



# Comparison of Fire Resistant Geopolymers for Passive Fire Protection of Concrete Tunnel Linings

Konstantinos Sakkas<sup>1,2</sup>, D. Panias<sup>1</sup>, P. Nomikos<sup>2</sup>, A. Sofianos<sup>2</sup>

<sup>1</sup>Laboratory of Metallurgy, School of Mining and Metallurgical Engineering, National Technical University of Athens, Athens, Greece

<sup>2</sup>Laboratory of Tunnelling, School of Mining and Metallurgical Engineering, National Technical University of Athens, Athens, Greece

Email: sakkasdin@yahoo.gr

**How to cite this paper:** Sakkas, K., Panias, D., Nomikos, P. and Sofianos, A. (2017) Comparison of Fire Resistant Geopolymers for Passive Fire Protection of Concrete Tunnel Linings. *Open Access Library Journal*, 4: e3327.

<http://dx.doi.org/10.4236/oalib.1103327>

**Received:** December 23, 2016

**Accepted:** January 13, 2017

**Published:** January 16, 2017

Copyright © 2017 by authors and Open Access Library Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

---

## Abstract

Fire resistant geopolymers are developed and the performance under thermal loading is examined and compared in this paper. The geopolymers were prepared by mixing the solid phase, metallurgical slag and metakaolin with a highly alkaline potassium hydroxide aqueous phase in order to create a paste that was subsequently cured at 70°C for a certain period of time. The developed materials were tested for the mechanical, physical and thermal properties. The behaviour of the geopolymers upon exposure on fire was studied following the EFNARC guidelines for testing of passive fire protection for concrete tunnels linings. The geopolymers were subjected to the most severe fire scenario, the Rijks Water Staat (RWS) temperature-time curve. Both geopolymers appeared great behaviour after the test reaching temperature lower than the RWS test requirement, proving the ability of both materials to work successfully as an efficient thermal barrier. Thus, the concrete slab protected by the geopolymers did not appear any form of spalling or degradation of its compressive strength.

## Subject Areas

Composite Material, Material Experiment

## Keywords

Geopolymer, Tunnel Linings, Passive Fire Protection

---

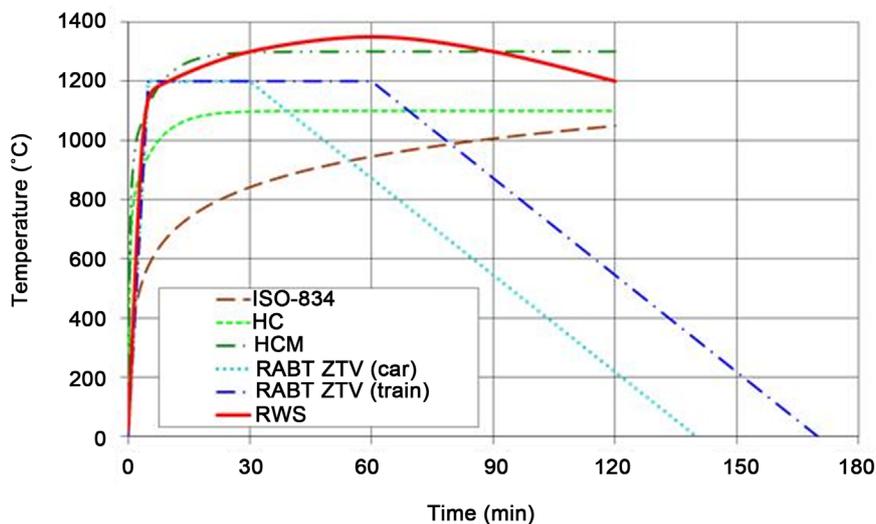
## 1. Introduction

A number of serious tunnel fire incidents have been reported worldwide that

have led to injuries and life loss, heavy damage in the concrete lining, thus threatening the stability of the tunnel structure, excess material damage, and significant time periods of tunnel restoration during which the tunnels were unavailable for traffic. Fires in tunnels can seriously damage their concrete lining rendering it to collapse. The damage is caused particularly by the spontaneous release of great amounts of heat and aggressive fire gases, resulting to spalling of concrete. Spalling is described as the breaking of layers or pieces of concrete from the surface of a structural element when it is exposed to the high and rapidly rising temperatures experienced in fires. The most severe spalling phenomenon is the so called explosive spalling, be described as a violent showering of hot pieces of concrete, which beyond to the detrimental effect on concrete lining can additionally cause very serious problems to the fire fighting service personnel rendering their work substantially more difficult and dangerous.

The spalling phenomena are expected at several temperatures depending on the strength of the concrete. The American National Institute for Standards and Testing (NIST) mentions that explosive spalling can be expected at temperatures between 300°C and 450°C [1], while it is generally accepted that concrete exposed at temperatures higher than 380°C is considered as damaged that should be removed and repaired [1]. This temperature is near to the calcium hydroxide dehydration temperature (400°C) which is a process that causes a significant reduction in the mechanical strength of the concrete [2]. The latter is considered to be significantly reduced at exposure temperatures higher than 300°C [3]. In addition to the damage caused by fire to concrete, special attention has to be paid to the damage caused to structural steel rebars that normally reinforce the concrete structures. Structural steels (especially some plain carbon and alloy steels) exhibit both an increase in strength and a substantial decrease in ductility, which is called “blue brittleness” effect, upon their heating at temperatures between 250°C and 300°C. They undergo significant deformations upon heating at temperatures higher than 430°C as well as stress relieving at temperatures ranging from 600°C to 650°C and generally are considered to have lose their strength at temperatures between 550°C and 600°C [1]-[6]. Therefore, steel and concrete are both fire sensitive construction elements requiring passive protection against fire in order to be capable of withstanding the effects of fire for an appropriate time period of time without loss of stability.

