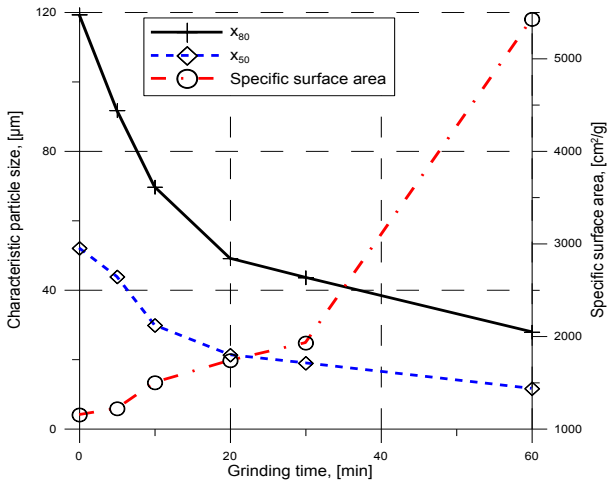

Figure 1. Changing of product fineness as function of grinding time

It was observed that the characteristic particle size became finer and specific surface area increased significantly by increasing grinding time even after 30 min residence time. The maximum fineness belongs to 60 minutes ground product (x_{50}=11.6 µm; x_{80}=27.9 µm; SSA=5425.55 cm^2/g).

The effect of grinding on the leachability of main structural elements: Si, Al, Fe is shown in Figure 2. An improving solubility can be reached for Si in alkaline solution as function of increasing fineness. These finding indicates that grinding breaking up the “spheres” of the fly ash resulting in the enhancement of soluble Si and Al which play important role in geopolymerisation reactions.

The effect of fly ash fineness on geopolymer mechanical properties (uniaxial compressive strength and specimen density) can be found in Figure 3.

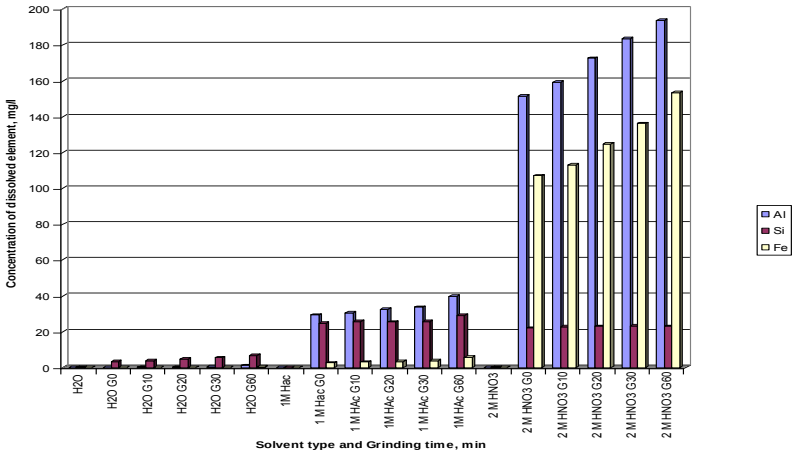

Figure 2. The effect of grinding on leachability of main structural elements of fly ash, Si, Al, Fe. Solid: Liquid ratio 1:50, contact time: 1 day

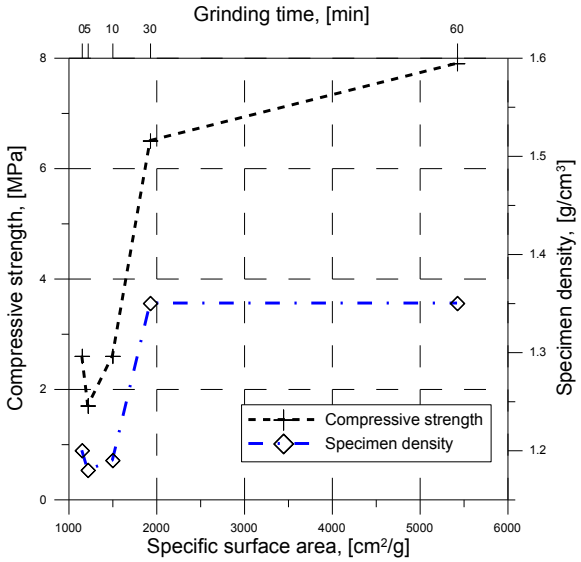

Figure 3. Geopolymer mechanical properties as function of fly ash fineness

The compressive strength improved by increasing specific surface area (or grinding time). The highest compressive strength (7.9 MPa) belongs to highest specific surface area (5425.55 cm^2/g). The tendency of specimen density change is similar to that of the compressive strength, good correlation achieved. The maximum density value was 1.35 g/cm^3.

