



Use of residual diatomaceous earth as a silica source in geopolymer production



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ABSTRACT

The use of binders as an alternative to Portland cement has gained importance in recent years. Among them, geopolymeric binders, developed by the reaction between an aluminosilicate precursor and a high alkalinity solution, have become one of the most promising alternatives. The activating solution generally comprises waterglass and sodium hydroxide. Since waterglass is the most expensive material and has a high environmental impact, using alternative silica sources will lead to more sustainable binders. Previous studies have successfully used rice husk ash (RHA) as a silica source. This research aims to assess the possibility of using diatomaceous earth (or diatomite) as an alternative silica source, like the previous studies with RHA. Diatomite is a sedimentary rock with a high amorphous silica content formed by fossilized diatom remains. In this work, the geopolymer was obtained using a fluid cracking catalyst residue as the precursor and six different activating solution types prepared with commercial products, residual diatomite (from beer and wine industries) and RHA. The results open a new possible route for the reuse and recovery of diatomaceous earth residue, although the compressive strength results of the mortars were slightly lower than those for mortars prepared with RHA or commercial reagents.

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1. Introduction

Cement production is responsible for ~5% of world CO₂ emissions [1]. On this basis, the use of alternative binders with lower carbon footprints has excellent potential for reducing greenhouse emissions. Geopolymeric cements could be the future of the construction industry. Geopolymers are prepared by using a solid precursor (aluminosilicate material) and an alkaline solution (NaOH-Na₂SiO₃). The alkaline solution is the weak point of this binder and commercial waterglass (CW) is a chemical reagent with a high cost, both economically and environmentally. In recent years, different authors have successfully used waste as an alternative way to substitute for CW [2–4].

The use of rice husk ash (RHA) as a silica source has been investigated and excellent results in terms of mechanical strength and minimization of CO₂ emissions have been reported, with a 50% reduction in CO₂ emissions compared with CW [5].

Some authors used diatomite as a precursor in mixtures with calcium aluminate cement [6] and others studied the combination

of RHA and diatomite in lightweight geopolymer manufacture [7]. Mejia et al. used diatomite as a source of silica in activating solution, which was used to activate a mixture of metakaolin and fly ash, with mortars of up to 38 MPa in strength developed [8].

The aim of this research is to investigate the viability of using four different diatomites as silica sources to produce fluid catalytic cracking catalyst residue (FCC) geopolymers. The results were compared with those obtained by the use of CW and RHA.

2. Experimental

2.1. Materials

The FCC was supplied by Omya Clariana S.A ($D_{\text{mean}} = 17.1 \mu\text{m}$). RHA was supplied by Dacsa S.A ($D_{\text{mean}} = 62.3 \mu\text{m}$). The composition of both materials is summarized in Table 1.

Four types of diatomites were studied: commercial diatomite (CD), supplied by JJS Minerals SL; a residual diatomite from the beer industry (BD), supplied by Heineken (Quart de Poblet, Spain); two residual diatomites from the wine industry, an as-received original waste residue (WD), supplied by Bodegas Vicente Gandia (Utiel, Spain) and the same one calcined at 650 °C for 1 h (WCD).

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Table 1
Chemical composition of FCC, RHA and diatomites (wt%).

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | Na ₂ O | P ₂ O ₅ | TiO ₂ | Cl | LOI ^a |
|-----|------------------|--------------------------------|--------------------------------|------|------|-----------------|------------------|-------------------|-------------------------------|------------------|------|------------------|
| FCC | 47.76 | 49.26 | 0.60 | 0.11 | 0.17 | 0.02 | 0.02 | 0.31 | 0.01 | 1.22 | – | 0.53 |
| RHA | 85.58 | 0.25 | 0.21 | 1.83 | 0.50 | 0.26 | 3.39 | – | 0.67 | – | 0.32 | 6.99 |
| CD | 82.97 | 2.83 | 0.95 | 0.30 | 0.34 | – | 0.51 | – | – | 0.16 | – | 11.81 |
| BD | 81.70 | 5.67 | 3.71 | 1.28 | 0.41 | – | 0.86 | 1.30 | 0.36 | 0.93 | – | 3.34 |
| WD | 71.89 | 6.95 | 1.77 | 1.20 | 0.26 | 1.89 | 2.58 | 1.33 | – | 0.45 | – | 11.05 |
| WCD | 80.88 | 7.49 | 1.87 | 1.11 | 0.36 | 1.15 | 2.80 | 1.54 | – | 0.43 | – | 1.63 |

^a Loss of ignition.

