Reuse of iron ore tailings in the production of geopolymer mortars

http://dx.doi.org/10.1590/0370-44672017720169

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Abstract

A great variety of silica and alumina-rich materials have been investigated in the production of alkaline activated binders (or geopolymers) with low environment impact, e.g. low CO_2 emissions. Geopolymer mortars and concretes may be more environmentally friendly if not only Portland cement but also natural aggregates (sand, gravel) are replaced with waste materials. This article presents results of geopolymers made with tailings from the iron mining industry. The geopolymer matrices are composed of metakaolin (MK) activated with a sodium silicate + sodium hydroxide solution. Two different iron ore tailings replaced a natural quartz aggregate in the geopolymers' formulation. The hardened properties assessed were compressive strength, water absorption, apparent density and porosity. Scanning electron microscopy (SEM) and x-ray micro computed tomography (μ-CT) were used to assess the changes in the microstructure when the tailings were incorporated into the geopolymers. Results show that the employment of iron ore tailings is not detrimental to the mechanical strength of geopolymers; however, geopolymers containing those alternative aggregates may present higher water absorption and porosity, and durability studies are required.

Keywords: geopolymer, alkali-activated binders, wastes, mine tailings, sustainable construction materials.

1. Introduction

Geopolymers are inorganic polymers with enormous potential to replace Portland cement (PC) for construction and building materials. These materials are produced from the alkaline activation of aluminosilicates, such as metakaolin, fly ash or blast-furnace slag. Most of the research so far confirmed that geopolymers offer great advantages over PC, such as low temperature of processing, high chemical durability and the development of alternative matrices for waste encapsulation (Shi *et al.*, 2011). One of the great environmental benefits of geopolymers is the possibility to activate natural materials as well as municipal, agricultural and industrial wastes (Mehta & Siddique, 2016). The wastes from the mining industry have also been investigated as geopolymer raw materials, although to a lesser extent. There are reports on the alkaline activation of tungsten mine waste mud (Pacheco-Torgal *et al.*, 2007); red mud from aluminum and slag from the ferronickel production (Giannopoulou *et al.*, 2009); vanadium silica-rich mine waste (Jiao *et al.* 2011); copper mine tailings (Ahmari& Zhang, 2012), among others. Most of those studies, however, employ fine tailings as geopolymer binders; the coarser materials, when used, are often ground to take part in the geopolymer matrix.

Geopolymer mortars and concretes may be more environmentally attractive if natural aggregates, i.e. sand and gravel, are also replaced with coarser tailings; this approach is little exploited. This may be of special interest for some countries where the mining industry currently generates large volume of wastes; the reuse of tailings as aggregates is more attractive than as binders, given the higher percentage of the first in mortars and concretes.

The annual disposal of iron ore tailings in Brazil is about 200 million tons, approximately 35% of the total generation of tailings in the country (IPEA, 2012). In addition to this large volume of waste materials, the environmental concerns have hampered the licensing areas for the construction of new tailing dams, raising the need for reuse and investment in new methods for disposal (Guimarães *et al*. 2012).

This article presents a first evaluation of geopolymers made with iron ore tailings as aggregate. The reference geopolymer matrix is based on metakaolin (MK) activated with a sodium silicate and sodium hydroxide solution. Two different iron ore tailings replaced a natural quartz aggregate in the geopolymer formulation. The main objective of this study is, therefore, to assess the changes in the mechanical behavior and microstructure of geopolymers when the tailings are employed as aggregates in the formulations.

2. Materials and methods

2.1 Iron ore tailings

Two mine tailings were used as aggregates in this study, both from the mineral processing of iron ore in Minas Gerais state, Brazil. The first is obtained from jig concentrator devices, used to separate particles within the ore body, based on their specific gravity (relative density); it has particles between 9.0-0.3 mm. The second is generated from spiral classifiers, used to separate mineral sand and fine mud in the gravity concentration, and clean mud and water in washing mineral process; its particle size ranges from 0.6-0.075 mm. The iron ore tailings will simply be referred to as jig and spiral wastes hereafter. The tailings were collected from their respective piles at the Mina de Água Limpa, Rio Piracicaba, Brazil. Five shallow holes were dug in random locations of the surface of the piles, from where the wastes were collected with a shovel at approximately 10 cm of the surface. A total of 90 kg of each waste was collected and taken to the laboratory, where it was dried and homogenized (quartered) prior to characterization. The mine tailings replaced natural quartz (river sand) in the geopolymer mortars.