Passive fire protection methods are generally divided in two categories: external (insulation) and internal (concrete design) ones. The former are more advantageous being applied in new as well as in existing tunnels and consists of the cladding of the concrete by a fire resistant material which creates a protective external insulation envelope. This work aims at evaluating the performance under thermal loading of a fire resistant geopolymers for external passive fire protection of concrete tunnels linings. Its efficiency under thermal loading is assessed by thermal exposure laboratory testing following the EFNARC guidelines. The thermal loading that was applied, was established from the Ministry of Public works in Netherlands and the TNO Centre for fire research and it is widely known as the RWS (**Figure 1**) (Rijswaterstaat) temperature-time which is com-



**Figure 1.** Time-temperature curves.

monly used for the evaluation of passive protecting materials for application in tunnels. This curve simulates a very severe hydrocarbon fire, rapidly exceeding 1200°C, peaking at 1350°C after 60 min and then falling gradually to 1200°C at 120 min at the end of the test. RWS curve is intended to simulate a 50 m<sup>3</sup> tanker carrying petrol in tunnel with a fire load of 300 MW causing a 2 hour fire. The RWS describes very severe fire incidents in tunnels concerning that the maximum temperatures attained in fires in tunnels (e.g. Channel, Mont Blanc, Tauern, Great Belt) do not usually exceed 1100°C.

## 2. Geopolymers

Geopolymers is a new family of synthetic aluminosilicate materials formed by alkali activation of solid aluminosilicate raw materials [7]. The term “alkali activation” refers to a heterogeneous chemical reaction between an aluminosilicate raw material and an activating phase composed primarily from an aqueous solution of an alkali metal (sodium or potassium) silicate and hydroxide [7]. The geopolymerization reaction is exothermic and takes place at atmospheric pressure and temperatures below 100°C [8] [9]. Under a complicated mechanism, this reaction results in the formation of durable and compact amorphous to semi-crystalline solid materials characterized by a specific three-dimensional polymeric structure. Therefore, geopolymers belong to the family of inorganic polymers, which are macromolecules linked by covalent bonds and having -Si-O-M-O- backbone, where M denotes principally aluminum and secondarily other metals such as iron [7] [8] [9].

The geopolymerization process has gained the scientific interest during the last decades. This is attributed to the large variety of solid aluminosilicate raw materials that can be used for the synthesis of geopolymers. Among the potential solid aluminosilicate raw materials, industrial minerals, such as kaoline, feldspars, perlite, etc. [10] [11] [12] [13], as well as solid industrial byproducts, such as fired-coal fly ash, alumina red mud, metallurgical slags, building demoli-

tion materials, etc. [14]-[20], are the most important raw materials. The latter class of potential raw materials is extremely attractive, mainly for environmental reasons. Geopolymers possess excellent physicochemical, thermal and mechanical properties, like low density, micro- or nano-porosity, high mechanical strength, notable surface hardness, thermal stability, fire and chemical resistance [7] [8]. Due to these properties, geopolymers are viewed as alternatives for construction materials with excellent mechanical and unique thermal properties. A series of fire resistant geopolymers have been developed earlier (Cheng, Chiu, Davivotis, Varela) which however have not been tested according to the international standardized time-temperature curves.

### 3. Experimental

#### 3.1. Materials

The metakaolin that was used in this study was provided from “AGS Mineraux”, a member of Imerys Minerals. Metakaolin had a mean particle size ( $d_{50}$ ) of 13.68  $\mu\text{m}$  measured on a MALVERN Laser Particle Size Analyzer. As is shown in **Table 1**, it is a material rich in silica and alumina oxide. Its mineralogical analysis showed that it is mainly composed of an X-ray amorphous silicate or aluminosilicate phase which is accompanied by crystalline mineralogical phases that belong to Illite [(K, H<sub>3</sub>O) (Al, Mg, Fe)<sub>2</sub>(Si, Al)<sub>4</sub>O<sub>10</sub>[(OH)<sub>2</sub>, (H<sub>2</sub>O)]], Quartz (SiO<sub>2</sub>), Anatase (TiO<sub>2</sub>) and Tridymite (SiO<sub>2</sub>).

Also pure silicon dioxide ( $d = 2.6 \text{ gr/cm}^3$ , particle size  $< 64 \mu\text{m}$ ) provided by “Sigma Aldrich” was used for the synthesis of metakaolin geopolymer. The slag used in the present study was provided by the metallurgical plant of the Greek company LARCO G.M.M.S.A. that treats laterites to produce ferronickel. The slag is generated during the reductive smelting of laterites in electric arc furnaces and is granulated using a flash water cooling process. For the synthesis of inorganic polymers, an adequate quantity of granulated slag was grinded to  $< 90 \mu\text{m}$  and the resulted powder had a mean particle size ( $d_{50}$ ) of 15.05  $\mu\text{m}$ . As shown in **Table 1**, the FeNi slag is a siliceous material very rich in iron oxides and rich in alumina. It also contains substantial amounts of trivalent chromium, magnesium

