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ScienceDirect

Ceramics International 41 (2015) 12967–12979

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Geopolymer technology for application-oriented dense and lightened materials. Elaboration and characterization

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Received 4 February 2015; received in revised form 30 June 2015; accepted 30 June 2015
Available online 8 July 2015

Abstract

In this paper, dense and lightened geopolymer materials based on calcined kaolin and different alkali activators were prepared and submitted to a physical and mechanical characterization: density measurement, mechanical tests (flexural and compressive tests) and thermal conductivity analysis were carried out.

First, pastes were prepared by using both sodium and potassium silicate solutions. It was found that the chemical composition of the alkali solution has a minor effect on the flexural strength, while it significantly affects compressive strength and stiffness in three-point-bending, being the best performance obtained with the sodium silicate solution.

Then, starting from this paste formulation, different dense materials were prepared, including mortars and composite samples containing a commercial acrylate emulsion (Primal B60A), used to improve the workability of the pastes and the mechanical properties of the cured samples. The Primal-free dense specimens showed good compressive strengths (20–30 MPa) in line with literature for metakaolin-based materials. However, Primal addition was effective in enhancing the compressive strength up to 46 MPa.

Finally, different sets of low-density materials were prepared: lightweight samples, produced with expanded glass spheres (Poraver®) and macroporous samples, foamed with hydrogen peroxide in different amounts. All these samples appeared homogenous with very limited segregation phenomena. The thermal conductivity ranged from 0.12 to 0.78 W/m K, in function of the density of the samples: the lowest values, presented by the macroporous materials, were comparable with those of most commonly used building insulation materials.

As a whole, this work has shown the versatility of geopolymers towards the elaboration of a variety of materials with different macroscopic features: from pastes, to mortars, to lightweight samples, to macroporous samples. Finally, the feasibility of producing bilayer materials has been assessed: samples made by superimposing a lightened layer over a millimetric layer of geopolymer paste or mortars after its partial curing were successfully prepared.

Keywords: B. Porosity; B. Microstructure-final; C. Mechanical properties; C. Thermal conductivity; Geopolymers

1. Introduction

Portland cement-based concrete is currently the highest volume product manufactured on Earth [1]. In fact, this material presents several advantages over other building materials, such as the highly reliable performance, the large availability of raw materials and their low cost. In spite of this, the manufacturing of Portland cement requires a considerable energy consumption, mainly imputed to the clinker calcination (which occurs at about 1450 °C) and grinding. The embodied energy is estimated to be about 3.8 GJ/t clinker [2]. Such high energy requirement is associated with high gas emissions: it was estimated that the manufacturing of a ton of clinker produces about 0.9 t of CO_2, deriving from raw materials decomposition (about 0.53 t) and from fuel combustion (about 0.37 t). As a result, the cement and concrete industry, as a whole sector, provides a contribution as high as 5–8% to the global anthropogenic CO_2 emissions [1,2]. It should be specified that the

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http://dx.doi.org/10.1016/j.ceramint.2015.06.140
0272-8842/

embodied energy intensity per functional unit of cement is still lower than those of other building materials [1]. However, the very large production volumes, required to meet the global demand, leads to such high emissions of greenhouse gases, associated to wide consumption of raw materials and formation of dust pollution.

Therefore, several energy saving measures in the field of construction are currently in progress [3] and many strategies are being used for reducing the emissions of the cement manufacturing plants. These strategies include the improvement of the energy efficiency, the use of bio-fuels and the replacement of limestone with other industrial by-products. Moreover, the clinker content can be reduced by using blast furnace slag, fly ash, natural pozzolans and silica fume [4–6]. Finally, new technologies can be applied, in order to make non-Portland cements, such as partially pre-hydrated C-S-H binders, belite-rich cements, magnesium oxy-carbonate cements, magnesium silicate cements, calcium carbonate cements etc. [4].

This last strategy also implies the use of *geopolymers*, term used to describe a family of alkali activated aluminosilicate binders [7]. The geopolymerization process starts with the dissolution of Al and Si (from the Al-Si-rich materials) in alkali solutions as hydrated reaction products with NaOH or KOH, hence forming a $[Mx(AlO_2)_y(SiO_2)_z \cdot nMOH \cdot mH_2O]$ gel. The curing time normally occurs at low temperatures (20–120 °C) between 3 and 10 h depending on the raw material and the composition used. The complete development of mechanical properties generally takes place after 5 days, as discussed in several researches [8–12].

