Ceramic tiles waste as replacement material in Portland cement

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The pozzolanic reactivity of real ceramic waste from different tile manufacturing companies was evaluated and its suitability as a partial Portland cement replacement was analysed. The raw material was finely ground and physico-chemically characterised using x-ray fluorescence (XRF), x-ray diffraction (XRD), scanning electron microscopy (SEM) and laser analysis particle size distribution (ADL). Percentages of ceramic waste (from 15 wt% to 50 wt%) to substitute Portland cement were used to assess this material's pozzolanic behaviour, and samples were cured at 20°C for different curing times. pH tests and conductivity measurements were used to evaluate its pozzolanic character, while mortars were utilised to evaluate compressive strength behaviour. The microstructural evolution of the developed binders was assessed in pastes by XRD, thermal analysis, Fourier transform infrared spectroscopy (FTIR) and SEM analyses. A strength gain due to pozzolanic activity was observed after 28 d and 90 d curing. The results prove that mortars with up to 35 wt% of tile ceramic waste comply with the requirements established for fly ash pozzolanic materials.

Introduction

Portland cement clinker is the dominant binder used in concrete because of an abundance of raw materials, its relatively low cost and its excellent mechanical and durability properties. However, as reported by Meyer (2009), its production process is energy intensive (850 kcal per kilogramme of clinker) and emits a high level of carbon dioxide emissions to the atmosphere (about a tonne of carbon dioxide per tonne of cement). It has also been estimated that cement companies are responsible for the emission of about two billion tonnes of carbon dioxide per year, which is 6–7% of the planet's total carbon dioxide emissions (Meyer, 2009). The cement industry is looking for alternatives to overcome these problems and to comply with Kyoto protocol obligations by making more sustainable binders and reusing wastes from other industries. Among the different options analysed, the scientific community has incorporated industrial by-products such as silica fume, fly ash, ceramic materials, glass and so on into the production of mortars and concretes (Frías *et al*., 2011; Lavat *et al*., 2009; Naceri and Hamina, 2009; Payá *et al*., 2002; Pereira de Oliveira *et al*., 2012). As explained by Frías *et al*. (2012) and Payá *et al*. (1999), the development of cement matrices that contain industrial

by-products brings environmental, economic and technological benefits, since it

- avoids the disposal of waste materials and minimises the use of natural resources, which implies energy savings and, therefore, fewer carbon dioxide emissions
- allows the use of waste to replace higher cost materials
- improves some properties of mortars and concretes.

Some of these by-products are ceramic in nature and have been successfully used in concrete and cement production (Ay and Ünal, 2000; Medina et al., 2012, 2013; Reig *et al*., Q2 2013a, 2014; Shi *et al*., 2011). Authors such as Medina *et al*. Q3 (2012a, 2012b, 2013a, 2013b) analysed the feasibility of using ceramic sanitary ware as a partial replacement for natural aggregates in concrete production. Contents of traditional coarse aggregates, ranging from 15 to 25 wt%, were substituted, and the microstructure, physical and mechanical properties, rheological and calorimetric behaviour, gas and water permeability of the developed concrete were analysed. Other types of ceramic waste such as bricks and sanitary ware (Alves *et al*., 2014), construction and demolition waste (Bezerra Cabral *et al*., 2010) and electrical insulators (Senthamarai *et al*., 2011) have

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also been successfully used as aggregates in concrete production. The suitability of other ceramic materials (e.g. red hollow bricks and ceramic tiles) as a source of aluminosilicate in alkali-activated binder production was also proved by Reig *et al.* (2013, 2014) and Sun *et al.* (2013). Similarly, Puertas *et al.* (2010) proposed the use of ceramic waste as a starting material for Portland cement manufacture while Silva *et al.* (2008) and Pereira de Oliveira *et al.* (2012) successfully proved the pozzolanic activity of ceramic materials. Different types of ceramic products (red clay brick waste, glass and tiles) were used by Pereira de Oliveira *et al.* (2012) to replace 10–40% Portland cement and 10% of red clay brick waste was used in the study reported by Silva *et al.* (2008). Although both studies reported the compressive strength evolution of the developed mortars, they provided very little information on the developed microstructure and the pozzolanic reaction.

As previously explained by Zanelli *et al.* (2011), the production process of ceramic materials determines the microstructure and phases developed, which greatly influence their potential reactivity. Among the different categories of ceramic products produced (structural products, tiles, sanitary ware, etc.), floor and wall ceramic tiles are produced in different temperature–time cycles, with peak firing temperatures usually falling within the range 1120–1220°C (García Ten, 2005). Global ceramic tile production has increased in recent years from 8581 million m^2 in 2009 to 11 913 million m^2 in 2013 (Stock, 2014). As reported by Stock (2014), Spain is the largest tile producer in the European Union and ranks fifth in global production, with 420 million m^2 made in 2013, which implies 3·5% of world production. It is the second largest exporting country in the world, with 318 million m^2 exported (75·7% of national production). As reported by Monfort *et al.* (2011), more than 215 companies related to the manufacturing process of ceramic tiles were registered in Spain in 2008; most (87%) were located in the Comunidad Valenciana (comprising Valencia, Alicante and Castellón in east Spain), which produced approximately 95% of the total national production. Ceramic waste is also generated in the construction sector: according to data from the Spanish National Institute of Statistics (2013), the construction sector in Spain produced 32·7 Mt tons of waste in 2011, of which about 54% was ceramics (GdE, 2010).