**Table 1.** Chemical analysis of metakaolin and slag.

Species	% w/w metakaolin	% w/w FeNi slag
SiO <sub>2</sub>	52.66	41.14
Al <sub>2</sub> O <sub>3</sub>	40.97	13.79
Fe <sub>2</sub> O <sub>3</sub>	1.83	34.74
K <sub>2</sub> O	1.18	-
MgO	-	3.59
TiO <sub>2</sub>	1.43	-
Cr <sub>2</sub> O <sub>3</sub>	-	5.41
Na <sub>2</sub> O	0.55	-

and calcium oxides, as well as traces of nickel. The mineralogical analysis of the slag showed that it is mainly composed of an X-ray amorphous silicate or aluminosilicate phase which is accompanied by crystalline mineralogical phases that belong to the Ferrite-spinels  $[(\text{Fe}^{2+}, \text{Mg})(\text{Fe}^{3+}, \text{Al}, \text{Cr})_2\text{O}_4]$ . Magnetite ( $\text{Fe}_3\text{O}_4$ ) was the principal constituent of spinels while magnesioferrite ( $\text{MgFe}_2\text{O}_4$ ) and chromite ( $\text{FeCr}_2\text{O}_4$ ) were the secondary ones. Also pure alumina, provided by the Aluminum Plant of Greece, was used in the mix design of material d. Alumina has a mean particle size ( $d_{50}$ ) of  $88.61 \mu\text{m}$  measured on a MALVERN Laser Particle Size Analyzer. Except for the aforementioned solid products, sodium hydroxide (Merck, anhydrous pellets), potassium hydroxide, sodium silicate solution (Merck,  $\text{Na}_2\text{O}:\text{SiO}_2 = 3.4$ ,  $\text{Na}_2\text{O} = 7.5\% - 8.5\%$ ,  $\text{SiO}_2 = 25.5\% - 28.5\%$  and  $d = 1.346 \text{ g}\cdot\text{l}^{-1}$ ) and deionized water were used for the synthesis. Finally, a strongly alkaline potassium hydroxide solution was also used for the synthesis of inorganic polymers. The solution was prepared by dissolving pellets (Merck, 99.5% purity) of anhydrous potassium hydroxide in deionized water.

### 3.2. Synthesis-Experimental Procedure

The fire resistant geopolymers were prepared according to the following procedure. A homogeneous viscous paste with the composition shown in **Table 2**, was initially prepared by mixing mechanically the raw material with the potassium hydroxide solution. Then, the paste was molded in appropriate open plastic (Ertacetal) molds and was cured at  $70^\circ\text{C}$  for 48 hours. After curing, the specimens were de-molded and the mechanical and thermophysical properties of the produced materials were measured.

### 3.3. Analysis and Tests

The geopolymer properties that were studied include uniaxial compressive strength, tensile strength, Young's modulus, thermal conductivity, apparent density, water absorption, porosity, shore hardness and behaviour upon exposure on fire. Compressive strength was measured according to ASTM C109 standard test using cubic specimens of 50 mm edge. The tensile strength was measured indirectly with the splitting tensile test (Brazilian test) performed on

**Table 2.** Synthesis and curing conditions of the geopolymer material.

Material	% w/w	% w/w
Metakaolin	40.2	-
Slag	-	42.24
$\text{SiO}_2$	17.6	-
$\text{Al}_2\text{O}_3$	-	25.03
KOH	17.95	8.09
$\text{H}_2\text{O}$	24.1	24.64
Curing temperature ( $^\circ\text{C}$ )	70	70
Curing time (h)	48	48

disc specimens of 55 mm diameter and 27.5 mm thickness, by adopting the relevant ISRM suggested method [ref]. The Young's modulus of the material was measured under uniaxial compression of prismatic specimens of  $50 \times 50 \text{ mm}^2$  cross section and 100 mm height. The axial strain was monitored by binding foil strain gauges in the middle-height of the specimen. The cold water absorption was determined according to the EN 771-1: 2003 standard test. The thermal conductivity of the material was measured with the HFM 436 Lambda Heat Flow Meter according to ASTM C518 standard test using a specimen of  $15 \times 15 \times 2 \text{ cm}$ . The apparent density was calculated by measuring the dimensions of the specimens with a precision electronic calliper as well as the weight of specimens with a precision balance. Open porosity was measured with Archimedes method. The hardness of the geopolymer was measured according to ASTM° D2240-00 standard test with shore D method.

The study of the material behaviour upon exposure on fire was based on the EFNARC guidelines for testing of passive fire protection for concrete tunnels linings. The laboratory tests were performed in a furnace which has the ability to simulate the temperature-time-curves employed in several international standards (such as the ISO-834 cellulose fire curve or the RWS tunnel fire curve). For this test a  $15 \times 15 \times 15 \text{ cm}$  (thickness) composite specimen was prepared, consisting of 5 cm thick geopolymer material and 10 cm thick concrete slab. The test was performed 28 days after the production of the specimen. The adhesion of the two materials was enhanced by the use of steel anchors, placed during curing of the material. During the test the free surface of the geopolymer material is exposed to a heat flux simulating a specific fire scenario. The developed temperature at the interface between the concrete and the geopolymer material was measured by using a "K"-type thermocouple, while the temperature of the back surface of the concrete slab was measured with a high performance infrared thermometer (RAYTEK, Raynger MX4). During the test any Acoustic Emission (AE) activity of the specimen was monitored. To capture the AE signals a piezoelectric AE transducer with 150 kHz resonant frequency was mounted on the back surface of the concrete. The mineralogical characterization of the fire resistant geopolymer after the fire test was performed by means of X-ray diffractometry (XRD) on a SIEMENS D 5000 diffractometer (**Figure 2**).



