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Comparative analysis between properties and microstructures of geopolymeric concrete and portland concrete☆

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ABSTRACT

High energy consumption and elevated emission of carbon dioxide are relevant problems of the Portland cement industry related to environmental issues. With the purpose of reducing such problems, geopolymerics cements constitute a new class of materials used as mineral binder capable to replace Portland cement owing to technical and environmental advantages. These advantages, particularly the "ecologically friendly" aspect, have been questioned and are currently the subject of research works. As possible applications, geopolymeric cements are known to rapidly develop mechanical strength with aging while maintaining dimensional stability. By also considering the excellent adherence to aggregates make geopolymer cements potential materials for civil construction. Indeed, they are currently being investigated for the production of geopolymeric concrete as possible substitute for Portland cement concrete. In this work a combined comparison between mechanical, thermal and microstructure characteristics of concretes made with geopolymeric and high performance Portland cements is presented. Results of compressive strength, X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermal analysis (DSC/TGA) are discussed, in order to gather information for a better understanding of the relation between properties and microstructure of both geopolymeric and Portland cements in the performance of concretes.

1. Introduction

The civil construction industry has been facing challenges in order to fulfill the growing demand for concrete, the second most used construction material after water. Common concrete requires not only water but also a significant amount of Portland cement (PC) as binder for the mineral aggregates. In this regard, a major challenge is due to PC production, which is highly energy intensive and could represent a substantial proportion (nearly 10%) of human-related CO_2 emission responsible for global warning [1]. Among the works conducted on materials that could contribute to mitigation in cement production, new low-CO_2 binders open the perspective for PC substitution. This is the case of geopolymers a promising class of inorganic binders considered a modern solution for "green" mortar and concrete [2–11]. Geopolymer is a name coined by Davidovits [12] encompassing a family of material based on synthetic aluminosilicates obtained by hydrothermal polymerization in a highly alkaline environment [13,14]. Depending on the molar composition of precursor reactants, it is possible to produce geopolymers with different characteristics and structures, including amorphous and semi-crystalline [15–17]. An important technical aspect of geopolymers is the binder behavior, which characterizes them as inorganic cementitious materials with potential applications in fire resistant composites, sealant ceramics and concretes for civil construction [18].

Typical precursor materials for geopolymer cement (GC) fabrication are metakaolin, as a source of Si and Al (basic aluminosilicate) and calcium containing industrial waste, like blast furnace slag, as well as KOH as an alkali reactant [18]. In practice the metakaolin is obtained by calcination of kaolin, a mineral component of kaolinitic clays. The calcination removes hydroxyl and creates a chemical instability improving the metakaolin reactivity. The blast furnace slag is a large scale available byproduct from steel fabrication. This slag is naturally granulated, due to the abrupt cooling process, which favors the reactions in alkaline solution, KOH, with metakaolin that characterize the geopolymerization [18]. All these precursors are relatively low cost allowing the GC to economically compete with PC.

As for the environmental advantages of GC, being claimed as a sustainable reason to replace PC [19–21], a Life Cycle Assessment study of Habert et al. [1] revealed that GC concrete might have a similar impact on global warming than PC concrete. In other words, this would not be an environmental advantage for GC cement in the civil construction industry.

On the other hand, the technical properties of GC cements might have advantages over PC, especially as binder for fabrication of concretes. Indeed Majidi [18] listed these unique properties as:

- High early strength;
- Extraordinary durability;
- Resistance to chemical attack;
- Ability to immobilize toxic atoms.

Moreover, the workability of fresh GC concrete is higher when compared with PC concrete. In spite of these technical advantages, applications of GC concretes are still incipient. As predicted by Majidi [18], it is not anticipated that GC concretes will supply a significant amount of global need in a near future. He also indicates that research community needs to address existing gaps in knowledge related to the properties of geopolymers, such as X-ray diffraction analysis and heating.

