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ECOLOGICAL ASPECTS IN THE APPLICATION OF GEOPOLYMER COMPOSITES ON ROAD SURFACES

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ABSTRACT: The article presents, based on preliminary research, the possibility of using a geopolymer composite as a protective layer of engineering structures, which protects it against the impact of harmful factors of the surrounding environment as well as the effects of mechanical interactions. The most common solutions of such layers are insulations based on synthetic feeds, bitumens – products obtained in the process of processing crude oil. The ecological aspect of the implementation of geopolymer materials and the process of their production are presented. Technological problems in the application of geopolymer protective layers on an industrial scale were considered. The paper presents the results of own research on the influence of the geopolymer composite layer thickness on adhesion to concrete based on Portland cement, in which the compaction method of the composite was considered.

KEY WORDS: geopolymers, CO_2 emission, cement, binder

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Introduction

The cement industry is responsible for 5% of global CO_2 emissions, which accounts for almost 20% of industrial emissions. Every ton of cement produced emits about 0.81 tons of CO_2 to the atmosphere (Benhelal et al., 2012; Siemieniuk, Szatyłowicz, 2018). In a short time, cement plants will be noticed as one of the main culprits of global warming, which will result in the imposition of new emission fees, as a result of which the price of Portland clinker can increase by up to several dozen percent. An excellent alternative to Portland cements seems to be geopolymer binders. They are characterized by better properties compared to concrete obtained from cements based on Portland clinker. These properties include: high compressive and bending strength, including high early strength, good chemical and thermal resistance, high degree of adhesion with steel, minimal shrinkage, no corrosion of reinforcement. In addition, the production of geopolymer, including all raw materials needed to obtain it, causes 4-8 times less CO_2 emissions (Mikuła et al., 2014; Zhang, 2015). One of the materials used to obtain it is fly ash which is a byproduct of combustion of coal dust in power units, and also created in fluidized bed boilers. This makes the technology of geopolymer concrete “green” with a large development potential.

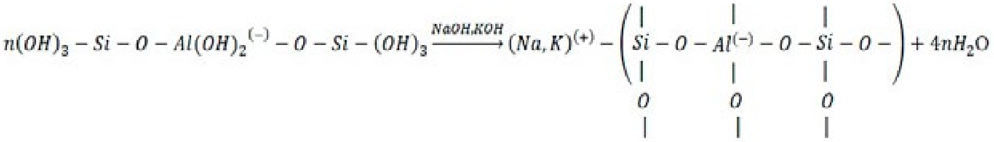
The process of obtaining and the structure of geopolymers

The synthesis of geopolymers consists in the alkaline activation of pozzolanic material. The material may be primarily fly ash from the combustion of coal dust, the activator is a solution of a strong base (NaOH or KOH) with sodium or potassium silicate. Obtained paste hardens after activation at elevated temperature giving an amorphous material, reminiscent of concrete based on Portland cement, but with other properties, i.e. high early strength, good chemical corrosion resistance, high strength at high temperatures, frost resistance (Hynowski et al., 2017).

The process of binding a geopolymeric paste is based on the polycondensation reaction, during which tetrahedrons $[SiO_4]^{4-}$, $[AlO_4]^5$ form amorphous structures, and the presence of Na^+ or K^+ ions in the chambers balances the structure charge. The stages of the formation of a composite based on geopolymers run differently than in cement concrete. The polymerization process consists of successive reactions, not permeating as in the case of classical cement bonding. In addition, the polymerization and hardening reaction of the geopolymer composite is not a spontaneous reaction and requires the heat to be supplied from the outside, usually heated in the 30-100°C range.

