

## PROPERTIES OF GEOPOLYMERS

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**Abstract.** *Especially geopolymers are novel environmental friendly materials, with promises of considerable progress in the near future. These materials, with unique physical, chemical and mechanical properties can be used for many different applications. They are produced by using waste-products from the industry, and turning them into a high value construction material needed for infrastructure developments.*

**Key words:** *Geopolymers, novel materials, ceramics, concrete, fly ash, organic materials, ecological material*

### 1. INTRODUCTION

Geopolymers are materials based on exceptional physical, chemical and mechanical properties, new binder for fiber composites and new cement for concrete. With their exceptional physical characteristics, being fire, heat, acid and corrosion resistant, as well as having high compressive strength, geopolymers are used for many different applications. Some of them are fire resistant and thermal insulation materials, low tech and low energy material such as tiles, cements and concretes [1].

These novel materials are created in inorganic polymeric materials geopolymerisation process, in inorganic polymeric materials geopolymerisation process made from aluminosilicate materials with alkali metal silicates in highly alkaline conditions. The first geopolymer was made in 1978 by Joseph Davidovits, after catastrophic fires happened in France, in 1970s, and consecutive investigations for fire resistant and non-flammable material. Geopolymer as a term was created and applied in 1978 as French "géopolymères", mineral polymers resulting from geochemistry or geosynthesis.

Geopolymers are a class of inorganic polymeric, amorphous materials consisting of alumina, silica, and alkali metal oxides. They are typically synthesized by mixing an

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aluminosilicate source (metakaolin or fly-ash) with silica dissolved in highly caustic alkaline solutions. These materials are inorganic polymers made from dissolution of the aluminosilicate source, polycondensation and precipitation under ambient temperature. Advantages of geopolymers are the usage of cheap waste materials in their production (such as slag, fly ash, various clays and even agricultural wastes), lower CO<sub>2</sub> emission (the low carbon footprint) into the atmosphere during manufacture, ambient temperature production and high compressive and flexural strengths, in particular as compared to cements. All this characteristics are placing them in a category of new eco-friendly materials and also new elements of sustainable architecture [2, 3, 4, 5].

In Figure 1 four different species of concrete are presented: first - PFA Based geopolymer concrete made with pozzolan fly ash, second-Geopolymer concrete based on Kaolinit, third is Ground granulated blast furnace (GGBS) based geopolymer concrete, and fourth is traditional concrete.



**Fig. 1** Range of geopolymer-concrete and ordinary-concrete [6].

## 2. GEOPOLYMERS DEVELOPMENTS

During 1930s and 1940s, sodium and potassium hydroxide were used to test ground slag with added Portland cement in iron blast furnace. This test was made to determine time needed for slag to set. In this kind of test for slag, Belgian scientist Purdon noticed that there was a rapid binder, with short time of hardening. Those types of reactions were used to make alkali-activated slag cements (Trief cements) for large scale construction in the 1950s [7].

During 1960s and 1970s, Victor Glukhovsky, a Ukrainian scientist at the KICE (Kiev Institute of Civil Engineering in the USSR), discovered that sodium alumino-silicate hydrates (zeolites) are created from rocks and clay mineral during alkali treatment. He called these materials soil silicate concretes and soil cements.

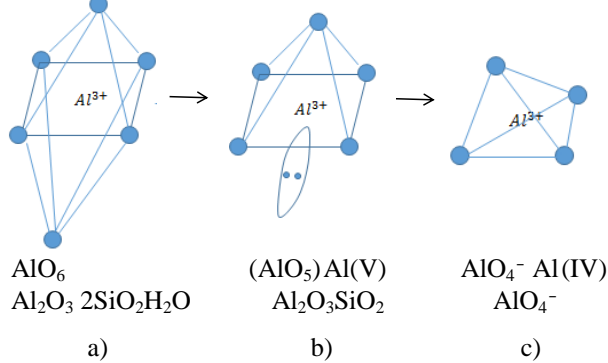
In 1972, at CORDI laboratory in Saint-Quentin a technology based on geosynthesis, natural kaolinite/quartz blended with mixed solid sodium hydroxide and water (Davidovits and Legrand, 1974) was developed. This kind of reaction was set relatively short, in hot pressed-thermosetting process for water evaporation at temperature 130-180°C with applied hydraulic pressure 10 - 30 bars [7]. A large contribution to the development and implementation of geopolymer composites was provided by the extensive research by Prof. Waltraud M. Kriven [8,9,10,11,12].