Sodium hydroxide pellets (Panreac-SA, 98% purity) and CW (Merck, 28% SiO₂, 8% Na₂O and 64% H₂O) were also used.

The different diatomites used were characterized mineralogically and microstructurally by X-ray fluorescence (XRF, Philips Magic Pro XRF), particle size distribution (PSD, Mastersizer 2000 by Malvern instruments, in a water suspension), powder X-ray diffraction (XRD, Bruker AXS D8 Advance), thermogravimetry (TGA, TGA 850 Mettler Toledo thermobalance, temperature range 35–600 °C at a heating rate of 10 C·min⁻¹ in a N₂ atmosphere) and field emission scanning electron microscopy (FESEM, ULTRA 55-ZEISS).

Six mixes were designed in this study, all of them using FCC as a precursor, and with different sources of silica in the activating solution: i) two controls were designed for comparative purposes, one of them with CW and the other one with the alternative system prepared with RHA and ii) four systems alkali-activated using the diatomites as an alternative source of silica (CD, BD, WD and WCD). Diatomites were used in their original particle size. The

alternative activating solutions were prepared by mixing water, NaOH and the corresponding solid silica source (RHA, CD, BD, WD and WCD) into a thermal bottle for 24 h.

Pastes and mortars were cured in a temperature and humidity controlled chamber (20 °C and 95% RH) for 7 and 28 d. The compressive strength of the mortars was tested, according to UNE-EN 196-1 standard [9], using a universal testing machine. Thermogravimetric tests were run in pastes.

3. Results and discussion

3.1. Characterization of diatomites

The composition of the diatomites given in Table 1 show that SiO₂ was the major compound, and significant amounts of Al₂O₃ and Fe₂O₃ were also identified. The sum of these acid oxides overpassed 80% for all of the diatomites, which suggested their signif-

