

## ANALYSIS REGARDING THE MECHANICAL PROPERTIES OF ALKALI-ACTIVATED FLY ASH-BASED GEOPOLYMER CONCRETE CONTAINING SPENT GARNET AS REPLACEMENT FOR SAND AGGREGATES

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### Abstract

*As research regarding the production and optimization of geopolymer materials is constantly increasing and is fundamentally motivated by the need, identified both in the global ecological context and at national level, new materials can be developed using this type of binder. Sustainable consumption of resources, focuses on the capitalization of existing waste and prevention of generating new ones, therefore adopting the Sustainable Development principles. The increase in the utilization of sand from rivers for various construction purposes, which also disturbs the environment can be considered another damaging factor for the environment. Recycling of garnets and their use as replacement for sand aggregates could provide an ecological solution for the production of the alkali-activated fly ash-based geopolymer binders. The aim of this paper is to present preliminary results regarding the use of spent garnet as replacement for sand aggregates in the production of alkali-activated fly ash-based geopolymer binders using Romanian local raw materials and to study its influence on the mechanical performances of the binder.*

**Keywords:** fly ash, spent garnet, alkali-activation, geopolymer.

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### Introduction

Worldwide, interest in the re-use and recycling of waste is growing. Therefore, consistent actions are taken in order to minimize the environmental impacts associated with waste treatment and disposal in order to minimize the further damage which has impact on the environment and to the people. The use of high-volume wastes in the production of alkali-activated binders is well known and could provide the transition to the implementation of the Circular Economy principles. The need to develop new and unconventional materials and technologies was determined not only by economic and social drivers, but also by the fact that with the exponential development of production, strong shortage of material sources and energy sources are arising, with increasing aggression of the environment. The development of alkali-activated binders, using different wastes as raw materials in their production, allows the industry to be strictly oriented towards the implementation of the above-mentioned principles, by creating materials with certain properties, so that the technical parameters are satisfy their intended field of use.

Studies regarding alkali-activated binders are still on-going and research regarding their mechanical properties and effects on the environment are also being intensively studied. Research

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regarding the development of alkali-activated binder is directly connected to the worldwide need of global CO<sub>2</sub> emissions reduction in all industries [1-4]. Literature shows that alkali-activated binders are characterised by excellent mechanical properties. Those binders also present high resilience in aggressive environments. Producing this type of materials can represent an opportunity for both the environment and the engineering fields, being considered a reliable alternative to the traditional technology [5-7]. When compared to existing construction materials, geopolymer binders show superior performances which can be used in specific applications. Since research regarding the production of alkali-activated fly ash-based geopolymer materials is extensively developing, their implementation requires special procedures and this conducts to more attention due to the several parameters that affect this type of material. Geopolymer binders are not subjected to unitary regulations governing the manufacture of this type of material, therefore the production of these binders is subjected to specific tests. All these tests should be carried out on the basis of special technical specifications, complementary to existing norms and available standards for construction materials [8,9].

Intensive research has proven that alkali-activated geopolymer binders obtained using waste, such as fly ash, as raw material, can lead to sustainable product development. Using waste materials in the geopolymerization process not only allow greener environmental growth in the construction sector but also protect the excessive consumption of natural fine aggregates, when compared to traditional techniques [10]. Garnets could be defined as a group of complex silicate minerals, with analogous lattice crystalline structures. They have varied chemical compositions and have major industrial uses (water jet cutting, abrasive blasting media, water filtration granules etc.) [11,12]. Garnets can be reused about 3–5 times during their use in the industry, keeping their overall properties intact. At some point, they degrade to an extent where they cannot be further reutilized. When garnets cannot be used for their intended use, those are stored in waste-yards and designated as “spent garnet” [13]. Studies have shown that by using spent garnet as sand replacement in the development of cementitious composites and also alkali-activated geopolymer binders open new perspectives in the production of this material [14-17].

