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Valorization of Industrial Waste for the Development of Fire-Resistant Materials

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Abstract

The development of a Fe-based geopolymer and its performance under thermal loading is examined. The geopolymer is developed by mixing industrial waste with a highly alkaline activator, KOH, in the aqueous phase. The mechanical, physical and thermal properties and their respective variation with time are measured. It is shown that the material presents adequate mechanical strength and excellent physical and thermal properties. Then, the geopolymer material is subjected to thermal loading with the modification of a standardized passive fire protection test. The temperature of the exposed surface of the material follows the ISO fire curve that is based on the burning rate of the materials found in general building materials. The material succeeded in the test without failing in any of the criteria concerning the temperature in the unexposed surface of the specimen and its internal integrity. During the test, the temperature in the material-concrete interface remained around 100˚C, which is below the test requirements. Thus, the concrete slab protected by the geopolymer did not appear any form of spalling. From this test, it is concluded that the specific geopolymer material by creating a high thermal gradient is able to resist adverse fire scenarios for temperatures up to 1049˚C (ISO 834 curve) rendering a proper fire-resistant material for building applications.

Subject Areas

Material Experiment

Keywords

Geopolymer, Fe Slag, Fire Resistant, Passive Fire Protection

1. Introduction

Geopolymerization process is based on a heterogeneous chemical reaction that

occurs between solid materials rich in alumino-silicate oxides and highly alkaline silicate solutions. The geopolymerization reaction is exothermic and takes place at atmospheric pressure and temperatures below 100˚C [1]. Under a complicated mechanism, this reaction results in the formation of durable and compact solid materials characterized by a specific three-dimensional polymeric structure. The produced materials comprise a family of novel inorganic polymeric materials, which are also called "geopolymers". The most proposed mechanisms for the geopolymerization process [2] [3] include the following four stages that proceed in parallel and thus, it is difficult to be distinguished: 1) Si and Al dissolution from the solid alumino-silicate materials in a strongly alkaline aqueous solution, 2) formation of oligomers (polynuclear hydroxy-complexes of silicon and aluminium) consisting of polymeric bonds of Si-O-Si and Si-O-Al type, 3) polycondensation of the oligomers to form a three-dimensional aluminosilicate framework (geopolymeric framework) comprising SiO_4 and/or AlO_4 tetrahedra linked alternately by sharing common oxygen ions and (iv) bonding of the non-dissolved solid particles into the geopolymeric framework and hardening of the whole system into a final solid polymeric material. Geopolymers are amorphous to semi-crystalline materials and possess excellent physicochemical and mechanical properties, like low density, micro- or nano-porosity, high mechanical strength, notable surface hardness, thermal stability, and fire and chemical resistance [1] [3]-[9]. Due to these properties, geopolymers are viewed as alternatives for certain industrial applications in the areas of construction and building materials such as pavement blocks and tiles.

In this research, the development of a fire-resistant geopolymer is examined [8] [10]-[15]. The purpose of the new product is to be used as a filler in paints and/or coatings providing fire-resistant properties. A number of standards have been developed to test and compare the performance of fire-proofing materials. The international standard ISO 834 contains the most commonly adopted fire curve and is based on a cellulose fire (**Figure 1**). This curve is the best to test the

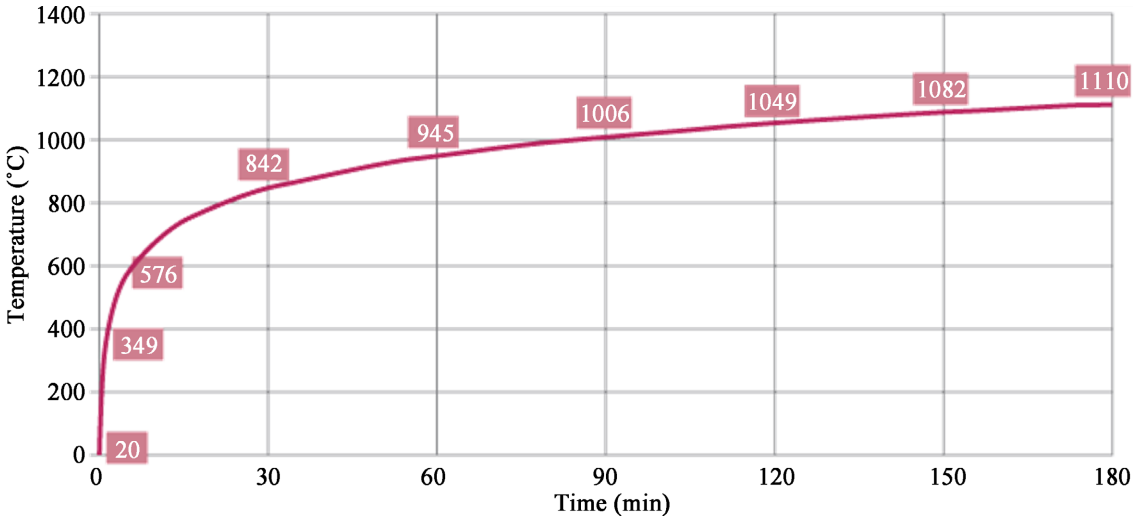

Figure 1. Time-temperature curve according to ISO 834.

