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Additional Information



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 residue  
28 as the precursor and six different activating solution types prepared with commercial  
29 products, residual diatomite (from beer and wine industries) and RHA. The results open  
30 a new possible route for the reuse and recovery of diatomaceous earth residue, although  
31 the compressive strength results of the mortars were slightly lower than those for mortars  
32 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 CO<sub>2</sub> emissions [1]. On this basis, the  
38 use of alternative binders with lower carbon footprints has excellent potential for reducing  
39 greenhouse emissions. Geopolymeric cements could be the future of the construction  
40 industry. Geopolymers are prepared by using a solid precursor (aluminosilicate material)  
41 and an alkaline solution (NaOH-Na<sub>2</sub>SiO<sub>3</sub>). The alkaline solution is the weak point of this  
42 binder and commercial waterglass (CW) is a chemical reagent with a high cost, both  
43 economically and environmentally. In recent years, different authors have successfully  
44 used waste as an alternative way to substitute for CW [2–4].

45 The use of rice husk ash (RHA) as a silica source has been investigated and excellent  
46 results in terms of mechanical strength and minimization of CO<sub>2</sub> emissions have been  
47 reported, with a 50% reduction in CO<sub>2</sub> emissions compared with CW [5].

48 Some authors used diatomite as a precursor in mixtures with calcium aluminate cement  
49 [6] and others studied the combination of RHA and diatomite in lightweight geopolymer  
50 manufacture [7]. Mejia et al. used diatomite as a source of silica in activating solution,

51 which was used to activate a mixture of metakaolin and fly ash, with mortars of up to 38  
52 MPa in strength developed [8].

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

56

## 57 2. Experimental

### 58 2.1. Materials

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

62 Four types of diatomites were studied: commercial diatomite (CD), supplied by JJS  
63 Minerals SL; a residual diatomite from the beer industry (BD), supplied by Heineken  
64 (Quart de Poblet, Spain); two residual diatomites from the wine industry, an as-received  
65 original waste residue (WD), supplied by Bodegas Vicente Gandia (Utiel, Spain) and the  
66 same one calcined at 650 °C for 1 h (WCD). Sodium hydroxide pellets (Panreac-SA, 98%  
67 purity) and CW (Merck, 28% SiO<sub>2</sub>, 8% Na<sub>2</sub>O and 64% H<sub>2</sub>O) were also used.

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

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	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

68

69 The different diatomites used were characterized minerallogically and microstructurally  
70 by X-ray fluorescence (XRF, Philips Magic Pro XRF), particle size distribution (PSD,

71 Mastersizer 2000 by Malvern instruments, in a water suspension), powder X-ray  
72 diffraction (XRD, Bruker AXS D8 Advance), thermogravimetry (TGA, TGA 850 Mettler  
73 Toledo thermobalance, temperature range 35–600 °C at a heating rate of 10 C·min<sup>-1</sup> in a  
74 N<sub>2</sub> atmosphere) and field emission scanning electron microscopy (FESEM, ULTRA 55-  
75 ZEISS).

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

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

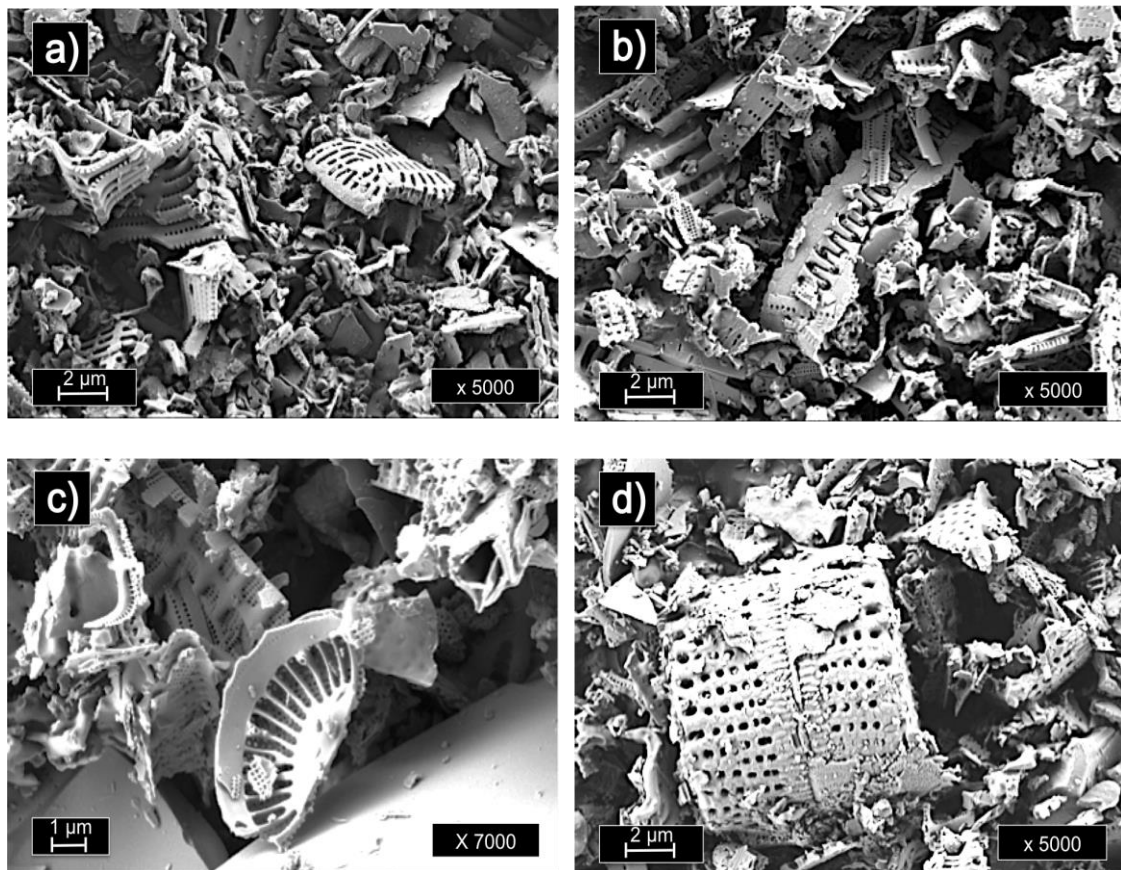
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### 89 **3. Results and discussion**