Based on preliminary results obtained regarding the production of alkali-activated fly ash-based geopolymer materials developed using Romanian local raw materials [18, 19], the aim of this paper is to study the possibility of using spent garnet as replacement for sand aggregates in the production of alkali-activated fly ash-based geopolymer binder and to study its influence on the mechanical performances of the binder.

## Materials and Methods

This chapter summarizes the raw materials used in the production of the alkali-activated fly ash-based geopolymer concrete, the mix design and curing conditions and also the testing methods used for the specific evaluation of the physical properties of the materials. A “trial-and-error” experimental research was adopted in order to produce the alkali-activated fly ash based geopolymer concrete using spent garnet as aggregate replacement, by using the full information and results regarding the production of the alkali-activated geopolymer concrete [18,19].

### Fly ash

The raw material used as main geopolymerization material was a low-calcium fly ash, obtained from a power plant in Romania. The chemical composition of the fly ash was established by X-ray fluorescence analysis (XRF analysis) (Table 1). The cumulative distribution of the fly ash particles was established using a HELOS RODOS/L, R5 instrument (Fig. 1).

### Alkaline activator

A combination between sodium silicate solution (Na<sub>2</sub>SiO<sub>3</sub> solution - SiO<sub>2</sub>=30%, Na<sub>2</sub>O=14% and H<sub>2</sub>O=56%) and sodium hydroxide solution (NaOH solution) was chosen as

alkaline activator for the production of the samples. The sodium hydroxide solution was prepared by dissolving NaOH pearls into water, until the desired concentration of the solution was achieved. The NaOH solution concentration used for the production of the samples was set to 10M (400g of NaOH flakes were dissolved in water, for one liter of solution).

**Aggregates**

Natural sand aggregates, granular class 0/4 mm (S), were used in this study for the production of the alkali-activated fly ash-based geopolymer binder. Spent garnet from a local provider in Romania was used in order to study the possibility of using this material as sand aggregates replacement. The physical properties of the sand and the spent garnet are presented in Fig. 2, Fig. 3 and Table 2. The chemical composition of spent garnet was also established by X-ray fluorescence analysis (XRF analysis) and is presented in Table 1.