The chemical composition of the jig and spiral wastes were determined by x-ray fluorescence (XRF) and the mineralogical composition was determined by XRD (with copper radiation; λ = 1,5418 Å; scanning from $5° \leq 2\theta \leq 80°$ with 0.02° step size at 1°/min) on samples ground below 75μm. The physical properties determined for the wastes were bulk density (unit weight) and specific gravity; clay lumps and friable particles were determined according to ASTM C142 (ASTM, 2010). These three tests were carried out to compare the wastes with standard aggregates used for concrete. The sieve analysis with calculation of the fineness modulus was conducted according to the ASTM C136 standard (ASTM, 2006). Ten samples of each waste were submitted to sieve analysis and the results are presented in terms of the mean and standard deviation.

The particle size distribution of the dry mix (binder + aggregates) used in this study (hereafter referred to as Geopolymer PSD curve) has been used in a previous article (Borges *et al*., 2014); it will also be used in this study for all geopolymer formulations containing either quartz aggregate or jig and spiral waste. In other words, the aggregates will not be used as collected, but rather sieved and mixed in fixed proportions to build the PSD curve (Sieves (% retained): 4.8 (15.3%); 2.4 (12.77%); 1.2 (10.85%); 0.6 (9.22%); 0.3 (7.83%); 0.15 (6.66%) and <0.075 (37.63%)). By doing this, it is possible to determine the effect of the addition of the tailings on the properties of geopolymers without the influence of their PSD.

2.2 Geopolymer matrix

The geopolymer matrices studied are based on the activation of metakaolin (MK) with sodium silicate and sodium hydroxide. Kaolin was provided by Imerys Brazil. The chemical and mineralogical composition of Kaolin was SiO_2 (44.9 %), Al_2O_3 (39.1%), Fe_2O_3 (0.5 %) and TiO_2 (0.4%). The Kaolin particle size distribution was such that 0.02% of particles were higher than 45 μm (#325) and 50% smaller than 2 μm was 50%) as determined from LASER particle size distribution. Metakaolin (MK) was obtained by calcination of kaolin at 750°C for 5 hours, which resulted in a material mostly amorphous and, therefore, suitable for geopolymerisation (Provis and Bernal, 2014).

The activation solution used herein was composed of sodium hydroxide and sodium silicate (SiO_2 = 66.67% Na_2O = 26.67%; H_2O = 6.66%); they were mixed to produce a final system (binder + solution) with molar ratios that give rise to MK-based geopolymers with appropriate mechanical properties (Barbosa *et al*., 2000). The solution to binder ratio (s/b) of geopolymers is determined according to the fineness of the precursor. Borges *et al*. (2014) studied the activation of the same MK and found that geopolymers with good workability were produced with s/b ratio ranging from 1.2 to 1.5. However, the choice of the s/b ratio is also a function of the density of the aggregates employed. Preliminary samples were cast to visually determine the segregation (i.e. settlement) of the mine tailings in the geopolymers. The s/b ratios studied in this work were then set to 1.2 and 1.3, in order to avoid settlement of waste particles and segregation of geopolymers.

2.3 Experimental factors, levels and responses (properties)

The experimental factors studied in this study are: (i) s/b ratio of the matrix (1.2 and 1.3); (ii) type of aggregate (spiral, jig and spiral + jig wastes); (iii) percentage of quartz replacement (50% and 100%). A general full factorial design with three factors was used, two of them with two levels and one with three levels, thus establishing 12 different runs. Table 1 shows all the formulations studied. Two reference formulations, REF1 with s/b = 1.3 and REF2 with s/b =1.2 contained only quartz aggregate and were used for comparison.

