

D.D. BURDUHOS-NERGIS¹, P. VIZUREANU^{1,2*}, D.C. ACHITEI¹,
A.V. SANDU^{1,3}, D.P. BURDUHOS-NERGIS¹, M.M.A.B. ABDULLAH^{4,5}

THE INFLUENCE OF SINTERING TEMPERATURE ON THE MICROSTRUCTURE OF COAL-ASH BASED GEOPOLYMERS

Currently, one of the main challenges of civil engineering and science materials engineers is to develop a sustainable substitute for Ordinary Portland Cement. While the most promising solution is provided by the geopolymerisation technology, most of the studied geopolymers are based on natural raw materials (kaolin). The metakaolin is mainly preferred because of its rapid rate of dissolution in the activator solution, easy control of the Si/Al ratio, and white color. However, its high cost prevents it from being widely used in geopolymer composites or other materials that can become an industrial alternative for Ordinary Portland Cement. Several studies have shown that geopolymers with good performance can also be obtained from secondary raw materials (industrial wastes such as coal ash or slag). This explains why countries with rapidly developing economies are so interested in this technology. These countries have significant amounts of industrial waste and lack a well-developed recycling infrastructure. Therefore, the use of these by-products for geopolymers manufacturing could solve a waste problem while simultaneously lowering virgin raw material consumption. This study evaluates the effect of replacing different amounts of coal ash with sand on the microstructure of sintered geopolymers. Accordingly, scanning electron microscopy and energy dispersive X-ray analysis were involved to highlight the morphological particularities of room-cured and sintered geopolymers.

Keywords: geopolymers; alkali activation; microstructural analysis; sintered structures; high temperature exposure

1. Introduction

Geopolymers are inorganic materials mainly used in the civil construction sector for the manufacturing of precast products [1]. From their chemical point of view, the geopolymers have a three-dimensional aluminosilicate structure activated using suitable alkaline or acid solutions [2]. Considering that almost any materials rich in aluminum and silicone can be used as raw materials, different types of secondary products were identified as suitable for geopolymerisation [3]. However, the researchers are still focusing on the natural material (kaolin) that has chemistry easier to control, compared to the aluminosilicate waste. Moreover, kaolin is an inorganic material that showed incredible properties when activated through geopolymerisation technology. Also, to increase its reactivity and make it even more suitable for in-situ application, kaolin can be subjected to calcination to obtain metakaolin which shows even higher reactivity in an alkaline environment [4].

Besides mechanical properties, the type of raw material will also influence the thermal behavior of geopolymers, during heating up to 900°C, aluminum species will start affecting the structure of geopolymers, while when the temperatures go up to 1200°C the calcium aluminosilicate frame fills the pores between the akermanite crystals [5]. When recycled aluminosilicates are used, the thermal behavior of geopolymers is changed significantly, especially, because this type of raw material contains different amounts of volatile compounds or water in multiple forms [6]. However, recently it was shown that this behavior and the type of compounds created during geopolymerisation can also be affected by the type of the activator [7]. In coal ash-based geopolymers activated with an alkaline solution, Differential Thermal Analysis (DTA) showed seven important reaction points that were related to water evaporation from hygroscopic pores, zeolitic channels, or crystallization compounds [8]. Moreover, when the temperature was increased above 180°C the hydrogel water was removed, while close to 230°C the water loss was

¹ GHEORGHE ASACHI TECHNICAL UNIVERSITY OF IASI, FACULTY OF MATERIALS SCIENCE AND ENGINEERING, D. MANGERON 41, 700050 IASI, ROMANIA

² TECHNICAL SCIENCES ACADEMY OF ROMANIA, DACIA BLVD 26, 030167 BUCHAREST, ROMANIA

³ ROMANIAN INVENTORS FORUM, ST. P. MOVILA 3, 700089 IASI, ROMANIA

⁴ CENTRE OF EXCELLENCE GEOPOLYMER AND GREEN TECHNOLOGY (CEGEOGTECH), UNIVERSITI MALAYSIA PERLIS (UNIMAP), ARAU 02600, PERLIS, MALAYSIA

⁵ UNIVERSITI MALAYSIA PERLIS (UNIMAP), FACULTY OF CHEMICAL ENGINEERING TECHNOLOGY, ARAU 02600, PERLIS, MALAYSIA

* Corresponding author: peviz2002@yahoo.com



associated with the molecules removed from the channels and pores specifically to calcium silicate hydrate (C-S-H), C-S-H with Al in its structure (C-A-S-H), and sodium aluminosilicate hydrate (N-A-S-H) structures. When the temperature exceeds 300°C, different amorphous phases, such as FeO(OH), were decomposed, while at around 500°C the Portlandite decomposition occurs. Between 500°C and 1000°C α -quartz is converted to β -quartz and different aluminum; titanium or zinc hydroxides will decompose. In the case of acid-activated geopolymers, the thermal behavior of the samples is similar in the range of water removal. However, above 300°C the phosphate-based geopolymers seem to be more stable, considering that no significant peak is shown on the DTA curves [6].