Therefore, the objective of the present work is to provide a contribution to the application of GC concretes by filling the knowledge gaps on mechanical properties, microstructural analysis and thermal behavior. As a novel approach, results were compared with corresponding ones high performance Portland cement (HPC) concrete with same aggregate particles trace (cement/sand/gravel) as well as same water/cement ratio.

2. Materials and methods

The basic precursor materials used for the geopolymer cement (GC) preparation were metakaolin, blast furnace slag and potassium hydroxide (KOH). The metakaolin was obtained by calcination at 850 °C for 2 h of natural kaolin supplied by Monte Pascoal SA, Brazil. The blast furnace slag was provided by steel making company Belgo Mineira Bekaert SA, Brazil. The KOH was purchased from Panamericana, Brazil. For comparison, a high performance (smaller particles and high specific surface) CP-V high performance Portland cement (HPC) supplied as ARI-RS by Holcim, Brazil was used. Aggregate raw materials composing both GC and HPC concretes were sand and gravel with characterization presented in Table 1. In this table points worth noticing are the almost equal densities and interval of sizes, which contributes to a good packed mixture during concrete fabrication.

The investigated GC was prepared by conventional method of dissolving the mixture of metakaolin and slag particles, sieved below 0.016 mm, in a highly alkaline, pH of approximately 14, KOH solution. This dissolution was carried out in a mixer at room temperature, about 25 °C, for a geopolymerization period of around 5 min. In continuous sequence, by

Table 1 – Characteristics of sand and gravel for both geopolymeric and high performance Portland concretes.

Concrete aggregate	Density (g/cm³)	Finess modulus	Maximum size (mm)	Minimum size (mm)	Organic impurities (ppm)
Fine sand	2.62	2.51	2.4	1.5	<300
Coarse gravel	2.75	5.93	9.5	5.9	[a]

[a] Gravel supplied by Pedreirra Vigné, Brazil, was cleaned to eliminate organic impurities.

considering that the geopolymer cement already developed binder capacity, volume fraction of 40 vol% gravel and 25 vol% sand were added inside the mixer onto the corresponding 18 vol% prepared geopolymer cement. The water/cement mass ratio was defined as w/c = 0.38 and trace (mass ratios of cement/sand/gravel/water) established as 1:1.56:2.54:0.38 for both GC and HPC concretes. The w/c ratio and trace attend the Brazilian standards for building construction and heavy traffic pavements [22].

Compression tests were performed in 5 specimens of both GC and HPC concretes after 1, 7 and 28 days of curing (onset time at mixing aggregates and water in cement) according to the Brazilian standard [23]. In addition, identical compression tests were also performed in 5 specimens of GC concrete after 2 h of mixing aggregates and water with GC. Under this short time condition the GC concrete was already solid, which is associated with one of its practical advantages [24]. On the other hand, a Portland cement (like HPC) concrete is not yet solid enough to be compression tested. All tests were conducted in a hydraulic driven model 13022 Contenco machine with 100 ton of capacity operating at room temperature with a stress rate of 0.25 MPa/s. After fracture, samples of the ruptured surface were observed by scanning electron microscopy (SEM) in a model JSM 5800 LV Jeol microscope operating either with secondary or backscattered electrons. The non-conducting concrete samples were gold sputtered before SEM observation.

X-ray diffraction (XRD) analyses were performed in powder samples of kaolin and metakaolin as well as in GC in a model D5000 Siemens diffractometer operating with CuKα radiation in the 2θ interval from 2 to 90°. Thermal behavior of both GC and HPC concrete were characterized by thermogravimetry (TGA) and differential scanning calorimetry (DSC) analyses in corresponding models TGA-50 and DSC-50 Shimadzu equipment operating from 25 to 690 °C under nitrogen atmosphere with a heating rate of 20 °C/min.

3. Results and discussion

Table 2 presents the results of compressive strength (maximum stress) for both geopolymer cement (GC) and high performance Portland cement (HPC) concretes after different curing (aging) periods. In this table one should notice that after 2 h of aging the GC concrete already displays a reasonable strength and after one day its resistance is within the standard of 30 MPa specified for heavy traffic pavements [22]. With increasing aging, after 28 days both concretes tend to acquire similar compressive strengths, within the standard deviation, up to 2 years.