**Figure 2.** (a) Specimen before test  $40 \times 40 \text{ cm}$ , (b) experimental setup during the fire test.

## 4. Results and Discussion

### 4.1. Mechanical and Thermophysical Properties

As it may be observed from **Table 3**, both geopolymers achieved almost 9 MPa compressive strength and 1 MPa tensile strength within the period of the first 28 days from its production. The Young Modulus in compression at 28 days was measured equal to 3GPa for both geopolymers.

The hardness of the geopolymers was measured equal to 90 shore A for the metakaolin geopolymer and 70 shore A for the slag geopolymer rating them as hard material which is considered good enough for a superficial material. In comparison to other, fire resistant materials (**Table 3**), the geopolymers have similar mechanical properties with the Fire Barrier 135 but lower mechanical properties from the Meyco Fireshield 1350. The thermal conductivity of the metakaolin geopolymer was measured to be 0.21 W/m·K at 300 K and 0.19 for the slag geopolymer which is substantially lower than the corresponding ones of the commonly used structural building materials, such as concrete blocks (0.5 - 0.6 W/m·K) and cement or gypsum plasters (0.2 - 0.8 W/m·K). It is slightly higher from the thermal conductivity value of the Fire Barrier 135 and significantly lower from that of the Meyco Fireshield 1350, as is seen in **Table 3**. This property is very crucial for the performance of fire resistant materials because it determines the ability of materials to operate as efficient heat flux barriers. In general, for a given heat flux the lowest the thermal conductivity, the highest the established temperature gradient across the fire resistant material. In addition, for given heat flux and predetermined temperature drop inside the fire resistant material the lowest the thermal conductivity, the lowest the thickness of the superficial fire resistant material.

### 4.2. Performance to Thermal Loading

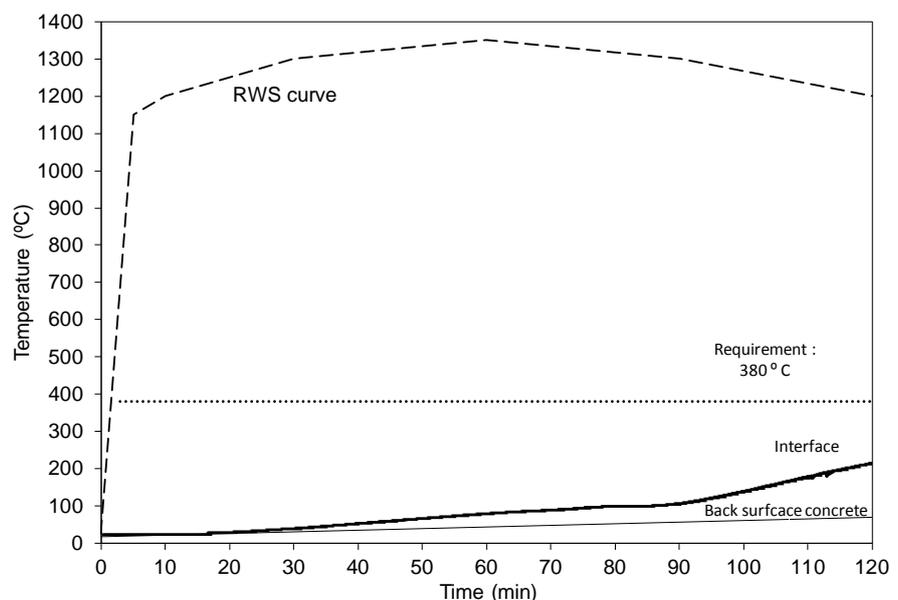
The behavior of the geopolymer during the passive fire protection test is shown

**Table 3.** Physical and mechanical properties of the geopolymers and other commercial fire resistant materials withstanding the RWS fire load curve.

	Fire barrier 135	Meycofireshield 1350	Slag geopolymer	Metakaolin geopolymer
Thermal conductivity at 300 K ( $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ )	0.185	0.41	0.16	0.21
Density ( $\text{kg}/\text{m}^3$ )	1150	1200 - 1800	1800	1700
Young modulus E (MPa)	4050	7900	3300	3000
Compressive/tensile strength (MPa)	9/0.8	15 - 18/1.5	8.7/0.94	9/1
Porosity (%)	66	52	40	29
Hardness	90 Shore A	-	70 shore A	90 shore A
Cold water absorption %	49%	18%	18 %	8.7%

in **Figure 3**, where the attained temperature at the concrete/geopolymer interface, the temperature at the unexposed concrete surface and the furnace temperature simulating the RWS fire load curve are drawn as a function of time.

As it is observed, the temperature at the geopolymer/concrete interface was lower than 220°C during the whole duration of the fire test. This temperature was at least 160°C lower than the performance requirements for an efficient fire resistant material set by the E.F.N.A.R.C for a passive fire protection test with the RWS fire loading curve. At the first 25 minutes, where the temperature in the furnace was increased rapidly from the ambient temperature to 1280°C, the interface temperature was remained at 30°C establishing a temperature gradient across the fire resistant geopolymer equal to 25°C/mm. Then, the interface temperature started increasing, with a low rate of 1.27°C/min reaching 100°C at about 80 minutes of test duration. During this time period the furnace temperature reached the maximum value of the test (=1350°C), while the temperature at the interface was just 80°C, establishing a temperature gradient equal to 25.4°C/mm which is attributed to its low thermal conductivity value (0.21 W/m·k). After the 80 minutes of the test, the temperature remained for 6 minutes constant at 100°C with a temperature gradient at 23.9°C/mm. The temperature plateau at 100°C was attributed to the removal of geopolymeric water through an endothermic water evaporation process consuming large amount of the incoming heat due to the large latent heat of water evaporation and keeping the interface temperature more or less constant at around 100°C. From this point onwards, the temperature at the geopolymer/concrete interface increased with an average rate of 3.41°C/min while the furnace temperature decreased to 1200°C. At the end of the fire test the interface temperature was 216°C and the temperature gradient was 19.7°C/mm. Finally, the temperature in the back surface of the