#### 90 *3.1. Characterization of diatomites*

91 The composition of the diatomites given in Table 1 show that SiO<sub>2</sub> was the major  
92 compound, and significant amounts of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> were also identified. The sum of  
93 these acid oxides overpassed 80% for all of the diatomites, which suggested their  
94 significant possibilities of reuse in geopolymer synthesis. Although the CD and WD  
95 diatomites exhibited LOI values higher than 10%, the calcination of WD reduced this

96 value to 1.63%, producing enrichment in acid oxides (80.61% for WD and 90.24 for  
97 WCD). The original mean particle diameters were 14.1  $\mu\text{m}$  for CD, 46.4  $\mu\text{m}$  for BD and  
98 34.7  $\mu\text{m}$  for WD and WCD. The XRD patterns showed that main crystalline phases in all  
99 the diatomites were quartz and cristobalite, two different forms of silica. Minor amounts  
100 of other crystalline phases were also identified, including tridymite ( $\text{SiO}_2$ ) in CD,  
101 anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) in BD and calcite ( $\text{CaCO}_3$ ) and anorthite in WD and WCD.  
102  
103



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

104  
105 The FESEM micrographs of each type of diatomite are presented in Fig. 1. In general,  
106 typical skeleton forms originated by the diatoms (microalgae) can be observed, with discs,

107 spheres and semi-spheres with micropores in their structures. No significant changes in  
108 the morphology and in the texture of the residual diatomite particles were observed when  
109 compared with CD.

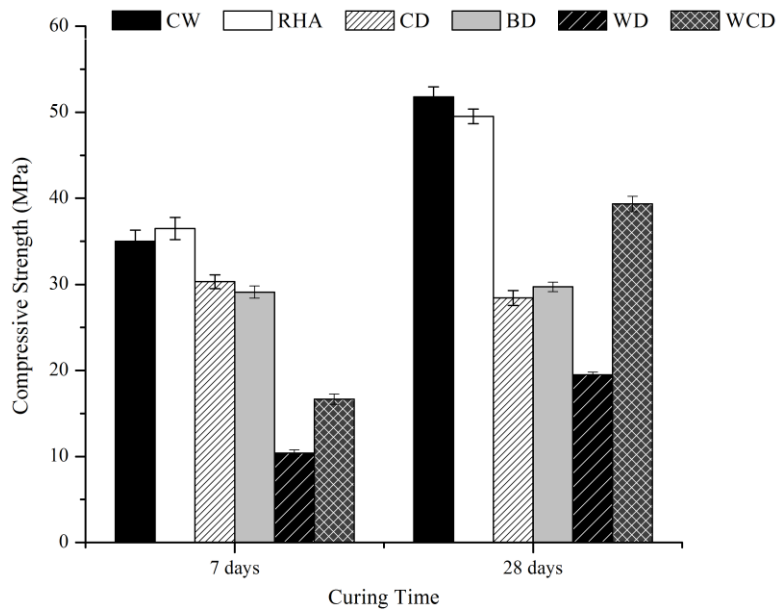
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### 111 *3.2. Diatomite behavior as silica sources in mortars*