The results in Table 2 reveal that the average compressive resistance of GC concrete is higher up to 7 days of cure but becomes, in average, practically identical to HPC concrete after the standard 28 days. Hardjito et al. [25] also found a fast initial gain in strength of a GC concrete with tendency to become equal or surpass Portland cement concrete after 28 days of cure.

Fig. 1 shows SEM micrographs of the fractured surface of GC concrete compressive specimens. In Fig. 1(a), with low magnification, one may notice a rather uniform distribution of well-adhered aggregates in the GC matrix. This kind of microstructure without evidence of large pores is desirable for the superior mechanical behavior of GC concrete in Table 2. The relatively rougher aspect of the matrix in Fig. 1(a) suggests that it might be associated with small-sized porosity. The higher magnification of Fig. 1(b) allows the observation of details in the aggregate/matrix interface. Fewer pores are seen in the faceted piece of an aggregate, left side of Fig. 1(b).

Table 2 – Compressive strength in GC and HPC concretes after distinct periods of curing.

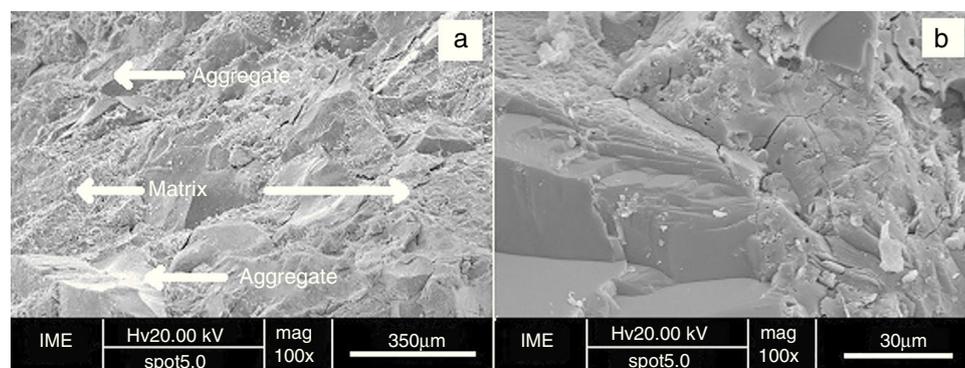| Concrete type	Strength (MPa) after curing time				
	2 h	1 day	7 days	28 days	2 years
GC	15.8 ± 1.7	39.2 ± 1.3	51.2 ± 1.3	57.4 ± 0.9	61.0 ± 1.1
HPC	[a]Paste like	29.1 ± 1.8	45.8 ± 2.3	57.9 ± 1.6	59.5 ± 1.4

[a] Too soft to be tested.

Fig. 1 – SEM micrograph of geopolymer concrete (a) low magnification and (b) geopolymer matrix/aggregate interface with high magnification.
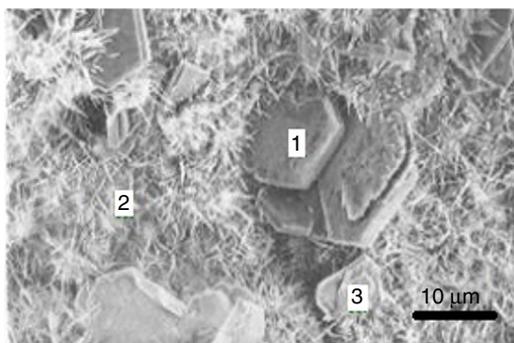
Fig. 2 – SEM micrograph of Portland cement concrete.

Fig. 3 – SEM-BSE micrograph of geopolymer concrete.

The microstructure of the GC matrix, right side, is massive with no defined morphology, which indicates amorphous or semi-crystalline cement [18]. In addition, several microcracks are observed, Fig. 1(b), in the GC matrix. Such microcracks, with mean size of approximately $3 \mu m$, were probably formed to accommodate the stress fields associated with the main cracks responsible for the concrete specimen rupture under compression. It is proposed that the microcracks, seen in the matrix of Fig. 1(b), might contribute to keep the integrity of the aggregate/matrix interface.