Increasing the NaOH molarity of activator solution has a positive effect on geopolymer mechanical stability until 10 M (Figure 4.). After it the compressive strength decreased from the maximum 12.3 MPa (10 M NaOH) to 9 MPa (14 M NaOH), however the specimen density still increased (maximum value was 1.61 g/cm^3 belongs to geopolymer activated by 14 M NaOH solution). This observation is different than that of reported by other authors [3] therefore further structural investigation (FTIR) is necessary.

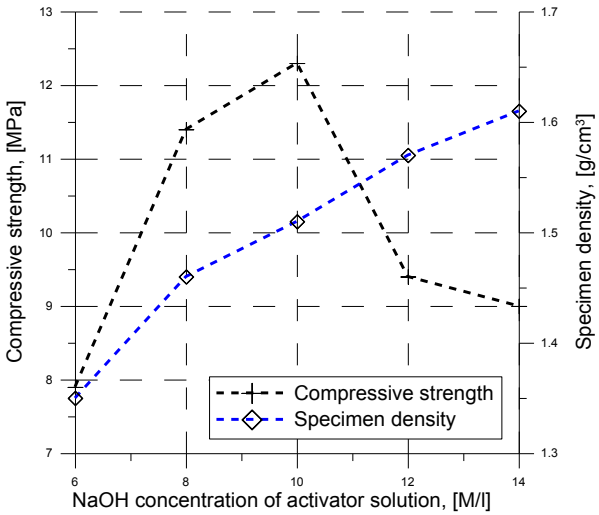

Figure 4. Effect of NaOH molar ratio on the geopolymer mechanical properties

Main peaks in FT-IR spectra (Figure 5) of geopolymer specimens corresponds to water molecules, O-C-O bonds and aluminosilicate bonds. In the case of geopolymer activated by 6 M NaOH solution the peak at 3353 cm^{-1} related to stretching vibrations of –OH, HOH bonds, while peak at 1646 cm^{-1} it is associated with HOH bending vibration. Peak at 1398 cm^{-1} related to O-C-O stretching vibration. Peak at 1012 cm^{-1} in case of fly ash shifted lower wavenumber (950 cm^{-1}; corresponds to asymmetric stretching vibration of Si-O-Si, Al-O-Si) which related to structural reorganization and formation of aluminosilicate gel phase associated with dissolution of fly ash amorphous phases in high alkaline condition. The peak at 950 cm^{-1} supplemented by a smaller peak at 905 cm^{-1} (in the case of geopolymers activated 10-14 M NaOH solution). Peaks at 797, 666, 615 and 561 cm^{-1} corresponds to Si-O-Si and Al-O-Si bonds symmetric stretching vibrations. It can be stated, that all of peak intensities became higher by increasing of NaOH concentration of activator solution.

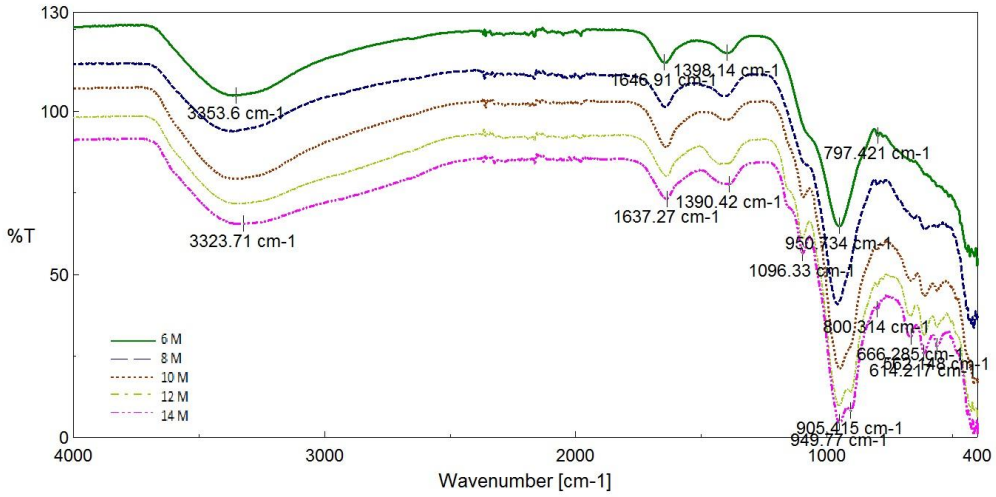

Figure 5. FT-IR spectra of geopolymers at various NaOH solution concentration

Based on FT-IR spectra it can be stated that, there are structural differences between geopolymer specimens, new peaks appeared in case of specimen spectra activated with 10-14 M NaOH solution in

the range of 800-400 cm^{-1} and increased its intensity. In order to clarify the reasons of strength decrease, X-ray diffraction measurements are necessary in the future.