## 4. CREATION OF GEOPOLYMERS

The geopolymerization reaction occurs with highly strained  $\text{AlO}_5^{2-}$  coordination polyhedra in the amorphous metakaolin which contains a lone pair of electrons and is susceptible to dissolution by the highly caustic sodium metasilicate solution (water glass) of standard composition  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot x11\text{H}_2\text{O}$  [5].

Tetrahedra  $\text{AlO}_4$  which attract charge balancing Group I cations that are formed in the highly alkaline solution of the  $\text{Al}^{3+}$  and then react with  $\text{SiO}_2$  to form an amorphous 3D network (Fig. 3).

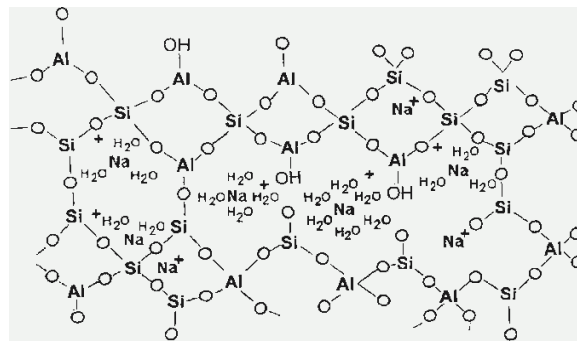


**Fig. 3** a) Crystalline kaolin b) Amorphous metakaolin c) Aluminate tetrahedron [5].

Dehydration of crystalline kaolinite, where the  $\text{Al}^{3+}$  is in 6-fold coordination, comes to dissolution of the aluminosilicate source (e.g. metakaolin on Figure 3. b) and in amorphous metakaolin that make a highly strained 5-fold coordinated  $\text{Al}^{3+}$  [5].

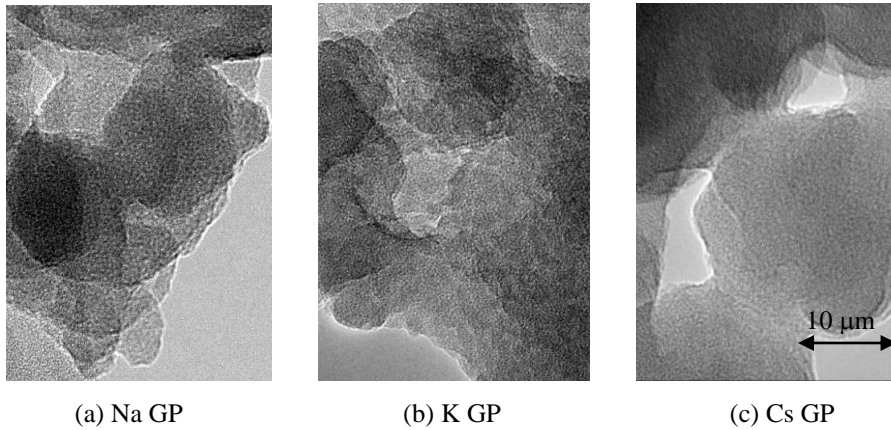
## 5. ATOMIC STRUCTURE AND MICROSTRUCTURE OF GEOPOLYMERS

At room temperature corner-shared tetrahedral units which contain amorphous atomic structure of two compounds (Figure 4),  $\text{SiO}_2$  and  $\text{AlO}_4$  are formed.



