

# PROCESSING AND PROPERTIES OF GEOPOLYMERS AS THERMAL INSULATING MATERIALS: A REVIEW

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**Abstract.** Geopolymers are inorganic polymers with 3D framework structures that exhibit superior mechanical and physical properties including high early strength, low shrinkage, good thermal resistance and good chemical resistance. The global warming scenario increased demands for the heat insulator material especially in the construction sector. Traditionally, ordinary Portland cement (OPC) has been used as the binder for concrete. However, the OPC has less resistance to thermal exposure. Therefore, development of other or alternative binders that can withstand the thermal exposure is considered vital in order to produce better thermal insulation material. Based on previous research, geopolymer offers good resistance to corrosion, abrasion and heat. Fly ash, metakaolin, kaolin, and slag are commonly used raw materials for the preparation of geopolymer composites. This geopolymer material also offers an innovative and sustainable solution for maintaining infrastructure. This paper summarizes review on the geopolymer processing and along with the potential of geopolymer composites for thermal insulating applications. This review includes geopolymer fundamentals and technology structure, geopolymerization mechanism, raw materials and preparation, and thermal performance of geopolymers.

## 1. INTRODUCTION

Due to the global warming scenario, demands for the material that can insulate heat are vital especially in the construction sector. Traditionally, ordinary Portland cement (OPC) has been used as the binder for concrete [1]. However, the OPC exhibits high thermal transmission. The development of heat insulation coatings are new energy-saving materials in recent years [2-4]. Cekon *et al.* [2] found that coatings of hollow microspheres with geopolymer paste can contribute to the thermodynamic performance up to 5% in daytime. Another study by Guo *et al.* [5] found that the heat reflective insulation coating made from geopolymer materials could re-

duce the exterior wall surface temperature effectively. The insulation coatings painted onto the building's exterior wall can effectively reduce the temperatures at the surface and within the building and thus protect the building, which obviously can reduce the energy absorption of a building's exterior wall, roof, and indoor area [6]. However, the currently available heat insulation coatings are organic binder coating so that they are easy aged under ultraviolet [7]. Therefore, development of other or alternative binders that resist heat transfer is considered vital in order to produce better thermal insulation material. Recently discovered geopolymers are materials that are produced by alkali activation of aluminosilicate raw materials, which transformed

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into reaction product by geopolymerization in a high pH environment and hydrothermal conditions at relatively low temperatures (which up to 120 °C). Considering the fact that the organic thermal insulation materials widely used today are flammable and the inorganic thermal insulation materials need complex processing conditions and high sintering temperature, which is high in manufacturing cost, the geopolymer material has good application potential as thermal insulation material in some situations [8]. Due to the low energy requirements of production from common raw materials and their inflammability at high temperatures, these compounds (geopolymer) are attracting increasing interest as ecologically friendly fireproof building materials, sound and heat insulators and materials for encapsulating hazardous wastes for storage or disposal [9,10].

Geopolymers are class of binder materials that are formed by the activation of aluminosilicate materials with alkaline or alkaline-silicate solutions and it was first named and introduced by Davidovits [11]. Geopolymers which are also known as inorganic polymers or alkali-activated binder have rapidly gained worldwide interests [12]. Geopolymer is considered as the third generation cement after lime and OPC. The term “geopolymer” is generally used to describe an amorphous alkali aluminosilicate. Other terms to describe geopolymers include “alkali-activated cements”, “geocements”, “alkali-bonded ceramics”, and “hydroceramics”. Although there is variety of nomenclature, all these terms describe materials synthesized utilizing the same chemistry. It essentially consists of a repeating unit of silicate monomer ( $-\text{Si}-\text{O}-\text{Al}-\text{O}-$ ) [13,14]. Geopolymers are amorphous to semi-crystalline three-dimensional silica-aluminate materials. They are prepared by mixing and activating the aluminosilicate sources such as fly ash, metal slag, kaolin or metakaolin with alkaline liquid (sodium hydroxide and/or sodium silicate) and curing at a moderate temperature [15]. Geopolymers are classified as one of the green materials that contain many exceptional properties such as high compressive strength, low shrinkage, and excellent fire and acid resistant [16].

In the 1950s, it is believed that Victor Glukhovsky was the first researcher attempting the modeling of the geological process of zeolite formation [17,18]. It was synthesized by alkali activation of aluminosilicates that normally present in industrial materials or wastes and some of them occur from natural sources [19]. These novel binders were initially known as ‘soil silicates’ [17]. Some researcher believes

that geopolymer compounds are the final and stable phase [20]. This is in agreement with the investigations on ancient Roman cements that have indicated the presence of amorphous compounds in it [21,22].

The outstanding performance and durability of ancient Roman cements and outcome of Glukhovsky’s research created interest in the potential to produce a new cementitious material that is high in strength and more durable. Later, Russian research during the 1980’s resulted in a better understanding of the setting reactions of alkali-activated slag cement and the hardening process which was found to be more complex than that proposed by Purdon [16]. The most comprehensive and successful research in this field was conducted by Davidovits [23] and applied the term ‘geopolymer’ to these alkali activated aluminosilicates.

The need for environmentally friendly construction materials (especially in the structure of the building and wall that insulate heat) to sustain the development is a critical environmental issue at this era in the construction industry. The production of concrete in industry is said to be one of the contributors of the global warming. This fact is due to the widely use of Portland cement as the main component in the production that said to be responsible for about 6% of the CO<sub>2</sub> emission worldwide [24]. Using geopolymer materials as concrete are able to offer comparable performance to the traditional cementitious binders in a wide range of applications, but with the extra advantage of lower greenhouse emissions [25-27]. Geopolymer technology is also attracting increasing attention because it provides viable economical alternative to organic polymers and inorganic cements in diverse applications, such as refractory adhesives and fire-proof [28]. The concern is also due to their excellent mechanical strength, adhesive behavior, long-term durability and exceptionally high thermal and chemical stability [29]. Thus, due to these excellent properties, geopolymers can be potentially thermal insulating materials that help conservation of energy and reduce the CO<sub>2</sub> footprints. Previous investigations by Davidovits [30], Barbosa and MacKenzie [31, 32] reported very good heat resistant properties of materials prepared using geopolymer, having thermal stability up to 1200–1400 °C.

In contrast to organic exterior wall coatings, geopolymer-based coatings have anti-ultraviolet and anti-aging capability [33-35]. It makes the geopolymer more suitable for fabricating inorganic exterior wall building coatings. In addition, a heat insulative paint, including pigments and fillers, was added to the film forming material and had an im-

**Table 1.** Chemical composition of fly ash, data from [42].

Composition	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>
Wt.%	55.3	25.8	5.5	2.9	0.8	0.3

**Table 2.** Chemical composition of rice husk ash, data from [43].

Composition	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO
Wt.%	0.45	89.34	2.58	0.90	4.98	0.76	0.40	0.49

portant effect on the heat insulation coating performance [36,37].