The objective of this research was to study the recycling of real ceramic waste arising from different tile manufacturing companies in order to produce pozzolanic cement. The properties of the ceramic waste were analysed and its pozzolanic reactivity was evaluated at different curing ages with replacements of various percentages of Portland cement.

Materials and methodology

Materials
The ceramic waste used in this study came from the Spanish tile ceramic industry and contained different types of tiles such as wall, stoneware and porcelain stoneware tiles. Portland cement type CEM I 42·5R (containing 4·5% calcium carbonate), partially replaced (0–50 wt%) with tile ceramic waste (TCW), was used to prepare pastes and mortars.

As-received TCW was dried in an oven at 100°C for 48 h, crushed in a jaw crusher (BB200, Retsch) to obtain a particle size smaller than 2 mm and ground in a porcelain ball mill (Gabbrielli Mill-2) in alumina media (450 g of waste, 90 balls) for 25 min. The mean particle diameter, determined by laser diffraction (Mastersizer 2000, Malvern Instruments), came close to 17·28 μm, with 90%vol of particles (d_{90}) under 43·02 μm. As shown in Figure 1, irregularly shaped particles with a smooth surface and sharp edges were observed by scanning electron microscopy (SEM) (JEOL JSM-6300).

Table 1 indicates the chemical composition of the TCW, as determined by x-ray fluorescence (XRF) analysis (Philips Magix Pro). As can be seen in the table, the TCW contained high levels of silicon dioxide and aluminium oxide (79·82 wt %), together with moderate amounts of calcium oxide, iron oxide and potassium oxide. The amorphous content (soluble fraction), determined according to UNE EN 196-2 specifications, was 60 wt%, which is higher than that determined for red clay brick waste (35 wt%) (Reig *et al.*, 2013b) and porcelain stoneware tiles (46 wt%) (Reig *et al.*, 2014).

Mineralogical composition was determined by x-ray diffraction (XRD) (Brucker AXS D8 Advance with CuKα radiation, 40 kV and 20 mA, 2θ from 5° to 70°). The data in Figure 2 indicate that quartz (Q, SiO$_2$; powder diffraction file (PDF) #331161) is the major crystalline phase, with mullite (M, Al$_6$Si$_2$O$_{13}$; PDF #150776), albite (A, NaAlSi$_3$O$_8$; PDF #190926), and the calcium magnesium silicate known as

20 μm
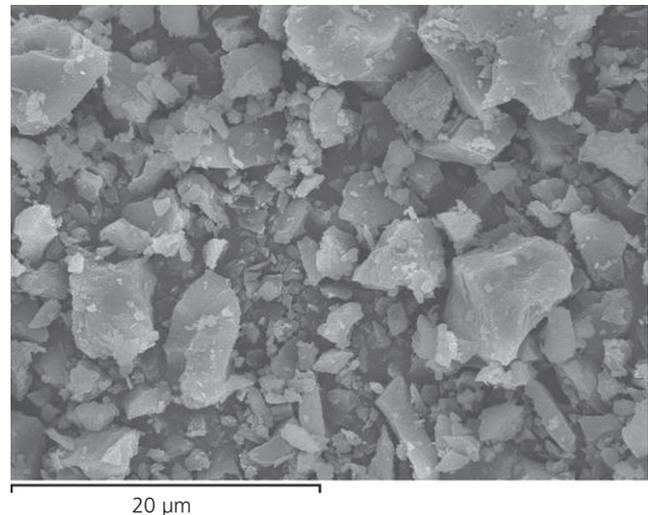
Figure 1. SEM micrograph of ground TCW

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Sodium oxide (Na$_2$O): wt%	1·49
Magnesium oxide (MgO): wt%	1·79
Aluminium oxide (Al$_2$O$_3$): wt%	18·60
Silicon dioxide (SiO$_2$): wt%	61·22
Phosphorus pentoxide (P$_2$O$_5$): wt%	0·25
Sulfur trioxide (SO$_3$): wt%	0·09
Potassium oxide (K$_2$O): wt%	3·33
Calcium oxide (CaO): wt%	5·77
Titanium dioxide (TiO$_2$): wt%	0·82
Iron oxide (Fe$_2$O$_3$): wt%	5·02
Zinc oxide (ZnO): wt%	0·22
Zirconium dioxide (ZrO$_2$): wt%	0·38
Barium oxide (BaO): wt%	0·14
Other	0·19
Loss on ignition at 1000°C	0·70

Table 1. Chemical composition of tile ceramic waste
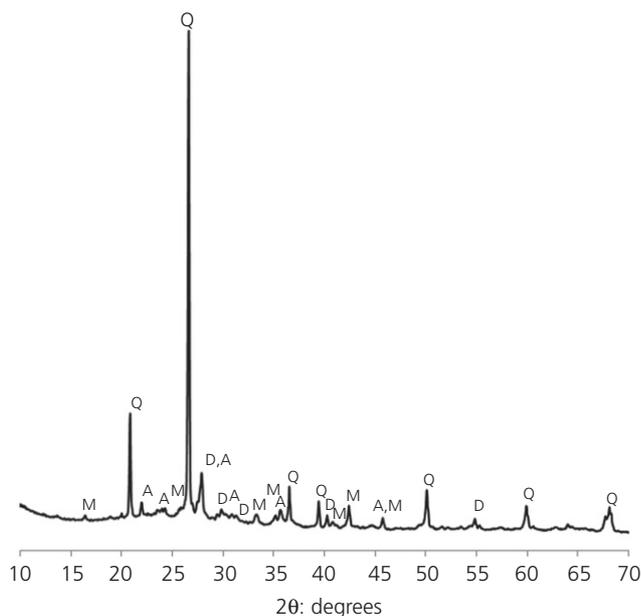
Figure 2. X-ray diffractogram of ground TCW: Q, quartz (SiO$_2$); M, mullite (Al$_6$Si$_2$O$_{13}$); A, albite (NaAlSi$_3$O$_8$); D, diopside (CaMg (SiO$_3$)$_2$)

diopside (D, CaMg(SiO$_3$)$_2$; PDF #190239), also present as minor constituents.

