New Eco-Friendly Inorganic Polymeric Materials for the Passive Fire Protection of Structures

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Abstract Passive fire protection of structures is of great importance nowadays. Several fires that broke out in buildings and other structures like tunnels, worldwide, resulted in the destruction of structures and more importantly, in the loss of human lives. However, the high cost of commercial fire-resistant products for construction often makes their application prohibitive. This paper deals with the development of new fire-resistant inorganic polymers (or geopolymers) based on recycled construction and demolition ceramic wastes, through the geopolymerization technology, which achieves a drastic reduction of energy use and CO_2 emissions, in comparison to the production technologies currently used for commercial fire-resistant products. The developed materials were tested at high temperatures, which simulated the anticipated temperatures developed in a fire case and their mechanical and physical properties were evaluated. According to the results, the developed geopolymers kept their form and shape up to 1050 °C, appearing with only negligible surface cracks, without phenomena of apparent deformation or creeping. The residual compressive strength of the developed materials ranged from 20 to 38 MPa, while their density was measured from 1430 to 1570 kg/cm^3, and their mass loss in between 4 and 10%, after their thermal testing at 1050 °C. Based on the findings of this study, the new materials are promising for the passive fire protection of buildings and constructions in comparison with conventional materials currently used in such applications.

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Introduction

The fire protection of buildings and civil engineering structures made of concrete and pre-stressed concrete is of great importance nowadays. Several serious fire incidents in buildings and road/railway tunnels, reported during the last decades worldwide, led to severe human casualties, serious structural damages, and dramatic injuries for the local communities and economies. When a building is exposed to high temperatures that normally occurred during fire incidents (>1000 °C), all the structural materials and elements, like cement, steel, bricks, and even natural stones, are significantly damaged or totally destroyed. From a structural point of view, the most critical damage occurred due to thermal loads in a fire is the 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 the fire. It is caused particularly by the spontaneous great amounts of heat release and the aggressive fire gases generated and should lead to the loss of the building's structural reliability and the failure of its operation. In general, spalling phenomena in concrete are expected at several temperatures, depending on the strength and the densification of the concrete; in dense concrete, explosive spalling has been observed at temperatures between 300 and 450 °C [1]. At temperatures higher than 300 °C, the mechanical strength of concrete is considered to be significantly reduced [1] and as it is generally accepted, concrete loses its carrying capacity when exposed to temperatures higher than 380 °C [2]. This temperature is close to the dehydration temperature of portlandite (400 °C) that comprises a basic constituent of cement and the exposure of concrete at this temperature, leads to structural disordering, thus causing a significant reduction of the concrete mechanical strength [3].

Therefore, to maintain the stability of structures in case of a fire and to avoid spalling of concrete, it is crucial to limit the spread of fire and at the same time, to protect the concrete structure against high thermal loads developed during this situation. This could be achieved through active and passive fire protection systems, which are currently used in buildings and structures. Active fire protection is referred to automatic fire detection and fire suppression systems, while passive fire protection is related to the so-called fire-resistant materials. These materials seek to limit a fire in the building location where it occurred for a crucial period and to maintain the temperature of important building components (steel rebars, electric installations, etc.) below a critical value, thus allowing for the building to withstand the anticipated temperatures of a fire without losing its structural stability. The fire-resistant materials currently used in structures include spray fireproofing inorganic plasters, boards, and sheets made of gypsum, calcium silicate, and expanded aggregates and cementitious plasters reinforced with cellulose fibers treated with ammonium sulfate or borate and mineral wool [4]. Among them, the cladding of structures with calcium silicate

(CaSi) is the most successful, traditional, and popular fireproofing method applied in Europe.