In this paper, the geopolymer processing, thermal properties and the suitability of geopolymers as thermal insulator are reviewed.

## 2. RAW MATERIALS FOR GEOPOLYMER FORMATION

### 2.1. Waste material

#### 2.1.1. Fly ash

Fly ash which is also known as flue-ash, is one of the residues generated in combustion, and comprises fine particles that rise with the flue gases [38]. Fly ash is normally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys of coal-fired power plants. Fly ash, together with bottom ash removed from the bottom of the furnace is in this case jointly known as coal ash [39]. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ashes contain substantial amounts of silicon dioxide (SiO<sub>2</sub>) (both amorphous and crystalline), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) and calcium oxide (CaO) [40]. Table 1 shows the chemical composition of fly ash. It is observed that fly ash consists mainly of silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) (more than 80%), which make it suitable to be the raw materials for geopolymer formation.

Omar *et al.* [41] in their studied on effects of elevated temperatures on the thermal behavior and mechanical performance of fly ash geopolymer stated that the use of fly ash geopolymeric structure along with the incorporation of lightweight aggregates enhances the mechanical and microstructural properties of the geopolymers at elevated temperatures. This study also found that fly ash geopolymer exhibits low thermal conductivity which leads to better thermal insulation. This was also

attributed to the low thermal conductivity characteristics of the lightweight aggregate which inhibits the heat diffusion through the structure.

#### 2.1.2. Rice husk ash

Rice husk ash (RHA) is originated from waste produced by burning rice husk primarily for the generation of electricity, a type of sustainable biomass energy. It is another pozzolanic material obtained from the combustion process of rice husk [43]. Rice husk which is the hard protective shell of rice grains is an agricultural by-product of rice mills [44]. The growing environmental concerns and need for energy from renewable biomass have led to a useful and economical solution which burning rice husk for electricity generation with zero net carbon output to the atmosphere. After burn process, the residual ash is known as rice husk ash (RHA).

The main component of the ash is silica (which consists of 90–95 wt.%). It exist predominantly in amorphous and partly in crystalline phases (although the duration and temperature of burning affect the ratio of amorphous to crystalline phases of silica), with remaining carbon as the major impurity and other trace elements such as K and Ca [45]. In general, after organic constituents of the rice husk are being burnt off, RHA consists of highly porous particles, leading to a low bulk unit weight and a very high external surface area [46]. The amorphous silica is found reactive and suitable to be used as a pozzolana. RHA has been successfully used in concrete for reduced permeability and enhanced sulfate resistance [44,47]. In addition, it has also been used to partially replace fly ash to regulate the Si/Al ratio in geopolymers [48]. Table 2 shows the chemical composition of rice husk ash. He *et al.* [49] studied the synthesis and characterization of red mud and rice husk ash based geopolymer composites. The study found that rice husk ash based geopolymer obtained good strength and have po-

**Table 3.** Chemical composition of kaolin, data from [54].

Chemical composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	ZrO <sub>2</sub>	K <sub>2</sub> O	MnO <sub>2</sub>	LOI
wt. (%)	54.0	31.7	4.89	1.41	0.10	6.05	0.11	1.74

**Table 4.** Composition of metakaolin geopolymer mixtures, data from [33].

Samples	Sodium silicate, wt.%	Metakaolin, wt.%	Sodium hydroxide pallet, wt.%	Water, wt.%
MK1	70.24	28.43	0.89	0.42
MK2	67.64	27.38	0.86	4.09
MK3	64.56	26.13	0.82	8.47

tential to use as construction material. It also stated that the rice husk ash show acceptable resistance towards thermal exposure [49, 50].

## 2.2. Natural resource

### 2.2.1. Clay

Kaolin is a clay mineral that conventionally has been used in the manufacture of porcelain. Kaolinite is the mineralogical term that applies and refers to kaolin clays [51]. Kaolin is a naturally occurring material composed primarily from fine-grained minerals and also the most abundant mineral found in the earth [52]. Kaolin basically is composed of alumina, silica, and water in variable combinations. It has the huge potential to replace the conventional OPC materials due to its unique properties and chemistry for producing environmentally friendly composites. Kaolinite is formed by rock weathering process and the process of kaolin formation is called kaolinization. It is white, greyish-white, or has slightly colored. The main constituent, kaolinite, is a hydrous aluminum silicate of the approximate composition  $2\text{H}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$  [53]. Table 3 shows the chemical composition of kaolin. As refer to Table 3, kaolin composed mainly of silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) (more than 85%), which make kaolin suitable to be the raw materials for geopolymer formation [54].

Jaarsveld *et al.* [55] study the effect of composition and temperature on the properties of fly ash and kaolinite based geopolymers. This study found that kaolin based geopolymer can withstand the temperature from 50 °C to 90 °C for long time without significantly affect the crystalline part of the geopolymer sample. It shows that the exposure of the geopolymer certain high temperature does not affects the structure of geopolymer. These prove that

geopolymer material can withstand temperature and able to insulate the thermal transmission.

Metakaolin (MK) is prepared from kaolin clay. According to Temuujin *et al.* [33], metakaolin is obtained by calcining kaolin at temperature 750 °C for 24 hours. The main reason metakaolin is suitable to be used as raw material for forming geopolymers is because it contains alumina and silica composition in it [56]. It is also common industrial mineral which can be obtained in a large quantity with homogeneous properties. Metakaolin is also environmentally friendly compared to OPC because its production requires much lower calcining temperature and emits 80–90% less CO<sub>2</sub> than OPC [57]. Temuujin *et al.* [36] reported that Si:Al ratio of 2.5 and Na:Al of 1.0 are the optimum composition to produce metakaolin-based geopolymers. Table 4 shows one of the design compositions to form metakaolin geopolymer mixtures [33].

Temuujin [58], used metakaolin in his study on the preparation and thermal properties of fire resistant metakaolin based geopolymer type for coatings. This study found that the metakaolin geopolymer coating samples showed up to 3% thermal expansion after heating to 800 °C. However, the geopolymer coatings also maintained high structural integrity with steel substrates when subjected to a heat treatment by a gas torch and formulations calcined at 1000 °C for 1 hour.