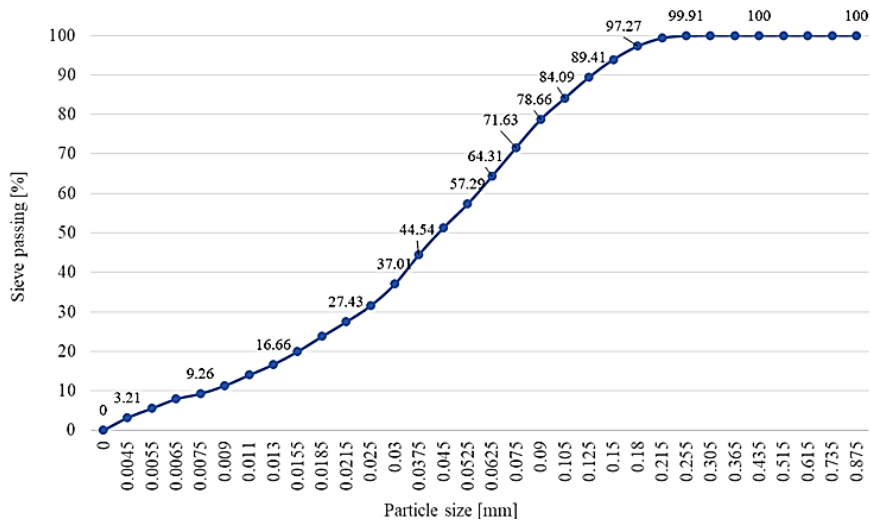


Fig. 1. Fly ash particle size distribution

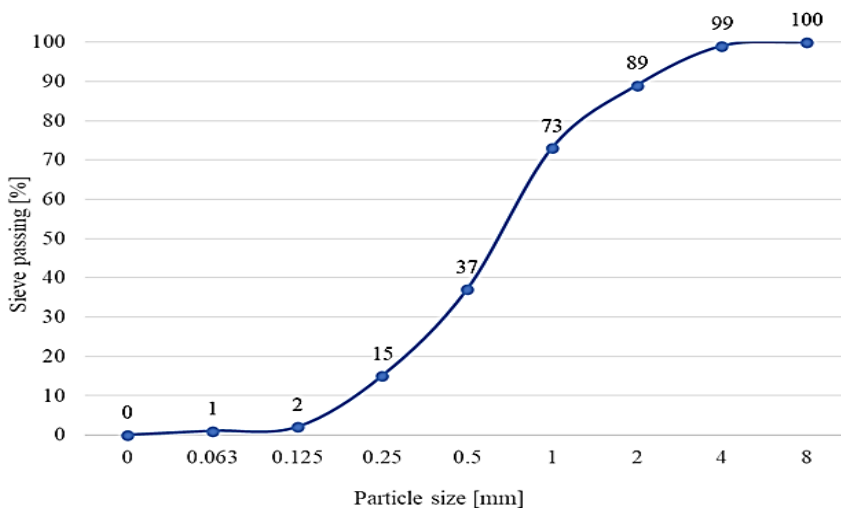


Fig. 2. Particle size distribution of granular class 0/4 mm sand

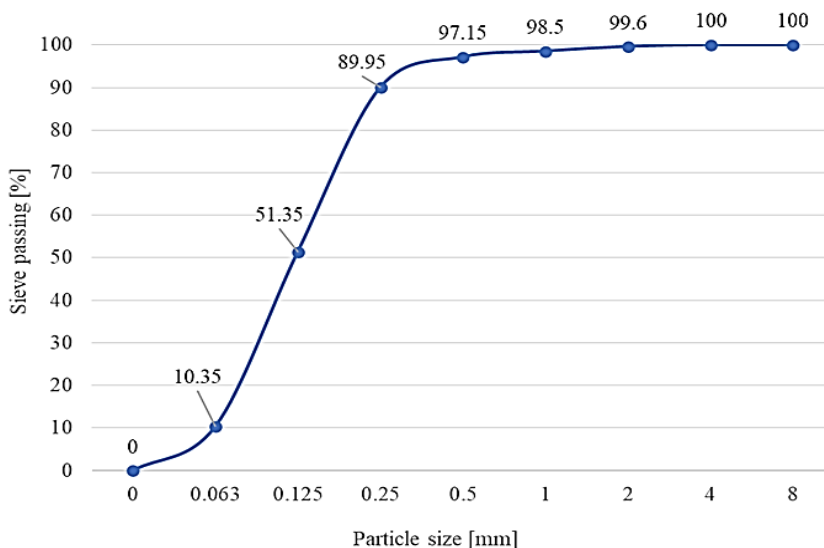


Fig. 3. Particle size distribution of spent garnet

Table 1. Fly ash and spent garnet chemical composition

Oxides	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	L.O.I.
wt.%	46.94	23.83	10.08	10.72	2.63	0.45	0.62	1.65	0.92	2.11
	36.65	17.54	28.58	6.27	5.88	0.05	0.22	1.07	2.12	-

Table 2. Physical properties of the granular class 0/4 mm sand and spent garnet

Characteristic	0/4 mm sand (S)	Spent garnet (G)
Absolute density, [kg/m <sup>3</sup> ]	2510	2880
Density determined after oven drying, [kg/m <sup>3</sup> ]	2448	2690
Density per saturated dry area, [kg/m <sup>3</sup> ]	2472	2760
Water absorption coefficient, [%]	1.00	2.40