The synthesis process is usually presented in the literature via two reaction equations (Zhang, 2015; Davidovits, 1994):

$$n(Si_2O_5, Al_2O_2) + 2nSiO_2 + 4nH_2O \xrightarrow{NaOH,KOH} n(OH)_3 - Si - O - Al(OH)_2^{(-)} - O - Si - (OH)_3 \qquad (1)$$



$$n(OH)_3 - Si - O - Al(OH)_2^{(-)} - O - Si - (OH)_3 \xrightarrow{NaOH,KOH} (Na,K)^{(+)} - \left(\begin{array}{c} | \\ Si \\ | \\ O \\ | \end{array} - O - \begin{array}{c} | \\ Al^{(-)} \\ | \\ O \\ | \end{array} - O - \begin{array}{c} | \\ Si \\ | \\ O \\ | \end{array} - O - \right) + 4nH_2O \qquad (2)$$

Substrates Si_2O_5, Al_2O_2, SiO_2 are firstly dissolved by alkali hydroxide solutions, such as NaOH and KOH, to release reactive aluminate and silicate oligomers, represented by $(OH)_3$-Si-O-$Al(OH)_2$ and $(OH)_3$-Si-O-$Al(OH)_2^{(-)}$-O-Si-$(OH)^3$ (1). In the alkaline environment, the polymerization reaction occurs along with the cross-linking of the structure (2).

Ecological aspect of the implementation of engineering products and constructions from geopolymers

The production of Portland clinker is a highly energy intensive process, the temperatures prevailing in the rotary kiln reach 1500°C (Kurdowski, 1981), however in this process it is not the fuel emission that has the largest share in CO_2 emissions, but the raw material emission (Duda, Tamasiak, 2015). This is because raw materials for the production of Portland clinker are dominated by carbonates – above all calcium carbonate, which is decarbonising at a temperature of approx. 850°C. The demand for cements based on Portland clinker is still growing. Therefore, the cement industry is becoming one of the main emitters of anthropogenic CO_2. The geopolymer composite has a great chance of reducing greenhouse gases in this industry sector, the synthesis of which consumes twice less energy with 4-8 lower CO_2 emissions than in the case of Portland clinker (figure 1).

An important aspect of geopolymer concrete technology is the use of incidental combustion products (ICP) in the process of obtaining geopolymer. ICP can include fly ash from conventional coal boilers with well-known properties as well as fly ash from fluidized bed boilers. The latter due to the unstable chemical composition of the fuel used for firing the boiler are characterized by variable parameters, which is why they are currently classified as arduous waste.

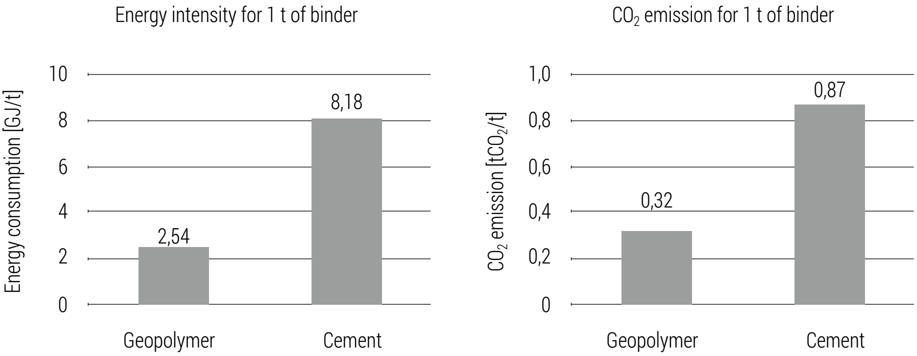


Figure 1. Comparison of CO_2 emissions and energy consumption in the production of cement and geopolymer binders

Source: Provis, Van Deventer, 2009, p. 195.

At Bialystok University of Technology, research on thin protective layers of concrete structures was carried out, resulting in patent protection of the number PL 230045 B1 "Method of ensuring durability of concrete structures and concrete mix in the protective layer" (Bołtryk et al., 2016). Further research is carried out to replace concrete based on Portland cement with geopolymer concrete and to use it as protective layers of road surfaces, both asphalt and concrete. This layer, protecting the road surface against harmful environmental factors and mechanical impacts, will prolong its service life, which in turn will reduce the consumption of bitumen in the form of asphalt or in the case of concrete Portland cement.