Although fire-resistant materials seem to be a preferable solution for the fire protection of buildings and constructions, and a variety of such commercial products already exists, the high cost substantiates a crucial drawback that limits their implementation. Therefore, it is imperative to develop new, cost-effective materials with improved thermal and mechanical properties for the passive fire protection of buildings and constructions. From this point of view, geopolymers or inorganic polymers, based on alkali-activated binders, seem to be advantageous materials. These materials are produced according to the geopolymerization process that involves a chemical reaction between materials rich in silicon and aluminum amorphous phases and alkali silicate solutions, under highly alkaline conditions. The geopolymerization reaction takes place at atmospheric pressure and temperatures below 100 °C and yields amorphous to semi-crystalline solid materials characterized by a specific three-dimensional polymeric structure, consisting of Si–O–T–O bonds, where T denotes principally, Al or Si and secondarily, other metals such as Fe [5, 6]. Geopolymers possess excellent physical, chemical, thermal, and mechanical properties, based on which they should be viewed as alternative materials for certain industrial and construction applications. Except for that, these materials have a very low embodied energy and CO_2 footprint, compared to conventional building materials, and exhibit rapid mechanical strength development, as well as durability in corrosive environments. However, their greatest advantage is that, based on the choice of raw materials and the design of the processing, geopolymers can meet a variety of requirements. This flexibility of geopolymer synthesis is of great importance when products with specific properties are required [7–9]. The solid alumino-silicate materials used for the production of geopolymers include natural minerals and rocks, such as clays and industrial minerals, as well as a wide range of industrial and urban waste available in large to enormous quantities, such as fly ash, metallurgical slags, mining overburdens and tailings waste glass, and construction and demolition wastes [5, 6, 8, 10]. Specifically, the latter group of raw materials is extremely attractive for the technological development of construction materials due to their low cost, as well as for environmental reasons.

In this paper, two specific streams of Construction and Demolition Waste (CDW), namely waste bricks (WB) and waste ceramic tiles (WCT) have been studied for the development of inorganic polymeric materials to be used for the passive fire protection of structures. CDW results from the construction, renovation, and demolition of buildings, roads, bridges, and other structures. This waste group comprises a wide range of waste materials, including concrete, bricks, tiles, gypsum, wood, glass, metals, plastic, organic materials, and excavated soil. In European Union (EU), the construction sector generated 531 million tons of CDWs in 2014, representing nearly, one quarter of the waste materials generated globally [11]. Accordingly, in USA, 534 million tons of CDW were generated in 2014, of which 28.9 million tons were during construction and 505.1 million tones during demolition activities [12]. Although the efforts to reuse and recycle CDW are constantly increasing worldwide, it is estimated that globally, about 35% of the quantities of CDWs produced are directed to

landfills. In EU, the management of CDW is steered by the EU Waste Framework Directive 2008/98/EC, which sets a target for the recycling of non-hazardous CDW at a minimum of 70% of its weight by 2020 [13]. Despite its potential, the level of recycling and material recovery of CDW varies greatly (between 0% and over 90%) across the Union [11]. In this paper, the geopolymerization of the selected waste streams to produce fire-resistant construction materials is investigated and the resulting materials are evaluated in terms of mechanical strength and thermal stability, after exposure at high temperatures ranging from 600 to 1050 °C.

Materials and Methods

Materials

In this study, two specific streams of recycled CDW were used as raw materials for the development of fire-resistant inorganic polymers: waste bricks (WB) and waste ceramic tiles (WCT). Both recycled waste materials were supplied from a recycling plant of CDW in Cyprus (Resource Recovery Cyprus). After manual sorting, representative samples of WB and WCT were crushed and milled to achieve homogeneity of the initial solid raw materials.

Table 1 presents the chemical analysis of WB and WCT, as it resulted from the analysis of four representative samples for each material. As shown in Table 1, both WB and WCT are rich in silicon oxide, the content of which is higher in WCT (~64%wt) than in WB (~54%wt). These materials have also increased and quite similar content of aluminum oxide (~14%wt.), as well as of iron oxides (18 to 21%wt), potassium oxide (~3.75%wt), magnesium oxide (~4%wt), and traces of sodium and titanium oxides. According to Table 1, the two solid raw materials differ mainly in the calcium oxide content, which reaches ~8 %wt. in the WB and ~1.5%wt. in the WCT.

