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.

Keywords: geopolymer, diatomaceous earth, waste valorization

1. Introduction

Cement production is responsible for ~5% of world CO_2 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 ($NaOH-Na_2SiO_3$). 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 CO_2 emissions have been reported, with a 50% reduction in CO_2 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_{mean} = 17.1 µm). RHA was supplied by Dacsa S.A (D_{mean} = 62.3 µm). 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 ºC for 1 h (WCD). Sodium hydroxide pellets (Panreac-SA, 98% purity) and CW (Merck, 28% SiO_2, 8% Na_2O and 64% H_2O) were also sed.

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

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5	TiO_2	Cl	LOI*
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

*Loss of ignition

The different diatomites used were characterized minerallogically 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 ºC at a heating rate of 10 C·min^{-1} in a N$_2$ 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 ºC 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 SiO$_2$ was the major compound, and significant amounts of Al$_2$O$_3$ and Fe$_2$O$_3$ were also identified. The sum of these acid oxides overpassed 80% for all of the diatomites, which suggested their

significant 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 ($CaAl_2Si_2O_8$) in BD and calcite ($CaCO_3$) and anorthite in WD and WCD.
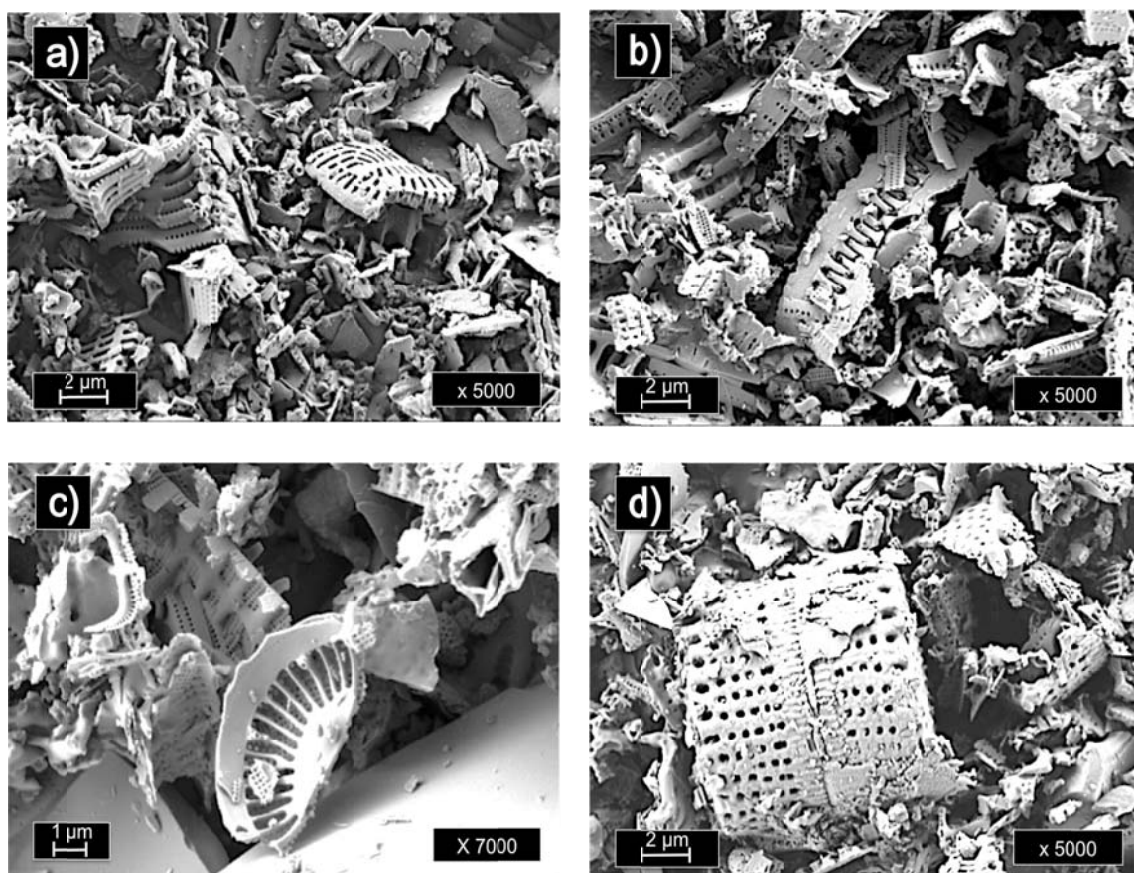