Own research in the field of thin protective layers from geopolymers

The aim of the conducted preliminary research was to assess the possibility of using geopolymer mortars as thin protective layers of cement composites. The research consisted in examining the dependence of the adhesion of the geopolymer layer to the cement concrete on its thickness. Standard sand was used as the aggregate. The activator used was a mixture of sodium water glass with a molar modulus of $1.6 < MR \leq 2.6$ with a substance content of approx. 35-43% ($Na_2O + SiO_2$) and a 14 molar NaOH solution. The mass ratio of the sodium silicate solution to the sodium hydroxide solution $Na_2SiO_2/NaOH$ was constant at 2.5. However, the ratio of activator to fly ash was 0.5. The fly ash used came from the combustion of coal dust in the

Ostrołęka Heat and Power Plant. The chemical composition and physical properties of the ash are presented in the table (table 1). The plain concrete used in the composite was designed for class C30/37 based on Portland cement CEM I 42.5 R (table 2) with a w/c ratio of 0.5. The thickness of the tested layers was 1.5 cm, 3.0 cm and 4.5 cm, respectively.

Table 1. Chemical composition and physical properties of fly ash

Component	% by weight
SiO_2	54,6
Reactive SiO_2	42,36
Al_2O_3	25,3
Fe_2O_3	4,97
Na_2O	0,84
CaO	2,14
Reactive CaO	1,84
Free CaO	<0,03
K_2O	2,8
MgO	1,8
TiO_2	1,07
P_2O_5	0,55
SO_3	0,37
BaO	0,15
SrO	0,07
Mn_3O_4	0,06
Ignition losses	4,37
Humidity	0,12

Source: external laboratory [31-12-2018].

The samples were formed by two methods in steel cubic molds with a side of 100 mm. The first method (I) was done by compacting the geopolymer concrete layer on the bottom of the mold by 30 second vibration. Then the mold was supplemented with ordinary concrete, then vibrated with a steel piston for 30 seconds. In the second method (II), both the geopolymer layer and the ordinary concrete were successively vibropressed for 30 seconds (figure 2).

Table 2. Technical parameters of Portland cement CEM I 42.5R used in the tests

Properties	Requirements according to the standard PN-EN 197-1	Test results	The basis of tests
Specific surface (Blaine method) [cm^2/g]	-	4124	PN-EN 196-6
The beginning of binding [min]	≥ 60	184	PN-EN 196-3
End of binding [min]	-	242	PN-EN 196-3
Change in volume [mm]	≤ 10	1,0	PN-EN 196-3
Compressive strength [MPa] - after 2 days: - after 28 days:	 ≥ 20,0 ≥ 42,5 ≤ 62,5	 30,1 60,2	PN-EN 196-1
SO_3 content [%]	≤ 4,0	2,95	PN-EN 196-2
Cl content [%]	≤ 0,1	0,089	PN-EN 196-21
Cr(VI) soluble content [ppm]	≤ 2,0	0,18	PN-EN 196-10
Insoluble residue [%]	≤ 5,0	0,57	PN-EN 196-2
Ignition losses [%]	≤ 5,0	3,33	PN-EN 196-2

Source: https://www.cemex.pl/cement-czerwony.aspx [03-01-2019].

The composite molds were seasoned for 24 h on the grate above the water surface, then placed for another 24 h in a laboratory dryer at 65°C to accelerate the activation of the geopolymer and accelerate the hydration of concrete based on Portland cement. The seasoning method was aimed at assessing the possibility of shortening the time that should be allowed to allow the surface to be used in the summer season.

After a 48 h curring period, the samples were subjected to testing, which consisted in applying a shear force at the interface between the two layers carried with a steel bar. Previously, the samples (rotated by 90° in relation to the forming direction) were placed on the pressure plate of the testing machine (figure 3).