**Figure 3.** Performance of the metakaolin geopolymer to thermal loading simulating the RWS fire load curve.

concrete slab did not exceed 70°C during the whole duration of the fire test as is seen in **Figure 4**, which means that across the concrete slab the temperature was varied in-between 70°C and 216°C, temperatures that do not create spalling to the concrete.

As it is seen in **Figure 4**, the metakaolin geopolymer after the end of the fire test has been exfoliated with an intense cracking on the surface due to the sudden loss of geopolymeric water at elevated temperatures. However the geopolymer remained fully bonded to the concrete without losing its structural integrity. Smelting or macroscopic creeping phenomena due to exposure at high temperatures were not observed in the geopolymeric material. Its adhesion with the concrete slab assisted by the steel anchors proved to be successful and any serious detachment at the materials interface was not observed. The geopolymer remained on top of the concrete slab without any change in its geometry.

The concrete slab protected by the metakaolin geopolymer did not appear any form of spalling or other mechanical damage and remained as it was initially before the fire test. This was also verified by the acoustic emission monitoring, since no AE signals were detected during the whole test duration. It was clearly observed by a simple comparison of the metakaolin geopolymer specimen before and after the fire test that the physical appearance of the material was changed. Its colour was changed from white to brown and grey indicating that mineralogical transformations took place during the exposure of material at high temperatures. In addition, colour variation across the material thickness was observed, as is shown in **Figure 5**, indicating that different phase transformations were taken place as a temperature gradient was established across the material during the fire test. Three distinct different thermal zones were observed.



**Figure 4.** (a) Face of geopolymer exposed to fire, (b) side view of concrete-geopolymer specimen after the fire test.

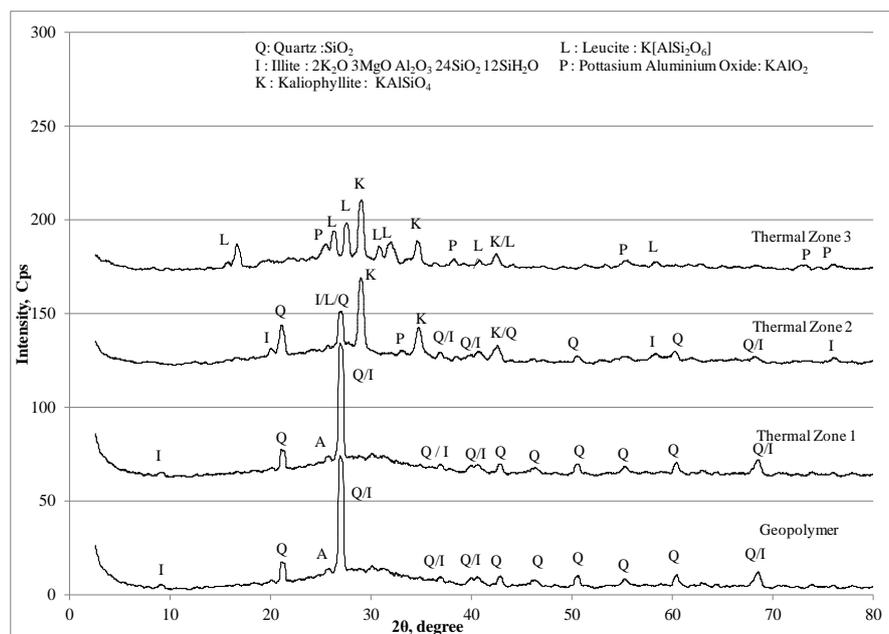


**Figure 5.** Colour variation across the metakaolin geopolymer after the fire test.

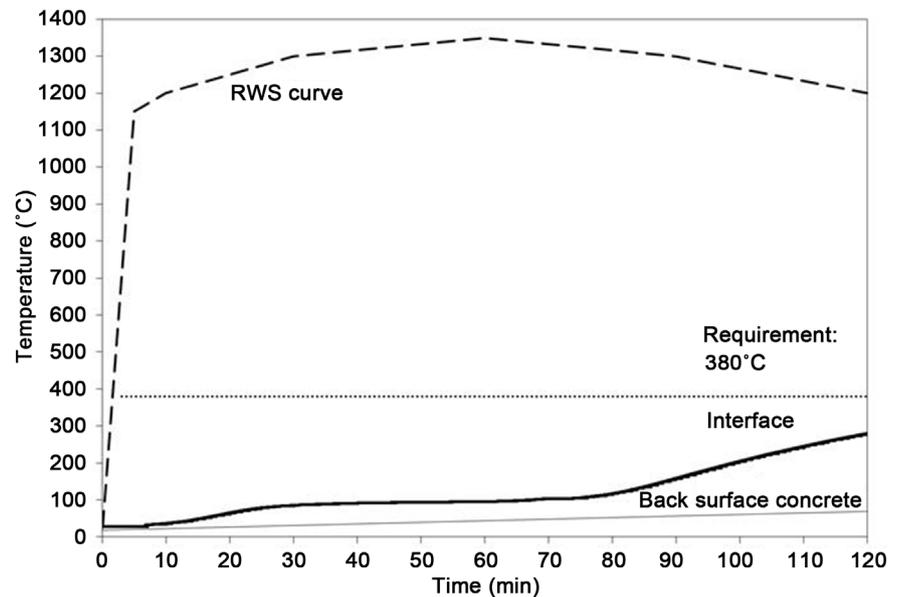
The material in thermal zone I resembled the initial metakaolin geopolymer (amorphous containing quartz, illite and anatase) as is seen in **Figure 6** where the X Rays Diffractograms of the material in the three thermal zones are shown. This observation indicates that the temperature in thermal zone I was too low to initiate mineralogical transformations. In the material in the thermal zone II, where the temperature was higher, the amorphous aluminosilicate phase had been crystallized and other mineralogical phases appeared, such as leucite and kaliophyllite together with remaining quartz and illite from the silicon dioxide and metakaolin respectively. Finally, the material in the very hot thermal zone III was further recrystallized. It was composed from the refractory mineralogical phases of leucite, kaliophyllite and potassium aluminium oxide which explains the successful behaviour of the material during the thermal test without macroscopic creeping phenomena.