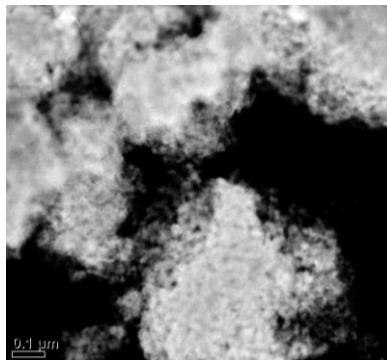
**Fig. 4.** Currently accepted atomic model of geopolymer structure [13].

The geopolymers microstructure can be nanoparticulate (approximately 20-40 nm in diameter) presented in Figure 5, and nanoporous (approximately 6.8 nm in diameter) presented in Figure 6.



**Fig. 5** High resolution transmission electron microscopy (HRTEM) of geopolymers precipitates [5].

It should be noted that the pure geopolymer is impermeable, although it is nanoporous. In the Table 1 is presented Summary properties of Porosimetry of pure geopolymer.

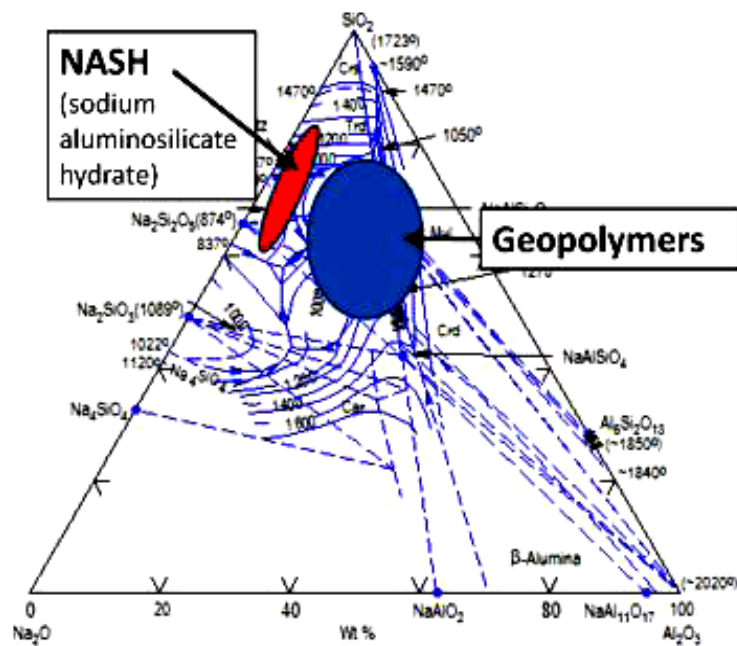


**Fig. 6** High angle annular Dark Field TEM micrograph of KGP showing nanoporosity [5].

There are numerous variants of the geopolymers that refer to alkali-activated aluminosilicates, but which are made from impure forms of aluminosilicate sources in industrial waste products such as slag or fly ash. These compositions tend to lie off the stoichiometric 1:1:4:11 compositions measured by TEM/EDS of metakaolin-derived geopolymers that is presented in Figure 7. As occur in cements, these composites tend to have significantly lower mechanical properties due to the presence of calcium silicate hydrate (C-S-H or N-A-S-H) binder phases [5].

**Table 1.** Porosimetry of pure K-GP measured by Porotech, Inc. [5].

Average logarithmic pore radius	0.4362 nm
Average pore radius	3.3711 nm
Porosity over weight	0.3165 cm <sup>3</sup> /g
Porosity over volume	0.4106 cm <sup>3</sup> /cm <sup>3</sup>
Meso- and macro-pore surface over weight	190.5778 m <sup>2</sup> /g
Meso- and macro-pore surface over volume	247.2794 m <sup>2</sup> /cm <sup>3</sup>
Total pore surface over weight	274.6912 m <sup>2</sup> /g
Total pore surface over volume	356.4186 m <sup>2</sup> /cm <sup>3</sup>
Density of solid phase	2.0481 g/cm <sup>3</sup>

**Fig. 7** Schematic comparison of alkali activated cements compounds such as sodium aluminosilicate hydrate (NASH) and stoichiometric geopolymers [5].