Table 1 Chemical analysis of WB and WCT raw materials

Oxide	WB	WCT
	Mass, %wt	
SiO_2	53.57	62.40
Al_2O_3	14.33	14.68
CaO	7.71	1.48
FeO	10.19	8.58
K_2O	3.74	3.76
MgO	4.07	3.68
Na_2O	0.66	0.98
TiO_2	1.46	
Fe_2O_3	11.32	9.54

The WB is principally crystalline, consisting mainly of quartz (SiO_2) and feldspars (albite-$NaAlSi_3O_8$); hematite (Fe_3O_3) and mullite ($3Al_2O_3 \cdot 2SiO_2$) were also detected as secondary phases and calcite ($CaCO_3$), as minor. In contrast, the WCT comprises of an amorphous aluminosilicate phase, with quartz (SiO_2) to be identified as the major crystalline constituent and feldspars (albite-$NaAlSi_3O_8$) as secondary. Hematite (Fe_3O_3), mullite ($3Al_2O_3 \cdot 2SiO_2$), and spinel ($MgAl_2O_4$) also occurred in WCT, as minor phases. Regarding the particle size of the two solid raw materials, WB has a particle size lower than 250 µm with a mean value (d_{50}) equal to 35.35 µm, while all particles of the WTL are minus 300 µm, with a mean diameter (d_{50}) equal to 48.34 µm.

Except of the two solid raw materials, i.e. WB and WCT, a strong alkaline aqueous silicate solution was used as an alkali activator in this study, for the preparation of the fire-resistant geopolymers. The activator consisted of a sodium silicate solution (Merck, $Na_2O = 8\%$, $SiO_2 = 27\%$, and $d = 1.346$ g/mL) and an aqueous solution of 8M KOH (potassium hydroxide) prepared by dissolving solid KOH in the form of pellets (Merck, 99.5% purity) in deionized water. The ratio of $Na_2SiO_3xH_2O$ to KOH solutions in the alkali activator was equal to 1.6.

Experimental Procedure

The inorganic fire-resistant polymers were prepared by mixing the pre-defined quantities of the alkali activator with the corresponding solid raw material in a mechanical mixer. A constant solid to liquid ratio (S/L) equal to 2.5 g/mL and 3.4 g/mL was designed for the inorganic polymers based on WB and WCT, respectively. The mixing time was determined at 5 min, after which a homogeneous paste was obtained. The paste was casted in cubic molds of two different dimensions, i.e. 50 x 50 x 50 mm and 100 x 100 x 100 mm, and left for curing in an oven for 7 days, at 50 °C. After oven curing, the cubic specimens were demolded and left for further hardening at ambient temperature and dry conditions for 7 days and 28 days, before measuring physical and mechanical properties and testing thermal stability at high temperatures.

The thermal stability of the developed fire-resistant materials was tested at 600, 800, and 1050 °C, using a muffle furnace with a maximum temperature capacity of 1200 °C. The specimens were placed in the furnace at room temperature and the furnace was heated at a rate of 4.4 °C/min until reaching the desired temperature, at which the specimens were left for 2 h. Then, the furnace was turned off and the specimens were allowed to cool down in open air conditions, to room temperature. After thermal treatment, weight loss, compressive strength, and density of materials were measured. Moreover, the surface of specimens was visually inspected and any observed micro-cracks or other surface defects were evaluated. For each studied temperature, 3 specimens were tested and used for the physical and mechanical properties measurements and visual observation.
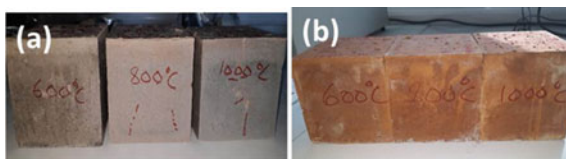
Results and Discussion

Visual Observation After Exposure at High Temperature

Alterations that take place during the heating of materials include moisture loss, evaporation, and transformation of mineralogical phases. Such alterations result in the disruption of the coherence of the materials' structure and thus, the development of deformation and also of creeping phenomena (Fig. 1).

As shown in Fig. 1, up to 600 °C, the specimens of both materials did not develop any kind of surface discontinuity or cracking.

After exposure at 800 °C, faint cracks appeared to form on the surface of specimens, mainly of the WCT-based materials; this cracking became more intense after exposure at 1050 °C, without, however, being considered as an indication of failure of specimens.

Physical Properties

Table 2 presents the Density and Mass loss of the WB- and WCT- based fire-resistant geopolymers, after their thermal exposure at different temperatures. The treated materials were cured at 50 °C for 7 days and left for hardening for another 7 days or 28 days. The mass loss reported in Table 2 is stated relative to the mass of materials after curing.

