Feasibility and strength properties of the geopolymeric binder made of fly ash suspension

Szymon Dawczyński^{1,*}, Marek Soczyński¹, and Marcin Górski¹

¹Silesian University of Technology, Department of Structural Engineering, 44-100 Gliwice, Poland

Abstract. Geopolymeric binders, or in general geopolymers, are nowadays applied in many different branches of the industry – also in building construction. This relatively new group of inorganic materials has similar strength properties as ordinary Portland cement (OPC) and in some features, it is even better (for example in terms of fire resistance or chemical resistance). It is also environmentally friendly material because industrial or mining tailings are used as its main components and the production process is not so energy consuming as in case of OPC. Paper presents laboratory research focusing on the curing temperature impact on strength properties of geopolymeric binder made of fly ash suspension. Besides the suspension which is a waste product from coal power plant, also recycled ground glass and metakaolin were used as the additions. The chemical activator of geopolymerisation reaction was prepared with the use of sodium hydroxide and sodium silicate. Prism samples 40x40x160 mm were done and then the flexural and compressive strength tests were performed. The paper also presents the impact of covering the moulds during heat curing on condition of geopolymeric binder samples.

1 Introduction

Industrial sector is nowadays responsible for release of enormous amount of pollutants into the environment. Almost every branch of industry produces plenty of by-products which may be hazardous for the natural environment. And particularly, the building construction industry is one of the main producers of wastes in the world [1]. The possibility of limiting the wastes and by-products in general, will significantly contribute both to the protection of natural resources and to stop the ongoing degradation of all elements of the natural environment.

Portland cement industry plays significant role in the economy of some developing countries. The demand of building construction market for OPC is systematically growing or at least is at a constant high level. Also, in Poland over the last few years the OPC production was on a stable level and was amounted to over 15 million tons per year [2]. Technology used during manufacturing process is responsible for constant release of carbon dioxide into the atmosphere. Unfortunately, the increasing content of carbon dioxide in the atmosphere leads to some global climate changes and particularly to the green-house effect. In Poland, cement industry is responsible for emission of CO₂ on the level of 9.6 million tons per year [2]. In the whole world OPC production has 6% share in overall of all man-made carbon emissions [3].

These basic facts were the stimulus to look for new material which would potentially substitute OPC and would use readily available industrial waste, reducing dependency on shrinking natural resources [4]. Hence,

the answer to this demand was laboratory research on wide group of alkali activated materials (AAM) and on geopolymers in particular. From the chemical point of view, geopolymeric binders are the outcome of reaction which combines solid precursor rich in silicon (Si) and aluminium (Al) with an alkaline solution. Main components are usually industrial by-products as blast furnace slags, fly ashes or mining tailings, while the activator (alkaline solution) is mix of sodium or potassium hydroxide with silicate products as for example water glass (sodium silicate). The modification of the geopolymers properties maybe also done with the use of some additives like ground glass or metakaolin [5, 6].

2 Heat treatment of geopolymers

In case of alkali activated materials, heat treatment during curing of the samples usually has significant impact on the final parameters of the product [7]. The practice shows that geopolymerisation processes occurs very slowly in ambient temperatures and the total curing time is much longer in such conditions. Alkali activated products should absorb enough amount of heat in order to develop inner processes of intermolecular bonds. There is no general answer for the optimal temperature value and optimal time duration of heat treatment of the geopolymers. However, there are some investigations suggesting that the optimal temperature is equal 60°C and optimal time is 24 hours [8, 9]. But practise shows that mainly it depends on mixture proportions and chemical compositions of the used precursor. In this case, due to the heat curing process with the use of

* Corresponding author: szymon.dawczynski@polsl.pl

special devices, the geopolymers are much more demanding in comparison to ordinary Portland cement-based materials.

3 Samples preparation

3.1. Components

Each set of samples (for each curing temperature) consisted of three prisms 40x40x160 mm. All the samples were prepared from following components:

- carbon fly ash suspension – solid precursor;
- sodium hydroxide and sodium silicate – the chemical activator;
- metakaolin – addition;
- recycled ground glass – addition.