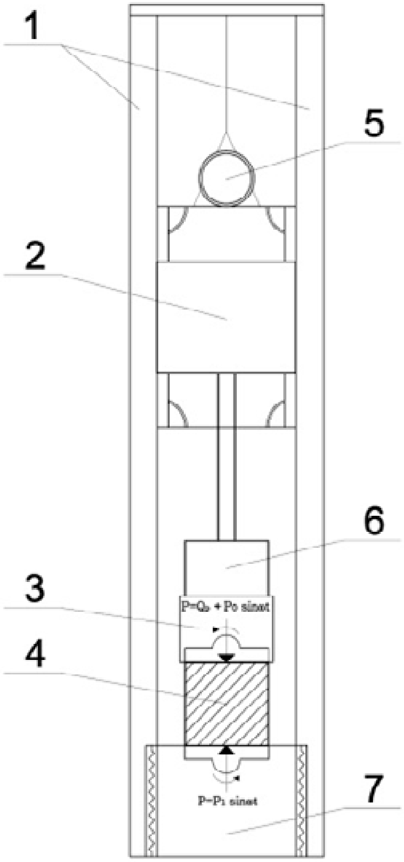


Figure 2. Schematic diagram of the vibrating station with vibropressing: Qp – pressure force, Po – force forcing the upper vibrator to vibrate, P1 – force forcing the vibrator to vibrate; 1 – guides, 2 – inertial load, 3 – extension, 4 – form, 5 – upper vibrator with adjustable force, 6 – pressure piston, 7 – bottom vibrator

Source: Falkowski, 2012, p. 27.

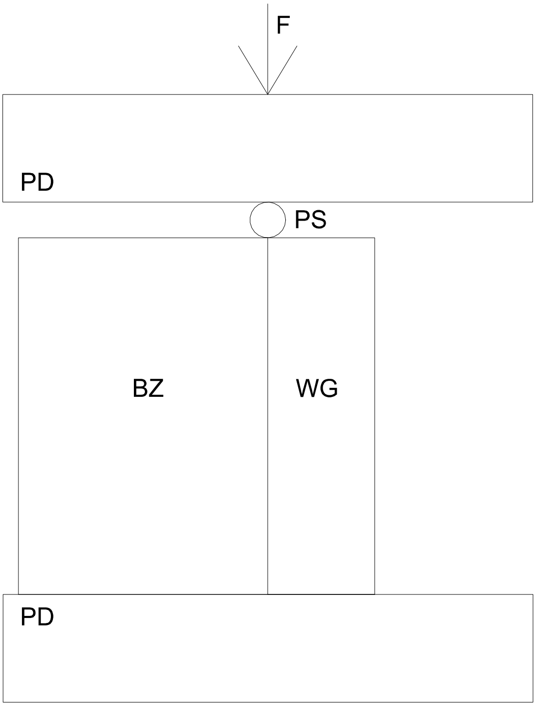


Figure 3. Scheme of the station for testing the adhesion between layers by splitting (PD – the press platens, BZ – ordinary concrete layer, WG – geopolymer layer, PD – steel bar carrying the load, F – the direction of load application)

Source: author's own work.

Results of the research

The results obtained are shown in the graph (figure 4). The dependence of the splitting force of the composite layer on both the compaction method and the thickness of the geopolymer layer is visible. Three samples were made and tested for each of the compaction methods. The average values of the destructive force of the combination of layers were: for a layer with a thickness of 1.5 cm: I method – 6.67 kN, II method – 14.0 kN; for the 3.5 cm layer: I method – 6.17 kN, II method – 19.17 kN; and for the 4.5 cm layer in the case of I method, 8.33 kN, and II, 35.83 kN.

In the case of the second compaction method, the mean values of shear force grow linearly with the increase of the geopolymer layer thickness, while with the application of the compaction method I the values differ slightly. It can be assumed, which requires further research, that better adhesion will be obtained by subjecting both layers to vibropressing.