## 3. ALKALINE SOLUTION

Alkaline solution is one of important parts in producing geopolymer. The main criteria for developing stable geopolymer are that the source materials must be highly amorphous and possess sufficient reactive glassy content, low water demand and be able to release aluminum easily. The alkaline activators such as sodium hydroxide (NaOH), potas-

sium hydroxide (KOH), sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and potassium silicate ( $\text{K}_2\text{SiO}_3$ ) are used to activate aluminosilicate materials. Geopolymer is synthesized by mixing the aluminosilicate-reactive material (raw material) with strong alkaline solutions [13,59]. Alkaline activating solution is very important for dissolving of Si and Al atoms to form geopolymer precursors and finally alumino-silicate material. The selection of different activators for aluminosilicate dissolution and its solidification into tetrahedral geopolymeric cementation structure is very important. In most cases, the alkaline reaction of aluminosilicates leads to formation of zeolite which is not a part of the cementation phase. Thus combination of different anionic group activator with alkaline chemicals is quite important to build stable tetrahedral structure of alumino-silicate phases for development of strength [60].

The most commonly used alkaline activators are NaOH and  $\text{Na}_2\text{SiO}_3$ . Compared to NaOH, KOH produced a greater level of alkalinity. But in reality, it has been found that NaOH possesses greater capacity to liberate silicate and aluminate monomers [61]. The potassium based alkaline solutions are usually very costly and are not suitable for economic viability for the production of geopolymer materials. The sodium based alkaline solutions are preferred and in such cases the formation of geopolymer matrix is also depended on its curing temperature. The curing of the product above normal atmospheric temperature is not a flexible option to adopt in commercial practice. Therefore, selection of proper chemicals with alkaline group for geopolymerization reaction at atmospheric temperature has been the focus of research [62]. Usually this alkaline activator is prepared by mixing water, sodium hydroxide and sodium silicate but other alkali metal systems or mixtures of different alkalis also can also be used. The solution strictly needs to be concentrated to avoid the end product to be a crystalline zeolite rather than a geopolymer [63, 64].

Joshi and Kadu [65] prepared the alkaline activator using commercially available sodium silicate liquid and sodium hydroxide pellets which contains  $\text{Na}_2\text{O} = 14.61\%$ ,  $\text{SiO}_2 = 25.18\%$ , and water = 59.99%. The alkaline solution was prepared with NaOH molar concentration varying from 8M to 16M and the mass ratio of sodium silicate to sodium hydroxide varied from 1.75 to 3.0. A study by Gharzouni *et al.* [66] stated the type of alkaline solution is important. The research found that the geopolymers based on a mixture of potassium silicate and KOH display higher mechanical proper-

ties compared to those based on sodium silicate and NaOH or potassium silicate/NaOH mixtures.

Another research by Xie and Ozbakkaloglu [67] used the alkaline activators that consisted of distilled water, sodium hydroxide (NaOH) solution and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) solution. The proportions of the three components of the alkaline activator solution were 65.3% of water, 24.8% of  $\text{Na}_2\text{SiO}_3$ , and 9.9% of NaOH by weight. The sodium hydroxide (NaOH) solution with 14M concentration was constantly used in all the mixes.

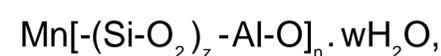
#### 4. GEOPOLYMER TERMINOLOGY AND GEOPOLYMERIZATION REACTION

Geopolymer involves the silicates and aluminates of by products to undergo process of geopolymerization. It is environmentally friendly and need moderate energy to produce. Geopolymerization is also known as a geosynthesis (reaction that chemically integrates minerals) that involves naturally occurring aluminosilicates [57,62].

Davidovits [68] observed the amorphous to semi-crystalline three dimensional silico-aluminate structures. Davidovits also further categorized the geopolymers structure based on the ratio of Si/Al as shown in Fig. 1. The chain structures of  $[\text{SiO}_4]^{4-}$  tetrahedra with cations and neutralizing anions build the mineral polymer framework in order to achieve the strength. These silicate minerals with OH bearing characteristics then possess excellent rock forming property [69].

Other alkaline activators that can be used for geopolymer formation are strong alkalis of chemical salts of  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{SO}_4$ , small amount of cement clinker [62,70]. Other chemical salts such as KCl,  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{K}_2\text{HPO}_4$  are also used as activator for geopolymeric reaction and solidification [70].

The following empirical formula has been postulated by Davidovits [30] to describe geopolymers:



where M is an alkali metal, z is 1, 2 or 3, and n is the degree of polymerization.

By dissolving an aluminosilicate powder in alkali solution such as NaOH, first  $\text{AlO}_2^{4-}$  and  $\text{SiO}_2^{4-}$  tetrahedra are formed and, according to the concentration of silicon in the solution, a type of monomers was naturally formed. The molecular arrangements in some geopolymer frameworks are shown in Fig. 2. A reaction mechanism for



geopolymerization proposed by Davidovits [57] involves the chemical reaction of precursors such as aluminosilicate oxides ( $\text{Al}^{3+}$  in IV-fold coordination) with alkali polysilicates, resulting in polymeric Si–O–Al bonds. To emphasize the IV-fold coordination of Al in these Al–Si minerals, these configurations are usually written as  $(\text{Si}_2\text{O}_5 \cdot \text{Al}_2\text{O}_3)$  rather than  $(2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3)$ . According to Davidovits the hardening mechanism for geopolymerisation essentially involves the polycondensation reaction of geopolymeric precursors, usually aluminosilicate oxides, with alkali polysilicates yielding polymeric Si–O–Al bonds [72] that are also depicted in Fig. 2.

In geopolymerization, aluminosilicate oxides firstly will dissolve in the alkali solution. Then the dissolved Al and Si complexes diffuse from the particle surfaces to the inter-particle spaces. Finally, a gel phase is formed from the polymerization of added silicate solution and Al and Si complexes and finally hardened to form hard solid [18, 57].

To produce geopolymer from kaolin, metakaolin or other clay materials, these three main steps are necessary [73]:

- a) Thermal activation, the aim of which is to obtain a clay material with high chemical activity. In this process dehydroxylation of clay mineral leads to an unstable amorphous solid.
- b) Alkali activation: activated aluminosilicate material is dissolved in highly alkaline solution to produce silicate and aluminate monomers.
- c) Reactive setting or polycondensation, in which the silicate and aluminate monomers condense to a stable polymer network.

To obtain a well structured geopolymer with acceptable mechanical properties, it is necessary to enhance the activity and solubility of Al–Si source materials in alkali solution. Thermal activation of the source material is one way to meet this condition and several investigations have examined the thermal activation process and its effects on final properties [74].

