Possibility of Using a Geopolymer Containing Phase Change Materials as a Sprayed Insulating Coating - Preliminary Results

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Abstract

Geopolymers have been known for decades and classified as inorganic polymers, characterized by high resistance to high temperatures. They can be successfully used for the thermal insulation of buildings, especially in the foamed form. The addition of phase change materials (PCMs) in such materials may also increase the heat capacity of the materials, therefore, using them for building cladding can increase the thermal comfort of the building and prevent it from overheating. This study tests the addition of PCMs to geopolymers by spraying and presents the results. Additionally, the study includes preliminary experience concerning the technology of applying these materials, along with selected test results that assess the properties of the produced coatings. The results indicate that the addition of PCMs in the amount of 15% can increase the heat capacity of geopolymer materials by about 150-180%, and the foamed geopolymer coatings produced have a thermal conductivity in the range of 0.07-0.09 W/mK.

Keywords: geopolymer, insulating materials, sprayed coatings, phase change material

1. Introduction

Geopolymer materials are gaining more and more interest in the scientific community due to their interesting properties [1]. Despite the development of this technology for over 40 to 50 years, mass-scale implementations are still not observed in the world. This is due to various implementation barriers, the largest of which include the appearance of efflorescence, lack of standards, and difficulties related to the appropriate technological regime. Additionally, due to the increasing inflation and armed conflict in Ukraine from 2022, there are related increases in the prices of raw materials and energy. Despite ongoing efforts to develop recipes for geopolymer mixtures capable of curing at ambient temperature, it has still not been possible to develop additives that would allow for a trouble-free implementation of this solution on a mass scale. The increase in raw material prices has made geopolymer materials more expensive than ready-mix concretes based on Portland cement. Such a situation stops the progress of this technology. However, it is worth noting that the higher price is not necessarily a barrier, as geopolymer materials offer many unique features that can be utilized in high-margin applications.

In addition, these materials are great for foaming processes and it is possible to produce insulating materials based on geopolymers [2-3]. Their applications can be diverse, ranging from the packaging industry to construction. However, to enable the industrial production of foamed geopolymers, efforts should be made to develop a technology for their production by spraying. This will allow the application of insulation layers on real, existing objects. This is a difficult issue because geopolymer foams have low stability and often suffer from foam structure collapses. The use of standard spray guns and aggregates is not suitable for this type of material [4-7].

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This study presents selected results of research and technological trials related to the possibility of applying foamed geopolymers containing phase change materials (PCMs) [8] by spraying. The addition of PCMs in this type of composite increases the heat capacity of such materials [9-12]. With the use of foamed geopolymers doped with PCM materials, it is possible to achieve decent insulation parameters with additionally increased thermal capacity. The addition of PCMs can increase the specific heat of such a composite by up to 180% without significantly worsening the insulating properties. This is a very attractive solution from the application point of view because the use of non-combustible insulation that can accumulate heat can bring great benefits when implemented on a mass scale.

PCMs placed in a matrix of porous insulating geopolymer cause the heat penetrating the building partition to be additionally retained by the PCM material. After the partition cools down, the heat is released, but due to the insulating nature of the partition, it does not enter the room in its entirety but is blocked by the porous structure of the matrix material. A building partition made with the use of such a solution will not cause overheating of rooms and buildings. The solutions and research results described in this study are undoubtedly an innovative approach to the use of PCM in building materials. They can contribute to the significant development of disciplines such as civil engineering and materials engineering. The presented test results and the results of spraying tests are only preliminary, as advanced work has just begun to establish an innovative pilot line for the additive application of geopolymers.

The refined geopolymer spray application technology may contribute to the development of geopolymer implementation in the industry. The technology of spraying non-foaming solid geopolymers can be used, among others, to protect concrete surfaces in various types of industrial pipelines and other similar facilities [13], and also be used in the production of fiber-reinforced panels [14]. The possibility of using devices for spraying foamed geopolymers makes their application easier and thus increases their use in industry. Geopolymer foam application technologies can be used both for pure geopolymers and geopolymer composites. Scientists around the world are constantly working on improving the parameters of foamed geopolymers [15] and composites, e.g., with EPS [16]. At the same time, efforts should be made to develop the technology of their application.