Concerning the slag geopolymer the behavior under the fire loading test is shown in **Figure 7**, where the attained temperature at the concrete/geopolymer interface, the temperature at the unexposed concrete surface and the furnace temperature simulating RWS fire load curve are shown as a function of time.

As it is observed, the temperature at the geopolymer/concrete interface was lower than 280°C during the whole duration of the fire test. This temperature was at least 100°C lower than the performance requirements for an efficient fire resistant material set by the EFNARC for a passive fire protection test with the RWS fire loading curve. In addition, the interface temperature remained below 100°C for almost the first 80 minutes of the fire test. At the first 5 minutes where the temperature in the furnace were increased rapidly from the ambient temperature to 1140°C, the interface temperature was remained at 30°C establishing a



**Figure 6.** X-ray diffractogram of the initial metakaolin geopolymer as well as the materials in the three different thermal zones after the fire test.



**Figure 7.** Performance of the slag geopolymer to thermal loading simulating the RWS fire load curve.

temperature gradient across the fire resistant slag geopolymer equal to  $22.2^{\circ}\text{C}/\text{mm}$ . Then, the interface temperature started increasing reaching a plateau at  $100^{\circ}\text{C}$  at about 35 minutes test duration. At this time the furnace temperature was  $1310^{\circ}\text{C}$  and the established temperature gradient across the slag geopolymer was even higher at  $24.2^{\circ}\text{C}/\text{mm}$ . The interface temperature remained at about  $100^{\circ}\text{C}$  for the next 45 minutes till the fire duration of 80 minutes. At 60 minutes, the furnace temperature reached its highest value of  $1350^{\circ}\text{C}$  establishing the highest temperature gradient ( $25^{\circ}\text{C}/\text{mm}$ ) across the fire resistant K-geopolymer during the entire duration of the fire test. Then, the furnace temperature started decreasing reaching  $1310^{\circ}\text{C}$  after 20 minutes establishing now a lower temperature gradient ( $24.1^{\circ}\text{C}/\text{mm}$ ). The temperature plateau at  $100^{\circ}\text{C}$  was attributed to the removal of geopolymeric water through an endothermic water evaporation process consuming large amount of the incoming heat due to the large latent heat of water evaporation and keeping the interface temperature more or less constant at around  $100^{\circ}\text{C}$ . From this point onwards, the temperature at the slag geopolymer/concrete interface started increasing while the furnace temperature decreased to  $1200^{\circ}\text{C}$ . At the end of the fire test the interface temperature was  $280^{\circ}\text{C}$  and the temperature gradient was  $18.4^{\circ}\text{C}/\text{mm}$ , which represented the lowest one measured value during the whole duration of the fire test. Finally, the temperature in the back surface of the concrete slab did not exceed  $70^{\circ}\text{C}$  during the whole duration of the fire test as is seen in **Figure 9**, which means that across the concrete slab the temperature was varied in-between  $70^{\circ}\text{C}$  and  $280^{\circ}\text{C}$ .

As it is seen in **Figure 8**, the slag geopolymer superficial material after the end of the fire test did not appear any mechanical damage. It remained on top of the concrete slab without any change in its geometry as well as without the appearance of any cracks. Even more, the surface of the slag geopolymer that was ex-



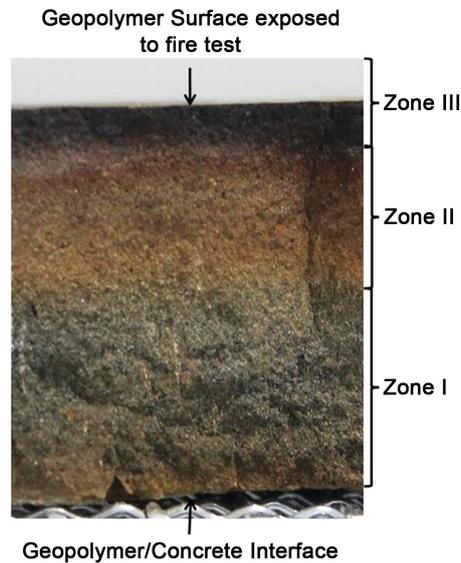
**Figure 8.** Face of geopolymer exposed to fire.

posed directly during the fire test at temperature as high as 1350°C remained almost intact without cracks or other mechanical damages except some local, small in extent and not deep, superficial scaling. The hardness of the surface of slag geopolymer after the end of the test was measured equal to 80 shore A, which is higher than the one of the green slag-geopolymer (**Table 3**) rating the material now as a hard one. Taking into account that in general hardness and mechanical strength are qualitatively analogue quantities, it can be assumed that after the fire test the superficial slag-geopolymer became tougher and stronger and the fire helped in improving the mechanical properties of material. The concrete slab protected by the slag-geopolymer did not appear any form of spalling or other mechanical damage and remained as it was initially before the fire test. This was also verified by the acoustic emission monitoring, since no AE signals were detected during the whole test duration.