As mentioned before, the jig waste has particles between 9.0-0.3 mm and the spiral waste has particles between 0.6-0.075 mm. The quartz aggregate was then replaced according to the particle size of each waste, i.e. the jig waste replaced 50% and 100% quartz in the range between 4.8-0.6 mm whereas the spiral waste replaced 50% and 100% quartz from 0.6-0.075 mm. Finally, the combination of both wastes replaced 50% and 100% of quartz from 4.8-0.075, which is the total PSD of the geopolymer.

Table 1
Formulations studied.

Experimental condition	Experimental factors		
	Solution/binder (s/b)	Type of waste	% Replacement
REF1	1.30	Quartz	0
REF2	1.20	Quartz	0
C1	1.30	Spiral waste	50
C2	1.30	Spiral waste	100
C3	1.30	Jig waste	50
C4	1.30	Jig waste	100
C5	1.30	Spiral +Jig waste	50
C6	1.30	Spiral +Jig waste	100
C7	1.20	Spiral waste	50
C8	1.20	Spiral waste	100
C9	1.20	Jig waste	50
C10	1.20	Jig waste	100
C11	1.20	Spiral +Jig waste	50
C12	1.20	Spiral +Jig waste	100

The geopolymer formulations were prepared with only one replicate and the analysis of variance (ANOVA) using the Software MINITAB determined the effect of the experimental factors on (i) water absorption, (ii) apparent density; (iii) apparent porosity and (iv) compressive strength. The P-values were considered statistically significant its value is less than or equal to 0.05.

2.4 Geopolymer preparations and testing

The raw materials were mixed in a high spin mixer at 400 rpm, which promotes dispersion of powder materials. The alkaline solution was added first and MK slowly afterwards. After approximately 5 minutes. the mix was fully homogenized and the aggregates were added. The mixing procedure continued until fully homogenized. Ten cubes (50x50 mm) were cast for testing in compression. The curing regime consisted of 45°C and 90% RH for 24 hours, then ambient curing (~25°C) in sealed plastic bags for another 6 days for all samples. Mechanical testing was carried out after 7 days using an EMIC D30000 universal testing machine. The rate for compression was 0.6 ± 0.2MPa/s (EN12390-3, 2009). Water absorption, apparent density and porosity tests were carried out at same age (7 days) using the split halves obtained from the bending tests. The vacuum saturation method (RILEM, 1984) was used. X-ray micro computed tomography (μ-CT) was carried out using a Skyscan 1172 high-resolution desktop system, the results of which were used to calculate the apparent porosity, total porosity and mean pore size.

3. Results and discussion

3.1 Characterization of the mine tailings

The chemical composition and physical properties of both wastes are similar; Fe_2O_3 and SiO_2 are the predominant oxides. The spiral waste contains 51.90% of Fe_2O_3 and 46.02% SiO_2; jig waste contains 56.75% of Fe_2O_3 and 37.83% SiO_2. The values found for unit weight, specific gravity and the percentage of clay lumps and friable particles are also similar: respectively 1.64 kg/dm^3, 3.05 g/cm^3 and 1.74% for spiral waste and 1.68 kg/dm^3, 3.10 g/cm^3 and 1.43% for jig waste. In addition, the loss of ignition values found for spiral waste and jig waste were 0.63 and 2.33, respectively. The high content of iron oxide is responsible for the higher unit weight and specific gravity of the wastes, compared with traditional aggregates (unit weight ~1.52-1.68 kg/dm^3 and specific gravity ~2.6-2.7 g/cm^3) (Mehta &Monteiro, 2005). Therefore, geopolymers containing these wastes may be denser materials and susceptible to segregation of the aggregates when the mix is still fresh, which had been observed in the preliminary tests for some mixes. The amount of clay lumps and friable particles is below 3% wt., which is the maximum percentage prescribed by the Standard ASTM C33 (ASTM, 2001). XRD showed that both wastes are crystalline materials; their XRD patterns are very similar, showing hematite and quartz as predominant phases (Fig. 1).

