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# 1 Properties and microstructure of alkali-activated red clay brick waste

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## 16 17 **Abstract**

18  
19 Sintered red clay ceramic is used to produce hollow bricks which are manufactured in enormous  
20 quantities in Spain. They also constitute a major fraction of construction and demolition waste. The  
21 aim of this research was to investigate the properties and microstructure of alkali-activated cement  
22 pastes and mortars produced using red clay brick waste. The work shows that the type and  
23 concentration of alkali activator can be optimised to produce mortar samples with compressive  
24 strengths up to 50 MPa after curing for 7 days at 65 °C. This demonstrates a new potential added  
25 value reuse application for this important waste material.

26  
27 *Keywords:* Ceramic waste (D), Waste Management (E), alkali-activated binder (D), mechanical  
28 properties (C).

## 1. Introduction

Red clay brick waste (RCBW) originating primarily from demolished brick walls represents approximately 54 wt.% of construction and demolition waste in Spain [1]. As previously reported [2], almost 30 million tonnes of structural ceramics and 608 million m<sup>2</sup> of tiles were manufactured by the Spanish ceramics industry in 2006. According to Pacheco-Torgal and Jalali [3], the amount of waste generated by the European ceramic industry is typically 3-7% by weight of total production, suggesting that millions of tonnes of RCBW are generated in Spain each year.

Significant quantities of RCBW are currently used as road sub-base in landscaping and as a coarse aggregate for the production of structural and non-structural concrete [3-5]. The use of sintered clay ceramics as a cementitious material to partially replace Portland cement (PC) clinker has also been investigated. The manufacture of Portland cement requires high amounts of energy (850 kcal per kg of clinker) and involves the emission of typically 0.8-1 Tonne of CO<sub>2</sub> per Tonne of clinker produced [6]. Different alternatives have been proposed to reduce the environmental impact of cement and these include reusing waste materials to produce low-CO<sub>2</sub> cement binders. In the study by Puertas et al. [6,7] ceramic waste materials were used to produce PC clinker, while other studies [3,8,9] investigated the potential of clay ceramics as a supplementary cementitious material. While only a portion of cement is replaced in these applications (usually 10–35 %), binders based on alkali-activation can be produced entirely or almost entirely from waste materials. In alkali-activation reactions aluminosilicate minerals are dissolved by a highly alkaline solution prior to precipitation reactions that form a gel binder [10]. The gel formed by alkali-activation of sintered clay is generally a zeolite precursor containing tetrahedral SiO<sub>4</sub> and AlO<sub>4</sub><sup>-</sup> in randomly distributed polymeric chains, cross-linked by bridging oxygen atoms. The negative charge on the AlO<sub>4</sub><sup>-</sup> group is balanced by alkali metal cations, typically Na<sup>+</sup> and/or K<sup>+</sup> [11-13].

The use of aluminosilicate minerals such as metakaolin, ground blast furnace slag and fly ash to produce alkali-activated cements has been extensively reported [12,14-17] and there is increasing interest in investigating the suitability of using other materials. Different wastes containing silica and alumina, such as hydrated-carbonated cement [18], glass [19], fluid catalytic cracking catalyst residues (FCC) [20] and waste ceramic materials [21,22] have been alkali-activated. In the work by

1 Puertas et al. [21], ceramic wastes were activated using NaOH and sodium silicate solution. Although  
2 compressive strengths between 7 and 13 MPa were achieved, it was concluded that further research  
3 was required to understand the influence of process parameters on the final properties of the binders  
4 developed.

5  
6 This research aimed to optimise alkali-activation of RCBW and understand the influence of the type  
7 and concentration of alkali activator used on the mechanical strength and microstructure of the binders  
8 formed.

## 9 10 **2. Experimental**

### 11 12 *2.1. Materials*

13  
14 As-received RCBW was crushed to give a granular material with particles less than 4 mm in diameter.  
15 This was dry milled using a porcelain ball mill with alumina milling media for 40 minutes to increase  
16 the specific surface area [22]. The particle size distribution of milled RCBW shown in Fig. 1 was  
17 determined using laser diffraction (Mastersizer 2000, Malvern Instruments). This indicates a mean  
18 particle size of approximately 20.9  $\mu\text{m}$ , a  $d_{90}$  (90% of volume less than this size) of 56.2  $\mu\text{m}$  and a  $d_{10}$   
19 value of 1.2  $\mu\text{m}$ .