## 6. TYPES OF GEOPOLYMERS

### 6.1. Phosphate-based geopolymer

Phosphate-based geopolymers in short period of time became conventional polymers. They contain naturally occurring mineral phases, and they are synthesized at room temperature and set rapidly. They represent variety of mineral geopolymer, formed by an acid-base reaction between a metal oxide and an acid phosphate, where Si is totally or

partially replaced by phosphorus. Any divalent or trivalent oxide that is diffuent may be used to form phosphate geopolymers [7].

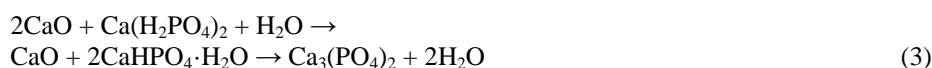
The main difference between phosphate geopolymers and polysilicate polymers is in their synthesis, because phosphate geopolymers are fabricated by acid-base reactions.

Applications of those polymers are in wide range of construction materials, oil and cements, dental cements, even radioactive waste stabilization.

### 6.1.1. Phosphate geopolymers

Phosphate geopolymers are synthesized in acid-base reaction between an acid phosphate and an inorganic oxide (divalent and trivalent metals). The reaction product is an anhydrous poly (phosphate) or a poly (hydrophosphate) that consolidates into a ceramic [7].

The following are the most common examples



If the rate of this reaction is controlled, ceramics can be formed even at room temperature. Ceramics also can be formed in reaction with trivalent oxides, but only at higher temperature [14].

An example is berlinite ( $\text{AlPO}_4$ ), formed by the reaction between alumina and phosphoric acid:



## 6.2. Organo-mineral geopolymers

### 6.2.1. Silicone

The siloxane (Si-O-Si) structure in organo-silicones is similar to the chains, rings, and networks of silicon and oxygen found in silica and the silicate minerals, for example in quartz. In the 1960s, studies shown that it is possible to pass from the polymeric silicate to the polymeric covalent molecules of an organosiloxane by replacing the bridging oxide ions of the silicate anions with methyl groups. The result of structures in this replacement are the silicate and aluminosilicate molecules: monomers, dimers, trimers, rings, chains, sheets and frameworks of corner-sharing silicate [ $\text{SiO}_4$ ] groups [7].

### 6.2.2. Hybrid organo-mineral geopolymers

By incorporating the geopolymer into the organic polymer structure and adapting the chemical composition of the components, the new class of compounds was obtained.

The resulting hybrid material has improved fire resistance and excellent mechanical properties. The new developments are focusing on improving the mechanical and physical properties of the geopolymer itself, because a homogeneous mixture without phase separation requires a new approach in studies [7].

### 6.2.3. Kerogen geopolymer (*Humic-acid based*)

Kerogen-geopolymer is the final alternating product in Earth and the most stable material within all geopolymeric materials. Some geopolymeric materials due to their unique geopolymeric structure can last for a long time [7].

Geopolymers are the materials which can be classified into two major groups: organic containing geopolymers and pure inorganic geopolymers. The key parameter in the strength and durability of material with a large volume of inorganics is the small content of organics. Unique geopolymer that contains a high content of organics is the kerogen. Kerogen geopolymers occur in numerous forms: with more or less organics and opposite. It is evident that both inorganics and organics are required in a mix at a certain ratio, which will result in a geopolymeric structure.

It is the most abundant form of organic carbon on Earth, about 1000 times more abundant than coal, which forms primarily from terrigenous remains of higher plants. This geopolymeric structure is similar to human bone and teeth, typical inorganic-organic composites that show extreme durability and mechanical strength [6].