The good results achieved in several studies allow to consider geopolymers as a possible alternative to Portland cement. Considering the mechanical properties, the cement mortars reaches a compressive strength between 10 and 30 MPa after 2 days, in relation to the Portland cement class. These values grow up to 32.5–52.5 MPa after 28 days of curing. Geopolymers develop a compressive strength in the range 5–40 MPa after 2 days and from 20 to 100 MPa after 28 days [13,14]. The compressive strength of geopolymers depends on several factors which include the gel-phase strength, the ratio of the gel phase/undissolved Al/Si particles, the distribution and the hardness of these undissolved particles and the amorphous nature of the geopolymer [15]. Moreover, this variability is related to the raw materials (fly ash, metakaolin or other silica aluminate powder) and technology used to process the samples. In fact, it is important to highlight that to date no standard method to produce geopolymer samples is defined; for this reason the extraction of homogeneous and unambiguous mechanical results from the literature is particularly difficult. Nevertheless, considering the geopolymers realized with metakaolin powder, several studies highlighted that the Si/Al ratio is the factor that mainly affects the mechanical properties of the materials. As reported in [12], the compressive strength of metakaolin based geopolymers, activated with sodium silicate and cured at 40 °C, increased linearly by approximately 400% from Si/Al = 1.15 to Si/Al = 1.90 where the samples achieved their maximum value (from 20 to 70 MPa), before decreasing again at the highest Si/Al ratio of 2.15 (60 MPa).

Similar observations were made by Kamseu et al. [16]. In this study, metakaolin-based geopolymers were designed with different Si/Al ratio. The specimens were activated with a mixture of sodium hydroxide, potassium hydroxide and sodium silicate and cured at room temperature. Mixes with high Si/Al ratio ranging between 1.79 and 2.07 developed higher values of compressive (50 ± 5 MPa) and flexural strength (7 ± 0.5 MPa). These materials developed a coarser microstructure: this reduction of the pore size contributed to increase the mechanical values and the durability.

The effect of the curing temperature on metakaolin geopolymer mortars activated with sodium silicate was investigated by Rovnanìc [17]. It was found that a high curing temperature (about 60° and 80 °C) increased the early age compressive and flexural strength of the samples which can achieve their target in 1 day (50 MPa and 12 MPa, respectively). However, the mechanical values of the same samples cured for 28 days were comparable or lower than the mechanical results achieved with samples cured at room temperature or 40 °C (compressive strength 60 MPa; flexural strength 12 MPa). In fact, at longer ages, when the geopolymerization degree is similar, the quality of reaction product is the predominant parameter: the quick formation of the hard structure probably does not result in such a good quality product. The samples cured at lower temperature grew slowly and developed lower porosity and higher toughness. On the contrary, an elevated temperature during the early-stage of the hardening process led to the formation of larger pores and to an increase in cumulative pore structure, which has a negative effect on the final mechanical properties. All these cited works confirmed that, through a correct design of the geopolymer mix, it is possible to achieve mechanical values comparable with those of ordinary Portland cement applying the same curing conditions.

Moreover, several studies reported that geopolymer mortars are less sensitive to chemical and physical degradation as compared to ordinary Portland cement [9,18–24]. Generally speaking, this behavior is imputable to the lower content of calcium compounds as well as to the lower permeability of the geopolymer-based binders. A key example of the superior chemical resistance of geopolymers as respect to concrete is provided by the work of Zhang et al. [19]. Here, metakaolin based geopolymers (activated with sodium silicate, with the addition of a small amount of blast furnace slags and cured at room temperature) were developed as innovative inorganic coating for marine concrete protection [19]. The geopolymer product was stable when immersed in sea water, displaying an excellent resistance in this condition and giving marine concrete chemical protection. This coating was applied in real conditions, showing the need of a correct formulation (use of aggregates and expansion agents) and controlled curing conditions to avoid undesirable large shrinkage as respect to the concrete substrate [20]. Bakkarev [22] showed that fly ash based geopolymers, immersed in 5% solutions of acetic and sulphuric acid, had in general a higher chemical resistance than the samples produced with ordinary cement.

In addition, contrary to standard Portland cement, geopolymers produced with fly ash or metakaolin and cured at room temperature show a high stability when submitted to high temperatures, even around 1000 °C [9,17] due to the lack or lower content of hydrated phases. In the study of Kong et al. [25] the effect of elevated temperatures on geopolymers manufactured using metakaolin and fly ash activated with sodium and potassium hydroxide and cured