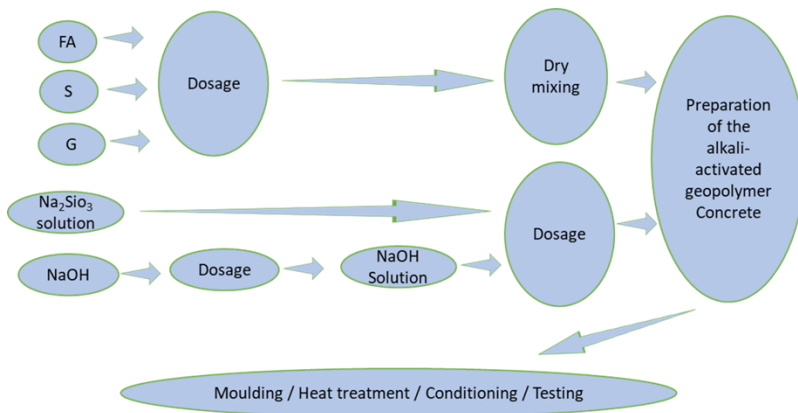
### Mix design, moulding and curing treatment

The following preliminary mixtures have been taken into consideration for the production of the alkali-activated fly ash-based geopolymer concrete, using the following constant parameters: alkaline activator to fly ash ratio, Na<sub>2</sub>SiO<sub>3</sub>/NaOH solution ratio and binder to aggregates ratio (Table 3).

The production of the alkali-activated fly ash-based geopolymer samples was based on principles already established for the preliminary production of the geopolymer binders used in the literature (Fig. 4) [18,19]. After casting the samples into moulds, with a corresponding 10 minutes vibration the samples were subjected to a (70°C/24 hours) heat treatment. After demoulding (Fig. 5), the geopolymer samples were kept in the climatic chamber at the temperature T (20±1)°C, with a relative humidity RH (60±5)%/ All the tests regarding their mechanical properties were determined at the age of 7 days, as preliminary studies shown that for heat cured geopolymer concrete, the mechanical properties reach their full strength at this age.

**Table 3.** Alkali-activated geopolymer paving blocks mix-design

Material/Parameter	%				
Fly ash	1.0				
AA/FA	1.0				
NaOH conc.	10M				
Na <sub>2</sub> SiO <sub>3</sub> /NaOH	2.5				
FA / Aggregates	0.5				
S / G	100:0	75:25	50:50	25:75	0:100
Binder / Aggregate	1:2				

**Fig. 4.** Technological production of the alkali-activated geopolymer**Fig. 5.** Alkali activated fly-ash based geopolymer concrete samples with spent garnet used as sand replacement

#### Alkali-activated fly ash-based geopolymer concrete density

The density of the alkali-activated fly ash-based geopolymer concrete produced using spent garnet as aggregate replacement was measured by weighing the samples and relating them to their volume. Initially, the samples were weighed immediately after demoulding, then, at the age of 7 days, they were immersed in water until they reached constant mass (saturated state density). Subsequently, the samples were dried in a drying oven at  $(105 \pm 5)^\circ\text{C}$  to dry state density.

#### Mechanical strength of the alkali-activated fly ash-based geopolymer concrete

Minimum three samples were tested in order to obtain the flexural and compressive strength of the samples. Tests regarding the mechanical properties of the alkali-activated fly ash-based geopolymer samples were conducted according to EN 196-1:2006. This standard is used for the evaluation of mechanical performances of OPC paste and standard type mortar.

### Water absorption of the alkali-activated fly ash-based geopolymer concrete

Total water absorption of the alkali-activated fly ash-based geopolymer concrete has been determined according to the current in force standard. The samples were initially submerged in water, at constant temperature of  $(20 \pm 5)^\circ\text{C}$ , until they reached constant mass. The minimum immersion period of the samples was 3 days until they reached saturated state constant mass and weighed (M1). Subsequently, the samples have been placed in the oven and dried to reach the constant mass at temperature of  $(105 \pm 5)^\circ\text{C}$  (M2). The  $W_a$  (water absorption) of each sample was expressed as a percentage by mass, acc. to the equation (1):