fire resistance of elements of building construction, but may also be used for tunnels. The temperature in this curve follows the equation:

$$T = 20 + 345\log_{10}(8t + 1) \quad (1)$$

where T is the furnace temperature (in ˚C) and t is the time (in min).

This curve follows three requirements:

Failure condition 1: The average temperature of the unexposed face of the test specimen exceeds the initial temperature by more than 140 K (˚C).

Failure condition 2: The temperature at any location on the unexposed face of the test specimen exceeds the initial temperature by more than 180 K.

Sample integrity: The failure in relation to integrity shall be deemed to have occurred upon collapse, the development of cracks, fissures or other openings through which flames or hot gases can pass. The standard notes that a crack is more than 6 mm wide and/or can be measured to be 25 mm deep using a gauge constitutes a failure of the sample's integrity.

2. Experimental

2.1. Materials

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 development of inorganic polymers, an adequate quantity of granulated slag was grinded to <90 lm and the resulted powder had a mean particle size (d_{50}) of 15.05 lm. As is 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 and calcium oxides, as well as traces of nickel. The mineralogical analysis of the slag (Figure 2) showed that it is mainly composed of an X-ray.

To develop the geopolymers an alkaline potassium hydroxide solution was also used for the synthesis of geopolymer. The solution was prepared by dissolving pellets of anhydrous potassium hydroxide (Merck, 99.5% purity) in deionised water.

Table 1. Analysis of slag.

Species	% w/w
SiO_2	41.14
Al_2O_3	13.79
FeO	34.74
Cr_2O_3	5.41
MgO	3.59
CaO	0.71
Ni	0.14

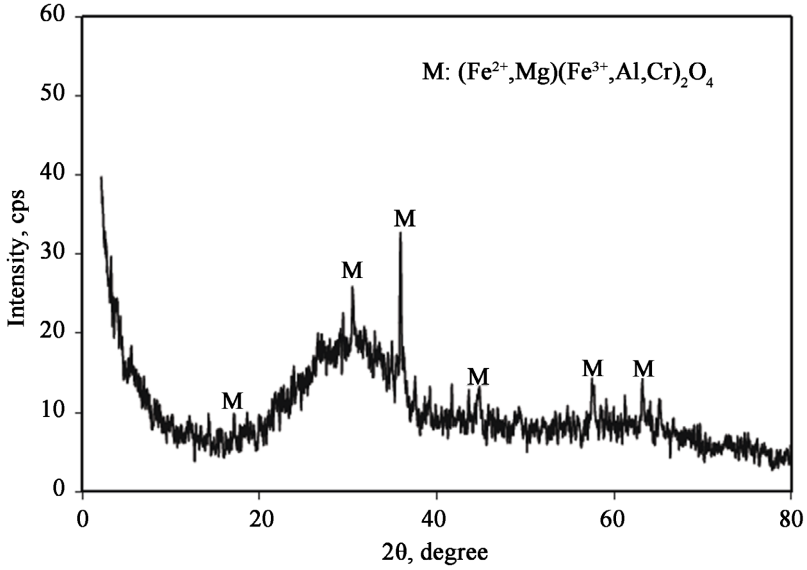

Figure 2. X-ray diffractogram of the FeNi-slag used in the present study.

Table 2. Synthesis of the geopolymer material.

Material	K-based geopolymer
Raw material	75.5
KOH	9.2
H_2O	15.16

2.2. Experimental Procedure

The geopolymer was prepared according to the following procedure:

A homogeneous viscous paste was initially prepared by mixing mechanically the FeNi slag (75.76% w/w) with 7 M potassium hydroxide solution (5.3% w/w) at a solid to liquid ratio equal to 4 g/ml. After mixing for 5 minutes the paste was casted in appropriate open plastic (Ertacetal) moulds and was cured at ambient temperature for 48 hours (Table 2).

After curing, the specimens were de-molded and the mechanical and thermophysical properties of the produced materials were measured through a set of tests.