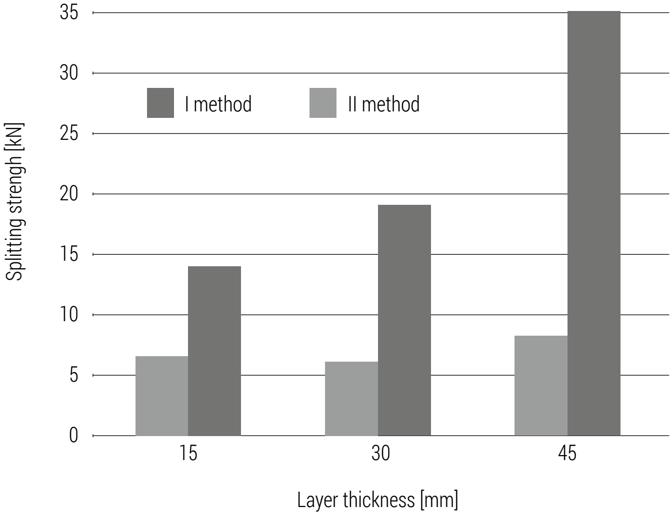


Figure 4. Graph of dependence of splitting force and compaction methods on geopolymer layer thickness

Source: author's own work.

Conclusions

Obtained results of preliminary tests on the application of geopolymers in the form of protective layers encourage further research on the use of geopolymer material as protective layers of concrete structures and road surfaces. At the further stage of testing, it is necessary to carry out tests such as: abrasion, roughness, thermal expansion, water absorption, frost resistance, compressive and tensile strength as well as stiffness of the obtained composite. An extremely important aspect is the development of the optimal technology of works, because the presented data unambiguously indicate that the value of the shear force needed to break the geopolymer protective layer is affected by both thickness and compaction method. When using this solution on an industrial scale, attention should be paid to the stability of the geopolymer embedment parameters to the structure being protected, because it will affect the quality of the obtained composite. The implementation of geopolymeric materials for general use will indirectly result in a decrease in anthropogenic CO_2 emissions and a reduction in the use of petroleum materials in construction.

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The contribution of the authors

All authors contributed equally to the manuscript.

Literature

Benhelal E., Zahedi G., Hashim H. (2012), *A novel design for green and economical cement 14 manufacturing,* "Journal of Cleaner Production" No. 22, p. 60-66

Bołtryk M., Stankiewicz N., Pawluczuk E. (2016), *Patent, Sposób zapewnienia trwałości konstrukcjom betonowym oraz mieszanka betonowa w warstwie ochronnej,* Polska PL 230045 B1

Davidovits J. (1994), *Properties of geopolymer cements*, First International Conference on Alkaline Cements and Concretes, Kiev

Duda J., Tamasiak J. (2015), *Redukcja emisji CO_2 w procesie produkcji cementu,* Konferencja Innowacje w Zarządzaniu i Inżynierii Produkcji p. 384-395

Falkowski K. (2012), *Technologia ochrony materiałowo-strukturalnej betonów cementowych w środowisku agresywnym,* "Civil and Environmental Engineering" No. 3, p. 25-31

Hynowski M. et al. (2017), *Wpływ granulowanego żużla wielkopiecowego na kształtowanie właściwości mechanicznych zaczynów geopolimerowych z popiołu krzemionkowego,* "Scientific Works of Institute of Ceramics and Building Materials" No. 34, p. 70-80

Kurdowski W. (1981), *Poradnik technologa przemysłu cementowego,* Warszawa

Mikuła J. et al. (2014), *Rozwiązania proekologiczne w zakresie produkcji.* Nowoczesne materiały kompozytowe przyjazne środowisku, part. 1, Politechnika Krakowska, Kraków

Provis L., Van Deventer J.S.J. (2009), *Geopolymers: structure, processing, properties and industrial applications,* New York

Siemieniuk J., Szatyłowicz E. (2018), *Zmniejszenie emisji* CO_2 *w procesie produkcji cementu*, "Civil and Environmental Engineering" No. 9, p. 81-87

Zhang M. (2015), *Geopolymer, Next Generation Sustainable Cementitious Material – Synthesis, Characterization and Modeling*, PhD thesis, Worcester Polytechnic Institute