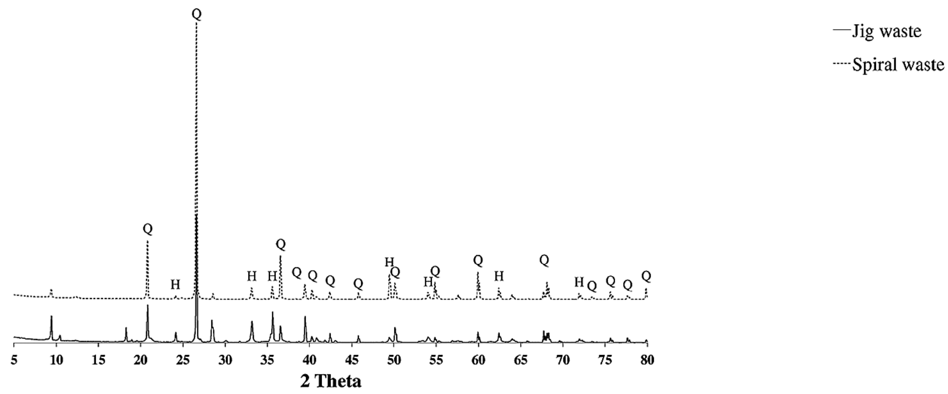

Figure 1
XRD pattern for jig and spiral waste
(H= hematite, Fe_2O_3; Q = quartz, SiO_2).

Figure 2 shows the particle size distribution (sieve analysis) of both mine tailings and the limits of natural and manufactured fine aggregates used for construction materials according to the ASTM standard C144 (ASTM, 2004). Figure 1 also shows the PSD geopolymer curve. It is noticeable that the PSD of both tailings lies outside the limits for fine aggregates for mortars. Their fineness moduli are 0.92 and 4.93, respectively for spiral and jig wastes; therefore, the tailings must be mixed with other materials to be employed as aggregates in Portland cement or geopolymer mortar and concretes. Alternatively, they may be blended among themselves to produce a better PSD curve (outside the scope of this paper).

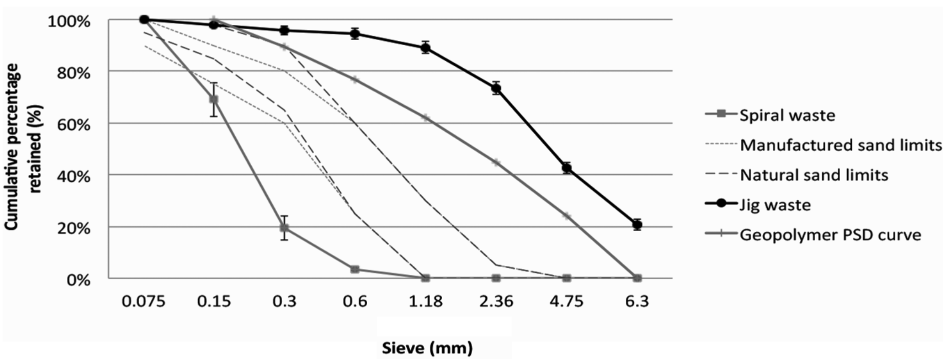

Figure 2
PSD of mine tailings, optimum and acceptable limits for concrete aggregates and geopolymer PSD curve for improved flow.

3.2 Mechanical and physical properties of geopolymers

3.2.1 Compressive strength

The mean compressive strength results ranged from 36.9 to 44.4 MPa and 36.3 to 49.5 MPa for formulations with s/b = 1.2 and 1.3, respectively. Those results are in the same range found in other studies of alkaline activation of MK (Bernal *et al.*, 2011). None of the investigated experimental factors affected the compressive strength, as the P-values are all above 0.05. Figure 3 shows the individual results for that response. Overall, the mean compressive strength was higher for those geopolymers made with s/b = 1.2. However, Figures 3a and 3b show that the standard deviation for compressive strength was significantly high for most of the geopolymers, and no conclusion can be drawn from the mean values. Other studies (Provis *et al.*, 2009) have also reported highly variable results for the compressive strength of alkali-activated metakaolin, without mentioning the cause. We believe that the stickiness of the MK-based geopolymer mortar jeopardize the compaction; thus, the failure in compression may be adversely affected by the presence of remaining large pores incorporated during the mixing procedure. In that sense, it is possible that the scattering of the data prevented the analysis of variance (ANOVA) and no experimental factor affected the compressive strength. Nonetheless, it is possible to observe that the replacement of quartz aggregate with jig / spiral wastes will not reduce the compressive strength of the geopolymers at a great extent (Fig. 3a and 3b). In addition, the error bars (i.e. standard deviation) in the same figure imply that the level of aggregate replacement (50% or 100%) did not affect the mechanical strength either.