2.3. Analysis and Tests

The geopolymer properties that were studied in this work include uniaxial compressive strength, tensile strength, flexural strength, Young's modulus E, thermal conductivity, specific heat, apparent density, water absorption, absorption coefficient, porosity, shore hardness, pH (alkalinity) and behaviour in the passive fire protection test. Compressive strength was measured according to ASTM C109 using cubic specimens of 50 mm edge. The flexural strength was measured according to ASTM C348 using prismatic beam specimens of 40 × 40 mm^2 cross section and 160 mm length. The thermal conductivity of the material was meas-

ured with HFM 436 LambdaTM Heat Flow Meter Heat according to ASTM C518 using a specimen of 15 × 15 × 2 cm. Specific heat (C) was measured through Differential Scanning Calorimetry (DSC). The apparent density (Apparent Density) of the geopolymer was calculated as the average of the values of the apparent density of three specimens. The passive fire protection test was performed in the laboratory by using a test furnace which was designed according to the EFNARC guidelines. The furnace has the ability to simulate the time-temperature curves employed in several international standards (such as the ISO 834 cellulose fire curve or the RWS tunnel fire curve). For this test a 20 × 20 × 13 cm (thickness) specimen was prepared, consisting of 3 cm thick geopolymer material and 10 cm thick concrete slab, constructed according to the EFNARC guidelines. The test was performed 28 days after the production of the specimen. 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).

3. Results and Discussion

3.1. Mechanical and Physical Properties

The compressive strength of the K-geopolymer specimens was increased from 6.2 MPa to 8.7 MPa within 28 days from initial curing. The 1-day and 28-days flexural strength was 1.08 MPa and 2.14 MPa respectively, which means that about 50% of the 28-days strength it was developed within 24 h after material curing. The 28-days Young's Modulus in compression was 3.3 GPa, while the 28-days indirect tensile strength was 0.94 MPa. The thermal conductivity of the material was measured to be 0.16 W/m·K at 300˚K. Thermal conductivity influences the rate of heat transfer into the structural member and thus it is most crucial for the performance of fire-resistant materials. In general, for a given heat flux, the lowest the thermal conductivity the highest the established temperature gradient across the fire-resistant material. The hardness of K-geopolymer was measured equal to 70 shore A, rating it as a medium hard material, which is good enough for a superficial coating material. Finally, the density of K-geopolymer was measured equal to 1800 kg/m^3. Cold water absorption was measured 18% and the porosity to 40% (**Figure 3**).

3.2. Performance to Thermal Loading

The passive fire protection test was performed as described in paragraph 2.3. In **Figure 4**, the temperature development at the concrete-geopolymer interface during time is shown, together with the measured temperature at the unexposed concrete surface and the furnace temperature prescribed by the ISO 834 curve. As it is observed, the interface temperature remained under 100˚C until a time

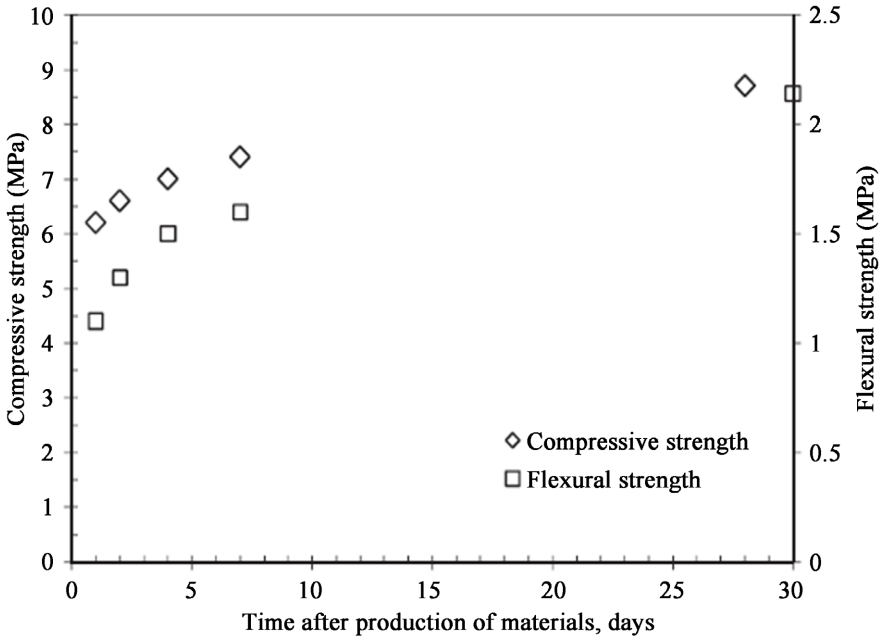

Figure 3. Mechanical properties of K-geopolymer versus time after production.