$$W_a = \frac{M1 - M2}{M2} \times 100 \quad [\%] \quad (1)$$

### Alkali-activated fly ash-based geopolymer concrete porosity

The porosity was evaluated by assimilation with standardized methods for characterizing the porosity of concrete. This method allows the determination of this parameter based on the apparent and real density of the material. The porosity of the alkali-activated fly ash-based geopolymer concrete was determined using the pycnometer method. The concrete samples were crushed and a representative amount was collected. The obtained material was placed in the mill and then passed through a 0.02 mm sieve. After sieving, it was dried at constant mass in the oven. The porosity of the samples was calculated by means of apparent density ( $\rho_{ap}$ ) and real density ( $\rho_{real}$ ), using the following equations (2), (3), (4):

$$\rho_{ap} = \frac{m_{dry}}{V_s} \quad (2)$$

where:  $\rho_{ap}$  – apparent density ( $\text{kg}/\text{m}^3$ );  $m_{dry}$  – dry state mass of the sample (kg);  $V_s$  – volume of the sample ( $\text{m}^3$ ).

$$\rho_{real} = \frac{m_1 - m_0}{V - \frac{m_2 - m_1}{\rho_{liq}}} \quad (3)$$

where:  $\rho_{real}$  – real density ( $\text{kg}/\text{m}^3$ );  $m_0$  – mass of the pycnometer (kg);  $m_1$  – mass of the pycnometer filled with sample (kg);  $m_2$  – mass of the pycnometer filled with sample and water (kg);  $V$  – volume of the pycnometer ( $\text{m}^3$ );  $\rho_{liq}$  – density of the liquid filling the pycnometer ( $\text{kg}/\text{m}^3$ ).

$$P = \frac{\rho_{real} - \rho_{ap}}{\rho_{real}} \times 100 \quad (4)$$

where:  $P$  – porosity of the material (%);  $\rho_{real}$  – real density ( $\text{kg}/\text{m}^3$ );  $\rho_{ap}$  – apparent density ( $\text{kg}/\text{m}^3$ ).

## Results and discussions

### Alkali-activated fly ash-based geopolymer concrete density

The results obtained regarding the density of the alkali-activated fly ash-based geopolymer concrete are presented in Fig. 6.

The average values of the results obtained for the density of the alkali-activated fly ash-based geopolymer concrete range from  $1620$  to  $1890 \text{ kg}/\text{m}^3$  in dry state, from  $1780$  to  $2000 \text{ kg}/\text{m}^3$  and from  $1905$  to  $2120 \text{ kg}/\text{m}^3$  in saturated state. It can be seen that as the amount of spent garnet

in the mixture increased, so did the corresponding densities, in accordance with the physical properties of the raw materials.

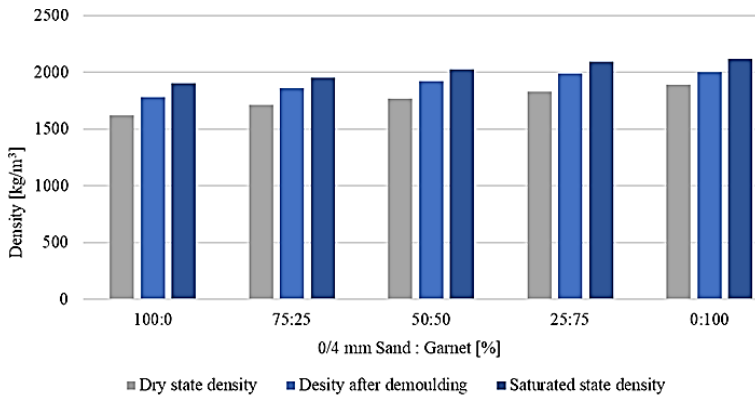


Fig. 6. Alkali-activated fly ash-based geopolymer concrete density

### Mechanical strength of the alkali-activated fly ash-based concrete

The flexural strength and compressive strength of the alkali-activated fly ash-based geopolymer concrete using spent garnet as sand replacement are shown in Fig. 7 and Fig. 8.