20  
21 The chemical composition of milled RCBW shown in Table 1 was determined by x-ray fluorescence  
22 (XRF). RCBW contains high levels of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , which are essential for alkali-activation, together  
23 with moderate amounts of CaO and MgO. The amorphous content, determined following UNE EN  
24 196-2, was around 35%, which is close to that obtained by Puertas et al. [21] for waste red clay tiles.  
25 According to Baronio and Binda [23], the amorphous content of bricks sintered between 800 °C and  
26 1000°C [9] originates at temperatures between 600°C and 900°C, due to loss of the combined water in  
27 clay minerals, which causes breakdown of the crystalline clay network, with the silica and alumina  
28 forming a disordered, amorphous phase. Pereira-de-Oliveira et al. [9] report that the amorphous  
29 content determines the degree of pozzolanic activity.

30

1 The mineralogical composition of RCBW was determined by x-ray diffraction (XRD, Philips  
2 diffractometer PW1710 with Cu K<sub>α</sub> radiation, 40 kV and 20 mA, 2θ from 5-55°). The data in Fig. 2  
3 shows that quartz (SiO<sub>2</sub>) is the major crystalline phase. Albite (NaAlSi<sub>3</sub>O<sub>8</sub>), calcite (CaCO<sub>3</sub>), anorthite  
4 (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) and sanidine ((K,Na)(Si,Al)<sub>4</sub>O<sub>8</sub>) were also present as minor constituents [3,8,21]. The  
5 particle morphology of milled RCBW was examined using scanning electron microscopy (SEM, JEOL  
6 JSM-6300) and this indicates mainly irregularly shaped particles as shown in Fig. 3.

7  
8 Sodium hydroxide pellets (98% purity, Panreac), water and sodium silicate (Merck, SiO<sub>2</sub>=28%,  
9 Na<sub>2</sub>O=8%, H<sub>2</sub>O=64%) were used to prepare alkali-activating solutions.

10

### 11 *2.2. RCBW paste and mortar sample preparation*

12 The alkaline activating solutions were prepared by dissolving NaOH pellets in water and adding the  
13 required amount of sodium silicate solution. The concentration of Na<sup>+</sup> provided by NaOH and sodium  
14 silicate ranged from 2.5 to 10 molal (mol.kg<sup>-1</sup>).

15

16 Table 2 summarizes the mix proportions investigated in this research. Mixes are coded 'w/m/r', where  
17 w is the amount of water per 100g of RCBW, m is the molality of Na<sup>+</sup> in the activating solution and r is  
18 the SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio in the activating solution.

19

20 Alkali-activated RCBW paste samples were obtained by mixing ground RCBW with the required  
21 alkaline solution for 4 minutes. Samples were cast in plastic containers, sealed and stored in a  
22 thermostatically controlled bath at 65 °C.

23

24 Alkali-activated RCBW mortar samples were prepared by mixing RCBW with activating solution for 2  
25 minutes. Siliceous sand (4.36 modulus fineness with maximum particle diameter of 2 mm) was then  
26 added using sand/RCBW ratios of 3/1 and 2/1, as shown in Table 2. Mixing continued for a further 3.5  
27 minutes and the mortar samples formed were then placed in a mould and vibrated for 4 minutes.

28 Samples were stored at 65 °C at a relative humidity of 90-95% for 3 and 7 days.

29

### 30 *2.3. Sample testing*

31

1 The compressive strengths of alkali-activated RCBW mortar samples were determined following UNE  
2 EN 196-1. The porosity of the mortars was evaluated by mercury intrusion porosimetry (MIP, AutoPore  
3 IV 9500) using pressures between 2 psia (13782Pa) to 32989 psia (227.4 MPa), equivalent to pores  
4 with diameters ranging from 91.2 microns to 5.5 nm. Pressures were converted to equivalent pore  
5 widths using the Washburn equation, assuming a contact angle of 130°.