pH and conductivity test method

The pozzolanic reactivity of ground TCW was assessed by pH and conductivity tests. As previously described by Tashima *et al*. (2014), this method consists of monitoring the electrical conductivity and pH of aqueous lime:pozzolan suspensions mixed in different proportions. Data were taken at 60°C

for up to 7 d curing in a micropH2001 pH-meter and a microCM2201 conductimeter (Crison).

The total mass of solid material was kept constant in all the tests (1 g) and the following lime:pozzolan proportions, expressed in mass, were used: 0·5:9·5, 1·0:9·0, 1·5:8·5, 2·0:8·0, 2·5:7·5 and 3·0:7·0. Suspensions, prepared by adding 50 ml of deionised water to the solid material, were introduced into a 100 ml Erlenmeyer flask. The containers were then tightly capped and placed in a water bath at 60°C. The different mixes were continuously agitated to facilitate the reaction processes, and electrical conductivity and pH data were collected every 24 h up to 7 d. A calcium hydroxide saturated solution was also prepared as the reference (control). The electrical conductivity measurements of the ground TCW ($C_{t,\text{poz}}$) suspended in water were also quantified to correct the results with the contribution of ions provided by ceramic waste.

Electrical conductivity curves were produced in terms of loss of conductivity (L_C), which was calculated as a percentage according to

1. $$L_C = \frac{C_0 - (C_t - C_{t,\text{poz}})}{C_0} \times 100$$

where C_0 is the initial conductivity of the calcium hydroxide suspension before adding pozzolan, C_t is the conductivity of the 'lime:pozzolan' mixture at a given time and $C_{t,\text{poz}}$ is the electrical conductivity of the ground TCW (pozzolan) measured in water.

After 7 d reaction, the suspensions were filtered to separate the solid and liquid fractions. Thermogravimetric analyses (TGA) were used to verify the presence of portlandite and other hydrated products formed by the pozzolanic reaction of ceramic waste. The concentration of calcium ions (Ca^{+2}) in the liquid was determined by chemical analysis titrating with 0·05M ethylenediaminetetraacetic acid (EDTA).   **Q7**

Paste and mortar sample preparation

Paste and mortar samples were prepared using Portland cement (PC) type CEM I 42·5R as the cementitious material and replacing it with different proportions of TCW (15%, 25%, 35% and 50% by weight). Paste samples were used to investigate microstructure evolution. For that purpose, the binder (PC + TCW) was mixed with water (w/b = 0·5) in plastic containers for 4 min, which were then sealed and stored in a thermostatically controlled chamber at 20°C at a relative humidity (RH) of 90–95%. Mortars were prepared following the process described in UNE EN 196-1:2005, using 1·0:3·0:0·5 **Q8** (binder:sand:water) weight proportions. Siliceous sand with a modulus of fineness of 4·36 and maximum particle size of 2 mm was used as the aggregate. Specimens were demoulded after being cured for 24 h (20°C, 90–95% RH) and were then

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immersed in water with calcium hydroxide until the testing age.

Mortar testing

Q9 The workability of fresh mortars was determined by the flow-table test according to UNE 83811:1992 specifications. The compressive strength of mortar specimens was determined following UNE EN 196-1. The compressive strength results are presented here in terms of strength activity index (SAI, in %) and strength gain (SG, in %). The SAI represents the ratio of the strength of the mortar with additions to that of the control mortar. SG is defined by Equation 2 and considers the proportion of cement used in the mixtures

$$2. \quad SG = \frac{\left| Cs_{poz} - (Cs_{control} \times cem\%) \right|}{Cs_{control} \times cem\%} \times 100$$

where Cs_{poz} is the compressive strength of mortar containing TCW, $Cs_{control}$ is the compressive strength of the control mortar, and cem% is the proportion of cement in the mortar with pozzolanic additions (in each unit).

The microstructure of the paste samples was examined by SEM-EDX (JEOL JSM-6300). XRD was used to identify mineralogical phases with the equipment described earlier in the section on materials. The Fourier transform infrared spectroscopy (FTIR) studies were done using a Bruker Tensor 27 Platinum ATR FTIR within the range 400–4000 cm^{-1}. TGA were performed in a Mettler-Toledo TGA850, with a horizontal furnace. Aluminium sealable crucibles (100 μl), with a pinhole in the lid to obtain the self-generated atmosphere, were used. The gas flow for the surrounding atmosphere was 75 ml/min of nitrogen and the test was performed at a heating rate of 10°C/min within the temperature range 35–600°C.

Results and discussion

pH and conductivity test results

The curves of conductivity and pH values for lime:pozzolan concentrations of 0·5:9·5 and 3·0:7·0 are plotted in Figure 3. As can be seen, the conductivity and pH values rapidly reduced in the mixtures that contained small amounts of lime (Figure 3(a)), which indicates that the calcium and hydroxide ions (Ca^{2+} and OH^-) of the dissolved lime were consumed by ceramic waste to generate cementitious products that precipitate. The 3·0:7·0 suspension, with a larger amount of lime, became saturated in calcium hydroxide from the very beginning. Despite TCW reacting with the lime dissolved through the pozzolanic reaction and the amount of ions in solution reducing, dissolution of new solid lime occurred. This was the reason for the slight variation noted in the conductivity and pH values in Figure 3(b) since, although the hydroxide ions in the solution were consumed by TCW, new solid lime was always dissolved.