As seen in Table 2, the density of both WB- and WCT- based fire-resistant inorganic polymers was remarkably decreased after their thermal testing at 600 °C, and then, it remained almost unchanged regardless of the temperature of materials exposure. In general, the WB-based geopolymer was less dense than the WCT-based one, at every tested temperature. Moreover, the hardening time of both materials seems to not affect their density (Table 2). The changes noted for materials density can be attributed to the removal of water from the geopolymeric binder that takes place in three different temperature ranges [14]. At approximately 100–115 °C, the water molecules absorbed on the surface of geopolymers start to evaporate. At higher temperatures, from 150 up to 600 °C, the dihydroxylation process occurs and the hydroxyl groups of the physically bound water molecules (-OH) are removed [14], resulting in the development of a capillary pore structure in geopolymers, which affects the weight of the materials specimens. At temperatures above 600 °C, the

Table 2 Physical properties of the developed fire-resistant materials

	Temperature (°C)	Density (kg/m^3)		Mass loss (%)	
		7 days	28 days	7 days	28 days
WB-based fire-resistant geopolymer	50	1554	1556		
	600	1475	1475	6.21	1.60
	800	1430	1430	7.53	1.91
	1050	1434	1436	7.97	2.13
WCT-based fire-resistant geopolymer	50	1736	1586		
	600	1583	1579	9.60	3.47
	800	1569	1579	9.55	3.59
	1050	1577	1566	9.91	3.64

dihydroxylation of silanol groups (>Si–OH) takes place [14] and the aluminosilicate gel of geopolymers starts to densify into a glass or ceramic state, resulting in contraction of the materials [15, 16].

Regarding the mass loss of the developed materials (Table 2), it was observed to be higher for the WCT-based geopolymer than for the WB-based one, in both cases of hardening time. Moreover, the mass loss was higher in the case of 7d hardening time than of 28d, for both materials developed. After 7d of hardening time, both materials exhibited high mass loss when exposed at 600 °C; this mass loss was increased slightly or kept almost constant, after materials testing at 800 and 1050 °C. More precisely, the mass loss of the WB-based geopolymer was 6.2% after its thermal testing at 600 °C and increased slightly (<2%), after its exposure at higher temperatures. Accordingly, the mass loss of the WCT-based geopolymer was 9.5% at 600 °C, without being changed at higher temperatures. In the case of 28d hardening time, the mass loss of both materials was negligible in all the tested temperatures, ranging from 1.60 to 2.13% for the WB-based geopolymer and from 3.47 to 3.64% for the WCT-based geopolymer. The mass loss of the geopolymers is strongly related to the structural deformations that occurred in their matrix and comprises a measure for the degree of geopolymerization. The mass loss of materials can be attributed to a capillary porosity, which is formed in the geopolymeric matrix after dehydration and dihydroxylation, both occurring up to 600 °C. When the temperature exceeds 650 °C, the aluminosilicate gel of geopolymers is densified into a glass or ceramic state due to softening and viscous sintering, resulting in the contraction of the materials [15, 16]. The amorphous aluminosilicate phase that existed in the WCT raw material enhanced its alkali activation, which resulted in the formation of a more extended geopolymeric gel phase, in comparison to the WB raw material. Therefore, the WCT-based geopolymer possessed higher mass loss than the WB-based one, during their thermal testing.

Fig. 2 Compressive strength of the developed fire-resistant geopolymers at the temperatures tested
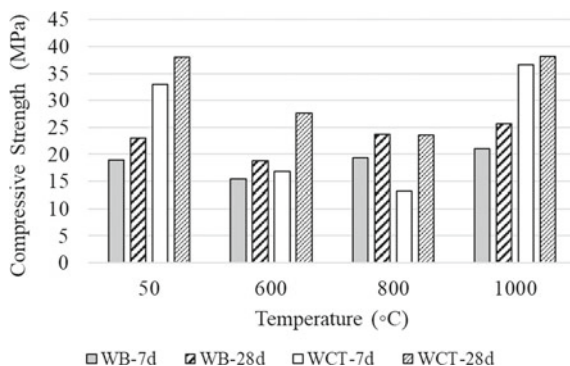
Mechanical Performance

Figure 2 presents the compressive strength of both WB- and WCT-based inorganic polymers, after curing (50 °C) and after their thermal testing at 600, 800, and 1050 °C.