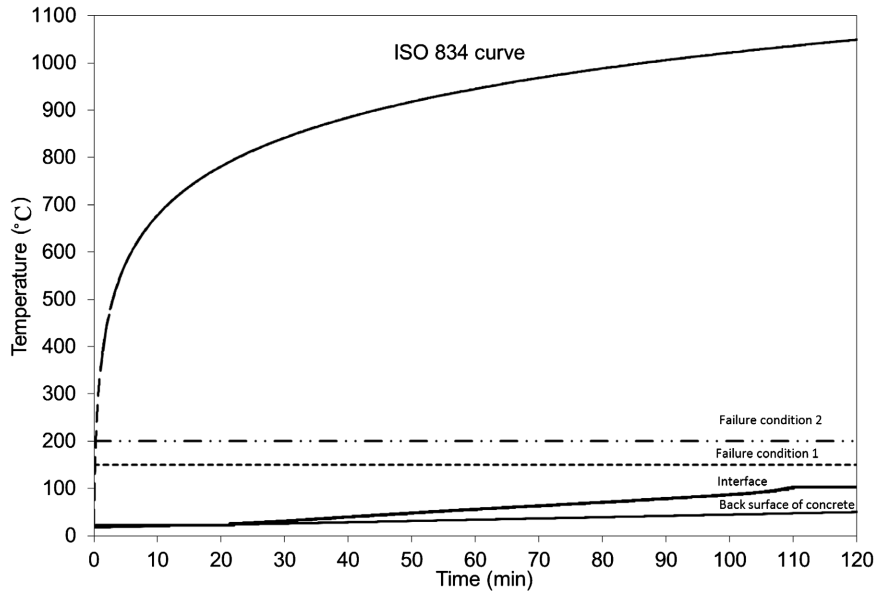

Figure 4. Fire protection test of the potassium based geopolymer according to ISO 834.

of 110 min and near 100˚C for the remaining 10 min of the test. This is much lower than the required temperature for maintaining the structural integrity of the concrete. The specimen did not exceed any of the failure conditions defined by ISO 834. At time 120 min of the test a temperature difference of 950˚C was attained between the exposed and unexposed surface of the geopolymer material, creating thus a local thermal gradient of 19˚C/mm. The temperature in the back surface of the concrete specimen did not exceed 50˚C, which is close to the ambient temperature (25˚C). Further, as it is clearly observed from the below photographs (**Figure 5**), the geopolymer material did not appear any creeping or

(a) (b)

Figure 5. Test specimen (a) before and (b) after the exposure to fire.

mechanical damage but only a change in colour, which is attributed to mineralogical transformations. In the front face of the specimen, some cracks were observed after the test due to the sudden loss of physically absorbed water that however they are less than 6 mm wide and 25 mm deep. The concrete slab protected by the sodium-based geopolymer did not appear any form of spalling or creeping.

4. Conclusions

A fire-resistant material that has been developed with the geopolymerisation technique by using a Fe reach slag as the raw material, is presented. The material is developed by mechanical mixing of the slag with a potassium hydroxide solution at a solid-to-liquid ratio equal to 4 g/ml, to produce a homogeneous viscous paste that is then molded and cured at ambient temperature for 48 hours.

The measured temperature at the geopolymer-concrete interface during the passive fire protection test simulating the ISO 834 time-temperature curve remained lower than the test requirements. Thus, the protected concrete slab did not appear any spalling phenomena, which was also verified by the absence of any acoustic emission signals. This very good performance is attributed to the low thermal conductivity. The geopolymer material itself did not appear any spalling phenomena and/or mechanical damage after the passive fire protection test. Some cracks formed at the exposed surface during the sudden loss of the physically absorbed water were found to be of limited width and depth.

It is concluded that the presented geopolymer may effectively set a temperature and a flame barrier during an ISO 834 fire temperature curve, protecting the construction elements from damage and spalling and limiting the possibility of spreading an incipient fire.

5. Next Steps

The developed material will be further tested as: 1) filler in plaster of ETICS system, replacing commercially available fillers, and 2) in paints and varnishes for metal, wood and concrete surfaces. Furthermore, the fire-resistant plaster will be

tested for its properties (open time, adhesion, stability, elasticity, colour retention) and fire resistance properties according to ISO 834 (for building applications) and also RWS (for tunnel applications).

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Conflicts of Interest

The authors declare no conflicts of interest.

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