Fig. 1. *FESEM micrographs (5000 and 7000×) of diatomites: a) CD; b) BD; c) WD and d) WCD.*

106   The FESEM micrographs of each type of diatomite are presented in Fig. 1. In general,

107   typical skeleton forms originated by the diatoms (microalgae) can be observed, with

108   discs, spheres and semi-spheres with micropores in their structures. No significant

109   changes in the morphology and in the texture of the residual diatomite particles were

110   observed when compared with CD.

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112   *3.2. Diatomite behavior as silica sources in mortars*

113   *Mechanical characterization of mortars*

114   The compressive strength of mortars cured for 7 and 28 days is shown in Fig. 2. The

115   CW and RHA mortars presented the highest strengths for both curing ages. After 7

116   days, the CW and RHA mortars exhibited 35.01 and 36.5 MPa, respectively, both

117   higher than the strength values presented by the diatomite-based samples: 30.27 MPa

118   for CD, 29.06 MPa for BD, 10.38 MPa for WD and 16.66 MPa for WCD. The CD and

119   BD mortars exhibited similar compressive strength results, and their mechanical

120   properties slightly varied from 7 to 28 days. Otherwise, a remarkable compressive

121   strength gain was observed for CW (47.95%), RHA (35.69%), WD (87.86%) and

122   WCDE (136%). The calcination of WD to produce WCD, which reduced the LOI by

123   ~10%, improved the mechanical properties of the mortars developed by 60.5% and

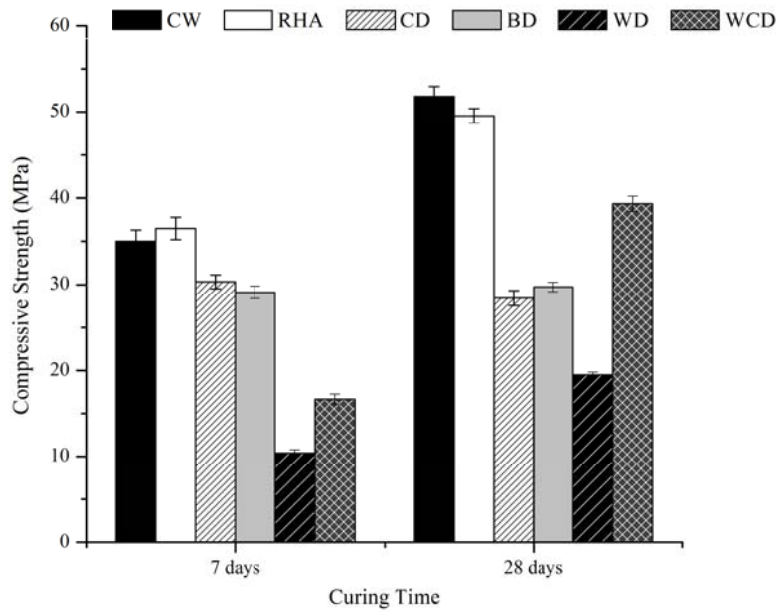124   101.8% after 7 and 28 days, respectively.