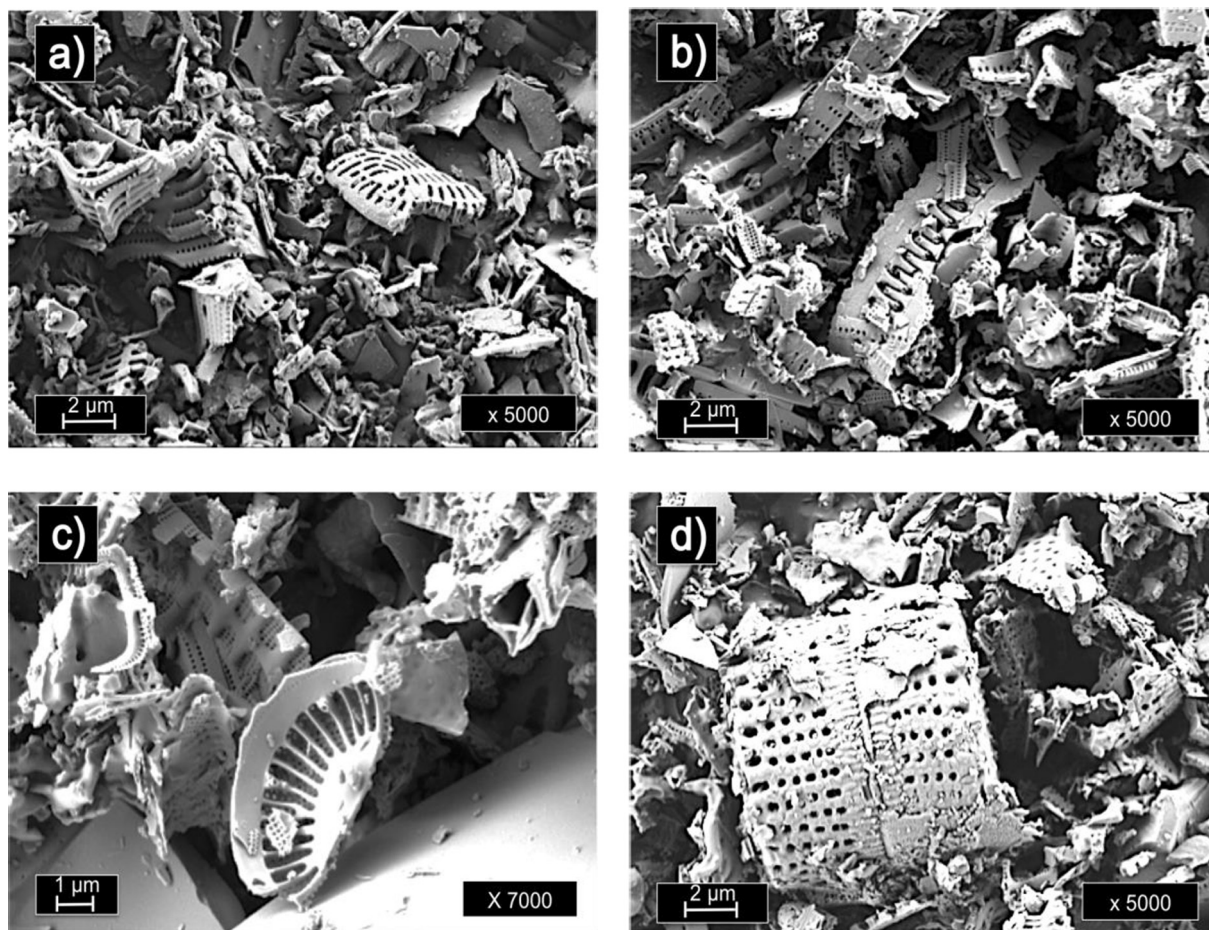


Fig. 1. FESEM micrographs (5000 and 7000×) of diatomites: a) CD; b) BD; c) WD and d) WCD.

icant possibilities of reuse in geopolymer synthesis. Although the CD and WD diatomites exhibited LOI values higher than 10%, the calcination of WD reduced this value to 1.63%, producing enrichment in acid oxides (80.61% for WD and 90.24 for WCD). The original mean particle diameters were 14.1 μm for CD, 46.4 μm for BD and 34.7 μm for WD and WCD. The XRD patterns showed that main crystalline phases in all the diatomites were quartz and cristobalite, two different forms of silica. Minor amounts of other crystalline phases were also identified, including tridymite (SiO_2) in CD, anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) in BD and calcite (CaCO_3) and anorthite in WD and WCD.

The FESEM micrographs of each type of diatomite are presented in Fig. 1. In general, typical skeleton forms originated by the diatoms (microalgae) can be observed, with discs, spheres and semi-spheres with micropores in their structures. No significant changes in the morphology and in the texture of the residual diatomite particles were observed when compared with CD.

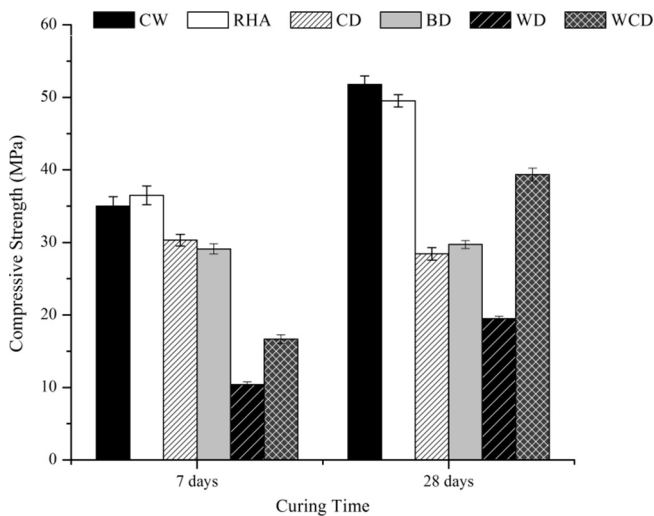


Fig. 2. Compressive strengths of CW, RHA, CD, BD, WD and WCD mortars after 7 and 28 days curing at room temperature.

3.2. Diatomite behavior as silica sources in mortars

3.2.1. Mechanical characterization of mortars

The compressive strength of mortars cured for 7 and 28 days is shown in Fig. 2. The CW and RHA mortars presented the highest strengths for both curing ages. After 7 days, the CW and RHA mortars exhibited 35.01 and 36.5 MPa, respectively, both higher than the strength values presented by the diatomite-based samples: 30.27 MPa for CD, 29.06 MPa for BD, 10.38 MPa for WD and 16.66 MPa for WCD. The CD and BD mortars exhibited similar compressive strength results, and their mechanical properties slightly varied from 7 to 28 days. Otherwise, a remarkable compressive strength gain was observed for CW (47.95%), RHA (35.69%), WD (87.86%) and WCD (136%). The calcination of WD to produce WCD, which reduced the LOI by $\sim 10\%$, improved the mechanical properties of the mortars developed by 60.5% and 101.8% after 7 and 28 days, respectively.