Figure 4 shows the evolution of loss of conductivity with time for the different lime:pozzolan concentrations in the solutions tested at 60°C. The suspensions that contained the smallest amounts of calcium hydroxide (0·5:9·5, 1·0:9·0, 1·5:8·5 and 2·0:8·0) showed significant loss of electrical conductivity (higher than 20%), which was attributed to the consumption
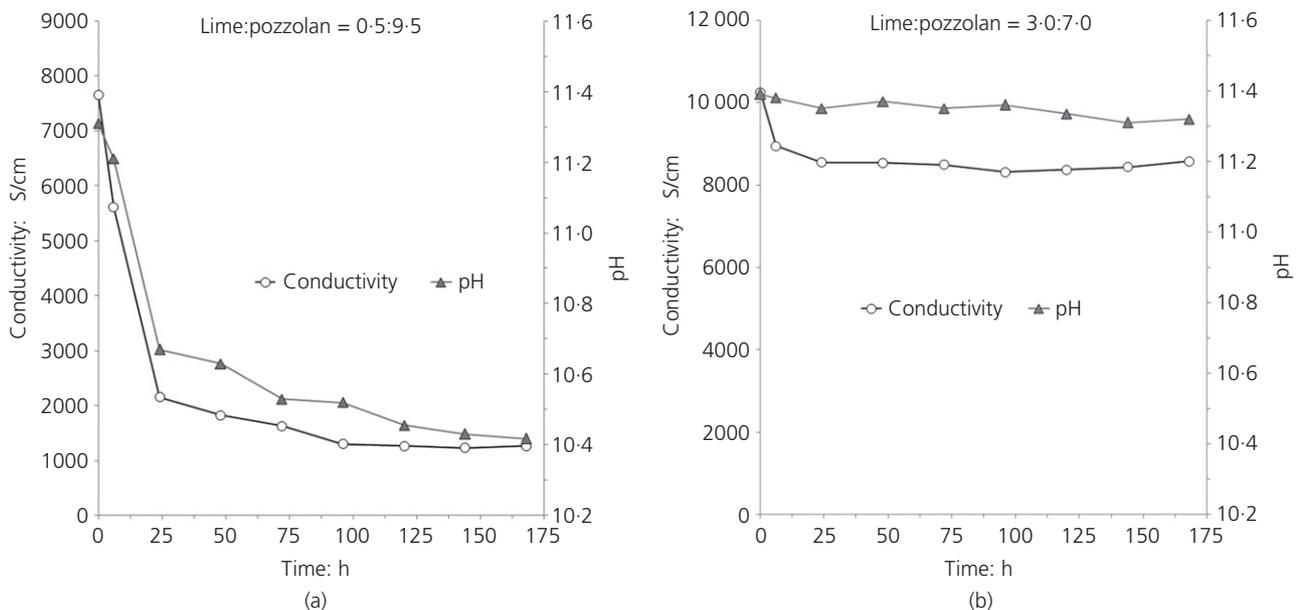

Figure 3. Electrical conductivity measurements and pH values for lime:pozzolan suspensions of 0·5:9·5 (a) and 3·0:7·0 (b)

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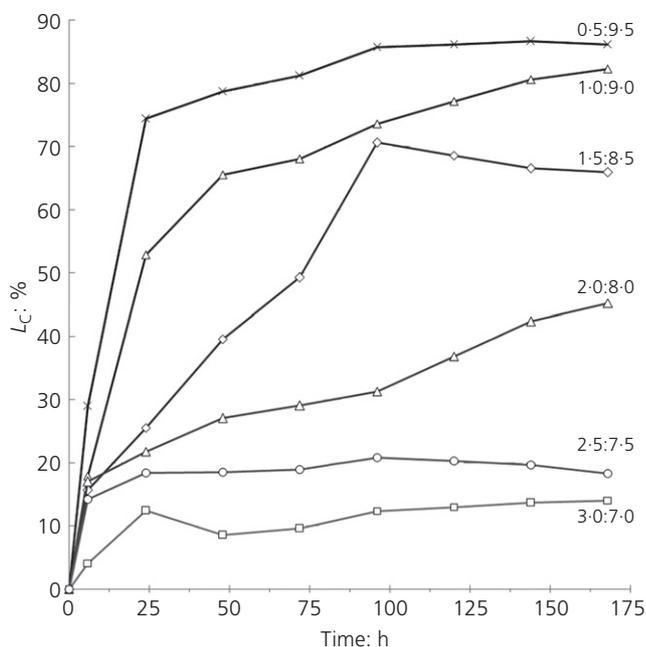
**Figure 4.** Loss of electrical conductivity, tested at 60°C, for different lime:pozzolan concentrations

of calcium and hydroxide ions (Ca^{2+} and OH^-) of lime by the TCW. On the contrary, no significant variation in electrical conductivity values was observed in the samples that contained greater calcium hydroxide ($Ca(OH)_2$) additions. This indicates that the ions were not completely consumed due to the low reactivity presented by the TCW at early curing ages. According to the method proposed by Tashima *et al.* (2014) to assess the pozzolanic reaction rate, suspensions 2·5:6·5 and 3·0:7·0 were saturated in calcium hydroxide since the loss of the conductivity values recorded after 7 d of testing was lower than 30% and the pH values reduced by less than 0·15 units. The results obtained when marking the lime:pozzolan proportion that yielded unsaturation at the testing temperature in the classification diagram provided by Tashima *et al.* (2014) showed that the reactivity of TCW was low compared to that presented by rice husk ash and silica fume, these being the pozzolanic materials used to develop the pozzolanic reactivity assessment method.