Carbon fly ash suspension (Figure 1) was derived from power plant filters. The exact chemical composition of that material is shown in Figure 2 and oxide composition in Table 1. It can be noticed that mentioned material has high Ca content (similar to class “C” of fly ashes).

Fig. 1. Carbon fly ash suspension.

Fig. 2. Print-out of the carbon fly ash suspension chemical composition analysis.

Table 1. Oxide composition of fly ash suspension.

Oxides	Mass [%]
Na ₂ O	0.42
MgO	1.54
Al ₂ O ₃	20.05
SiO ₂	39.56
SO ₃	7.27
CaO	23.45
TiO ₂	1.83
Fe ₂ O ₃	5.72
K ₂ O	0.17

Recycled ground glass was made from soda-lime glass type which is usually used for glass containers. The standard composition of such a glass is rich in silica, sodium oxide and calcium. The oxide composition is shown in Table 2.

Table 2. Standard oxide composition of recycled ground glass.

Oxides	Mass [%]
Na ₂ O	13.9
MgO	3.9
Al ₂ O ₃	1.1
SiO ₂	72.6
CaO	8.4
minors	<1.0

Metakaolin used for the samples preparation was a commercial product, available on the market – the oxide composition was not done.

As a chemical activator of the geopolymerisation reaction the combination of sodium hydroxide and sodium silicate was applied. Pellets for preparation of the NaOH solution had 99.5% of purity and molar mass equal to 40 g/mol. The sodium silicate was R-145 type and had purity higher than 99%. The molar ratio was between 1.6 and 2.6, while the density was about 1.45 g per cubic centimetre. The ratio of sodium silicate to sodium hydroxide was equal 2.0.

3.2. Mixture

Percentage share of the solid precursor in the mixture was about: carbon fly ash suspension (80%), metakaolin (10%) and ground glass (10%). The ratio of precursor to activator was equal 1.0, while the ratio of precursor to sodium silicate was equal 1.5.

The exact mass of all components was checked with a laboratory scale with accuracy to 1.0 mg. All dry and weighted components were mixed together carefully. Then the precursor and activator were combined and mixed.

Fresh geopolymeric mixture with high alkaline conditions may react with steel, that is why it was casted in a mould made of Plexiglas (PMMA). Then the mould was placed in the climatic chamber with constant temperature and humidity.

3.3. Heat curing

Reaction of geopolymerisation may be faster and influenced positively with a higher temperature of curing [10]. Heat curing usually influences the final mechanical parameters as flexural and compression strength. The exact curing temperature which has the most favourable consequences on the final geopolymers was checked during this investigation. All samples were prepared exactly in the same way and from the same mixture and then put into the climatic chamber for 24 hours. After the first day of heat curing, samples were put in the ambient temperature for 27 days. Heat curing influence was checked with the following temperatures: 20°C, 40°C, 60°C and 80°C. Firstly prepared samples were destined for curing in 60°C. Half of the samples were cured in covered mould and half of them in uncovered mould, to check if there will be any significant impact of that factor on the final product. The humidity in the climatic chamber was constant and equal 40%.

During the heat-treatment, every specimen was unharmed, although taking samples from the mould had to be done carefully, due to adhesive reaction between geopolymeric binder and the mould. Even before the main testing of mechanical properties, it was noticeable that different temperatures have a completely different influence on the geopolymerisation reaction. Structure matrix was various but the biggest difference and probably the most unfavourable situation was seen in case of samples cured in 20°C. Surface of these samples was still sticky after first 24 hours (Figure 3). Samples were actually still wet and further drying in the ambient temperature caused surface-cracking and shrinkage (Figure 4).

Fig. 3. The surface of the sample after 24 hours curing in 20°C.

Fig. 4. The surface of the sample after 28 days curing in 20°C.

Samples cured in 60°C (Figure 5) and 80°C (Figure 6) seemed to have similar matrix and the only difference was the colour. As it was already mentioned, half of the samples from 60°C was cured in covered mould while the other half not. Even though the humidity in climatic chamber was constant and at the level of 40%, heat-curing caused drying and cracking of the surface which seemed to have unfavourable influence on the mechanical parameters (Figures 7, 8).

Fig. 5. Samples cured in 60°C in covered mould.

Fig. 6. Samples cured in 80°C.

Fig. 7. Over-dried samples cured in 60°C in uncovered mould.