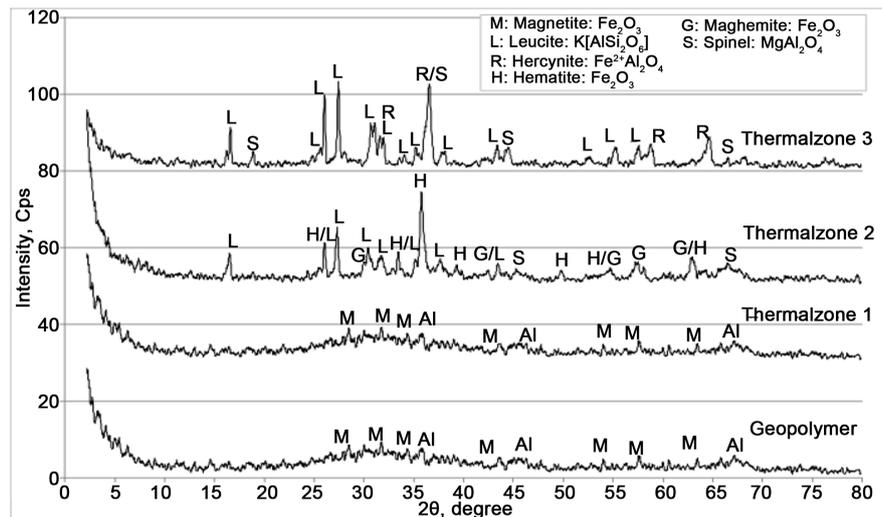
Also colour variation across the geopolymeric material was observed as is shown in **Figure 9** indicating that different phase transformations were taken place as a temperature gradient was established across the material during the fire test. Three distinct different thermal zones were observed. The material in thermal zone I resembled the initial slag geopolymer (principally amorphous containing magnetite as the only crystalline phase) as is seen in **Figure 10** where the X Rays Diffractograms of the material are shown. This observation indicates that the temperature in thermal zone I was too low to initiate mineralogical transformations. The material in the thermal zone II, where the temperature was higher, had been recrystallized losing its initial amorphous character. Magnetite disappeared and its oxidation products maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) were observed changing the colour from deep green gradually to yellow and red. The amorphous aluminosilicate phase had been crystallized to leucite as is seen in **Figure 10**. Finally, the material in the very hot thermal zone III was further recrystallized. It was composed from the refractory mineralogical phases of leucite and hercynite together with remaining hematite.

## 5. Conclusions

The comparison of these two fire resistant geopolymers showed the following:



**Figure 9.** Colour variation across the slag geopolymer after the fire test.



**Figure 10.** X-ray diffractogram of the initial slag geopolymer as well as the materials in the three different thermal zones after the fire test.

- The performance of both geopolymers to RWS thermal load was excellent. The material proved to have the ability to put an efficient heat flux barrier protecting the tunnel concrete lining as well as the steel reinforcement from the most severe fire incidents that may happen in underground constructions.
- No concrete spalling was observed during or after the thermal loading test for both geopolymers. This was also verified by the absence of any acoustic emission signals during the whole test duration. The compressive strength of the concrete remained similar to the one measured before the test.
- The macroscopic behaviour after the fire test seems to be quite better for the slag geopolymer than the metakaolin geopolymer. The slag geopolymer did not appear cracks or any damage while at the same time the metakaolin geo-

polymer showed intense cracking and damage. The reason is attributed to the raw material used since the metakaolin is a clay in contrast with the slag. The cracking of metakaolin geopolymers is a usual problem referred in the literature.

- The slag geopolymer did not appear any mechanical damage or deformation which suggests that there is no need for serious repairs after a fire incident. The material will remain on top of the concrete lining necessitates only minor interventions which will not close the tunnel for more than a week.
- Concerning the properties, both materials showed similar properties. More specific the 28 days compressive strength reached the value of 9 MPa with a Young's Modulus in compression equal to 3 GPa, and a tensile strength of 1 MPa. The mechanical properties of the geopolymers are comparable with those of the existing fire proofing materials.

As a final conclusion, the developed geopolymers have been proved, through small scale passive fire protection test, to possess excellent fire resistant properties. It can put an effective heat flux barrier allowing for a successful passive fire protection to the tunnels concrete linings from the most severe fire incidents that can happen in underground constructions. This anticipated behavior should also be verified with large scale as well as pilot tests before any application in practice.

## Acknowledgements

Greek Scholarship Foundation (IKY) Fellowships of excellence for postgraduate studies in Greece. Siemens Program.