From the point of view of the results obtained for the flexural strength, it can be seen in Fig. 7 that it increases as the amount of spent garnet in the mixture increases. An observation can be made about the rate of increase of the tensile strength. When spent garnet was added to the mixture, the tensile strength values increased by 12%. Subsequently, as the amount of spent garnet increased, the increases averaged from 3-5%, up to a maximum of 4.3 N/mm<sup>2</sup>.

In terms of the results obtained for the compressive strength (Fig. 8) the same behavior of the mixtures can be observed. The development of the compressive strength at the time of adding spent garnet in the mixture had an increase of 32%, then as the amount of spent garnet increased, the increases had an average of 9-12%, up to a maximum of 31.9 N/mm<sup>2</sup>, for the alkali-activated fly ash-based geopolymer concrete produced only with spent garnet as aggregate.

Another important factor in the development of mechanical strengths is the particle size of the aggregates. It can be seen that the particle size of spent garnet is smaller than that of 0/4mm sand. A smaller particle size favors the development of mechanical strengths of the materials.

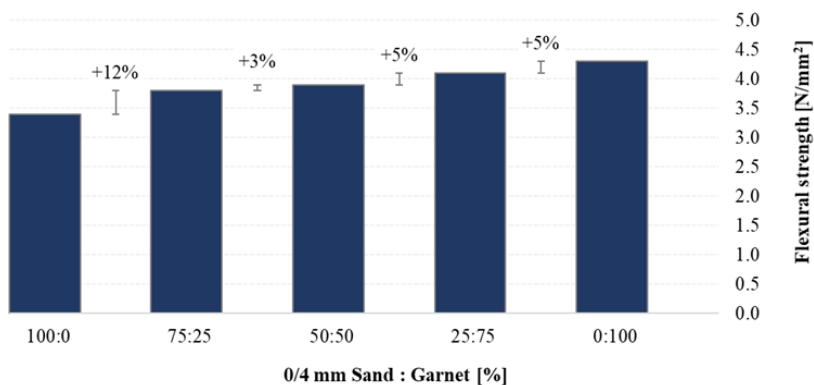


Fig. 7. Alkali-activated fly ash-based geopolymer concrete flexural strength

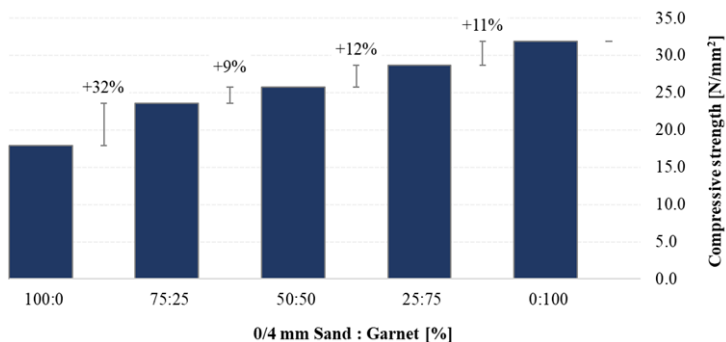


Fig. 8. Alkali-activated fly ash-based geopolymer concrete flexural strength

### Water absorption of the alkali-activated fly ash-based geopolymer concrete

The results obtained regarding the water absorption of the alkali-activated fly ash-based geopolymer concrete are presented in Fig. 9.