6

7 The microstructure of RCBW paste samples was examined using SEM-EDX (JEOL JSM-6300). X-ray  
8 diffraction (XRD) was used to identify mineralogical phases (Philips diffractometer PW1710 with Cu K $\alpha$   
9 radiation, 40 kv and 20 mA, 2 $\theta$  from 5-55°). Fourier transformed infrared spectroscopy (FTIR) analysis  
10 of the nanostructure of the materials obtained was conducted with a Mattson Genesis II spectrometer.

11 The KBr pellet method was used to prepare the samples, with spectra collected in transmittance mode  
12 from 1500 to 400 cm<sup>-1</sup>.

13

14 Thermogravimetry (TG, 850 Mettler-Toledo) was used to investigate weight loss of samples under a  
15 N<sub>2</sub> atmosphere, using sealed pin holed aluminium crucibles at a heating rate of 10 °C min<sup>-1</sup>, from 35  
16 °C to 600 °C. Samples were analyzed after 3 and 7 days of curing at 65 °C (relative humidity 90-95%).  
17 Samples for TG and XRD analyses were crushed using a pestle and mortar and passed through a 125  
18  $\mu$ m sieve. Hydration reactions were inhibited by immersing samples in acetone and then placing them  
19 in the oven at 60°C for 30 minutes.

20

## 21 **3. Results and discussion**

22

### 23 *3.1. Compressive strength*

24

#### 25 *3.1.1. Effect of NaOH concentration*

26

27 Fig. 4 shows the effect of NaOH concentration (molality: 2.5, 5, 7 and 10) on the compressive strength  
28 of RCBW mortars prepared at a constant water to binder (w/b) ratio of 0.45. The best alkali-activated  
29 samples were obtained using 5.0 molal NaOH ('45/5.0/0.0') after curing for 7 days, while the  
30 mechanical properties decreased significantly for higher concentrations of NaOH. This concentration  
31 is close to the optimum established by Puertas et al. [21] who also showed that mechanical properties

1 did not exhibit significant differences when the type or amount of activator was varied. The existence  
2 of an optimum concentration was previously reported by Palomo et al. and Tashima [24, 25] for alkali-  
3 activated fly ash and vitreous calcium silico-aluminates, respectively. According to Barbosa et al. [26],  
4 the optimum concentration of activator depends on the precursor, and must be sufficient to balance  
5 the charges of the Si and Al tetrahedral, without providing an excess of NaOH, that may cause the  
6 formation of carbonate salts resulting from atmospheric carbonation.

### 7 8 *3.1.2. Influence of SiO<sub>2</sub>/Na<sub>2</sub>O ratio*

9  
10 Fig. 5 shows the compressive strengths of RCBW mortars prepared using a constant 5 molal NaOH  
11 concentration with different SiO<sub>2</sub>/Na<sub>2</sub>O molar ratios (0.73, 1.46, 1.60), for samples cured at 65 °C for 3  
12 and 7 days. The compressive strength increases as the amount of sodium silicate increased.  
13 However, higher silicon contents increased the mortar viscosity and reduced setting time. It was  
14 impossible to produce mortars with a SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio higher than 1.60 for samples with 5 molal  
15 NaOH because these samples set within a few seconds of mixing. Results are in agreement with  
16 previous studies [20,25,27] where compressive strength generally increase with the addition of more  
17 activator. According to Pacheco-Torgal et al. [11], this is due to the presence of sodium silicate in the  
18 activating solution which increases the Si/Al ratio, accelerating the geopolymerization process. Provis  
19 et al. [27] used dilatometry measurements to prove that the optimum amount of silica depends on the  
20 precursor, and must be appropriate to form a highly cross-linked alumino-silicate network and avoid  
21 the presence of unreacted silica.