The effect of increasing amount of waterglass to NaOH solution on compressive strengthis shownin figure6. At 90°C the increasing waterglass ratio improved the compressive strength with a maximum value of 11.1 MPa belongs to 75 m/m% waterglass concentration. In case of lower temperature the highest compressive strength reached when activator solution was 100% Na-K silicate (13.1 MPa at 60°C, 21.3 MPa at 30°C). The lower temperature has positive effect on the compressive strength, which different from literature, where most of the results shows better mechanical properties in case of higher temperature [3]. The main cause presumably, that by increasing the amount of waterglass the molar ratios were changed and because the K based network formation became slower, therefore more timewould be needed to the diffusion of molecules and connect it. In case of higher temperature the reaction was so fast, that these diffusion processes couldnot be occurred and the formed structure will be disordered.

The effect of increasing ratio of waterglass to NaOH solution on specimen density is shown in Figure7. The results are correlated well with that of the compressive strength data.

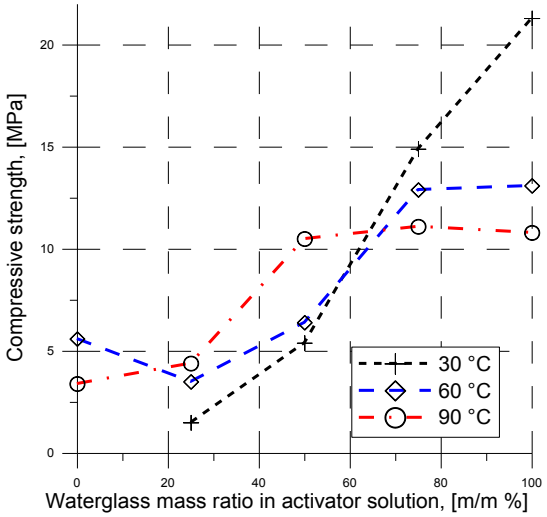

Figure 6. Waterglass addition to activator solution and its effect on compressive strength at various curing temperatures

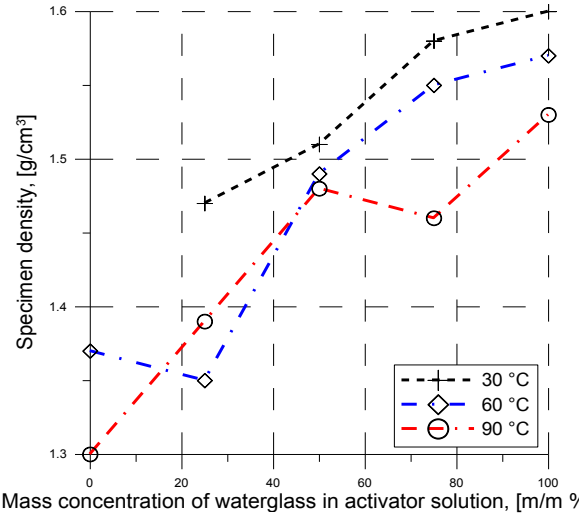

Figure 7. Waterglass addition to activator solution and its effect on specimen density at various curing temperatures

Leaching characteristics of geopolymers 1 M Acetic-acid for the main structuralelements are given in Figure 8. The leached Na concentration indicates the unconsumed NaOH. The other elements concentrations are also higher than it was in case of fly ash, which indicated that the new structure formed in the geopolymersis more sensitive than it was in the fly ash. However, it is important to note that other authors observed the leaching behaviour of various solvents resulted in more moderated leachability of structural as well as toxic components [9]. Moreover, it was found that toxic elements were mobilized in the geopolymer.

Based on the results presented in Figure 8 no significant effect of grinding fineness was found on the leachability of structural elements in strong acidic media.