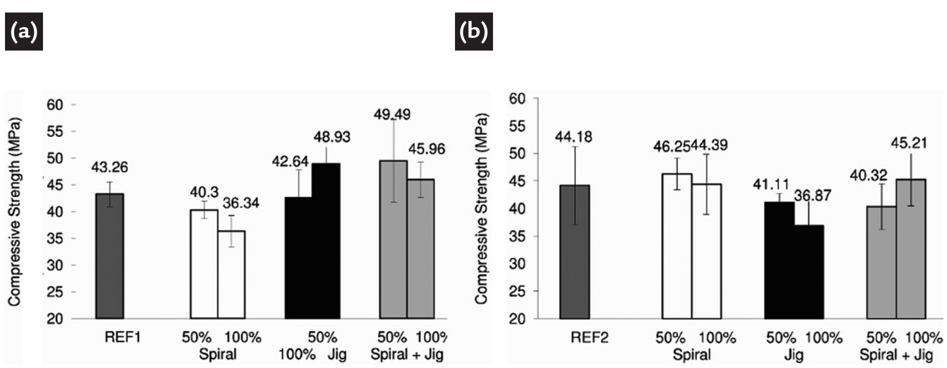

Figure 3
Compressive strength of geopolymers with (a) s/b = 1.2 and (b) s/b = 1.3.

3.2.2 Apparent dry density, water absorption and apparent porosity

Overall, the data of apparent density of the geopolymers ranged from 1.84 to 1.98 g/cm^3 and from 1.81 to 1.95 g/cm^3 for formulations with s/b ratio = 1.20 and 1.30, respectively. The experimental factor "% quartz replacement" affected the apparent density of geopolymers (P-value = 0.023). The percentage increase of 2.96 % occurs in the apparent dry density when the level of quartz replacement increased from 50% to 100% (analyses via "main-effect"). This is a direct consequence of the high density of the tailings. The water absorption values ranged from 9.1% to 11.6 % and from 10.7% to 12.4% for formulations with s/b = 1.20 and 1.30, respectively and the experimental factor "s/b ratio" affected the response (P-value = 0.006). By analyses via "main-effect", it was observed that a percentage increase of 9.4 % in the water absorption when the s/b ratio increased from 1.20 to 1.30. The apparent porosity also increased with a rise in the s/b ratio. The apparent porosity data ranged from 20.6 to 27.0% and from 24.19 to 29.4 % for formulations with s/b = 1.20 and 1.30, respectively. The main effects that affected the porosity were "s/b ratio" and "type of waste" ((P-value =0.001 for both). The main effect analyses for s/b ratio shows an average increase of 9.65 % when the s/b ratio rises from 1.20 to 1.30, which is consistent with the results of water absorption.

The main effect "type of waste" revealed a 13.1% increase in the apparent porosity when the jig waste was employed rather than the spiral jig. In fact, the jig waste appears to be more irregular in shape, which could be detrimental to particle packing. The combination of the two wastes (jig and spiral), however, reduces this detrimental effect of the jig waste. Figures 4a and 4b show that, for all cases, the reference formulations (REF1 and REF2, with quartz aggregate) have lower porosity than those with mine tailings. Nevertheless, the porosity is not governed solely by the percentage of waste in the geopolymer. Figure 5 shows that geopolymers containing 50% wt. mining waste have porosity equivalent to those with 100% waste. So, the employment of mine tailings as aggregates in geopolymers should be conditional to a systematic study of particle packing.