A comparison with the typical SEM micrograph of HPC concrete is shown in Fig. 2. This figure discloses relevant differences to the GC concrete micrograph in Fig. 1. With EDS analysis, three distinct phases were found to compose the cementitious HPC matrix:

- Portlandite, which the brittle $Ca(OH)_2$;
- Hygrated Ca silicate;
- Hydrated Ca aluminate.

The main points of difference to the one phase GC matrix in Fig. 1 are the brittle portlandite and the very porous aluminate. In principle, the higher porosity and less homogeneous, triphasic, HPC matrix could justify a lower mechanical strength. However, results in Table 2 do not support this reasoning.

While Figs. 1 and 2 were generated from SEM secondary electrons, backscattered electrons (BSE) could also reveal significant differences between both concretes. Fig. 3 shows a SEM-BSE image of ruptured surface of the GC concrete. This image confirms the relative amount of porosity as well as microcracks in the matrix, as also observed in Fig. 1. The importance of the BSE image is that, except for the dark microcracks and pores, the same uniform gray contrast is observed throughout the matrix and aggregates in Fig. 3. On the contrary, sharp dark and white contrast was reported by Scrivener [26] in similar HPC concrete. In one of his figures, the white cement particles inside the matrix were interpreted as only partially reacted with other phases. Again, this could be associated with lower strength although not supported by the results in Table 2.

As aforementioned, in the present work the kaolin is an essential precursor for the production of GC. Therefore its participation in the geopolymerization was investigated by XRD. Fig. 4 shows the diffractograms for (a) the as-received
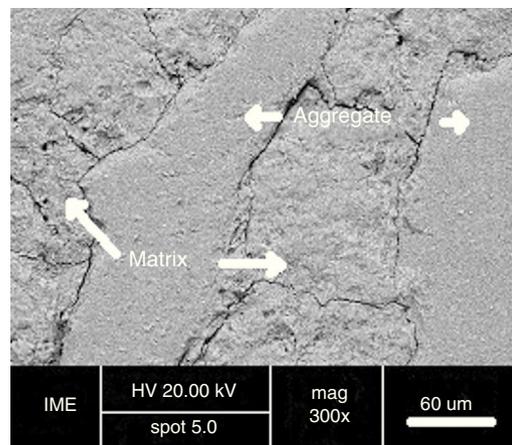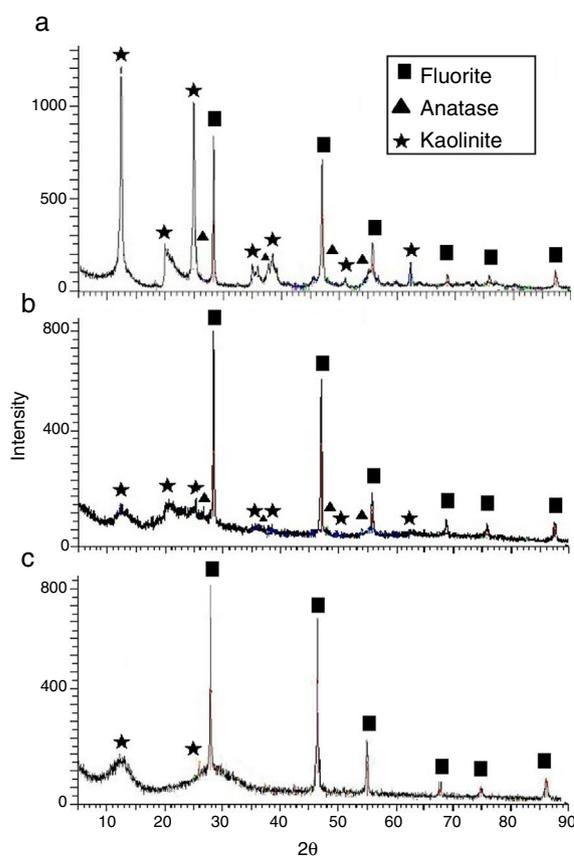