## 5. MANUFACTURING OF GEOPOLYMER

Geopolymer is usually prepared by mixing material (raw material) with the alkaline activator solution. The raw materials previously were ground by a centrifugal ball mill until fine particles were obtained [75]. The mixture of aluminosilicate and alkali activator solution then were turned into a slurry or paste and was cured at 70–80 °C for 24 hours. Normally, the dissolution of sodium hydroxide was modified in one liter of distilled water in a volumetric flask to obtain

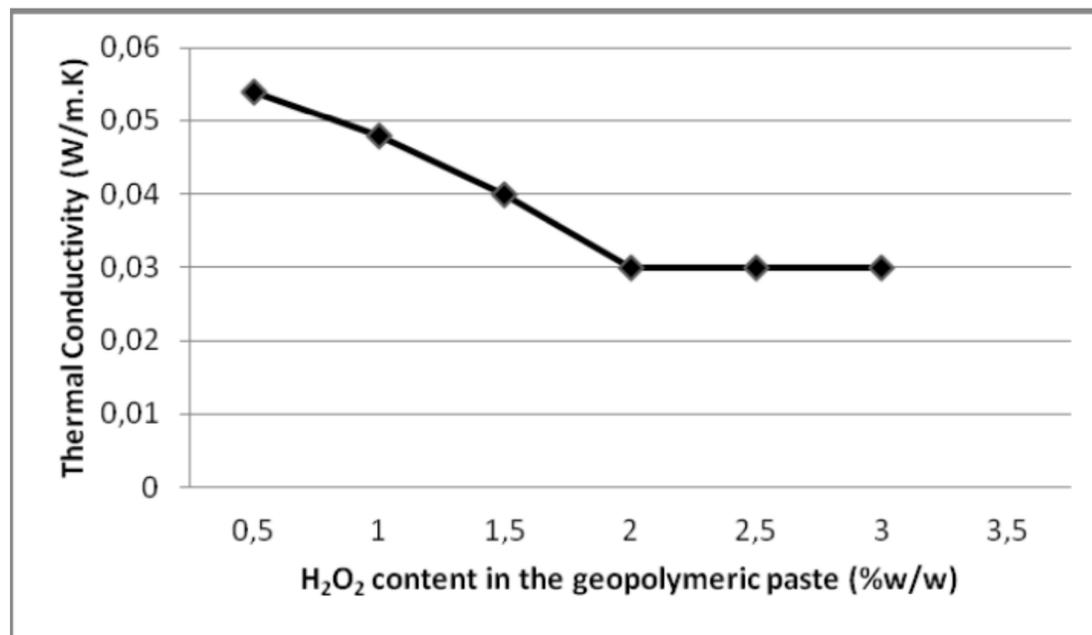
a 12M concentration of NaOH [76]. Mustafa *et al.* [77] in his research mixed the raw material with alkaline activator in the mixer. Further, the geopolymer was placed in the 50x50x50 mm mold and vibrated for 20s on the vibrating table. The geopolymer samples were cured at different curing temperatures.

Castel and Forster [14] in their research on manufacture the geopolymer used alkaline solution from a mixture of 12M concentration of sodium hydroxide (NaOH) solution and sodium silicate solution. The mass ratio of alkaline solution to aluminosilicate material was 0.55. The specimens then were cured for 24 hours. The ratio of the raw material with the alkaline activator is important in forming the geopolymer [78]. The Si:Al composition for geopolymer prepared from raw material were 2.5 and 3.5 respectively [79]. At the same time, Cheng and Chiu [80] used  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the range of 3.16–3.46. Mustafa *et al.* [81], in his research used 2.5 as ratio of  $\text{Na}_2\text{SiO}_3/\text{NaOH}$ . Normally the ratio for solid to liquid (S/L) started from 0.6 and above.

Liu *et al.* [82] in their research on thermal behavior of the geopolymer concrete used the ratios of the sodium silicate solution to sodium hydroxide solution and the alkaline solution were 2.5 and 0.55 by mass, respectively. They also used the sodium hydroxide with 14M molarity. The mixture of the solution was prepared at least 1 day prior to its use to allow the exothermically heated liquid to cool to ambient temperature. Wang *et al.* [83] studied the thermal conductivity of the geopolymer using raw materials with theoretical composition of  $\text{SiO}_2/\text{Al}_2\text{O}_3=4.0$ , the ratio of  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3=1.0$  and  $\text{H}_2\text{O}/\text{K}_2\text{O}=11.0$  (molar ratio).

## 6. THERMAL INSULATION

Thermal insulation is the reduction of heat transfer (the transfer of thermal energy between objects of differing temperature) between objects in thermal contact or in range of radiative manipulated [84]. Thermal insulation is also known as a single material or combination of materials that when properly applied, will retard the rate of heat flow by conduction, convection, and radiation. It retards heat flow into or out of a object or building due to its high thermal resistance [85]. Thermal insulation is the reduction of heat transfer (the transfer of thermal energy between objects of differing temperature) between objects in thermal contact or in range of radiative influence. Thermal insulation can be achieved with specially engineered methods or processes, as well as with suitable object shapes and materials. Thermal insulation provides a region of



**Fig. 3.** Thermal conductivity of foamy materials with different H<sub>2</sub>O<sub>2</sub> contents in the geopolymeric paste. Reprinted with permission from [V. Vaou and D. Pantias // *Minerals Engineering* **23** (2010) 1146. © 2010 Elsevier Ltd.]

insulation in which thermal conduction is reduced or thermal radiation is reflected rather than absorbed by the lower-temperature body [86]. The insulating capability of a material is measured with thermal conductivity ( $k$ ). Low thermal conductivity is equivalent to high insulating capability ( $R$ -value). In thermal engineering, other important properties of insulating materials are product density ( $\rho$ ), and specific heat capacity ( $c$ ) [87].

Heat flow resisted by thermal insulating materials as a result of the countless microscopic dead air-cells, which suppress (by preventing air from moving) convective heat transfer. It is the air entrapped within the insulation which provides the thermal resistance, not the insulation material. By making small cells (closed cell structure) within thermal insulation across which the temperature difference is not large also reduces radiation effects. It causes radiation 'paths' to be broken into small distances where the long-wave infrared radiation is absorbed and/or scattered by the insulation material (low energy materials can also be used to minimize radiation effects). However, conduction usually increases as the cell size decreases (the density increases) [85].

There are many types of material that suitable for thermal insulation is available which fall under the following basic materials and composites [85]:

#### 1. Inorganic Materials

- Fibrous materials such as glass, rock, and slag wool, fly ash.
- Cellular materials such as calcium silicate, bonded perlite, vermiculite, ceramic products and geopolymer.