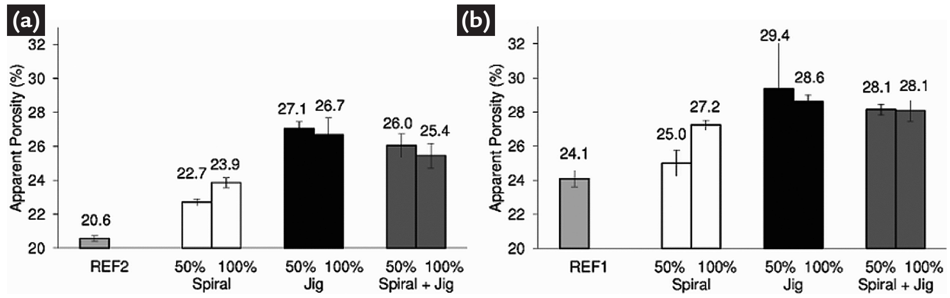

Figure 4
Apparent porosity of geopolymers with (a) s/b = 1.2 and (b) s/b = 1.3.

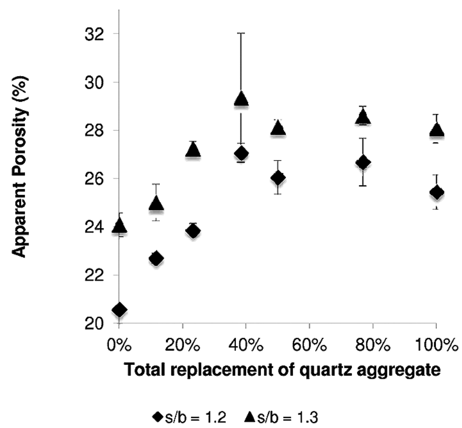

Figure 5
Apparent porosity as a function of the amount of waste in the geopolymers.

3.3 Micro computed tomography (µ-CT)

Table 2 shows the results of µ -CT for formulations REF1, C2, C4 and C6. It is possible to observe that the reference formulation (REF 1, without mine tailings) had significantly lower porosities (apparent and total) than any other with jig and spiral wastes (C2, C4 and C6). The highest apparent and total porosities are found when the jig waste replaced the quartz aggregate (C4). The combination of the two wastes (spiral and jig) decreased the apparent and total porosities, compared to others containing waste aggregate (C2 and C4). As mentioned before, we believe that the combination of the two wastes provide better particle packing, which is consistent with the results obtained for the apparent porosity by a water saturation method (section 3.2.2).

In general, the addition of mine tailings apparently increased the apparent and total porosity (TP and OP) and the mean pore size (MPS). It is important to note that the µ - CT analysis is carried out in a very small area (~ 1 µm^2); therefore, this technique did not assess the interface between aggregate and matrix. Nevertheless, we observed that the employment of waste aggregates altered the microporosity of geopolymers, which is also visible on the 3-D model of Figure 6. In this figure, the dark shades of gray represent the pores, whereas the lighter portion represents the geopolymer matrix. REF1 (Fig.6a) has a smaller fraction of pores and mean size. There is no marked difference between the C2 and C6 geopolymers. The geopolymer containing jig waste (C4), however, has a different pore structure, characterized by higher volume and pore connectivity.

Formulation	TP (%)	OP (%)	MPS (μm)
REF1	37.1 ± 1.1	27.0 ± 1.1	16.9 ± 0.1
C2	48.5 ± 0.6	44.3 ± 0.9	15.5 ± 0.4
C4	49.8 ± 1.1	44.3 ± 1.6	18.0 ± 0.3
C6	45.3 ± 0.8	35.7 ± 1.4	20.0 ± 0.3

TP = total porosity; OP = open porosity; MPS = mean pore size

Table 2
Main morphological parameters obtained by μ-CT for the geopolymers studied.