### 22 23 *3.1.3 Influence of Na concentration for a constant SiO<sub>2</sub>/Na<sub>2</sub>O ratio*

24  
25 Fig. 6 summarises the compressive strength data of mortars with a constant SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio  
26 (1.60) and different sodium concentrations, cured at 65 °C for 3 and 7 days. Although the compressive  
27 strength remained almost the same after curing for 3 days for all mortars (14-17 MPa), the mix  
28 prepared using 7 molal Na<sup>+</sup> exhibited good workability and gave the highest strengths of 28 MPa after  
29 7 curing days. These results are consistent with previous studies in which the compressive strength  
30 was found to depend not only on the SiO<sub>2</sub>/Na<sub>2</sub>O ratio but also on the activator/binder ratio [17,28,29].  
31 This is related to the optimum concentration of activator for the RCBW. As discussed in sections 3.1.1

1 and 3.1.2, the  $\text{Na}^+$  concentration increases as the sodium silicate content is increased in the alkali-  
2 activating solution.

### 3 4 *3.1.4 Influence of water/binder (w/b) ratio*

5  
6 The effect of w/b ratio for different Na concentrations on compressive strength is summarized in Fig. 7.  
7 For the lowest w/b mixes (except '30/7.0/2.00') the amount of  $\text{Na}^+$  and  $\text{SiO}_2$  with respect to the RCBW  
8 was constant and equal to those prepared for mix '45/7.0/1.60' at 3.15 mol of  $\text{Na}^+$  and 2.52 mol of  
9  $\text{SiO}_2$  per kg of ceramic waste. Consequently, the concentration  $\text{Na}^+$  in the solution increased for  
10 mixtures with w/b ratio of 0.40 (8 molal) and 0.35 (9 molal). Two main results are observed. The  
11 compressive strength increases as the w/b ratio decreases when the activator/binder and  $\text{SiO}_2/\text{Na}_2\text{O}$   
12 ratios are kept constant ('45/7.0/1.60', '40/8.0/1.60', '35/9.0/1.60'). According to Lampris et al. [17], this  
13 implies that a 0.35 w/b ratio provides sufficient water to effectively wet all the grains of the source  
14 material, which react with the activating solution. As observed by Komnitsas et al. [30], the reduction in  
15 compressive strength when the water volume is increased is due to the water not being consumed  
16 during hydration resulting in increased porosity.

17  
18 For every concentration of  $\text{Na}^+$ , the compressive strength increased as the w/b ratio decreased  
19 ('45/8.0/1.60' - '40/8.0/1.60'; '45/9.0/1.60' - '35/9.0/1.60'). This effect was observed after both 3 and 7  
20 days curing, and means that reduced amounts of reagents were used at lower w/b ratios. This is an  
21 important result from both an environmental and economic point of view, because the compressive  
22 strength increased while reducing the  $\text{Na}^+$ /binder and  $\text{SiO}_2$ /binder ratios.

23  
24 The binder/sand ratio (b/s) was modified in sample '30/7.0/2.00' in order to increase the workability of  
25 the fresh mortar and this allowed the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio to be increased to 2.0. A significant improvement  
26 in compressive strength was observed, especially for samples cured for 3 days (42.3 MPa), when  
27 compared to sample '45/7.0/1.60', which gave the best results with a w/b ratio of 0.45. For this mix,  
28 with the lowest w/b ratio, only 2.1 mol of  $\text{Na}^+$  and 4.2 mol of  $\text{SiO}_2$  were used per kilogram of RCBW. It  
29 can be concluded that the amount of water is the dominant parameter in achieving high compressive  
30 strengths.

31



### 1 3.2 Mercury intrusion porosimetry

2

3 Porosity studies were carried out on selected mortars. These were samples '45/5.0/0.0' and  
4 '45/7.0/1.60' with a constant w/b ratio which had the highest compressive strengths for the samples  
5 with and without sodium silicate addition.

6

7 The total porosity of mortars was reduced when sodium silicate was added to the activating solution:  
8 19.8% for sample '45/5.0/0.0' (without sodium silicate), and 12.0% for sample '45/7.0/1.60' (with  
9 sodium silicate). Therefore, higher durability alkali-activated RCBW samples with sodium silicate can  
10 be expected due to the reduced ability of aggressive chemical agents to penetrate the microstructure.