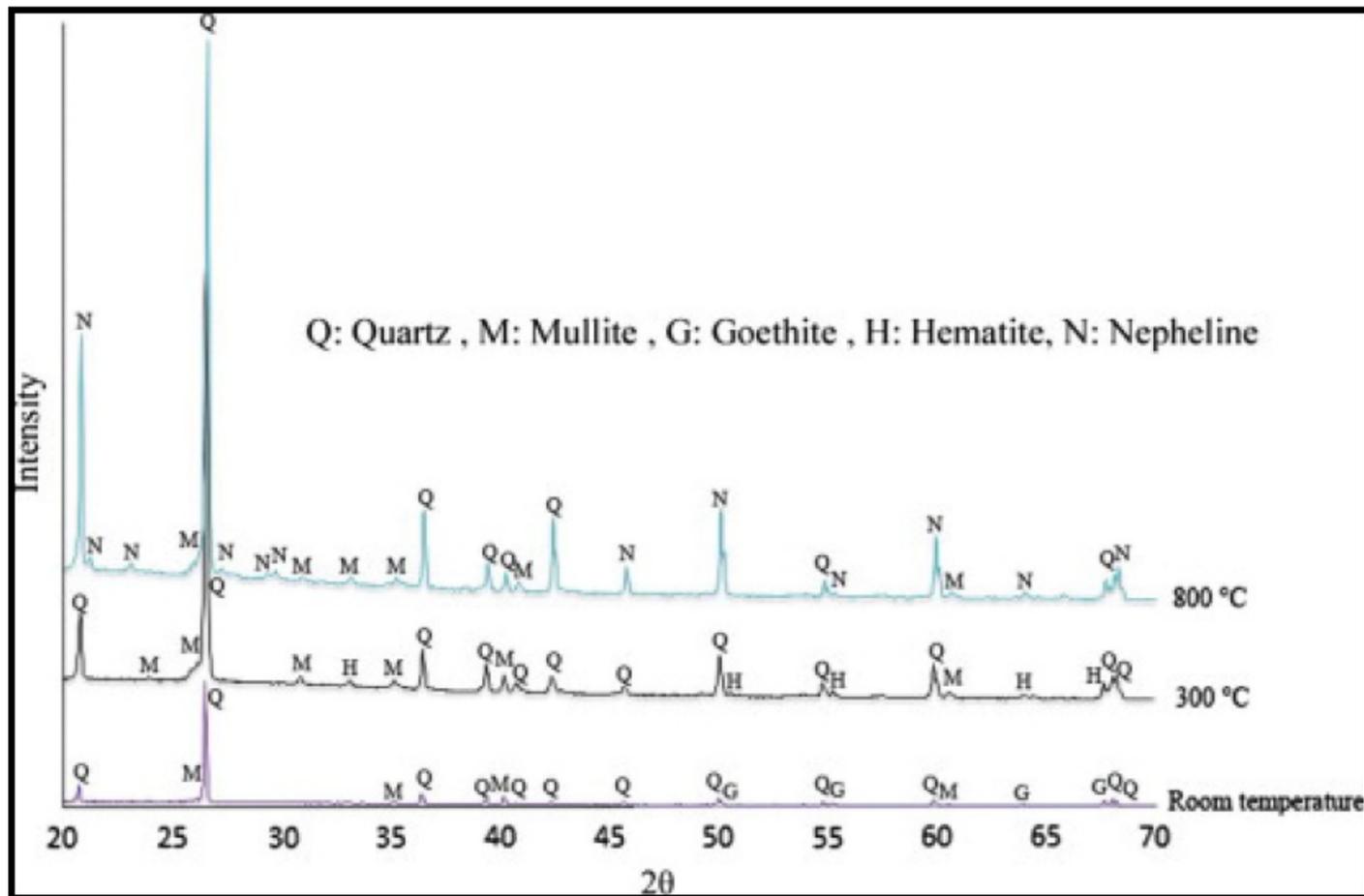
#### 2. Organic Materials

- Fibrous materials such as cellulose, cotton, wood, pulp, cane, or synthetic fibers.
- Cellular materials such as cork, foamed rubber, polystyrene, polyethylene, polyurethane, polyisocyanurate and other polymers.

There are several type of thermal insulation standard testing based on American Society for Testing and Materials (ASTM). ASTM's thermal insulation standards are instrumental in specifying and evaluating the materials and methods used to reduce the rate of heat transfer. The flow of heat can be delayed by understanding the conductive, convective, and/or radiative behavior of the material in consideration. The ASTM that suitable for thermal insulation testing for geopolymer are ASTM C163 - 05, ASTM C166 - 05, ASTM C411 - 11, ASTM C447 - 03, ASTM C870 - 11, ASTM C195 - 07, ASTM C165 - 07, ASTM C335 / C335M - 10e1, ASTM C1058 / C1058M - 10 and ASTM E831 [88]. Khaliq and Kodur [89] in their research used ASTM E 831-06 by using thermo-mechanical analysis (TMA) apparatus to study the thermal conductivity and insulation of geopolymer. Another study by Rickard *et al.* [90] also used ASTM E831 to study the thermal insulation of material from geopolymer. They used thermal expansion testing to determine the insulation of material.

## 7. THERMAL PROPERTIES OF GEOPOLYMER

Vaou and Pantias [91] showed that the thermal conductivity of foamy geopolymeric materials as shown in Fig. 3. Thermal conductivity of the geopolymer paste was decreased substantially from 0.053 W/



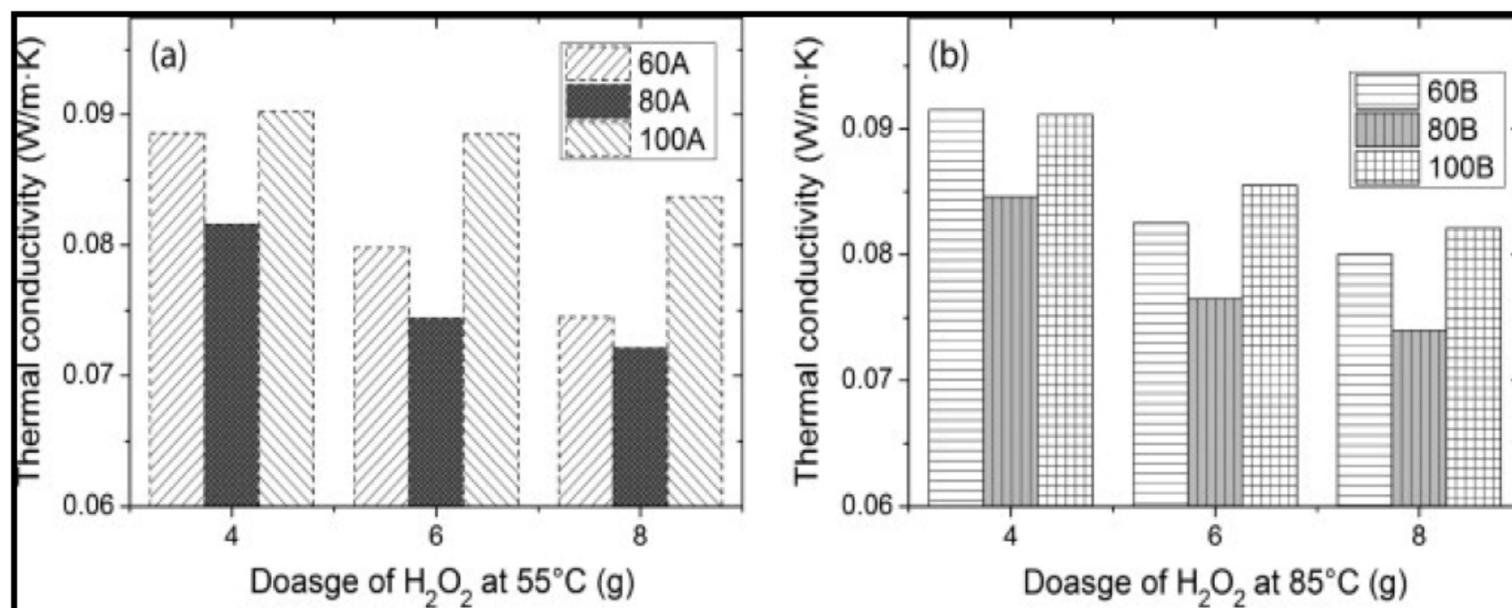
**Fig. 4.** XRD patterns of the FA based geopolymer. Reprinted with permission from [N. Ranjbar, M. Mehrli, U.J. Alengaram, H.S.C. Metselaar and M.Z. Jumaat // *Construction and Building Materials* **65** (2014) 114. © 2014 Elsevier Ltd.]