3.2.2. Thermogravimetric analysis of pastes

The DTG curves and mass losses obtained from the thermogravimetric analysis are depicted in Fig. 3. In general, a main peak arose in the 100–200 $^{\circ}\text{C}$ range, which is attributed to the dehydration of the N-A-S-H gel formed during the geopolymerization process. Minor variations of the mass loss with the curing time were observed in the pastes developed using waste as an alternative silica source (RHA, CD, BD, WD and WCD). This suggests that no significant amounts of new N-A-S-H gel formed from 7 to 28 curing days. However, a slight displacement of the bands towards higher temperatures was observed in the RHA, WD and WCD thermogravimetric curves, which implies that higher temperatures were required to dehydrate the formed gel. This behavior denotes a modification of the hydrated products formed with the curing time, which would be explain the minor variations of the strength values observed from 7 to 28 days in the CD and BD mortars, and the improvement of the mechanical properties exhibited by the RHA, WD and WCD mortars.

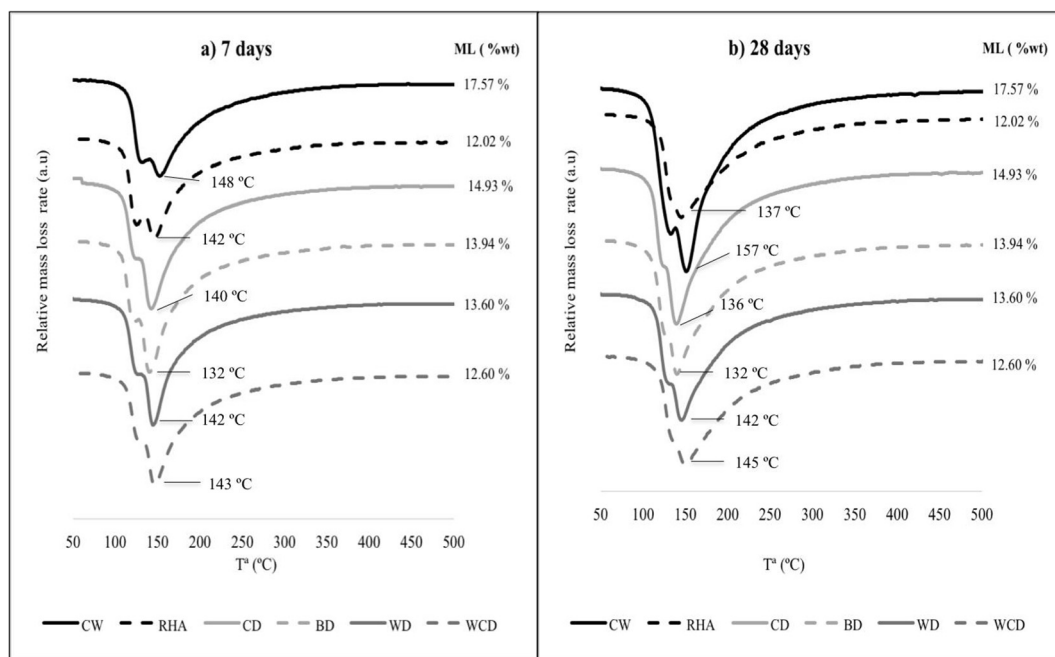


Fig. 3. DTG curves and mass losses by weight of WC, RHA, CD, BD, WD and WCD pastes after: a) 7 days and b) 28 days.

4. Conclusions

This research has demonstrated that residual diatomaceous earth can be successfully used as a silica source to prepare the activating solution in geopolymeric systems. Although wine and beer industrial diatomite-derived residues were less reactive than the RHA, the obtained results provide new promising alternatives to reuse and valorize this significant industrial waste (considering only the beer production in 2016, about 0.27–0.48 Mtons of residual diatomaceous earth were generated due this industrial activity). The use of residual diatomites obtained similar (BD) and even better (WCD) results than those obtained with commercial ones (CD). The calcination process of the WD improved the mechanical properties of the mortars developed (WCD), which was attributed to the organic matter elimination.

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