2. Materials and Methods

Fly ash from the Skawina heat and power plant was used to produce foamed geopolymer materials. The fly ash that was used came from the combustion of hard coal in 2022. It was class A fly ash (below 5% loss on ignition). The chemical composition of the precursor is determined by the X-ray fluorescence (XRF) method, as shown in Table 1.

Oxide CaO MgO K_2O P_2O_5 SiO₂ Al_2O_3 Fe_2O_3 Na₂O SO_3 TiO₂ BaO 55.89 23.49 5.92 2.72 0.59 3.55 0.161.09 Content [%] 2.61 0.82 0.20

Table 1 Chemical composition of the fly ash from the Skawina power plant

The geopolymers were produced using technical sodium hydroxide flakes and an aqueous sodium silicate solution of R-145 module 2.5 (SiO2/Na2O molar module), with a molar density of about 1.45 g/cm3. The mixture did not use distilled water. The alkaline solution was prepared by pouring the solid sodium hydroxide over an aqueous solution of sodium silicate and water. The solution was thoroughly mixed and allowed to equilibrate until a constant concentration and temperature were achieved.

The geopolymer foams were prepared by first mixing solid constituents such as fly ash, microspheres, solid PCM, and sand until they reached a homogeneous state. Subsequently, an alkaline solution consisting of a 10 M sodium hydroxide solution with the addition of sodium silicate in the ratio of 1:2.5 was introduced. The material was mixed for 10 minutes, followed by the addition of an appropriate amount of hydrogen peroxide, which was continuously mixed for approximately 1 minute. After the completion of the mixing process, the material was poured into a mold and subjected to a temperature of 75

°C for 24 hours. Alternatively, the mixed mass was transferred to a spray gun and applied to various surfaces using these devices. After the heating process, the element was dismantled and stored under laboratory conditions for 28 days to obtain full strength. The list of materials used to perform the tests is presented in Table 2. Hydrogen peroxide was used as a blowing agent both in the production of cast materials and in spray tests.

Table	2	Character	istics o	f test	samnl	es
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Sample ID	Sand mass [g]	Microsphere mass [g]	Fly ash mass [g]	Cement mass [g]	PCM mass [g]	Alkaline activator [ml]
Reference sample	100	200	800	100	0	350
PCM 15% MikroCaps	100	200	800	100	215	400

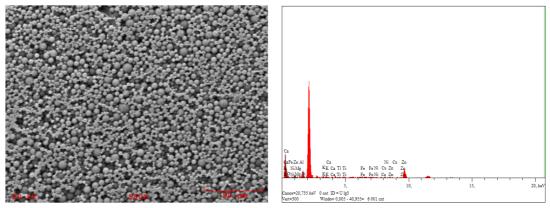


Fig. 1 PCM microstructure (MikroCaps)

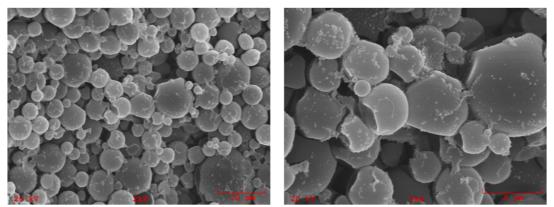


Fig. 2 SEM micrograph of PCM (MikroCaps)



Fig. 3 MicroCaps PCM in the form of a suspension

MikroCaps PCM 28 Slurry (MikroCaps, Slovenia) was used as the PCM. The basic parameters of this material are a melting point of 28 °C, a heat storage capacity of 174 kJ/kg, and a specific heat of 2 kJ/kg·K [17], which is a material used in the form of a suspension of microcapsules containing paraffin. The particle morphology is shown in Figs. 1-3. PCM

particles/capsules with an average size of 1 to 10 microns are shown in Fig. 1 and Fig. 2. Scanning electron microscopy (SEM) observations were made on samples previously dried to a constant weight. In the delivery state, there are visible particles suspended, as shown in Fig. 3. These particles, in suspension, were added to the geopolymer mass.