m K to 0.03 W/m K along with the increasing of hydrogen peroxide ( $H_2O_2$ ) content from 0.7% and 2.02%. Further increment of the  $H_2O_2$  content in the geopolymeric paste has considerably does not produce an effect on the thermal conductivity value. The results showed that the thermal conductivity of foamy geopolymers is correlated to their cellular structure. A substantial decrease of the thermal conductivity value also can be achieved by controlling appropriately cells type, size, shape and volume. The results from these studies are in good agreement with the state-of-the-art on thermal insulation foamed plastics where the thermal conductivity is correlated firstly to the thermal conductivity of the filling gas followed by the apparent density of foams and then the morphology of the cellular structure [92].

Ranjbar [963] studied on compressive strength and microstructural analysis of fly ash/palm oil fuel ash based geopolymer mortar under elevated temperatures showed the XRD analysis of the samples. Fig. 4 shows the XRD patterns of fly ash (FA) based geopolymers. The patterns were taken after the sample was exposure to room temperature, 300 °C and 800 °C. These studies state that the strong peaks in FA base geopolymer identify the presence of quartz, mullite, and goethite at room temperature. Mullite is the only stable crystalline phase of the  $Al_2O_3-SiO_2$  system under atmospheric condi-

tion and is a refractory. Mullite retains its room temperature strength at elevated temperatures and has high temperature stability with low thermal expansion and oxidation resistance [94]. After the exposure to 300 °C, peaks of quartz are still stable while peaks of mullite become progressively stronger. The phase transition from goethite to hematite occurs at about 300 °C. At this temperature, most of the constitutional water molecules have been released. The pattern of XRD analysis for FA based geopolymer subjected to 800 °C shows hematite starting to disappear while crystalline nepheline  $AlNaSiO_4$  (sodium aluminum silicate) was present in the specimen although quartz remains the major phase. The mullite was still present [95]. These prove that the main structure of geopolymer does not significantly affect by the high temperature. It also prove that geopolymer material suitable to use and apply as thermal insulator [31,96].

Feng *et al.* [8] studied the thermal conductivity of porous fly ash based geopolymer. Fig. 5 showed the thermal conductivity of the porous fly ash based geopolymer material. At the same curing temperature and when same amount of sodium water glass ( $H_2O_2$ ) were added, the increasing of the  $H_2O_2$  leads to reduction in density and thermal conductivity along with increasing apparent porosity. The  $H_2O_2$  were added in 60 g, 80 g, and 100 g. In addition, with the increase of  $H_2O_2$  amount, numbers of voids



**Fig. 5.** Thermal conductivity of the porous fly ash based geopolymer material. Reprinted with permission from [J. Feng, R. Zhang, L. Gong, Y. Li, W. Cao and X. Cheng // *Materials & Design* **65** (2015) 529. © 2014 Elsevier Ltd.]

inside the material with air contained could be generated, thus resulting in the reduction of density and thermal conductivity and increase in apparent porosity. Density and apparent porosity are generally correlated with thermal conductivity. This is because higher porosity means more voids and the thermal conductivity of air within the voids is much lower than that of solid substance, thus leading to a comparatively lower thermal conductivity of the whole material [97]. It clearly proved from Fig. 5, for sample of 80 A, starting from 2 g, 4 g, and 6 g H<sub>2</sub>O<sub>2</sub>, the thermal conductivity values are 0.0816, 0.0744, and 0.0721 W/m K, respectively and the relevant density and apparent porosity are 335, 260, and 239 kg/m<sup>3</sup> and 79.1%, 79.9%, and 81.2%, respectively.

Comparing the thermal conductivity of this porous fly ash-based geopolymer material with other thermal insulation materials, it can be seen that the thermal conductivity of this material is greater than those of expanded perlite and kenaf insulation board [98, 99], but close to that of cotton stalk insulation board [97] and even smaller than that of lightweight aggregate [100]. Meanwhile, considering its non inflammability, simple technology, cost saving and environmental contribution, the material synthesized in present work shows potential for building thermal insulation application [101].

## 8. CONCLUSION

This paper summarized the processing, thermal properties and suitability of geopolymer materials to be used for thermal insulating application. Besides, geopolymer exhibits excellent properties which offer sustainable solution and environmental friendly for extending the service life of infrastruc-

ture and maintenance cost. Development of geopolymer seems to present a greener alternative to ordinary Portland cements. Although extensive researches have already been carried out, the development of geopolymer as a thermal insulator are less been explored. It is hoped that future research in this field will drive a new era of greener materials in the construction industry.

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## REFERENCES

- [1] P.K. Sarker, S. Kelly and Z. Yao // *Materials & Design* **63** (2014) 584.
- [2] M. Cekon, M. Kalousek, J. Hraška and R. Ingeli // *Energy and Buildings* **77** (2014) 343.
- [3] C. Escudero, K. Martin, A. Erkoreka, I. Flores and J.M. Sala // *Energy and Buildings* **59** (2013) 62.
- [4] I. Hernández-Pérez, G. Álvarez, J. Xamán, I. Zavala-Guillén, J. Arce and E. Simá // *Energy and Buildings* **80** (2014) 81.
- [5] W. Guo, X. Qiao, Y. Huang, M. Fang and X. Han // *Energy and Buildings* **50** (2012) 196.
- [6] Y. Ma, B. Zhu, Y. Li and H. Yu // *Journal of Tongji University* **40** (2012) 1876.
- [7] E. Kamseu, B. Ceron, H. Tobias, E. Leonelli, M. Bignozzi, A. Muscio and A. Libbra //