The properties of geopolymers could also be affected by the type and addition of aggregates. Aggregates are widely used in civil engineering applications, especially in the manufacture of concrete. Therefore, by increasing the need for both residential and industrial constructions, the demand for aggregates will also increase considering that 60 wt.% to 70 wt.% of concrete is aggregates [9]. The major problem related to aggregate consumption is related to the negative effects on the environment, due to landscape changes [10]. Moreover, since most of the aggregates are non-renewable resources, their increased consumption will accelerate both the environmental effects and the need of finding alternative resources. Accordingly, in the construction sector, different types of lightweight aggregates were identified as suitable substitutes [11,12]. Compared to conventional aggregates, this new class is much more eco-friendly and can contribute to the sustainable development of this sector. Moreover, these materials will also provide different advantages, such as reduced permeability, reduced early cracking, and increased lifespan [13,14]. The lightweight aggregates can be natural or by-products. The natural ones may need further processing (shale, slate, clays etc.) or they can be used as it is (volcanic tuff, limestone, lava foam etc.). However, to preserve the environment only a few places in the world can be considered (only those places where these materials represent a problem to the environment due to their presence). Considering this geographic limitation, the need of finding alternative aggregates was extended to different types of wastes, such as coal ash, blast furnace slag, mine tailings etc. [15,16].

Currently, geopolymers remain the ideal alternative to OPC-based materials for sustainable development [17,18]. Not only because geopolymers have OPC-like performance in many applications, but they also have many additional benefits, including fast curing, high acid resistance, excellent adhesion to aggregates, immobilization of toxic and hazardous materials, and a significant reduction in energy consumption and greenhouse gas emissions (approximately 62%–66% lower than CO₂ emissions for the manufacture of concrete based on equivalent OPC) [19]. However, similar to OPC concrete, geopolymers exhibit brittle behavior with low tensile strength [20]. Moreover, due to the high cost of sodium silicate, their industrial use is significantly reduced. These shortcomings not only impose constraints on structural design but also affect the long-term sustainability of products. To date, numerous studies have been conducted involving the use of steel

or carbon fibers to eliminate these disadvantages of geopolymers. However, although steel or carbon fibers can effectively increase the tensile strength, ductility and hardness of geopolymers, their manufacture involves high energy consumption and very limited recycling possibilities [21]. Thus, the growing awareness of the negative effects on the environment and the need to ensure the sustainability of building materials have led to a high interest in alternative fibers. This explains the high interest in this technology, especially in developing industrialized countries [22]. These countries accumulate large amounts of industrial waste and have not identified a developed recycling route. The use of waste for the production of geopolymers could not only solve an environmental problem but also reduce the consumption of non-renewable raw materials. Construction is one of the most important economic sectors in Europe. In 2019, the total value of construction works was 1.324 billion euros, representing 9.5% of EU27 GDP, according to data from the European Federation of the Construction Industry [23]. The European Federation of the Construction Industry was established in 1905 and brings together 33 national federations from 29 European countries (EU25 + Norway, Switzerland, Ukraine, Turkey). According to the same federations, 3 million companies are active in the field, of which 95% are small and medium-sized companies, and 93% are companies with less than 10 employees. The field covers 6.1% of the total number of employees at the EU27 level (12.7 million employees) and a multiplier effect of 1 to 2 has been identified (each job created in the construction sector generates 2 jobs in another domain), according to the data for 2019 [24].

The European housing stock is made up of 85% of buildings built before 2001 (approximately 220 million units), with an estimated 85 to 95% of which will be up and running by 2050. Most of them have a low level of energy efficiency, the real estate area being responsible for the consumption of 40% of energy in the EU and the production of 36% of greenhouse gases [25].