3. Results and Discussion

The produced samples of foamed geopolymer were subjected to thermal conductivity tests. As depicted in Fig. 4, the device and cut to the appropriate size $(20 \times 20 \times 2.5 \text{ cm})$ samples of foamed geopolymer containing PCM were utilized. Thermal conductivity tests were conducted on cast samples before the spray test, revealing that the reference sample exhibited a thermal conductivity of 0.068 W/mK, whereas the sample with the addition of 15% PCM displayed a lambda coefficient of 0.092 W/mK.





(a) A device for testing the thermal conductivity coefficient

(b) Samples of foamed PCM geopolymers

Fig. 4 Testing device and examples of test samples

The addition of PCMs deteriorates the insulating properties, but at the same time, it can increase the specific heat. Therefore, it was considered that the introduction of PCM is justified. The obtained thermal conductivity coefficients are not comparable with popular insulating materials such as polystyrene or mineral wool (0.025-0.035 W/mK) [18]. Nevertheless, foaming plays a crucial role in substantially reducing the thermal conductivity coefficient of geopolymer materials. For comparison, the non-foamed geopolymer material in the form of a solid plate, as shown in Fig. 5, had a thermal conductivity coefficient of 0.889 W/mK (The values of thermal conductivity of geopolymers depending on the density are given in Table 3).



Fig. 5 Solid geopolymer plate (without the addition of foaming agents)

Table 3 Values of thermal conductivity of geopolymers depending on the density

Density of geopolymer (kg/m3)	1890	1430	1210	800	650	310
Thermal conductivity (W/mK)	0.889	0.629	0.540	0.120	0.980	0.070

Geopolymer materials can also be used in a foamed form for the production of lightweight aggregates, both in terms of granules obtained on granulators or lightweight aggregates obtained in the controlled crushing process. The Cracow University of Technology has investigated the possibility of using this type of aggregate. Examples of aggregates of various fractions obtained from foamed geopolymer based on fly ash are presented in Fig. 6, which is a source from previous author research.



Fig. 6 An example of foamed lightweight geopolymer aggregates (different fractions)

The topic of obtaining stable geopolymer foams has been known for several decades and widely described in the scientific literature. The problem arises when there is a need to apply these materials to an uneven substrate, such as a steel or concrete structure that cannot be covered with thermal insulation panels. During the tests, geopolymer foams produced without any problems obtained a stable, non-falling structure, which is confirmed by the samples presented in Fig. 7. These samples had dimensions of $10 \times 10 \times 10$ cm. Currently, the production of foamed geopolymers presents no research challenge. The primary challenge lies in developing the technology required to efficiently apply such a challenge is the technology of applying such materials to steel and concrete structures for insulation purposes. Fig. 8 presents the results of preliminary tests of spray application of foamed geopolymers using a paint gun (air gun, using a special cup as a material reservoir).





Fig. 7 Examples of foamed geopolymer samples with the addition of phase change materials

In Fig. 8, it is evident that the foamed structure was not obtained with this method, with the air pressure generated for material propulsion eliminating the gas pores formed by the hydrogen peroxide (36%) blowing agent. This method seems to be completely useless, although literature reports indicate that it is possible [19-20]. Despite many attempts to use this method by the authors, the intended effects have not been achieved. Analysis of the hydrodynamic method also showed that the prevailing pressures and the size of the pipes transporting the material, spraying of foamed geopolymers will not be possible with these methods. It was decided to use a standard plastering unit for applying plasters and putties. Preliminary research has confirmed the legitimacy of using this deposition technology, as shown in Fig. 9. However, refinement of this method still requires significant expenditures and extensive research. The results presented in this study should be treated as preliminary test results. Work will be continued in this area and presented to the scientific community in subsequent publications. Some of the previous research was presented in the article [7].