Fig. 8. Surface layer cracking caused by shrinkage in samples cured in 60°C in uncovered mould.

4 Results

After 28 days of curing time (24 hours in climatic chamber and 27 days in ambient conditions), the samples were tested. As there are no standards for geopolymeric binders testing methodology, the procedure for mortars according to the Polish standard [11] was used. For performing the strength tests, the PILOT automatic compression-flexural tester was used.

4.1. Three-point flexural strength test

The scheme of the test is shown in Figure 9.

Fig. 9. Flexural strength test scheme.

Flexural strength of all geopolymeric binder samples cured in different temperatures are shown in Table 3. These values are the average ones from all of the samples cured in the same temperature conditions. Diagram (Figure 10) shows relationship between the heat-treatment temperature and the flexural strength of tested samples.

Table 3. Results of three-point bending tests.

Curing temperature	Mean value of destructive force F [kN]	Flexural strength f_t [MPa]
20°C	0.323	0.81
40°C	0.966	2.26
60°C	0.855	2.00
80°C	0.938	2.20

Fig. 10. Dependence of flexural strength (average values) and heat-treatment temperature.

Results of bending test shows that the flexural strength of the samples varies with the growing temperature of heat-curing treatment. The highest growth of the strength can be seen between the ambient temperature (20°C) and temperature 40°C – the difference is equal 1.44 MPa. After reaching the maximal value of the bending strength which is equal 2.26 MPa and represents samples treated with 40°C, a drop of that mechanical parameter is noticeable. However, it is also noticeable that samples which actually were treated with temperature higher than ambient one, are characterised by similar values of flexural strength. The differences between the results varies from 3% (for 40°C and 80°C) to 13% (for 40°C and 60°C). An example of the geopolymer sample failure is shown in Figure 11.

Fig. 11. Failure of the sample during bending test.

As it was mentioned before, there were 6 samples cured in 60°C and only half of them were in covered mould. Climatic chamber provided constant temperature and humidity level equal to 40%. However, 24 hours in those conditions caused drying shrinkage at the top surface of the uncovered samples which actually resulted in lowering of the flexural strength of those samples. Table 4 and diagram (Figure 12) show difference in results of bending test for covered and uncovered samples.

Table 4. Results of three-point bending tests.

Curing temperature	Mean value of destructive force F [kN]	Flexural strength f _f [MPa]
60°C samples covered	0.855	2.00
60°C samples uncovered	0.816	1.91

Fig. 12. Dependence of flexural strength (average values) and covering up the mould during heat-treatment (60°C).

4.2. Compression strength test

The values of compression strength were determined on the basis of the destructive forces magnitudes. The results of those tests are presented in Table 5. While diagram (Figure 13) shows relation between compressive strength of geopolymeric binder samples and temperature of the heat-treatment. An example of sample compression failure is presented in Figure 14.

Table 5. Results of uniaxial compression strength tests.

Curing temperature	Mean value of destructive force P [kN]	Compression strength R [MPa]
20°C	19.30	12.69
40°C	23.29	14.56
60°C	34.89	21.80
80°C	40.67	25.42

Fig. 13. Dependence of compression strength (average values) and heat-treatment temperature.

Fig. 14. Failure of samples after the uniaxial compression strength test.

Analysing the results of the compression tests it is noticeable that the compression strength of geopolymeric binder samples increases gradually with the raising heat-treatment temperature. The biggest raise of the compressive strength can be seen between samples from 40°C and 60°C and the difference here is equal 7.24 MPa (which is almost 50%), while the smallest raise occurs in the range of two first temperatures (20°C and 40°C) and it is equal 1.87 MPa (almost 15%). A similar percentage of strength increase (17%) was observed between samples cured in 60°C and 80°C.

The compression strength test also showed that the lack of the cover during the heat-treatment process had unfavourable influence on the mechanical properties of the geopolymer samples. The difference between obtained results are presented in Table 6 and in Figure 15. In case of the compression strength test, in terms of absolute values the results vary less than it was observed for the flexural strength test results. It can be noticed the change of the compression strength in that case is equal only 0.87 MPa.

Table 6. Results of uniaxial compression strength tests.