Mortar workability

The workability of the mortars containing TCW was similar to that presented by the control mortar (with no TCW) and all the values were close to 155 ± 5 mm regardless of the amount of TCW added. These results are close to those previously reported by Pereira de Oliveira *et al.* (2012), who did not observe a significant reduction in the workability of mortars when incorporating TCW and red clay brick waste (4·5% and 7·3% respectively in samples that contained 40% ceramic powder). Although a greater specific surface and porous

additions usually require larger amounts of water, this was not the case for TCW, which was attributed to the smooth surface and low porosity of the ceramic particles.

Compressive strength of mortars

Table 2 summarises the compressive strength results for the mortars with increasing TCW additions, cured for 3–90 d. Although a significant reduction in strength with increasing TCW contents was observed at short curing ages (3 d and 7 d), the values came closer to that of the control mortar after curing for 90 d. This behaviour was consistent with the pH and conductivity test results, and corroborated the low level of reactivity of TCW, which was enhanced at long curing ages.

The SAI results are shown in Figure 5. The obtained results meet the specifications set out in UNE EN 196-1, and were

TCW: wt%	Compressive strength: MPa			
	3 d	7 d	28 d	90 d
0	44·00 ± 0·58	47·19 ± 1·10	51·02 ± 1·84	55·48 ± 2·01
15	32·11 ± 1·49	43·36 ± 1·13	45·30 ± 1·79	53·13 ± 2·10
25	32·21 ± 0·86	38·46 ± 1·02	45·07 ± 1·58	50·48 ± 2·37
35	29·02 ± 0·85	34·30 ± 0·71	40·15 ± 1·41	49·83 ± 1·89
50	19·09 ± 0·49	24·63 ± 0·80	33·82 ± 0·84	40·20 ± 0·92

Table 2. Evolution of compressive strength of mortars with TCW additions, cured at 20°C for 3–90 d
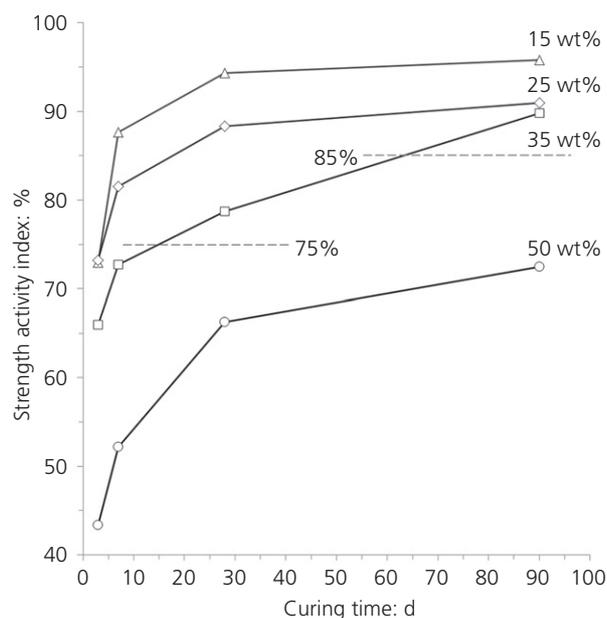

Figure 5. Strength activity index of mortars with TCW additions cured at 20°C for 3–90 d

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higher than 75% and 85% in the mortars that contained 25% TCW cured for 28 d and 90 d respectively. The SAI values **Q10** improved with curing time and came closer to ~~the unit~~ after 90 d curing. This was attributed to the enhanced reaction between pozzolan and portlandite generated during Portland cement hydration. Although the low reactivity of TCW
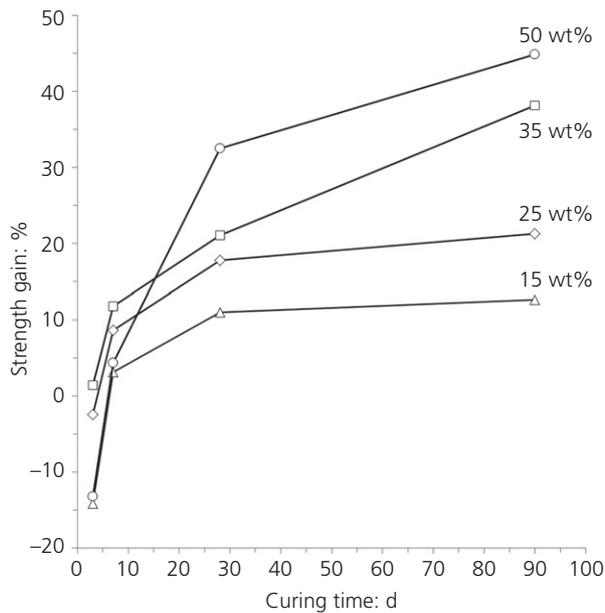
observed at early curing ages makes these materials inadvisable in applications where speed of construction is required, the mechanical requirements set out in fly ash regulations can be satisfied after 28 d curing by replacing up to 35 wt% of Portland cement with TCW. This, together with the geographic proximity between Spanish ceramic tile and Portland cement manufacturing companies, makes TCW a potential alternative as a pozzolanic admixture. This would result in environmental and economic advantages, allowing waste that would otherwise be landfilled to be reused.