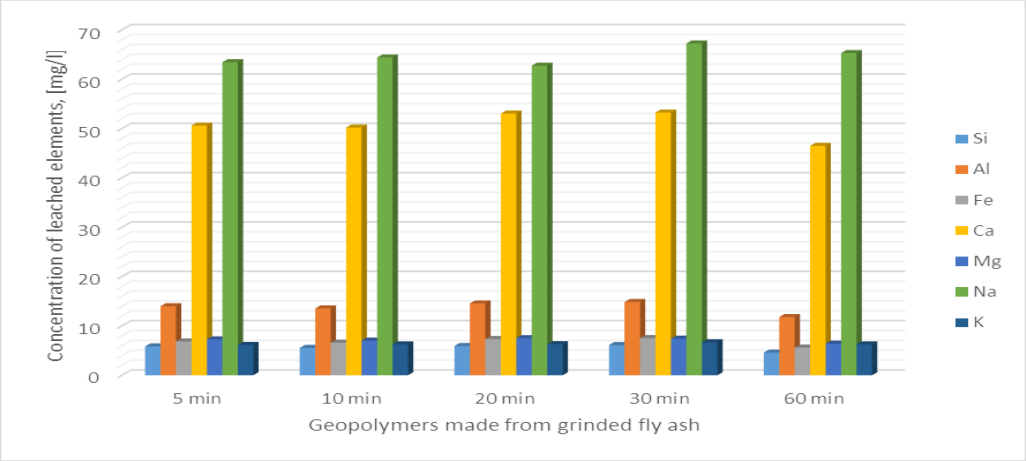

Figure 8. Dissolution of main elements from different geopolymers in 1 M Acetic-acid

4. Conclusions

Based on the experimental resultsthe following conclusions can be drawn:

- Increasing residence time in ball mill higher specific surface area, finer median particle size and x_{80}were reached.The finest product given by 60 minutes grinding time (SSA= 5425.55 cm^2/g, x_{50}=11.6 µm, x_{80}=27.9 µm).
- The fly ash fineness has positive effect on geopolymer physical properties. The finest fly ash (60 minutes ground) resulted the best compressive strength (7.9 MPa).
- Higher NaOH concentration increases the compressive strength to 12.3 MPa using 10 M NaOH solution. After it the compressive strength decreased.
- Na-K-silicate has positive effect on geopolymer compressive strength, 21.3 MPa reached when only Na-K-silicate solution was used.
- The compressive strength increased when lower temperature (30 °C) heat curing was used.
- FT-IR shows structural differences between geopolymers activated with different NaOH solutions.
- According to leaching experiments on ground fly ash it can be stated; grinding breaking up the "spheres" of the fly ash resulting in the enhancement of soluble Si and Al.
- No significant effect of grinding fineness was found on the leachability of structural elements in strong acidic media.

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References

[1] Kumar S, Kumar R, Alex T C, Bandopadhyay A, Mehrotra S P 2007 *Adv Appl Ceram***106**, No 3 pp. 120-127
[2] Álvarez-Ayuso É, Querol X, Plana F, Alastuey A, Moreno N, Izquierdo M, Font O, Moreno T, Diez S, V´ázquez É, Barra M 2008*J Hazard Mater***154** 175–183
[3] Mucsi G, Lakatos J, Molnár Z, Szabó R 2014*9th International Conference "Environmental Engineering"*, Vilnius, Lithuania, 22–23 May 2014

[4] Mucsi G, Molnár Z, Papp A2014*XXVIII. microCAD International Multidisciplinary Scientific Conference*, University of Miskolc, 10-11 April 2014
[5] Mucsi G, Csőke B, Mádai F, Debreczeni Á, Rácz Á, Molnár Z 2013*XV Balkan Mineral Processing Congress* Sozopol, Bulgária, 12.06.2013-16.06.2013. Sofia, pp. 864-868. (ISBN: 978-954-353-218-6)
[6] Mucsi G, Csőke B, Molnár Z 2010*Proceedings of the XIIth International Mineral Processing Symposium* 6-8. October 2010. Cappadocia Nevsehir, Turkey ISBN: 978-975-491-295-1, pp. 1235-1242
[7] Provis J L, van Deventer J S J 2009*Geopolymers, structure, processing, properties, and industrial applications*. (Woodhead publishing in materials, New York), ISBN: 978-1-84569-638-2 (e-book) p. 421-436
[8] Izquierdo M, Querol X, Davidovits J, Antenucci D, Nugteren H, Pereira C F 2009 *J Hazard Mater* **166** pp. 561-566
[9] Mucsi G, Szenczi Á, Molnár Z, Lakatos J 2016 *J Environ Eng Landsc* **24** pp. 48-59