- Journal of thermal analysis and calorimetry* **108** (2011) 1189.
- [8] J. Feng, R. Zhang, L. Gong, Y. Li, W. Cao and X. Cheng // *Materials & Design* **65** (2015) 529.
- [9] R.E. Lyon, *Fire Response of Geopolymer Structural Composites* (DTIC Document, 1996).
- [10] H.M. Khater // *Advances in Cement Research* **26** (2014) 1.
- [11] L. Zeng, C. Dan-Yang, Y. Xu, F. Chun-Wei and P. Xiao-Qin // *Applied Clay Science* **101** (2014) 637.
- [12] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo and J.S.J. van Deventer // *Journal of Materials Science* **42** (2007) 2917.
- [13] B. Singh, G. Ishwarya, M. Gupta and S.K. Bhattacharyya // *Construction and Building Materials* **85** (2015) 78.
- [14] A. Castel and S.J. Foster // *Cement and Concrete Research* **72** (2015) 48.
- [15] J. Temuujin, A. Minjigmaa, W. Rickard and A. Van Riessen // *Journal of thermal analysis and calorimetry* **107** (2012) 287.
- [16] J. Liyana, H. Kamarudin, A.M. Mustafa Al Bakri, M. Binhussain, C.M. Ruzaidi and A.M. Izzat // *Australian Journal of Basic and Applied Sciences* **7** (2013) 182.
- [17] V.D. Glukhovskiy, *Soil Silicates* (Gosstroyizdat Ukrainy Publishing, Kiev, 1959), In Russian.
- [18] B. Majidi // *Materials Science and Technology* **24** (2009) 79.
- [19] V.D. Glukhovskiy, *Oil silicates: their properties, technology and manufacturing and fields of application* ( DTech.Sc. Thesis, Civil Engineering Institute, Kiev, Ukraine, 1965), In Russian.
- [20] M.L. Granizo, *Activación alcalina de metacaolín: desarrollo de nuevos materiales cementantes* (PhD Thesis, University Autonoma of Madrid, 1998), In Spanish.
- [21] D.H. Campbell and R.L. Folk // *Concrete Int.* **29** (1991) 44.
- [22] J. Van Jaarsveld, J. Van Deventer and L. Lorenzen // *Minerals Engineering* **10** (1997) 659.
- [23] J. Davidovits, In: *Proc. 1st Int. Conf. on Geopolymers* (Compiègne, France, 1998), p. 19.
- [24] F.U.A. Shaikh // *Construction and Building Materials* **43** (2013) 37.
- [25] J. Davidovits // *World Resource Review* **6** (1994) 263.
- [26] A. Fernández-Jiménez and A. Palomo, In: *Geopolymers: Structures, Processing, Properties and Industrial Applications* (Woodhead Publishing Limited, 2009), p. 167.
- [27] M. Sofi, J. van Deventer, P. Mendis and G. Lukey // *Journal of Materials Science* **42** (2007) 3107.
- [28] J.L. Bell, P.E. Driemeyer and W.M. Kriven // *Journal of the American Ceramic Society* **92** (2009) 607.
- [29] T. Alomayri, F.U.A. Shaikh and I.M. Low // *Ceramics International* **40** (2014) 14019.
- [30] J. Davidovits, In: *Proc. Int. Conf. Geopolymer '99* (France, 1999), p. 9.
- [31] V.F. Barbosa and K.J. MacKenzie // *Materials Research Bulletin* **38** (2003) 319.
- [32] V.F.F. Barbosa and K.J.D. MacKenzie // *Materials Letters* **57** (2003) 1477.
- [33] J. Temuujin, A. Minjigmaa, W. Rickard, M. Lee, I. Williams and A. van Riessen // *Applied Clay Science* **46** (2009) 265.
- [34] Z. Zhang, K. Wang, B. Mo, X. Li and X. Cui // *Energy and Buildings* **87** (2015) 220.
- [35] X. Li, X. Cui, S. Liu, B. Mo and L. Cui // *Key Engineering Materials* **537** (2013) 261-264.
- [36] J. Temuujin, A. Minjigmaa, W. Rickard, M. Lee, I. Williams and A. van Riessen // *Journal of Hazardous Materials* **180** (2010) 748.
- [37] J. Davidovits // *J. Mater. Educ.* (1994) (1994) 91.
- [38] P.S. Deb, P. Nath and P.K. Sarker // *Materials & Design* **62** (2014) 32.
- [39] T. Tho-in, V. Sata, P. Chindaprasirt and C. Jaturapitakkul // *Construction and Building Materials* **30** (2012) 366.
- [40] A. Adam and A. Horianto // *Procedia Engineering* **95** (2014) 410.
- [41] A.A. Omar, A.M. Mustafa Al Bakri, H. Kamarudin, I. Khairul Nizar and A.A. Saif // *Construction and Building Materials* **50** (2014) 377.
- [42] G.S. Ryu, Y.B. Lee, K.T. Koh and Y.S. Chung // *Construction and Building Materials* **47** (2013) 409.
- [43] A. Kusbiantoro, M.F. Nuruddin, N. Shafiq and S.A. Qazi // *Construction and Building Materials* **36** (2012) 695.
- [44] P. Chindaprasirt, S. Homwuttivong and C. Jaturapitakkul // *Construction and Building Materials* **21** (2007) 1492.
- [45] D.S. Chaudhary and M.C. Jollands // *Journal of Applied Polymer Science* **93** (2004) 1.