Fig. 8 Example of air-sprayed geopolymer using a spray gun (cup gun)





Fig. 9 Process of applying layers of foamed geopolymers (preliminary tests) using a plastering unit (without using compressed air)

4. Conclusions

As mentioned in the introduction, geopolymer materials can become a viable and interesting alternative to other commonly used insulation materials in construction as well as building materials with much better insulation parameters [21-23]. However, this requires the use of appropriate foaming agents and a large technological regime that allows for obtaining stable porous structures. Laboratory tests prove that it is possible to produce geopolymer foams with parameters similar to those of porous cellular glass. The addition of PCMs allows such materials to obtain high specific heat, which makes them not only insulating materials but also materials with accumulation properties. However, it is necessary to develop a unique technology for applying such layers because their production in the form of boards is difficult in terms of application. The results presented in this article show that it is possible to spray foamed geopolymers using plaster aggregates. The application technology is extremely important because the use of inappropriate devices can lead to very unfavorable effects as shown in the article (Fig. 8).

The article presents the preliminary results of tests related to the spray application of geopolymers. Currently, no solutions are enabling the industrial application of foamed geopolymers sprayed on various structures and building elements, making this issue of great importance from the application point of view. Research on the material research conducted on the composition of foamed geopolymers with PCMs exhibits the aptitude for excellent insulation parameters. While the achieved thermal conductivity coefficients do not align with the parameters of commonly used insulating materials, such as polystyrene or polyurethane foam, one undeniable advantage of utilizing geopolymers is their enhanced environmental friendliness. The advantage is also their very high resistance to high temperatures, even of the order of 1000 °C.

- (1) Several key variables must be considered when applying geopolymers via spraying. These include the stability of foamed structures, the optimal spray pressure, and the duration of action of the foaming agent, which is essential for activating after applying the geopolymer layer's application. However, these issues require further advanced research and testing.
- (2) It is possible to apply foamed geopolymers using popular plastering aggregates. The use of this type of equipment allows the application of much greater material thicknesses.
- (3) The use of cup guns for applying foamed geopolymers causes several difficulties and the quality of the coating is heterogeneous.
- (4) For the implementation of insulating geopolymers to make sense, efforts should be made to develop methods for their application.

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Conflicts of Interest

The authors declare no conflict of interest.

References

- [1] J. Davidovits, Geopolymer Chemistry and Applications, 4th ed., Saint-Quentin France: Institut Géopolymère, 2015.
- [2] E. Liefke, "Industrial Applications of Foamed Inorganic Polymers," 2nd International Conference Geopolymere Geopolymere, pp. 189-200, July 1999.
- [3] N. A. Jaya, L. Yun-Ming, M. M. A. B. Abdullah, and H. Cheng-Yong, "Porous Metakaolin Geopolymers with Tailored Thermal Conductivity," IOP Conference Series: Materials Science and Engineering, vol. 551, article no. 012088, 2019.
- [4] M. Łach, K. Korniejenko, and J. Mikuła. "Thermal Insulation and Thermally Resistant Materials Made of Geopolymer Foams," Procedia Engineering, vol. 151, pp. 410-416, 2016.
- [5] M. Łach, D. Mierzwiński, K. Korniejenko, and J. Mikuła, "Geopolymer Foam as a Passive Fire Protection," MATEC Web of Conferences, vol. 247, article no. 00031, December 2018.
- [6] M. Łach, K. Pławecka, A. Bąk, K. Lichocka, K. Korniejenko, A. Cheng, et al., "Determination of the Influence of Hydraulic Additives on the Foaming Process and Stability of the Produced Geopolymer Foams," Materials, vol. 14, no. 17, article no. 5090, September 2021.
- [7] K. Kaczmarski, K. Pławecka, B. Kozub, P. Bazan, and M. Łach, "Preliminary Investigation of Geopolymer Foams as Coating Materials," Applied Sciences, vol. 12, no. 21, article no. 11205, November 2022.
- [8] M. Łach, K. Pławecka, A. Bąk, M. Adamczyk, P. Bazan, B. Kozub, et al., "Review of Solutions for the Use of Phase Change Materials in Geopolymers," Materials, vol. 14, no. 20, article no. 6044, October 2021.
- [9] Bak, K. Pławecka, P. Bazan, and M. Łach, "Influence of the Addition of Phase Change Materials on Thermal Insulation Properties of Foamed Geopolymer Structures Based on Fly Ash," Energy, vol. 278, article no. 127624, September 2023.
- [10] M. Muraleedharan and Y. Nadir, "Geopolymer Mortar Integrated with Phase Change Materials for Improvement of Thermal Efficiency in Buildings: A Review," Materials Today: Proceedings, vol. 44, part 1, pp. 878-885, 2021.
- [11] V. D. Cao, S. Pilehvar, C. Salas-Bringas, A. M. Szczotok, J. F. Rodriguez, M. Carmona, et al, "Microencapsulated Phase Change Materials for Enhancing the Thermal Performance of Portland Cement Concrete and Geopolymer Concrete for Passive Building Applications," Energy Conversion and Management, vol. 133, pp. 56-66, February 2017.
- [12] R. Shadnia, L. Zhang, and P. Li, "Experimental Study of Geopolymer Mortar with Incorporated PCM," Construction and Building Materials, vol. 84, pp. 95-102, June 2015.
- [13] J. Matthews, A. Selvakumar, S. Vaidya, and W. Condit, "Large-Diameter Sewer Rehabilitation Using a Spray-Applied Fiber-Reinforced Geopolymer Mortar," Practice Periodical on Structural Design and Construction, vol. 20, no. 4, article no. 04014050, November 2015.