Similar results were reported by Pereira de Oliveira *et al.* (2012), who did not observe significant compressive strength differences among mortars that contained brick, tiles, amber and green glass waste as pozzolanic admixtures. Only the mortar with brick powder did not follow the minimum SAI established at 90 d in UNE EN 196-1 (85%), which was attributed to its production process as it did not result in a structure with potential pozzolanic reactivity.

Figure 6 shows the strength gains of mortars containing different percentages of TCW (15–50 wt%) cured at 20°C for up to 90 d. Although the compressive strength results reduced with increasing TCW additions (Table 2), an excellent contribution of pozzolanic addition to the mechanical properties was observed after 28 d curing, which became more significant with increasing TCW additions. These results agree with those reported by ~~Heidari *et al.*~~ (2013) for concrete produced **Q11** using ground ceramic tile waste as a substitute for Portland cement (0–40 wt%). As described by ~~Heidari *et al.*~~ (2013), **Q12**


Figure 6. Strength gain index of mortars with TCW additions cured at 20°C for 3–90 d
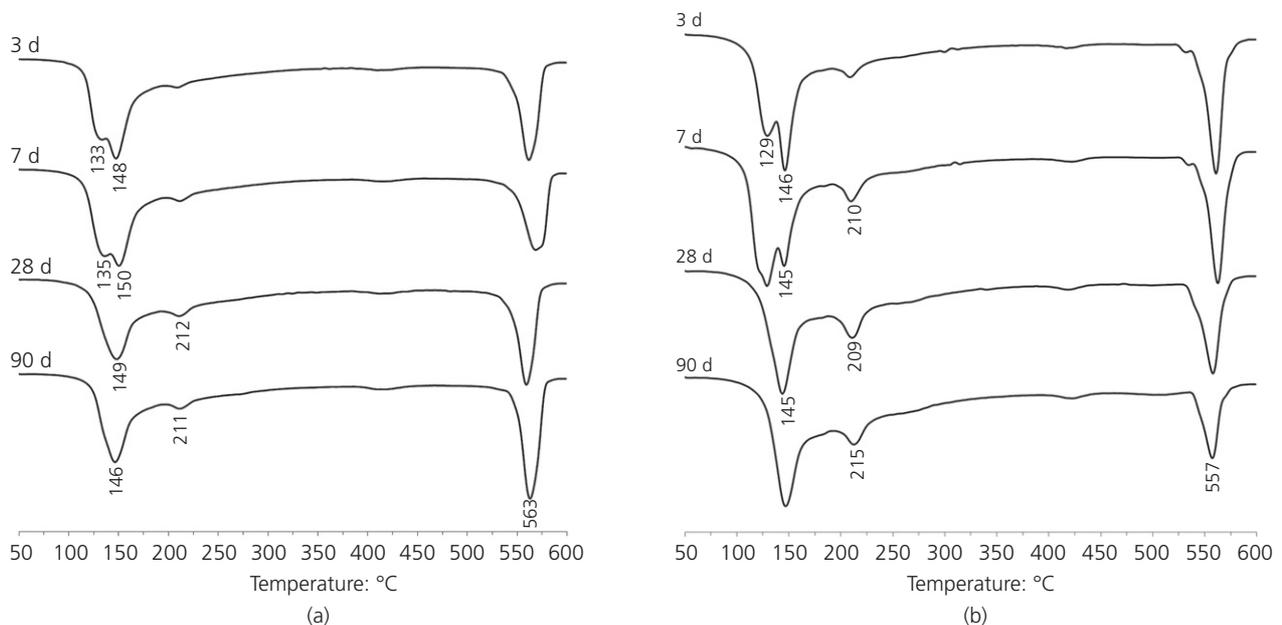
Figure 7. DTG curves of pastes cured for 3–90 d at 20°C: (a) control; (b) 50 wt% TCW

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TCW: wt%	Component: wt%															
	3 d curing				7 d curing				28 d curing				90 d curing			
	TWL	CH	H	FL	TWL	CH	H	FL	TWL	CH	H	FL	TWL	CH	H	FL
0	17·8	3·2	14·6		18·8	3·2	15·6		18·2	3·2	14·9		19·1	3·7	15·4	
15	16·1	2·8	13·3	−2·0	17·3	2·8	14·6	−3·1	16·5	2·6	13·9	5·4	17·4	2·9	14·6	7·9
25	15·0	2·5	12·5	−4·9	16·5	2·8	13·7	−19·8	15·9	2·5	13·4	−4·4	16·3	2·4	13·9	15·1
35	14·4	2·5	11·9	−19·6	14·4	2·4	12·1	−15·9	14·3	2·1	12·1	−1·8	15·3	1·5	13·8	37·0
50	11·7	2·0	9·7	−22·6	13·3	1·9	11·3	−24·1	12·5	1·5	11·0	−6·2	13·0	0·9	12·1	48·5

Table 3. Results obtained after TGA: TWL, total weight loss; CH, water loss attributed to decomposition of portlandite; H, percentage of hydrates originated during hydration; FL, fixed lime

the addition of up to 20 wt% ceramic powder did not considerably affect compressive strength behaviour, with average decreases of 14·60% and 1·45% recorded after 7 d and 90 d curing respectively.