#### 112 *Mechanical characterization of mortars*

113 The compressive strength of mortars cured for 7 and 28 days is shown in Fig. 2. The CW  
114 and RHA mortars presented the highest strengths for both curing ages. After 7 days, the  
115 CW and RHA mortars exhibited 35.01 and 36.5 MPa, respectively, both higher than the  
116 strength values presented by the diatomite-based samples: 30.27 MPa for CD, 29.06 MPa  
117 for BD, 10.38 MPa for WD and 16.66 MPa for WCD. The CD and BD mortars exhibited  
118 similar compressive strength results, and their mechanical properties slightly varied from  
119 7 to 28 days. Otherwise, a remarkable compressive strength gain was observed for CW  
120 (47.95%), RHA (35.69%), WD (87.86%) and WCDE (136%). The calcination of WD to  
121 produce WCD, which reduced the LOI by ~10%, improved the mechanical properties of  
122 the mortars developed by 60.5% and 101.8% after 7 and 28 days, respectively.

123



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

124

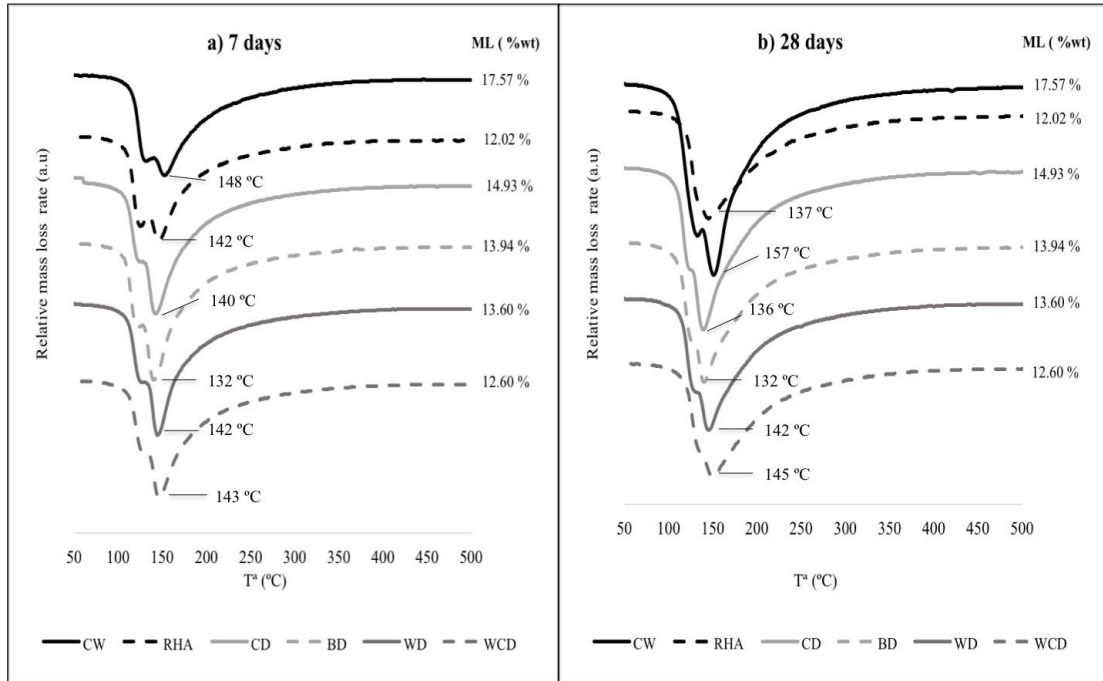
125 *Thermogravimetric analysis of pastes*

126 The DTG curves and mass losses obtained from the thermogravimetric analysis are  
 127 depicted in Fig. 3. In general, a main peak arose in the 100–200 °C range, which is  
 128 attributed to the dehydration of the N-A-S-H gel formed during the geopolymerization  
 129 process. Minor variations of the mass loss with the curing time were observed in the  
 130 pastes developed using waste as an alternative silica source (RHA, CD, BD, WD and  
 131 WCD). This suggests that no significant amounts of new N-A-S-H gel formed from 7 to  
 132 28 curing days. However, a slight displacement of the bands towards higher temperatures  
 133 was observed in the RHA, WD and WCD thermogravimetric curves, which implies that  
 134 higher temperatures were required to dehydrate the formed gel. This behavior denotes a  
 135 modification of the hydrated products formed with the curing time, which would be  
 136 explain the minor variations of the strength values observed from 7 to 28 days in the CD



137 and BD mortars, and the improvement of the mechanical properties exhibited by the  
 138 RHA, WD and WCD mortars.

139



**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.

140

#### 141 4. Conclusions

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

150 mechanical properties of the mortars developed (WCD), which was attributed to the  
151 organic matter elimination.

152

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157

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