## References

- [1] Graham, E. (2005) Solutions for Explosive Problems. *Journal of Tunnels & Tunneling International*, **39**, 44-45.
- [2] Fletcher, I., Welch, S., Torero, J., Carvel, R. and Usman A. (2007) Behaviour of Concrete Structures in Fires. *Journal of Thermal Science*, **11**, 37-52. <https://doi.org/10.2298/TSCI0702037F>
- [3] Sakkas, K., Nomikos, P., Sofianos, A. and Panias, D. (2013) Inorganic Polymeric Materials for Passive Fire Protection of Underground Constructions. *Journal of Fire and Materials*, **37**, 140-150. <https://doi.org/10.1002/fam.2119>
- [4] Edwards, W.T. and Gamble, W.L. (1986) Strength of Grade 60 Reinforcing Bars after Exposure to Fire Temperatures. *Journal of Concrete International*, **8**, 17-19.
- [5] National Codes and Standards Council of the Concrete and Masonry Industries (1994) Assessing the Condition and Repair Alternatives of fire Exposed Concrete and Masonry Members. Fire Protection Planning Report, 14.
- [6] American Petroleum Institute Publication (2000) API RP 579 Fitness-for-Service. 1st Edition. American Petroleum Institute Publication, USA.
- [7] Davidovits, J. (1999) Geopolymer'99. *2nd International Conference*, Saint-Quentin, 9-39.
- [8] Van Deventer, J.G.S., Van Deventer, J.S.J. and Lukey, G.C. (2002) The Effect of Composition and Temperature on the Properties of Fly Ash- and Kaolinite-Based

- Geopolymers. *Chemical Engineering Journal*, **89**, 63-73.  
[https://doi.org/10.1016/S1385-8947\(02\)00025-6](https://doi.org/10.1016/S1385-8947(02)00025-6)
- [9] Davidovits, J. (1988) Geopolymer Chemistry and Properties. *Proceedings of the 1st International Conference on Geopolymer'88*, Compiègne, 1-3 June 1988, 25-48.
- [10] Cioffi, R., Maffucci, L. and Santoro, L. (2003) Optimization of Geopolymer Synthesis by Calcination and Polycondensation of a Kaolinitic Residue. *Journal Resource, Conservation and Recycling*, **40**, 27-38.  
[https://doi.org/10.1016/S0921-3449\(03\)00023-5](https://doi.org/10.1016/S0921-3449(03)00023-5)
- [11] Xu, H. and Van Deventer, J. S. J. (2000) The Geopolymerisation of Alumino-Silicate Minerals. *International Journal of Mineral Processing*, **59**, 247-266.  
[https://doi.org/10.1016/S0301-7516\(99\)00074-5](https://doi.org/10.1016/S0301-7516(99)00074-5)
- [12] Wang, H., Li, H. and Yan, F. (2005) Synthesis and Mechanical Properties of Meta-kaolinite-Based Geopolymer. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **268**, 1-6. <https://doi.org/10.1016/j.colsurfa.2005.01.016>
- [13] Vaou, V. and Panias, D. (2010) Thermal Insulating Foamy Geopolymers from Perlite. *Journal of Minerals Engineering*, **23**, 1146-1151.  
<https://doi.org/10.1016/j.mineng.2010.07.015>
- [14] Swanepoel, J.C. and Strydom, C.A. (2002) Utilisation of Fly Ash in a Geopolymeric Material. *Journal of Applied Geochemistry*, **17**, 1143-1148.  
[https://doi.org/10.1016/S0883-2927\(02\)00005-7](https://doi.org/10.1016/S0883-2927(02)00005-7)
- [15] Wu, H.C. and Sun, P. (2007) New Construction Material from Fly Ash Based Lightweight Inorganic Polymer. *Journal of Construction and Building Materials*, **21**, 211-217. <https://doi.org/10.1016/j.conbuildmat.2005.06.052>
- [16] Panias, D., Giannopoulou, I. and Perraki, T. (2007) Effect of Synthesis Parameters on the Mechanical Properties of Fly Ash-Based Geopolymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **301**, 246-254.  
<https://doi.org/10.1016/j.colsurfa.2006.12.064>
- [17] Bakharev, T. (2005) Geopolymeric Materials Prepared Using Class F Fly Ash and Elevated Temperature Curing. *Cement and Concrete Research*, **35**, 1224-1232.  
<https://doi.org/10.1016/j.cemconres.2004.06.031>
- [18] Cheng, T.W. and Chiu, J.P. (2003) Fire-Resistant Geopolymer Produced by Granulated Blast Furnace Slag. *Journal of Minerals Engineering*, **16**, 205-210.  
[https://doi.org/10.1016/S0892-6875\(03\)00008-6](https://doi.org/10.1016/S0892-6875(03)00008-6)
- [19] Maragkos, I., Giannopoulou, I. and Panias, D. (2008) Synthesis of Ferronickel Slag-Based Geopolymers. *Journal of Minerals Engineering*, **22**, 196-203.  
<https://doi.org/10.1016/j.mineng.2008.07.003>
- [20] Giannopoulou, I., Dimas, D., Maragkos, I. and Panias, D. (2009) Utilization of Solid By-Products for the Development of Inorganic Polymeric Construction Materials. *Global NEST Journal*, **11**, 127-136.



**Submit or recommend next manuscript to OALib Journal and we will provide best service for you:**

- Publication frequency: Monthly
- 9 [subject areas](#) of science, technology and medicine
- Fair and rigorous peer-review system
- Fast publication process
- Article promotion in various social networking sites (LinkedIn, Facebook, Twitter, etc.)
- Maximum dissemination of your research work

Submit Your Paper Online: [Click Here to Submit](#)

Or Contact [service@oalib.com](mailto:service@oalib.com)