Curing temperature	Mean value of destructive force P [kN]	Flexural strength R [MPa]
60°C samples covered	34.89	21.80
60°C samples uncovered	33.49	20.93

Fig. 15. Dependence of compression strength (average values) and covering up the mould during heat-treatment (60°C).

5 Conclusions

Basing on the results of performed flexural and compression strength tests the following conclusions are drawn:

- The heat-treatment is necessary in case of curing geopolymers based on the fly ash suspension. Samples cured only in the ambient temperature represents poor mechanical properties.
- The compression strength of tested geopolymer samples increases with an increase of the heat-treatment temperature, although the maximal temperature was not established during that investigation.
- The most favourable temperature (within the investigated range) in case of compression strength was equal to 80°C.
- The highest flexural strength was obtained in case of samples cured in 40°C. However, the results obtained in 80°C were almost the same (the difference was less than 3%).
- During the heat-treatment the samples should be isolated (tightly covered) to avoid excessive surface drying and shrinkage cracks.

Summing up, the analysed fly ash suspension-based geopolymeric binder shows tendency to perform better mechanical properties, while the heat-treatment temperature is higher. This general statement is consistent with other geopolymers studies presented in the literature (the intermolecular bonds development is stronger when heat is delivered).

In this research, due to the technical capabilities the highest checked temperature was limited to 80°C. Further investigations should check the behaviour in the wider range of temperature. However, it should be also noted that the excessive growth of curing temperature in laboratory conditions is possible, but in practical applications it would be a significant hindrance. That is why from the practical point of view, it is desirable to maintain an optimal balance.

Study proved also possibility of shrinkage cracking while the sample is exposed to excessive drying. These conclusions should be helpful in case of next laboratory research.

This paper has been prepared with the financial support of the Silesian University of Technology (BK-235/RB6/2017); European Union's Horizon 2020 Research and Innovation Staff Exchange (RISE) programme (Marie Skłodowska-Curie Actions) under grant agreement no. 645696, project REMINE (Reuse of Mining Waste into Innovative Geopolymeric-based Structural Panels, Precast, Ready Mixes and Insitu Applications) and Polish Ministry of Science and Higher Education project no. 341284/PnH/2016.

References

1. J. Brol, S. Dawczyński, K. Adamczyk, *Wtórne wykorzystanie budowlanych elementów konstrukcyjnych (Reuse of structural elements)*, Wyd. Pol. Śl. (2014)

2. Polish Cement Association, *2017 przemysł cementowy w liczbach (2017 cement industry in numbers)*, Online : <http://polskicement.pl/files/Pages/490/uploaded/informator%202017%20www2.pdf>

3. M.S. Imbabi, C. Carrigan, S. McKenna, *Int. J. of Sust. Built Envir.* **1**, 194-216, (2012)

4. L. Vickers, A. van Riessen, W.D.A. Rickard, *Fire-Resistant Geopolymers. Role of Fibres and Fillers to Enhance Thermal Properties*, SpringerBriefs in Materials (2015)

5. S. Dawczyński, M. Górski, R. Krzywoń, Geopolymer as an alternative ecological material for buildings. *Proceedings of 14th International Conference on New Trends in statics and Dynamics of Buildings*, Bratislava, Slovakia (2016)

6. S. Dawczyński, P. Cieśla, M. Górski, R. Krzywoń, Impact of recycled ground glass addition on strength properties of tungsten mine waste geopolymeric binder. *Proceedings of International Congress on Engineering ICEUBI*, Covilha, Portugal (2017)

7. V.A. Kirschner, H. Harmuth, *Ceramics – Silikaty* **48 (3)**, 117-120, (2004)

8. D. Hardjito, B.Y. Rangan, *Development and Properties of Low-Calcium Fly Ash-based Geopolymer Concrete*, Research Report GC1, Curtin University of Technology

9. P. Chindaprasirt, T. Chareerat, V. Sirivivatnanon, *Cem. & Concr. Compos.* **29 (3)**, 224-229, (2006)

10. A.A. Adam, H. Horiato, *Proc. Engin.* **95**, 410-414, (2014)

11. PN-EN 1015-11:2001: Methods of test for mortar for masonry – Part 11: Determination of flexural and compressive strength of hardened mortar.