## 7. PROPERTIES OF GEOPOLYMERS

The physical, chemical and mechanical properties of geopolymeric materials indicate that they offer a wide range of industrial applications, although the formation of geopolymers is not still completely understood. The Si/Al molar ratio and curing, setting and hardening conditions in the geopolymeric structures determines the properties and the application fields of geopolymers [1].

Geopolymers are fire resistant up to 1400°C, heat resistant, and acid resistant materials. Also, they exhibit high early compressive strength, important fracture toughness, long-term durability, low apparent porosity or nano-porosity and freeze-thaw resistance.

Geopolymeric cements and concretes present ideal mechanical properties in comparing to Portland cement. Their compressive and tensile strengths are twice to three times bigger and the Moh's hardness ranges from 4 to 7.

Geopolymers are introduced into the construction materials and road building industrial sectors. Regarding their properties, geopolymers have a wide range of important industrial uses as pure, with fillers or reinforced materials [1].

In order to improve their mechanical properties, such as flexure, tension, shear and flexural fatigue at high temperatures, geopolymers are reinforced by different types of fabrics (carbon, glass, minerals or steel) to produce binders for advanced composite materials. Fiber reinforced geopolymeric binders and concretes are used as fire safety advanced materials into the transportation (air, sea, rail, car, etc.), nuclear and pharmaceutical industrial areas.

## 8. APPLICATION OF GEOPOLYMERS

Composite geopolymers are used for the production of electronic devices, moulds for thermoplastic material and metals casting, cutting tools, containers for hazardous chemicals and radioactive wastes, components for high performance engines, lightweight materials and prototype automobile components [1].



For construction applications all new materials must meet a set of high standards and procedures which is extremely expensive and time-consuming for manufacturers. Beside the lack of knowledge, especially on the long term behaviour of geopolymers, an important reason for the slow development of markets for geopolymers is a conservative view of new materials. However, a geopolymer industry is developing and an increasing number of geopolymer supplier companies are established based on research activities in universities and research institutes. Although there is no firm data on the market size, geopolymer concrete is now used in the transport sector in the USA and more recently in Australia. The short setting time of geopolymer cement makes it an ideal solution for repairing highways and airport runways [15].

Figure 8 shows the example of construction Queensland's University GCI building in Australia made from geopolymer concrete. It has 3 suspended floors built from structural slag/fly ash-based geopolymer concrete. This geopolymeric concrete has been branded by Australian architect Wagner and it is named as Earth Friendly Concrete (EFC) [16]. Three floors in this building were made from 33 structural pieces of floor construction. In Figure 9 is presented one of the structural floor panel made from geopolymer concrete (EFC) [17].

Recently, geopolymers are examined as potential technological solutions for the management of toxic and radioactive waste materials. Selecting an Al-Si material allowing acceptable levels of mechanical properties to be obtained is the key to produce cheaper geopolymer concretes. Production of cheaper concrete can be done by using low concentrations of alkali atoms and silicate units. The effect of carbon taxes on the cement and concrete industry also will help the geopolymer industry to enhance its competitiveness with Portland cements [18].

Another promising application of geopolymers is advanced fire resistant geopolymer composites. Geopolymers reinforced with carbon or glass fibres exhibit extraordinary mechanical properties. At elevated temperatures geopolymers are ideal materials for aerospace applications. In 1994, a geopolymer matrix composite was successfully used in a Formula 1 racing car by replacing titanium parts in exhaust system with geopolymeric composite. Subsequently these composites have been widely adopted in racing cars where their thermal properties are effective. Carbon fibre reinforced geopolymer composites do not burn or release any smoke after exposure to severe heat flux, which makes them appropriate materials for aircraft cabin fire protection, substituting for ordinary polymer matrix composites. The US Air Force now uses bombers equipped with geopolymer composites as fire resistant materials [15].



**Fig. 8** Queensland's University building [16]. **Fig. 9** Construction of floor [17].

It should be noted that several advantages of geopolymers are related to the following.