Fig. 4 – XRD pattern for: (a) as received kaolin; (b) calcinated metakaolin; and (c) geopolymer cement.

kaolin and (b) the resulting metakaolin after calcination at $850\,^{\circ}C$ for 2 h and (c) the GC. In this figure the identified peaks correspond to kaolinite, anatase and fluorite. The kaolinate, $Al_2Si_2O_5(OH)_4$, is the basic compound of the mineral kaolin, while anatase, TiO_2, is a minor constituent. The fluorite, CaF_2, was added into all XRD diffraction samples as standard for control of peaks position owing to its high crystallinity and few well-defined peaks non-coincident with those of kaolinite and anatase.
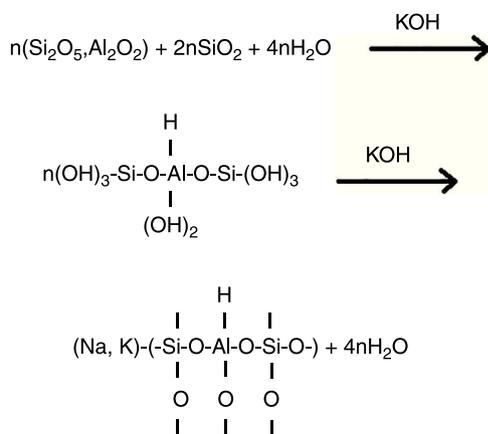
$$n(Si_2O_5,Al_2O_2) + 2nSiO_2 + 4nH_2O \xrightarrow{\text{KOH}}$$

$$n(OH)_3\text{-Si-O-Al-O-Si-}(OH)_3 \xrightarrow{\text{KOH}}$$

with H above and (OH)₂ below:

$$n(OH)_3\text{-Si-O-Al-O-Si-}(OH)_3$$

$$(Na, K)\text{-(-Si-O-Al-O-Si-O-)} + 4nH_2O$$

Fig. 5 – Geopolyymeric reaction of metakaolin proposed by Davidovits [27].

Fig. 6 – Thermal analysis of (a) GC and (b) HPC concretes.

The major presence of kaolinite is evident by its corresponding peaks intensities in Fig. 4(a) particularly that at 12.5° 2θ associated with the {0001} interplanar distance of 0.707 nm. After calcination, Fig. 4(b), these peaks are significantly reduced in intensity and become more like shoulders on the background noise. Actually, with calcination the kaolinite suffers dehydroxilation and a very reactive amorphous phase is formed, the metakaolin (Si_2O_5,Al_2O_2) [18].$A1_2Si_2O_s(OH)_4 \Leftrightarrow (Si_2O_5, A1_2O_2) + 2H_2O$ EQ.1

In the present work the basic GC aluminosilicate precursor was this metakaolin, which undergoes the following geopolymerization reaction proposed by Davidovits [27], resulting in polymeric Si-O-Al bonds chemically shown in Fig. 5.

Fig. 4(c) presents the XRD pattern of the GC obtained in this work. Except for the sharp fluorite peaks, used as control, only shoulders are observed at about 11–13° and 27–30° 2θ. Duxson et al. [24] indicated that typical amorphous diffractograms of geopolymers derived from metakaolin reveal a "featureless hump" centered at approximately 27–29° 2θ. This coincided with the same event observed in the XRD pattern of Fig. 4(c), which also has another "featureless hump" centered at 12.5° 2θ coinciding with the kaolinite peak in Fig. 4(a).

The importance of the metakaolin based amorphous structure of the GC is that it corroborates with the matrix details observed in Fig. 1(b) and in Fig. 3. Indeed, small porosity and stress accommodation microcracks would be characteristic features of an amorphous ceramic phase. Moreover, an amorphous matrix in a GC concrete renders a superior resistance to chemical attacks, as compared to Portland cement concretes [28].

Fig. 6 shows DSC and TGA curves for both GC and HPC aged for 28 days. These curves provide basic information on the thermal behavior of the investigated cements up to 690 °C.