11 These values are close to those previously reported for Portland cement pastes and mortars with  
12 similar water-to-cement (w/c) ratios. Cook and Hover [31] observed a minimum total porosity of 16.0%  
13 for Portland cement paste specimens mixed with a w/c ratio of 0.3 and cured for 56 day, and higher  
14 values when increasing the w/c ratio and reducing the curing time (56% for a w/c of 0.7 cured for 1  
15 day). Similar results were reported by Willis et al. [32], who observed a total porosity of 16 and 23% for  
16 mortars with a w/c ratio of 0.4 and 0.6, respectively.

17

18 Figure 8 shows the pore size distribution for the mortar samples analyzed. There are significant  
19 differences between the volume percentages. The capillary porosity was higher for the sample  
20 activated with NaOH, with a total volume of 75-80% in the 10nm-1 $\mu$ m range, while this was only 40-  
21 45% for the mortar containing sodium silicate. The volume of air voids in the 1-10  $\mu$ m range was  
22 higher for the mortar containing sodium silicate, which could be attributed to the high viscosity of the  
23 paste, which allows greater air retention in the mix. These results are contrary to those previously  
24 reported by Sindhunata et al. [33], who observed smaller pore sizes with increasing additions of  
25 soluble silicate to the activating solution. After analyzing the hydration mechanisms of Portland cement  
26 and inorganic polymer pastes, Lloyd et al. [34] also concluded that larger pores may be expected in  
27 samples activated without silicate. In Portland cement pastes C-S-H gel grows outwards from the  
28 surface of hydrating cement grains, forming "C-S-H gel" pores 1.5 nm in diameter and "capillary"  
29 pores, which are much larger and are the remains of originally water-filled spaces that have not  
30 become filled with C-S-H gel [35]. The growth of C-S-H gel in alkali-activated systems occurs through  
31 the sample, which explains the absence of capillary pores, as much of the volume between the

1 particles fills concurrently with C-S-H gel to form the hardened binder structure. However, in the  
2 absence of dissolved silicate the mechanism of inorganic polymer gel formation is more similar to that  
3 of Portland cement, i.e. growth of reaction products outwards from the surface of the binder grains,  
4 and therefore capillary pores may be expected in samples activated only with NaOH. However, it was  
5 observed that, unlike the capillary pores present in Portland cement pastes, these pores were  
6 separated by regions of C-S-H gel. Access to these pores, via the smaller pores of the gel, would  
7 cause a pronounced “ink bottle” effect. Consequently, the MIP results may be misrepresenting the  
8 pore size distribution [32,33,35]. This is because the pore size measurement is based on the diameter  
9 of access throat through which the mercury penetrates the pore.

### 11 *3.3 Thermogravimetric analysis*

13 Table 3 shows thermogravimetric analysis data giving the total weight loss of pastes cured for 3 and 7  
14 days. A general increase in water loss with curing time is observed, which may be associated with a  
15 greater degree of alkali-activation [20]. Weight loss generally increases with Na<sup>+</sup> concentration which,  
16 according to Bernal et al. [36], can be related to a higher degree of chemically bounded water and OH<sup>-</sup>  
17 groups, provided by NaOH, in the binding phase. Samples with the same SiO<sub>2</sub>/Na<sub>2</sub>O ratio (1.60) gave  
18 similar thermogravimetric loss without a specific trend. The reduction in the w/b ratio did not decrease  
19 the total weight loss, suggesting that the water molecules and OH<sup>-</sup> groups bonded to the geopolymer  
20 matrix are not related to the initial mix water.

22 As observed in Fig. 9, all paste samples showed a peak weight loss between 120 and 150 °C which,  
23 according to several authors [20,25, 36], is attributed to free or loosely bound water present in these  
24 samples. As shown in Fig. 9a, among the pastes activated without sodium silicate, only sample  
25 ‘45/5.0/0.0’ presented two peaks in the DTG curve. Although Stakebake [37] associated the second  
26 peak centred at 185 °C to a weight loss from zeolitic phases, these could not be clearly identified by  
27 XRD. In the studies performed by Bernal et al. [36] signals related to zeolitic reaction products could  
28 not be distinguished by thermogravimetry, because they tend to show a broad dehydration peak in the  
29 same temperature range attributed to the loosely bound water present in the samples (60-160 °C).