Romania has one of the highest rates of overcrowding (46.30%) and one of the highest housing shortages (16.10%) [25], which will help maintain high growth rates. In order to improve the situation in the housing market, the Romanian Government has introduced several investment schemes. In terms of innovation, Romania is the country with the lowest level of innovation in the European Union. Although there is an environmentally friendly legislative climate for innovation and research and development and a broadband internet network with capacities above the European average, Romania has few innovative firms, mainly due to low investment and insufficient human resources. In the field of construction, in the period 2010-2017, there was an increase of 556% in spending on innovation and research and development, from 2.9 million euros to 19.2 million euros [26]. Regarding the evolution of the field, it is expected that the construction sector will remain on a positive trajectory based on investments in the field of residential and non-residential buildings, but also civil engineering [25].

Among the principles of EU policy on increasing the energy efficiency of real estate is the rethinking of the life cycle and circularity [27]. Thus, it is desired to adopt policies that promote

The components of the studied samples

Sample code	Mixture component	Activator		Solid component		
		Na ₂ SiO ₃ , wt.%	NaOH, wt.%	Coal ash, wt.%	Glass powder, wt.%	Sand, wt.%
100CA		30	20	50	—	—
70CA_30GP		30	20	35	15	—
30CA_70S		30	20	15	—	35
15CA_15PG_70S		30	20	0.75	0.75	35

droxide solution has been used. The density of Na₂SiO₃ solution was 1.37 g/cm³ and a pH of 11.5, while the molar concentration of NaOH solution was 10M. The activator was prepared 24 h before use to avoid the thermal effect of the NaOH dissolution over the geopolymerisation. The composition of the studied samples is given in TABLE 2.

3. Results and discussions

As can be seen from the microstructural analysis of the 100CA sample, the high temperature converts the inhomogeneous matrix [7] into a highly porous structure that showed a very high

dissolution of the coal ash particles (Fig. 3). Moreover, in terms of chemical homogeneity, the elemental mapping shows a uniform distribution of the elements over the entire surface of the analyzed samples. As can be seen from Fig. 4, all the chemical elements from the raw material and activator are present in the sample after sintering, while the Si, Al and Na show a great distribution.

After replacing 15 wt.% of coal ash with glass microparticles, the microstructure of the sintered geopolymer is significantly changed. Instead of multiple small pores, the 70CA_30PG sample shows multiple large pores, with diameters above 100 μm (Fig. 5). However, at high magnification, the matrix is homogeneous and compact with clear edges and delimitations. Moreover, compared to the sample without glass particles, multiple large

