

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

26 sedimentary rock with a high amorphous silica content formed by fossilized diatom
27 remains. In this work, the geopolymer was obtained using a fluid cracking catalyst
28 residue as the precursor and six different activating solution types prepared with
29 commercial products, residual diatomite (from beer and wine industries) and RHA. The
30 results open a new possible route for the reuse and recovery of diatomaceous earth
31 residue, although the compressive strength results of the mortars were slightly lower
32 than those for mortars prepared with RHA or commercial reagents.

33

34 **Keywords:** geopolymer, diatomaceous earth, waste valorization

35

36 **1. Introduction**

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

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

49 Some authors used diatomite as a precursor in mixtures with calcium aluminate cement
50 [6] and others studied the combination of RHA and diatomite in lightweight

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

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

57

58 **2. Experimental**

59 *2.1. Materials*

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

63 Four types of diatomites were studied: commercial diatomite (CD), supplied by JJS
 64 Minerals SL; a residual diatomite from the beer industry (BD), supplied by Heineken
 65 (Quart de Poblet, Spain); two residual diatomites from the wine industry, an as-received
 66 original waste residue (WD), supplied by Bodegas Vicente Gandia (Utiel, Spain) and
 67 the same one calcined at 650 °C for 1 h (WCD). Sodium hydroxide pellets (Panreac-SA,
 68 98% purity) and CW (Merck, 28% SiO₂, 8% Na₂O and 64% H₂O) were also used.

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*
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

69

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

77 Six mixes were designed in this study, all of them using FCC as a precursor, and with
78 different sources of silica in the activating solution: i) two controls were designed for
79 comparative purposes, one of them with CW and the other one with the alternative
80 system prepared with RHA and ii) four systems alkali-activated using the diatomites as
81 an alternative source of silica (CD, BD, WD and WCD). Diatomites were used in their
82 original particle size. The alternative activating solutions were prepared by mixing
83 water, NaOH and the corresponding solid silica source (RHA, CD, BD, WD and WCD)
84 into a thermal bottle for 24 h.

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

89

90 **3. Results and discussion**

91 *3.1. Characterization of diatomites*

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

103 significant possibilities of reuse in geopolymer synthesis. Although the CD and WD
104 diatomites exhibited LOI values higher than 10%, the calcination of WD reduced this
105 value to 1.63%, producing enrichment in acid oxides (80.61% for WD and 90.24 for
106 WCD). The original mean particle diameters were 14.1 μm for CD, 46.4 μm for BD and
107 34.7 μm for WD and WCD. The XRD patterns showed that main crystalline phases in
108 all the diatomites were quartz and cristobalite, two different forms of silica. Minor
109 amounts of other crystalline phases were also identified, including tridymite (SiO_2) in
110 CD, anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) in BD and calcite (CaCO_3) and anorthite in WD and WCD.
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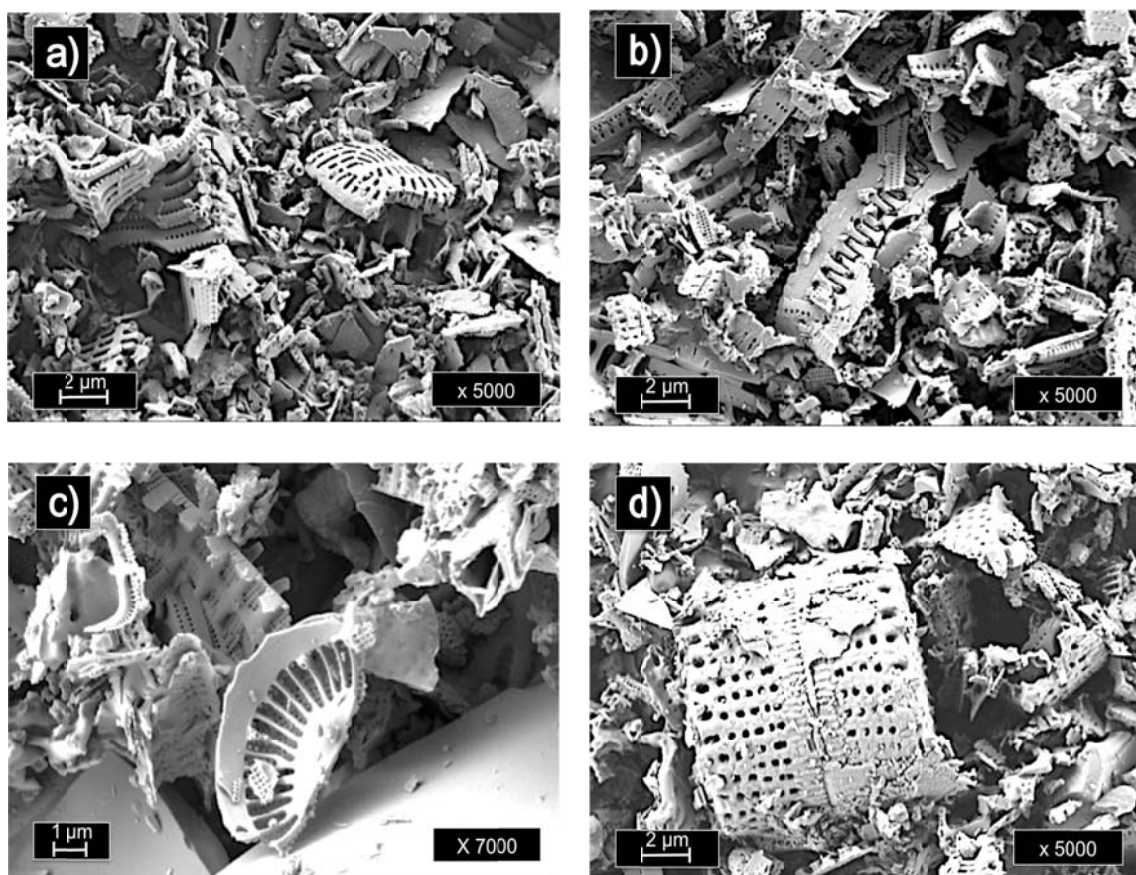