The DSC curve for GC in Fig. 6(a) disclosed only a single endothermic peak at 115 °C, which might be assigned to water release. As for the TGA curve, a relatively small total mass loss of 9.61% was found from 25 up to 690 °C for GC in Fig. 6(a).

The DSC curve for the HPC in Fig. 6(b) revealed two endothermic peaks. The peak at 145 °C is attributed to the loss of absorbed water by hydrated calcium silicate (C-S-H), one of the HPC phases detected in Fig. 2. The peak at 480 °C is ascribed
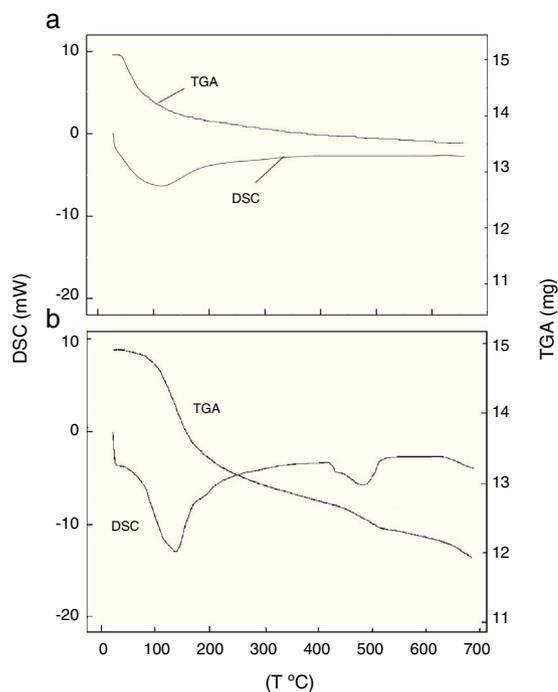
to the decomposition of portlandite, $CaOH_2$ which is another HPC phase detected in Fig. 2. This decomposition is indicated to cause significant damage to Portland cement-based mortars and concretes [29]. The TGA curve in Fig. 6(b) is associated with a total mass loss of 20.46% which is more that the double of that of GC in Fig. 6(a). These basic DSC and TGA results emphasize an important thermal stability of GC for possible high temperature applications. In fact, thermal advantages of GC over Portland cements, such as fire resistance, are being applied in geopolymer composites [18]. In the present work it is suggested that thermal stability of GC shown in Fig. 6 (a) could also be used in concretes that may eventually be subjected to raising temperature conditions. Our thermal results could also contribute to elucidate the contradictory findings reposted by Pan et al. [30] that sometimes geopolymer strength increases and other times decrease after exposure to elevated temperatures.

4. Summary and conclusion

- A comparative analysis between mechanical and thermal behavior as well as microstructure characteristics of same trace concretes made with geopolymer (GC) and high performance Portland (HPC) cements revealed novel results that might contribute to civil construction applications.
- The GC concrete, as expected, develops a reasonable compressive strength after 2 h of aging, while HPC concrete is still paste-like soft. From 7 days up to 2 years of aging, both concretes present similar compressive strengths above the standard limits specified not only for building constructions but also heavy traffic pavements.
- The GC concrete fractographs reveal aggregates well-adhered to a uniform single phase geopolymeric matrix

with small pores and microcracks. On the other hand, the three phases HPC matrix displays higher porosity and cracks associated with aggregates interfaces.

- X-ray diffraction analyses confirm the expected transformation of crystalline kaolinite into amorphous metakaolin, which is the main constituent of the investigated GC concrete matrix. This corroborates the corresponding microfractograph features of porosity and microcracks.
- The thermal analyses by DSC and TGA, from 25 to 690 °C, discloses a comparatively higher thermal stability of GC with significant lower mass loss and no phase decomposition as happens with portlandite, $Ca(OH)_2$, in HPC concrete. These experimental results support high temperature applications of GC concrete while restricting the use of HPC concrete above 400 °C.

Conflicts of interest

The authors declare no conflicts of interest.

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