- [46] F. Adam, J.N. Appaturi and A. Iqbal // *Catalysis Today* **190** (2012) 2.
- [47] P. Chindaprasirt, P. Kanchanda, A. Sathonsaowaphak and H.T. Cao // *Construction and Building Materials* **21** (2007) 1356.
- [48] S. Songpiriyakij, T. Kubprasit, C. Jaturapitakkul and P. Chindaprasirt // *Construction and Building Materials* **24** (2010) 236.
- [49] J. He, Y. Jie, J. Zhang, Y. Yu and G. Zhang // *Cement and Concrete Composites* **37** (2013) 108.
- [50] S. Detphan and P. Chindaprasirt // *International Journal of Minerals, Metallurgy and Materials* **16** (2009) 720.
- [51] Z. Yunsheng, S. Wei and L. Zongjin // *Applied Clay Science* **47** (2010) 271.
- [52] G. Varga // *Epitoanyag* **59** (2007) 6.
- [53] C.Y. Heah, H. Kamarudin, A.M. Mustafa Al-Bakri, M. Luqman, K. Nizar and Y.M. Liew // *Australian Journal of Basic and Applied Sciences* **5** (2011) 1026.
- [54] C.Y. Heah, H. Kamarudin, A.M. Mustafa Al Bakri, M. Binhussain, M. Luqman, I. Khairul Nizar, C.M. Ruzaidi and Y.M. Liew // *Construction and Building Materials* **35** (2012) 912.
- [55] J.G.S. Van Jaarsveld, J.S.J. Van Deventer and G.C. Lukey // *Chemical Engineering Journal* **89** (2002) 63.
- [56] P. Rovnanik // *Construction and Building Materials* **24** (2010) 1176.
- [57] J. Davidovits, In: *Proc. First international conference on alkaline cements and concretes* (1994), p. 131.
- [58] J. Temuujin, W. Rickard, M. Lee and A. van Riessen // *Journal of Non-Crystalline Solids* **357** (2011) 1399.
- [59] S.H. Sanni and R. Khadiranaikar // *International Journal of Research in Engineering and Technology* **2** (2013) 366-371.
- [60] A. Fenandez-Jimenez and A. Palomo // *Journal of Fuel* **82** (2003) 2259.
- [61] P. Duxson, A. Fernández-Jiménez, J. Provis, G. Lukey, A. Palomo and J. Van Deventer // *Journal of Materials Science* **42** (2007) 2917.
- [62] D. Khale and R. Chaudhary // *Journal of Materials Science* **42** (2007) 729.
- [63] J. Davidovits, In: *Proc. 99 International Conference* (Saint-Quentin, France, 1999), 9-40.
- [64] D. Hardjito, *Studies of fly ash-based geopolymer concrete* (Curtin University of Technology, 2005).
- [65] S. Joshi and M. Kadu // *International Journal of Environmental Science and Development* **3** (2012) 5.
- [66] A. Gharzouni, E. Joussein, B. Samet, S. Baklouti and S. Rossignol // *Journal of Non-Crystalline Solids* **410** (2015) 127.
- [67] T. Xie and T. Ozbakkaloglu // *Ceramics International* **41** (2015) 5945.
- [68] J. Davidovits, *Geopolymer Chemistry and Sustainable Development, The Poly(sialate) Terminology : A Very Useful and Simple Model for the Promotion and Understanding of Green-Chemistry* (Institute of Geopolymer, Saint-Quentin, France, 2005).
- [69] S.D. Muduli, J.K. Sadangi, B.D. Nayak and B.K. Mishra // *Greener Journal of Physical Sciences* **6** (2013) 204.
- [70] D. Hardjito, S. Wallah, D. Sumajouw and B. Rangan, In: *Proc. 8th CANMET/ACI International Conference on fly ash, silica fume, slag and natural pozzolans in concrete* (Las Vegas, USA, 2004), 111.
- [71] W. Lee and J. Van Deventer // *Cement and Concrete Research* **32** (2002) 577.
- [72] J. Davidovits // *J. Materials Education* **16** (1994) 91.
- [73] H. Xu and J. Van Deventer // *International Journal of Mineral Processing* **59** (2000) 247.
- [74] J. Davidovits // *J. Therm. Anal.* **37** (1991) 1633.
- [75] C. Tippayasam, P. Keawpapasson, P. Thavorniti, T. Panyathanmaporn, C. Leonelli and D. Chaysuwan // *Construction and Building Materials* **53** (2014) 455.
- [76] A.M. Mustafa Al Bakri, L. Jamaludin, H. Kamarudin, M. Binhussain, M. C. Ruzaidi and A.M. Izzat // *Advanced Materials Research* **686** (2013) 227.
- [77] A.M. Mustafa Al Bakri, H. Kamarudin, M. Binhussain, I.K. Nizar, Y. Zarina and A.R. Rafiza // *Physics Procedia* **22** (2011) 286.
- [78] E. Kamseu, B. Nait-Ali, M.C. Bignozzi, C. Leonelli, S. Rossignol and D.S. Smith // *Journal of the European Ceramic Society* **32** (2012) 1593.
- [79] Z. Zhang, X. Yao and H. Zhu // *Applied Clay Science* **49** (2010) 1.
- [80] T. Cheng and J. Chiu // *Minerals Engineering* **16** (2003) 205.

- [81] A.M. Mustafa Al Bakri, L. Jamaludin, K. Hussin, M. Bnhussain, C. M. Ruzaidi and A.M. Izzat // *International journal of molecular sciences* **13** (2012) 4388.
- [82] M.Y.J. Liu, U.J. Alengaram, M.Z. Jumaat and K.H. Mo // *Energy and Building* **72** (2014) 238.
- [83] M.R. Wang, D.C. Jia, P.G. He and Y. Zhou // *Ceramics International* **37** (2011) 1661.
- [84] M.S. Al-Homoud // *Journal of Thermal Envelope and Building Science* **27** (2004) 235.
- [85] F.J. Snow // In: *Thermal Infrared Sensing Applied to Energy Conservation in Building Envelopes* ( International Society for Optics and Photonics, 1982), p. 94.
- [86] V.K.R. Kodur and M.A. Sultan, In: *Proceedings, International Symposium on High Performance and Reactive Powder Concrete, Concrete* (Sherbrooke, Canada, 1998), p. 217.
- [87] M.S. Al-Homoud // *Journal of Building Physics* **33** (2009) 65.
- [88] K.P. Menard, *Dynamic mechanical analysis: a practical introduction* (CRC press, 2008).
- [89] W. Khaliq and V. Kodur // *Cement and Concrete Research* **41** (2011) 1112.
- [90] W.D.A. Rickard, J. Temuujin and A. van Riessen // *Journal of Non-Crystalline Solids* **358** (2012) 1830.
- [91] V. Vaou and D. Papias // *Minerals Engineering* **23** (2010) 1146.
- [92] A.M. Papadopoulos // *Energy and Buildings* **37** (2005) 77.
- [93] N. Ranjbar, M. Mehrali, U.J. Alengaram, H.S.C. Metselaar and M.Z. Jumaat // *Construction and Building Materials* **65** (2014) 114.
- [94] N. Kawai, K.G. Nakamura and K.I. Kondo // *Journal of Applied Physics* **96** (2004) 4126.
- [95] S. Gialanella, F. Girardi, G. Ischia, I. Lonardelli, M. Mattarelli and M. Montagna // *Journal of thermal analysis and calorimetry* **102** (2010) 867.
- [96] T. Bakharev // *Cement and Concrete Research* **36** (2006) 1134.
- [97] X.Y. Zhou, F. Zheng, H.G. Li and C.I. Lu // *Energy and Buildings* **42** (2010) 1070.
- [98] J. Xu, R. Sugawara, R. Widyorini, G. Han and S. Kawai // *Journal of Wood Science* **50** (2004) 62.
- [99] S. Panyakaew and S. Fotios // *Energy and Buildings* **43** (2011) 1732.
- [100] D. Zorić, D. Lazar, O. Rudić, M. Radeka, J. Ranogajec and H. Hiršenberger // *Journal of thermal analysis and calorimetry* **110** (2011) 489.
- [101] R. Demirboğa and R. Gül // *Cement and Concrete Research* **33** (2003) 723.