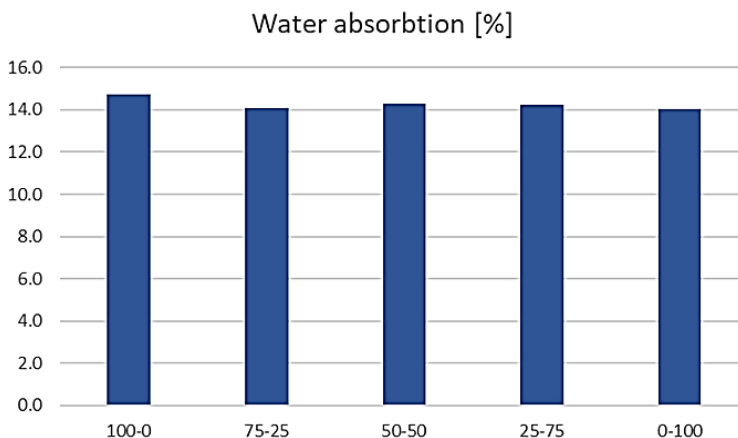


Fig. 9. Alkali-activated fly ash-based geopolymer concrete water absorption

### Alkali-activated fly ash-based geopolymer concrete porosity

Whatever the nature of the primary raw material from which products are produced, the packaging and the architecture of the porous permeable structure, a porous material is considered to consist of two component phases: the solid skeleton (solid matrix) and the intercommunicating pores [20,21]. Open pores, or intercommunicating pores, communicate both with each other and with the outer surfaces of the porous matrix, performing the function of filtering and permeating liquids [22].

The totality of the open pores determines the open intercommunicating porosity of the material. Closed pores do not provide permeability and are not of interest from the point of view of water absorption properties [23]. Results regarding the porosity of the alkali-activated fly ash-based geopolymer concrete with spent garnet replacement for 0/4 mm sand are presented in Fig. 10.

Analyzing Fig. 10, it can be seen that the porosity of the alkali-activated fly ash-based geopolymer concrete decreases as the amount of spent garnet in the mixture increases, from 45.1% to 24.0%. This can be attributed to the increase in the density of the material, as spent garnet is much finer than sand, which leads to a much better filling of the spaces within the geopolymer matrix.



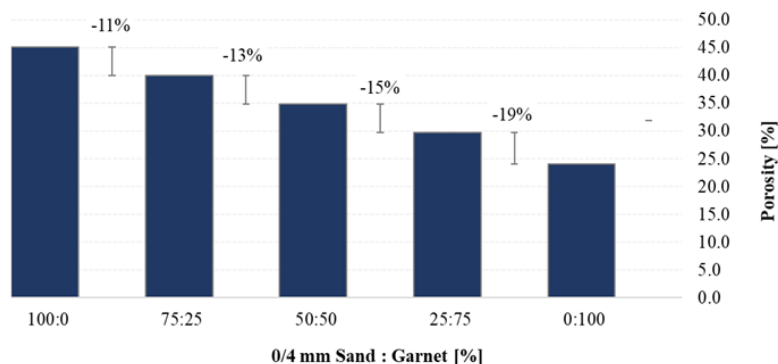


Fig. 10. Alkali-activated fly ash-based geopolymer concrete porosity

Correlating the porosity data with the water absorption data, it can be stated that as the spent garnet content in the mixture increases, the porosity of the material decreases, but the water absorption remains constant. This can be taken as an indirect indicator that as the amount of spent garnet increases, the number of closed pores in the geopolymer matrix decreases. Based on the results obtained it can be stated that the porosity of a material can be directly responsible for the development of its subsequent mechanical properties.

## Conclusions

Research regarding the production of alkali-activated geopolymer materials using Romanian local raw materials could be definitely a possible answer and direction responding to the need of producing and developing greener concrete, therefore adopting the Sustainable Development principles.

Results regarding the use of spent garnet as 0/4 mm sand aggregate substitution has shown the following data:

- As the amount of spent garnet in the mixture increases, the density of the alkali-activated fly ash-based geopolymer concrete increases;
- As the material is denser, the mechanical properties of the alkali-activated fly ash-based geopolymer concrete, both in terms of flexural strength and compressive strength increase;
- By correlating the porosity data with the water absorption data, it can be stated that as the spent garnet content in the mixture increases, the porosity of the material decreases, but the water absorption remains constant, meaning that the geopolymer matrix becomes denser.

Using spent garnet as replacement for sand aggregates opens new perspectives in the production of alkali-activated fly ash-based geopolymer materials, using local raw materials from Romania. Further research focuses on implementing the same principles regarding the production of alkali-activated fly ash-based geopolymer materials, but using spent garnet as replacement for fly ash, in order to study the effects on the production of the material and also, on the physical-mechanical properties.

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