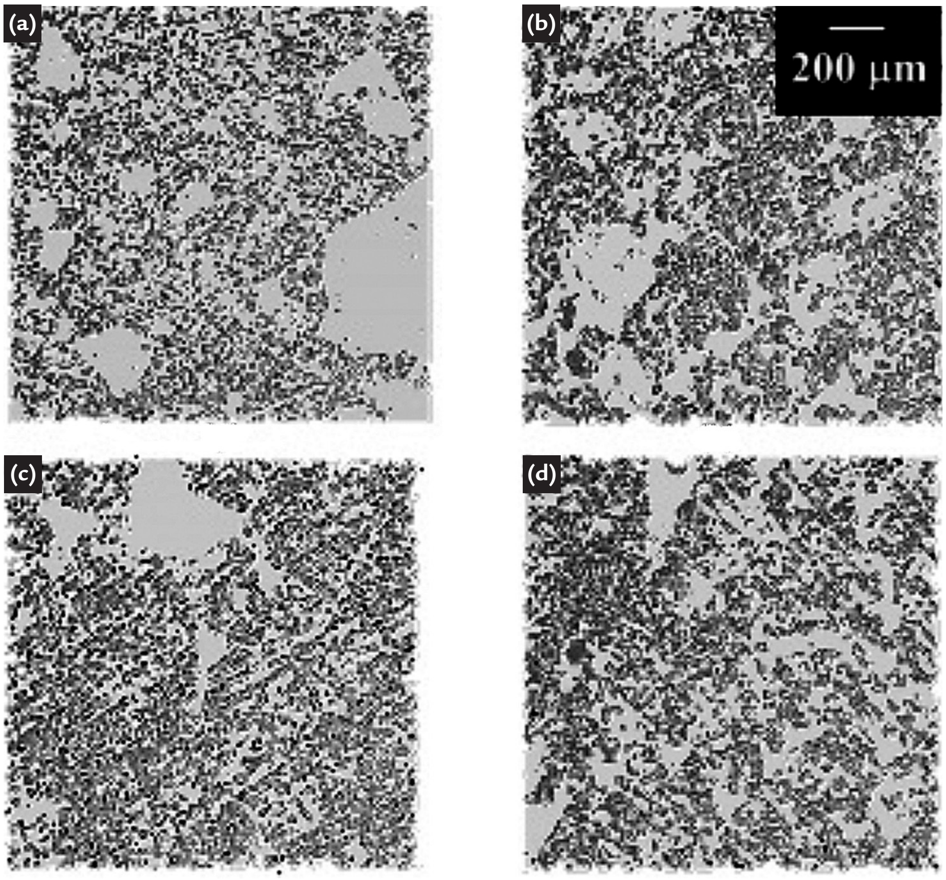

Figure 6
3D-models based on μ-CT for geopolymers
(a) REF1; (b) C2; (c) C4; (d) C6.

4. Conclusions

This study investigated the replacement of quartz aggregates with jig concentration and spiral classifier mine tailings in the production of geopolymer mortars. The main conclusions are:

• Both tailings (jig and spiral) are rich in hematite (Fe_2O_3) and quartz (SiO_2); therefore, geopolymers made with these wastes are denser compared to others made with quartz aggregate. Overall, geopolymers produced with up to 50% iron ore tailings with that composition had no major changes in density; higher percentage of tailings increase the density of geopolymers.

• The main parameter affecting the properties studied is the solution to binder ratio; the geopolymers made with mine tailings exhibited good performance with respect to the mechanical properties, without significant reductions in compressive strength.

• Geopolymers containing mine tailings presented higher water absorption and porosity compared to the reference formulation (with quartz aggregate). This could jeopardize the durability of the first, making them more prone to chemical attack. The combination of the two tailings, however, appears to promote the particle packing, thus reducing the porosity of the geopolymer containing these alternative aggregates.

In general, it is possible to conclude that iron ore tailings may be suitable as aggregates in the production of structural geopolymer mortars and concretes, in order to increase the sustainability of the construction industry and reduce the environmental impact associated with the large volume of land filled tailings. However, further studies should be carried out to ensure long-term durability of such materials.

Acknowledgements

The authors would like to thank FAPEMIG-VALE S.A. (grant number TEC- RDP-00186-10), CAPES, FAPEMIG and CEFET-MG for funding this research.

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Received: 24 November 2017 - Accepted: 10 July 2019.