1 Thermogravimetric data for alkali-activated RCBW paste samples using sodium hydroxide and sodium  
2 silicate are shown in Fig. 9b. These tend to have a broader first peak when the amount of reagents is  
3 increased. The second peak can only be clearly distinguished for lower  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio paste (0.73),  
4 and it progressively overlaps with the first peak when the concentration of the solution is increased.  
5 According to Duxson et al. [13], this is because zeolitic-like phases are less likely to form in highly  
6 concentrated solutions due to increased difficulties in phase transport and reorganization.

7

### 8 *3.4 X-ray diffraction studies*

9

10 Fig. 10 shows XRD diffraction data for pastes '45/5.0/0.0' and '45/7.0/1.60', after curing for 7 days at  
11 65 °C. The XRD data for the as-received RCBW is shown for comparison. The quartz phase was  
12 found to be largely unreactive [12], and remained in the sample after the alkali-activation process.  
13 Paste '45/5.0/0.0' showed a peak that did not appear in the raw material, denoting the formation of  
14 natrite (N,  $\text{Na}_2\text{CO}_3$ ). This did not appear in samples prepared with sodium silicate. Results are in  
15 agreement with thermogravimetry data reported by Provis et al. [27], who observed that silicate-  
16 activated samples presented low mass loss between 200 °C and up to approximately 800 °C.  
17 However, hydroxide-activated samples showed an additional mass loss, which was attributed to the  
18 decomposition of carbonates, resulting from atmospheric carbonation formed during the preparation of  
19 the samples prior to analyses. Bernal et al. [36] attributed the DTG peaks observed at temperatures  
20 between 650 °C and 670 °C and 770 to 790 °C to carbonates.

21

22 Previous studies [12,13] have demonstrated that crystalline phases are less likely to form when  
23 sodium silicate solutions are used because high  $\text{SiO}_2$  concentrations confer greater stability to the  
24 amorphous phases. Despite authors such as Duxson et al. [13] and Criado et al. [28] having noted the  
25 formation of semi-crystalline to crystalline phases from the geopolymeric gel, usually zeolitic in nature,  
26 these could not be clearly identified in these samples.

27

### 28 *3.5 Scanning electron microscopy*

29

30 Fracture surfaces of alkali-activated RCBW pastes are shown in Fig. 11. RCBW particles can be  
31 observed, indicating that some larger particles had only partially reacted during alkali-activation as

1 complete reaction depends on the particle size. This has led to the development of different  
2 morphologies, giving rise to a heterogeneous microstructure containing unreacted ceramic waste  
3 particles surrounded by alkali-activation reaction products. It seems that smaller particles were  
4 completely dissolved by the alkali solution, while the larger ones are only partially reacted. The  
5 strengthening or weakening effect will depend on whether the particles themselves are strong or  
6 weak, and also whether they are bonded on the surfaces to the matrix. Studies performed by Yungsen  
7 et al. [38] showed that the unreacted particles reduced the compressive strength while Kourti et al.  
8 [19] found that unreacted glass could increase strength and toughness.

9  
10 As expected from XRD results, crystalline phases were developed in samples with 10 molal Na<sup>+</sup> as  
11 shown in Fig. 11b. EDX analysis confirmed the high concentration of Na<sup>+</sup> had produced sodium  
12 carbonate (natrite) by atmospheric carbonation [39]. This, together with the mechanical properties  
13 obtained, confirmed that this concentration of activator was in excess for this sample and this is  
14 deleterious to the alkali activation process [17]. Although the development of crystalline phases was  
15 observed in some samples as in Fig. 11d, these could not be clearly identified by XRD.