According to Fig. 2, the initial compressive strength that developed the WCT-based fire-resistant inorganic polymer after curing was substantially higher than that of the WB-based material. In particular, the compressive strength of the WCT-based geopolymer was 33 MPa and 38 MPa, after 7 days and 28 days of hardening, respectively, while the corresponding compressive strength values of the WB-based material were 19 and 23 MPa. This difference can be attributed to the differences in the chemical and mineralogical composition of the two types of solid materials. The existence of an amorphous aluminosilicate phase in the WCT raw material provided the chemical system with easily dissolved Si and Al, which enhanced the development of the Si- and Al-based polymerized network in the material's matrix [14]. This has as a result the production of more compact and stable structures. In addition, the high content of calcium in the WB raw material affected negatively the mechanical performance of the WB-based geopolymer. In the presence of calcium, the product of the geopolymerization reaction could be a Ca-containing geopolymeric gel in the form of C, N-A-S-H (where C = Ca, N = Na, A = Al, S = Si, and H = H_2O) or a mixture of gels in the forms of C-S-H and N-A-S-H that coexist in the geopolymeric system [17]. The high content of Ca in a geopolymeric system promotes the formation of C-S-H gels that keep relatively lower strength than the C, N-A-S-H gels [17]. The hardening time also improved the material's compressive strength (Fig. 1), as it favors the formation of a more ordered geopolymeric network and denser material.

As shown in Fig. 2, the exposure of both fire-resistant geopolymers at high temperatures resulted in important changes in their compressive strength, which are more characteristic in the case of the WCT-based geopolymer. More precisely, the residual compressive strength of the WCT-based material was substantially reduced up to 800 °C, and then, it was sharply increased as the temperature raised to the highest

value tested (1050 °C). At this temperature, compressive strength reached a slightly higher value than the initial one, regardless of the time of hardening (7d or 28d). The residual compressive strength of the WB-based material followed a similar trend, but with less abrupt changes (Fig. 2). The decrease of the residual compressive strength, observed at 600 and 800 °C for both fire-resistant geopolymers developed in this study, is strongly related to the softening of the geopolymeric matrix, which happens at 550–650 °C [15]. The alkali activation of a solid aluminosilicate material involves the surface attack of the material's particles and the formation of an amorphous phase of alkali-aluminosilicate composition (geopolymeric gel) around them, which bonds these particles in stable structures. At 800 °C, the amorphous geopolymeric phase could be transformed to a crystalline one, which in the case of sodium (nepheline) starts to melt, resulting in a loose structure with decreased mechanical strength. Above 800 °C, sodium acts as flux, causing partial sintering of the unreacted solid particles in the contact zone, between them and the melted geopolymeric binder, which results in more durable structures [18]. This process improved the residual compressive strength of the developed materials at 1050 °C.

Conclusions

Waste bricks and waste ceramic tiles from construction and demolition waste were proven suitable raw materials for the development of inorganic polymers to be used for the passive fire protection of structures. The developed fire-resistant materials remained stable, after being exposed to temperatures up to 1050 °C.

The temperature range between 600 and 800 °C was considered critical for the properties of the developed materials. Density and weight loss of both WB- and WCT- based fire-resistant inorganic polymers were decreased after their exposure at these temperatures. Both properties remained almost constant at higher temperatures.

The compressive strength of the WCT-based geopolymer was higher than that of the WB-based one, regardless of the hardening time of materials. When both materials were exposed at 600 and 800 °C, their compressive strength decreased and this decrease was more significant for the WCT-based material. As the temperature was raised to 1050 °C, the compressive strength of both materials increased and reached almost the initial value, after curing. The changes in the material's mechanical strength observed at the tested temperatures should be attributed to the structural transformations taking place in the geopolymeric gel matrix due to melting and sintering phenomena that occurred at elevated temperatures.

During the heating exposure up to 1050 °C, there were no signs of spalling or deformation for both studied materials. Only small size cracks appeared on the specimen's surface of both materials at 800 °C, which became more intense and larger after their heating exposure at 1000 °C.

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