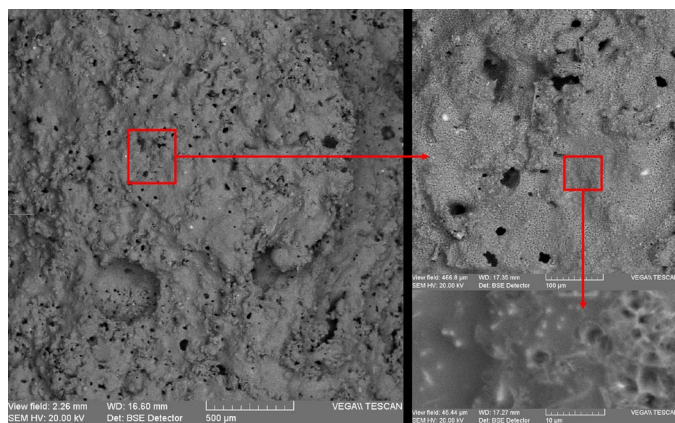


Fig. 3. SEM micrographs of 100CA geopolymer exposed to 1000°C

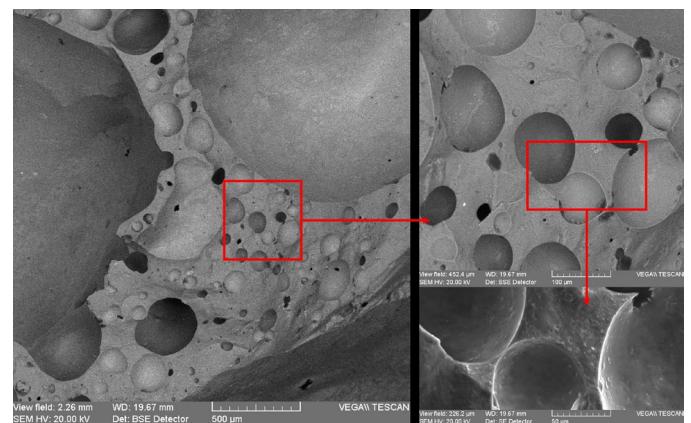


Fig. 5. SEM micrographs of 70CA_30PG geopolymer exposed to 1000°C

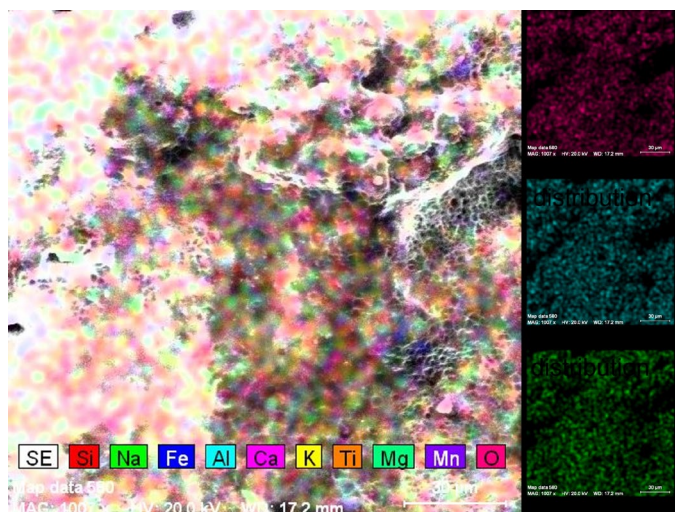


Fig. 4. The chemical elements distribution in 100CA geopolymer exposed to 1000°C

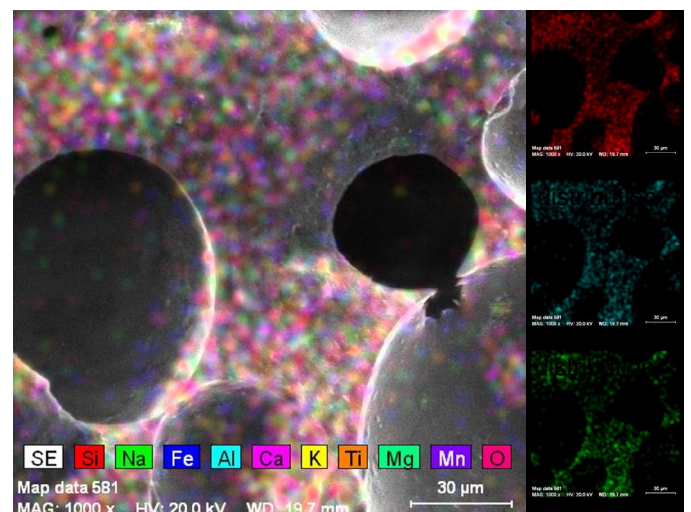


Fig. 6. The chemical elements distribution in 70CA_30PG geopolymer exposed to 1000°C

diameter (>1 mm) pores can be observed in the structure, while the chemical elements are uniformly distributed over the entire surface (Fig. 6).

In the sample with 35 wt.% sand, the sintered microstructure seems to contain small porous zones and large compact areas. As can be seen from Fig. 7, the 30CA_70S sample shows a mixture of aggregates and coal ash matrix. During heating, the matrix was converted to a porous structure, while the sand particle remained compact. Moreover, on the studied surface a zone rich in calcite [8] was observed (Fig. 8). Because the structure of calcite is made of small particles with low adherence to each other, it can be stated that a high content of calcite will result in low mechanical properties. Therefore, the high content of Ca in geopolymers can negatively affect the performances of these materials when exposed to high temperatures.

The geopolymer sample with both sand and glass particles showed the most compact and homogenous matrix. Fig. 9 showed a smooth surface with fewer zones where small size pores can be observed. Considering the effect observed in 70CA_30PG, i.e., glass particle addition will increase pore size, it can be concluded that the porous zones are related to glass particle

presence. However, considering the similarities between the chemical composition, the elemental mapping (Fig. 10) doesn't show a clear correlation between these particles and the pores formation.

4. Conclusions

The microstructural particularities of four types of alkali-activated geopolymers sintered at 1000°C have been studied. Accordingly, it was observed that by exposing a coal ash-based geopolymer to high temperatures, a highly porous matrix will be obtained. However, when glass particles will be introduced as fine aggregates, the pores will increase in size significantly, while the matrix will become crystalline.

In the coal ash-based geopolymers with sand addition, a compact sample was observed even after exposure to 1000°C for 4 hours. Also, in this case, the coal ash matrix was converted to a highly porous structure, while the aggregates keep their structural integrity and provided better performance in terms of high-temperature resistance.