- (1) The low cost production, considering that they are based on alumino-silicate materials, which both occur naturally in abundance on the Earth as clay minerals and derive from industrial wastes as fly ash, blast-furnace slag [18].
- (2) The energy-effectiveness of the production procedure since geopolymers are cured and hardened at relatively low temperature. The energy consumed for geopolymeric tiles fabrication is less than 16% of that of conventional ceramic bodies.
- (3) The environmental contribution provided that:
  - (a) a number of waste materials can be transferred into added value innovative products.
  - (b) greenhouse gas emissions are essentially reduced during geopolymeric materials production (the geopolymeric cement manufacture emits 80% less CO<sub>2</sub> than that of Portland cement).
  - (c) geopolymeric composites can be utilized for safe stabilization and immobilization of radioactive and toxic wastes [1].

## 9. CONCLUSION

A brief history of geopolymers and highlights of research activities in this area have been presented. Geopolymer technology has a history of a more than half a century. Desirable properties, abundant raw materials and successful applications of geopolymers promise considerable progress in large scale production of geopolymers in the near future.

In the last two decades, considerable research has been carried out through the world, providing a large volume of useful data and important findings on geopolymerisation and the properties of geopolymers.

Geopolymer concrete offers environmental protection by means of upcycling low-calcium fly ash and blast furnace slag, waste-products from the industries, into a highvalue construction material needed for infrastructure developments.

A large contribution to the development and implementation of geopolymer composites has been provided by the extensive research by Prof. Waltraud M. Kriven [10,11,12].

Geopolymer concrete has excellent compressive strength and is suitable for structural applications. The main factors that influence the properties of the fresh concrete and the hardened concrete have been identified. Simple guidelines for the design of mixture proportions are included. The elastic properties of hardened geopolymer concrete and the behavior and strength of reinforced geopolymer concrete structural members are similar to those in the Portland cement concrete. Fly ash-based geopolymer concrete also shows excellent resistance to sulfate attack and fire, good acid resistance, undergoes low creep, and suffers very little drying shrinkage.

A lack of information on some aspects of geopolymerisation is apparent and the incoming researches should focus on these gaps. Despite the current status and wide acceptance of Portland cement, the desirable properties of geopolymers, their environmental benefits, suggest that geopolymer technology should make significant progress in the near future.

It is very important to evolve the knowledge on this topic, considering there are a lot of possibilities of applying these novel materials in our area, further exploration of geopolymer usage is important. Also, it should be very useful to explore the possibilities for applying geopolymers in our region. One of the aspects of geopolymer research can be focused on the fractal analysis of geopolymer microstructure, which would significantly contribute to understanding and analysis of these new materials' properties.[19,20,21].