Microstructural studies

Thermogravimetric analysis

Figure 7 shows the TGA derivate curves (DTG) of the control paste (Figure 7(a)) and the 50 wt% TCW paste (Figure 7(b)) cured for 3, 7, 28 and 90 d. According to Payá *et al.* (2003), the first and second peaks appearing in the diagram overlap within the 100–180°C region, and are attributed to the dehydration of calcium silicate hydrates (CSH) and ettringite (AfT). The peak centred at 180–240°C corresponds to the dehydration of calcium aluminate hydrates and calcium aluminosilicate hydrates (CAH and CASH), while the peak appearing at 520–580°C is due to dehydroxylation of portlandite. As expected, the intensity of the last band was stronger in the control paste and diminished with TCW content, which was attributed to the dilution of Portland cement and pozzolanic effects. While this band increased with curing time in the control paste, it progressively decreased with curing age in the samples that contained TCW because of the pozzolanic reaction that occurred between the ceramic waste and portlandite.

Table 3 summarises the main quantitative data obtained after TGA; that is, total weight loss (TWL), water loss attributed to the decomposition of portlandite (CH), the percentage of hydrates originated during the hydration process (H, calculated as the difference between TWL and dehydroxylation of portlandite) and fixed lime (FL). The percentage of fixed lime was determined according to

3. $$FL = \frac{CH_c \times cem\% - CH_{poz}}{CH_c \times cem\%} \times 100$$

in which CH_c is the lime (portlandite) present in the control paste for a given curing time, CH_{poz} is the lime in the paste with TCW addition at the same curing age and cem% is the proportion of cement in the paste with pozzolanic additions.

As shown in Figure 8, negative fixed lime values were obtained at early curing ages which, as explained by Cyr *et al.* (2005) and Payá *et al.* (2003), were attributed to the particle effect that prevailed over the pozzolanic reaction. According to Cyr *et al.* (2005), this effect accelerated Portland cement hydration due to heterogeneous nucleation, since
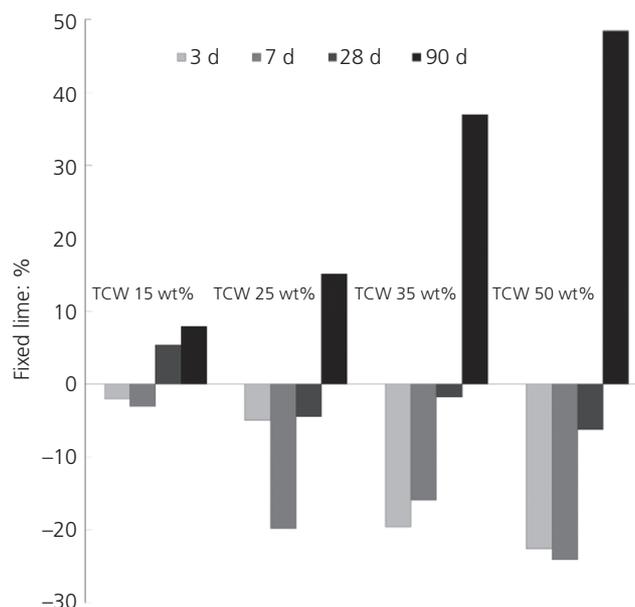