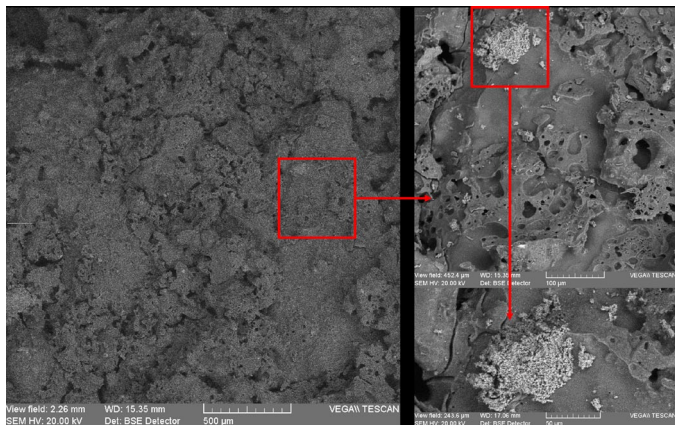


Fig. 7. SEM micrographs of 30CA_70S geopolymer exposed to 1000°C

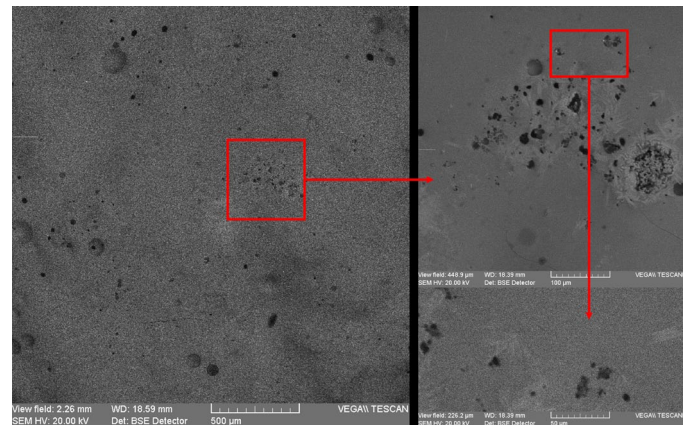


Fig. 9. SEM micrographs of 15CA_15PG_70S geopolymer exposed to 1000°C

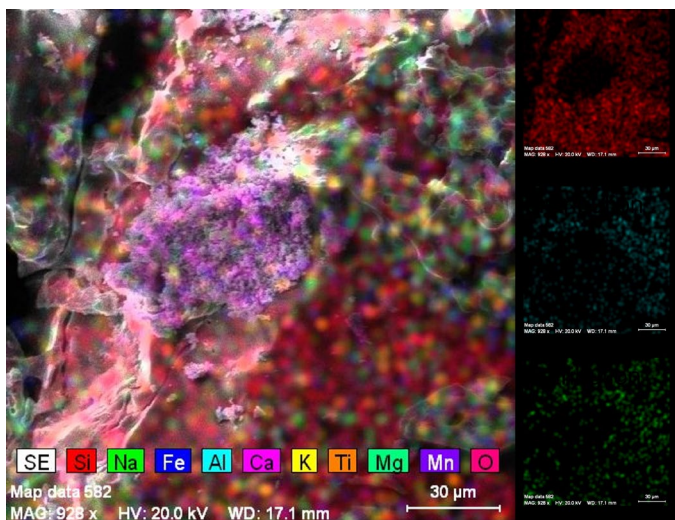


Fig. 8. The chemical elements distribution in 30CA_70S geopolymer exposed to 1000°C

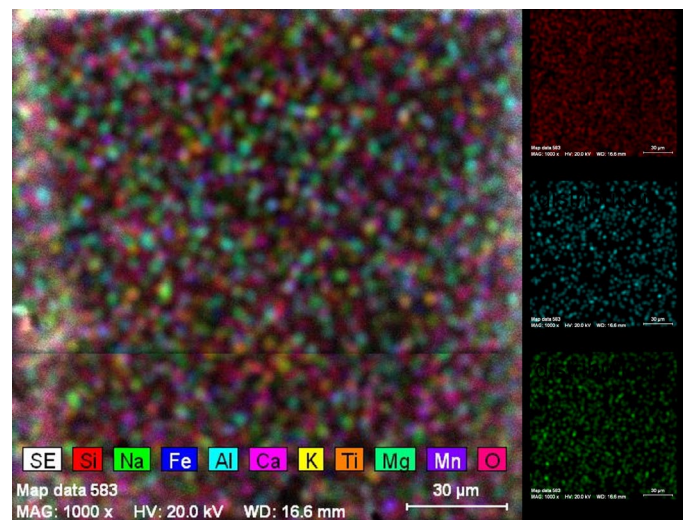


Fig. 10. The chemical elements distribution in 15CA_15PG_70S geopolymer exposed to 1000°C

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