#### REFERENCES

1. Dimitrios Panias, Ioanna Giannopoulou, "Geopolymers: a new generation of inorganic polymeric novel materials", National Technical University of Athens, Proc. of 1<sup>st</sup> International Conference on Advances in Mineral Resources Management and Environmental Geotechnology, AMIREG 2004, June 2004, pp.407-412
2. Zoran Grdić, Gordana Topličić-Ćurčić, "Ekološki materijali – komponenta održive arhitekture", Zbornik radova Građevinskog fakulteta u Nišu, br. 25, pp. 87-94, Niš, 2010.
3. Gordana Topličić-Ćurčić, Zoran Grdić, Nenad Ristić, Iva Despotović, "Environmental building materials and their application in civil engineering", International symposium about research and application of modern achievements in civil engineering in the field of materials and structures, DIMKS, XXV Kongres, Tara, 20 – 21. oktobar 2011, pp. 487 – 495.
4. Gordana Topličić-Ćurčić, Dušan Grdić, Nenad Ristić, Zoran Grdić, "Ceramic facade cladding as an element of sustainable development", Facta Universitatis, Series: Architecture and Civil Engineering vol. 13, no 3, 2015, pp. 219 – 231,
5. Waltraud M. Kriven, "For NSF proposal with Ange", private conversation, December 2015
6. <http://blogs.qub.ac.uk/geopolymer/geopolymer-background/>
7. Joseph Davidovits, "Geopolymer Chemistry & Applications", Institut Géopolymère, November 2015
8. "Intrinsic Microstructure of Geopolymers and Geopolymer-based Materials," W. M. Kriven, J. Bell, M. Gordon and Gianguo Wen, in "Geopolymer, Green Chemistry and Sustainable Development Solutions," edited by Joseph Davidovits. Proc. World Congress Geopolymer, 2005, St. Quentin, France. Published by the Geopolymer Institute, St. Quentin, France, pp 179-183 (2005)
9. S.S. Musil, W.M. Kriven, "In Situ Mechanical Properties of Chamotte Particulate Reinforced, Potassium Geopolymer," J. Am. Cer. Soc., 97(3) 907-915 (2014)
10. Daniel R. Ribeiro, Waltraud M. Kriven, "Properties of Geopolymer Composites Reinforced with Basalt Chopped Strand Mat or Woven Fabric," J. Am. Ceram. Soc., 99 [4] 1192-1199 (2015)
11. Brayden E. Glad, Waltraud M. Kriven, "Highly Porous Geopolymers Through Templating and Surface Interactions," J. Am. Ceram. Soc. 98 [7] 2052-2059 (2015)
12. Ruy A. Sa Ribeiro, Marilene G. Sa Ribeiro, Kaushik Sankar, Waltraud M. Kriven, Potassium-based Geopolymer Reinforced with Bamboo Fibers," J. Am. Ceram. Soc., 100 [1] 49-55 (2017)
13. Joseph Davidovits, "Geopolymers-Inorganic polymeric new material, Reprint of Journal of Thermal Analyses (1991)", Institut Géopolymère, 1997
14. A.S. Wagh, and S.Y. Jeong, "Chemically Bonded Phosphate Ceramics: I. A Dissolution Model of Formation", J. Ceramic Society, 2003
15. Behzad Majidi, "Geopolymer Technology, from Fundamentals to Advanced Applications: A Review", Materials Technology, vol. 24, no.2, pp. 79-87 June 2009
16. <https://www.geopolymer.org/news/worlds-first-public-building-with-structural-geopolymer-concrete/>
17. <http://www.architectureanddesign.com.au/awards-1/2013-awards-finalists/innovation-of-the-year/suspended-geopolymer-concrete-floor-panels>
18. Vijaya Rangan, "Geopolymer concrete for environmental protection", The Indian Concrete Journal April 2014
19. Vojislav V. Mitica, Vesna Paunovica, Ljubisa Kocic, Fractal approach to BaTiO<sub>3</sub>-ceramics micro-impedances, Ceramics International, Ceramics International 41 (2015) 6566–6574
20. V.V. Mitić, Lj. Kocić, V. Paunović, F. Bastić, D. Sirmić, The Fractal Nature Materials Microstructure Influence on Electrochemical Energy Sources, Science of Sintering, 47(2015) 195-204
21. A. Terzić, V. V. Mitić, Lj. Kocić, Z. Radojević, S. Pašalić, Mechanical Properties and Microstructure Fractal Analysis of Refractory Bauxite Concrete, Science of Sintering, 47 (2015) 331-346.

## **SVOJSTVA GEOPOLIMERA**

*Geopolimeri su novi ekološki materijali, koji imaju potencijala za veliki napredak u bliskoj budućnosti. Ovi materijali, sa jedinstvenim fizičkim, hemijskim i mehaničkim svojstvima mogu biti iskorišćeni na mnogo načina. Proizvedeni su korišćenjem industrijskih otpadnih materijala, a mogu se pretvoriti u visoko kvalitetne konstruktivne materijale potrebne za razvoj infrastrukture.*

**Ključne reči:** *geopolimeri, novi materijali, keramika, beton, leteći pepeo, organiski materijali, ekološki materijali*