- [14] Kuqo, T. Koddenberg, and C. Mai, "Use of Dry Mixing-Spraying Process for the Production of Geopolymer-Bonded Wood and Seagrass Fibreboards," Composites Part B: Engineering, vol. 248, article no. 110387, January 2023.
- [15] R. Szabó, I. Gombkötő, M. Svéda, and G. Mucsi, "Effect of Grinding Fineness of Fly Ash on the Properties of Geopolymer Foam," Archives of Metallurgy and Materials, vol. 62, no. 2B, pp. 1257-1261, 2017. (In Polszczyzna)
- [16] T. Magyar, J. Faitli, and R. Szabó, "Experimental- and Theoretical Investigation of the Resultant Thermal Conductivity of Geopolimer-EPS Composite Insulating Materials," Journal of Silicate Based and Composite Materials, vol. 69, no. 3, pp. 74-82, 2017. (In Magyar)
- [17] MikroCaps, https://www.mikrocaps.com/, November 30, 2022.
- [18] S. Klarić, D. Samic, J. Katica, A. Kurtović, M. Duerod, and M. R. Popovac, Guidelines Energy Efficiency in Buildings as a Basis for Sustainable Social and Economic Development in Bosnia and Herzegovina, Sarajevo: Savjet za zelenu gradnju Green Council, 2016. (In Bosnian)
- [19] Y. Mao, L. Biasetto, and P. Colombo, "Metakaolin-Based Geopolymer Coatings on Metals by Airbrush Spray Deposition," Journal of Coatings Technology and Research, vol. 17, no. 4, pp. 991-1002, July 2020.
- [20] L. V. Su, N. V. Vu, K. Buczkowska, T. Bakalova, L. Volesky, P. Los, et al., "Fire Resistance of Geopolymer Foam Coating," Geopolymer Camp 2021, pp. 1-17, August-September 2021.
- [21] M. M. Ahmed, K. A. M. El-Naggar, D. Tarek, A. Ragab, H. Sameh, A. M. Zeyad, et al., "Fabrication of Thermal Insulation Geopolymer Bricks Using Ferrosilicon Slag and Alumina Waste," Case Studies in Construction Materials, vol. 15, article no. e00737, December 2021.
- [22] D. Tarek, M. M. Ahmed, H. S. Hussein, A. M. Zeyad, A. M. Al-Enizi, A. Yousef, et al., "Building Envelope Optimization Using Geopolymer Bricks to Improve the Energy Efficiency of Residential Buildings in Hot Arid Regions," Case Studies in Construction Materials, vol. 17, article no. e01657, December 2022.
- [23] M. Maafa, A. Abutaleb, N. Zouli, A. M. Zeyad, A. Yousef, and M. M. Ahmed, "Effect of Agricultural Biomass Wastes on Thermal Insulation and Self-Cleaning of Fired Bricks," Journal of Materials Research and Technology, vol. 24, pp. 4060-4073, May-June 2023.



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