Fig. 1. FESEM micrographs (5000 and 7000 \times) of diatomites: a) CD; b) BD; c) WD and
d) WCD.

106

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.

111

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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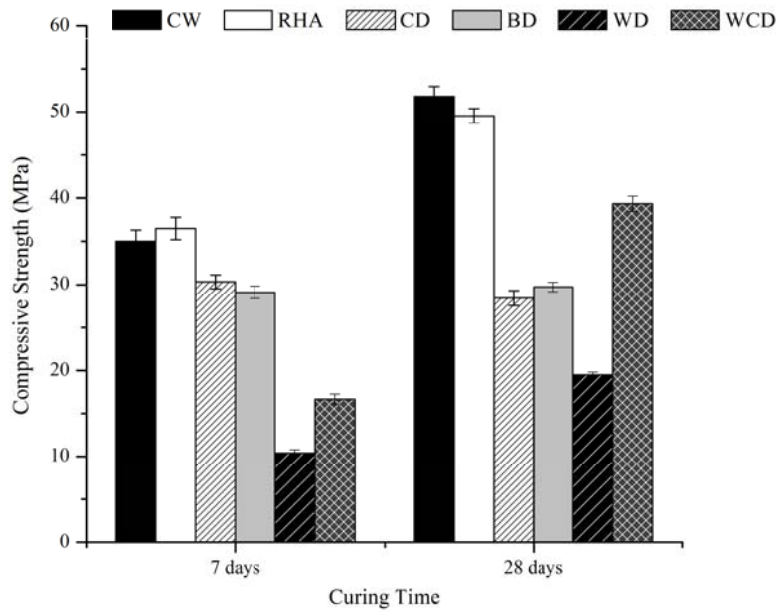


Fig. 2. Compressive strengths of CW, RHA, CD, BD, WD and WCD mortars after 7 and 28 days curing at room temperature.

127

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 °C 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

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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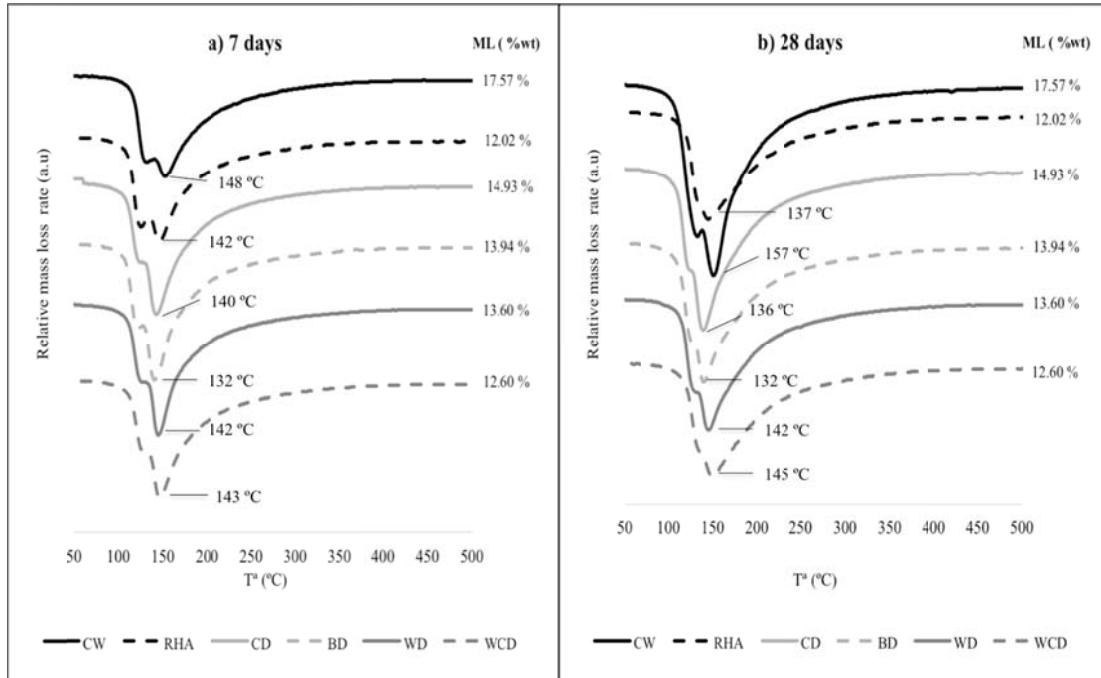


Fig. 3. DTG curves and mass losses by weight of WC, RHA, CD, BD, WD and WCD pastes after: a) 7 days and b) 28 days.

143

144 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.

154

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