### 16 17 *3.6 Fourier transformed infrared spectroscopy (FTIR)*

18  
19 Infrared spectra of the as-received RCBW and pastes '45/5.0/0.0' and '45/7.0/1.60', cured for 7 days  
20 at 65 °C, are shown in Fig. 12. The spectra obtained were normalized in order to allow direct  
21 comparison between them. The presence of unreacted particles, previously observed by SEM and  
22 XRD, was corroborated by FTIR. According to Criado et al. [28], the quartz gives rise to a series of  
23 bands located at 1145, 1084, 796-778, 697, 668, 522 and 460 cm<sup>-1</sup> in the IR spectrum. Although these  
24 bands persist after activation, a reduction in intensity is observed, which indicates that quartz has  
25 partially reacted. The higher reduction observed for the sample containing soluble silica ('45/7.0/1.60')  
26 implies greater reactivity, which leads to further development of the alkali-activation reaction products.  
27 These results are consistent with the lower porosity and improved compressive strength presented by  
28 the samples alkali-activated with sodium silicate.

29  
30 A wide and intense band appears from 950 cm<sup>-1</sup> to ~1200 cm<sup>-1</sup>. The interpretation of this region may  
31 be difficult, as bond vibrations of different compounds tend to overlap, producing a highly complex

1 spectrum. While in the unreacted RCBW this band appears at  $\sim 1045 \text{ cm}^{-1}$ , in the activated samples it  
2 shifts to lower wave numbers ( $\sim 1011 \text{ cm}^{-1}$ ). According to authors such as Rees et al. [40] and  
3 Hajimohammadi et al. [41], this shift occurs due to the formation of aluminosilicate gel, as the  
4 asymmetric stretching vibrations of the newly formed Si-O-T (T = Al, Si) bonds originate a new band  
5 growing at  $960 \text{ cm}^{-1}$ . Although a gel with a higher Si/Al ratio is expected for the '45/7.0/1.60' sample,  
6 the nature of the gel formed could not be clearly distinguished from FTIR results, due to the Al-  
7 enriched gel phase band ( $\sim 1020 \text{ cm}^{-1}$ , from [41]), and the primary band of the Si-O-T bonds in the gel  
8 overlap. Furthermore, the bands associated with the vitreous phases of the raw material were also  
9 expected to appear in this region ( $950 \text{ cm}^{-1}$  to  $1100 \text{ cm}^{-1}$  [28]). Although they could not be  
10 distinguished, the intensity was expected to decrease as the alumino-silicate gel formation proceeded.

11  
12 The bands appearing at  $871 \text{ cm}^{-1}$  and  $1415 \text{ cm}^{-1}$  in the raw material spectrum are associated with  
13 pure  $\text{CaCO}_3$  [42], attributed to out-of-plane deformation and asymmetric stretching vibrations,  
14 respectively. Both bands shift to higher wave numbers after the activation process which, according to  
15 Zaki et al. [43] relates to  $\text{CO}_3^{2-}$  impurity species. This, together with the higher intensity of the peaks  
16 appearing in the spectrum of the sample activated with only NaOH ('45/5.0/0.00'), correlates well with  
17 XRD and SEM results, where the presence of Natrite ( $\text{Na}_2\text{CO}_3$ ) was observed.

18  
19 No definite peaks were observed in the regions highlighted by Rees et al. [44] as zeolite characteristic  
20 regions. This is in good agreement with XRD results, and confirms that it is unlikely that the system  
21 contains significant quantities of zeolite nanocrystals.

22

#### 23 **4. Conclusions**

24

25 This research has demonstrated that red clay brick waste (RCBW) can form alkali-activated cement  
26 pastes and mortars using NaOH and sodium silicate solution as activators. Although  
27 thermogravimetric analysis identified initial formation of zeolitic structures, these tend to disappear  
28 when the concentration of the alkaline solution increased. The optimum mix was found to be  
29 '45/7.0/1.60', and this gave compressive strengths close to 30 MPa after 7 curing days. The  
30 mechanical properties were further increased up to 50 MPa by optimising the w/b, b/s and  $\text{SiO}_2/\text{Na}_2\text{O}$   
31 ratios.

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