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

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128   *Thermogravimetric analysis of pastes*

139   The DTG curves and mass losses obtained from the thermogravimetric analysis are

140   depicted in Fig. 3. In general, a main peak arose in the 100–200 ºC range, which is

141   attributed to the dehydration of the N-A-S-H gel formed during the geopolymerization

142   process. Minor variations of the mass loss with the curing time were observed in the

143   pastes developed using waste as an alternative silica source (RHA, CD, BD, WD and

144   WCD). This suggests that no significant amounts of new N-A-S-H gel formed from 7 to

145   28 curing days. However, a slight displacement of the bands towards higher

146   temperatures was observed in the RHA, WD and WCD thermogravimetric curves,

147   which implies that higher temperatures were required to dehydrate the formed gel. This

148   behavior denotes a modification of the hydrated products formed with the curing time,

149   which would be explain the minor variations of the strength values observed from 7 to

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141 28 days in the CD and BD mortars, and the improvement of the mechanical properties

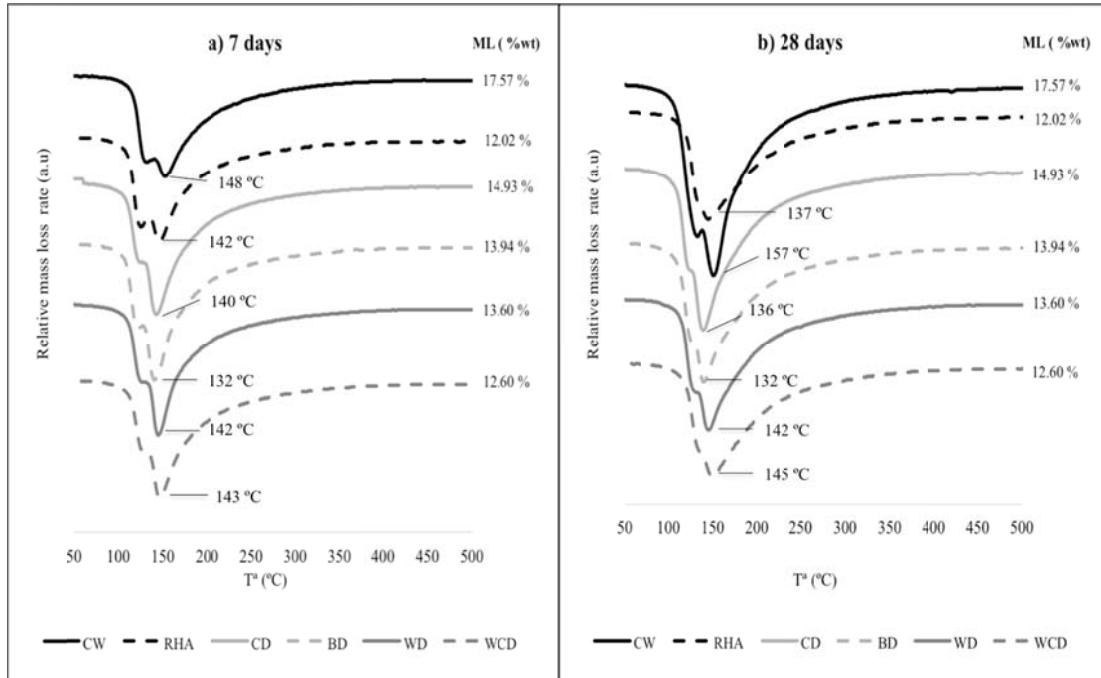142 exhibited by the RHA, WD and WCD mortars.

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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.*

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4. Conclusions

152 This research has demonstrated that residual diatomaceous earth can be successfully

153 used as a silica source to prepare the activating solution in geopolymeric systems.

154 Although wine and beer industrial diatomite-derived residues were less reactive than the

155 RHA, the obtained results provide new promising alternatives to reuse and valorize this

156 significant industrial waste (considering only the beer production in 2016, about 0.27 –

157 0.48 Mtons of residual diatomaceous earth were generated due this industrial activity).

158 The use of residual diatomites obtained similar (BD) and even better (WCD) results

159 than those obtained with commercial ones (CD). The calcination process of the WD

152 improved the mechanical properties of the mortars developed (WCD), which was

153 attributed to the organic matter elimination.

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