Figure 8. Fixed lime content in pastes with TCW cured at 20°C for 3–90 d

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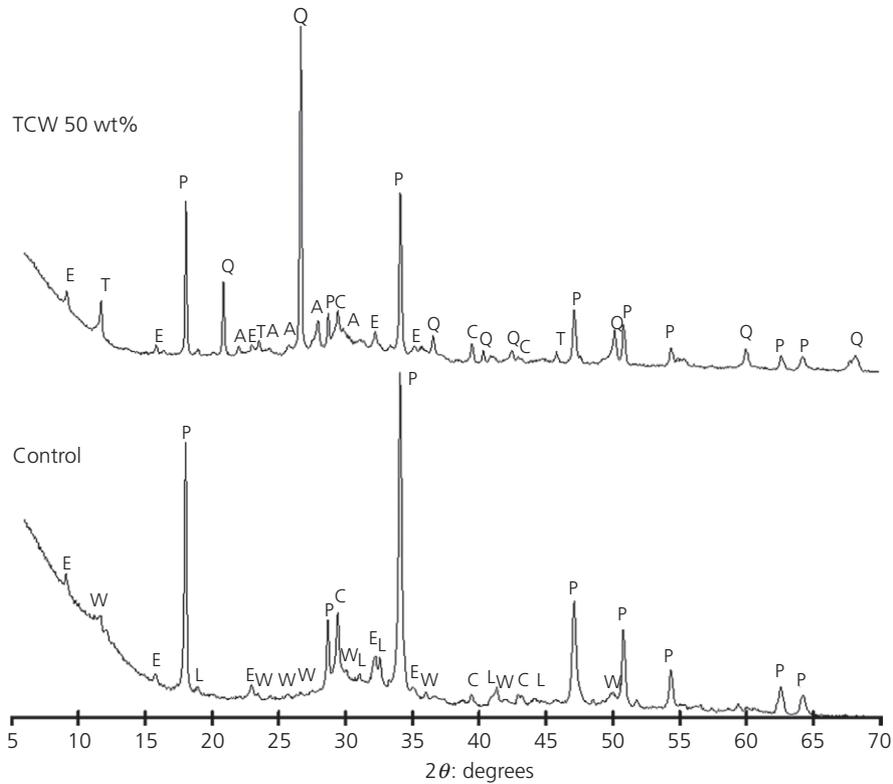
Figure 9. XRD patterns of control and 50 wt% TCW pastes cured at 20°C for 28 d: Q, quartz (SiO_2); E, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O$); T, hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot$ $4(H_2O)$); P, portlandite ($Ca(OH)_2$); A, albite ($NaAlSi_3O_8$); C, calcite ($CaCO_3$); W, wollastonite ($CaSiO_3$); L, larnite (β-Ca_2SiO_4)
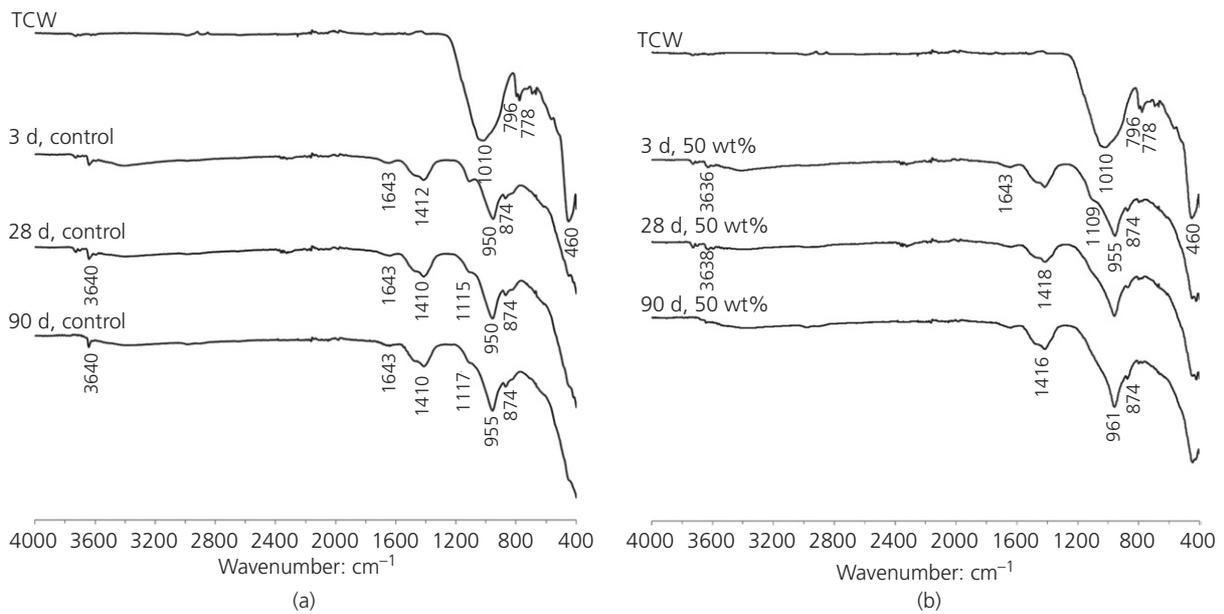
Figure 10. FTIR spectra of the TCW and pastes cured at 20°C for 3–90 d: (a) control; (b) 50 wt% TCW

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TCW particles provided an extra surface upon which the first hydration products to form could be deposited, thus leaving more free area to continue cement hydration. Then, the cement hydrated faster with increasing ceramic waste contents, producing more negative values. These rates progressively increased to become positive after 90 d curing, given the consumption of portlandite by ceramic waste in the pozzolanic reaction.

X-ray diffraction studies

Figure 9 shows the XRD patterns for the control paste and the paste with 50 wt% TCW, both cured for 28 d. Portlandite (P, $Ca(OH)_2$, PDF #040733) was the main phase detected in the control paste, together with other minor compounds such as ettringite (E, $Ca_6Al_2(SO_4)_3(OH)_{12}$·$26H_2O$, PDF #411451) and calcite (C, $CaCO_3$, PDF #050586). The latter was due to the presence of a limestone filler in the Portland cement composition, which is corroborated by the corresponding peak registered in the paste that contained 50 wt% TCW, whose intensity diminished due to the dilution effect. Traces of other phases, such as dicalcium silicate larnite (L, β-Ca_2SiO_4, PDF #330302) and calcium silicate wollastonite (W, $CaSiO_3$, PDF #100489), were also detected.

In agreement with the TGA results, the intensities of peaks on the XRD spectrum attributed to portlandite, calcite and ettringite were less for the 50 wt% TCW paste than for the control paste. The main crystalline phases corresponding to the ceramic residue, such as quartz (Q, SiO_2, PDF #331161) and albite (A, $NaAlSi_3O_8$, PDF #090466), were also identified in the pastes that contained TCW, along with traces of carboaluminate hydrotalcite (T, $Mg_6Al_2CO_3(OH)_{16}$·$4(H_2O)$, PDF #141191).

Fourier transform infrared spectroscopy

The FTIR spectra of the control paste and the 50 wt% TCW paste cured at 20°C for 3–90 d are plotted in Figures 10(a) and 10(b) respectively. The FTIR spectrum of the TCW is included in the figures for reference purposes: the ceramic material presented a main band within the 1200–950 cm^{-1} region, centred at 1009 cm^{-1}, together with a signal at 460 cm^{-1} and lower intensity bands at 796–778 cm^{-1} (double peak). These bands were attributed to the asymmetric stretching vibrations of Si–O and Al–O bonds (Frías et al., 2011) and were distinguished in all the pastes that contained TCW, which denoted the presence of unreacted TCW.

As reported by Yu et al. (1999), the bands that appeared within the 950–1100 cm^{-1} region in all the hydrated pastes are typically originated by the Si–O stretching vibrations of newly formed calcium silicate hydrates. The bands that arose at 1630 cm^{-1} and 3450 cm^{-1} were attributed to the bending (H–O–H) and stretching vibrations (–OH) of the hydroxyl groups in hydrated products. These bands appeared together with the sharp peak that originated at 3640 cm^{-1}, which also corresponded to –OH stretching vibrations (Parande et al., **Q13** 2011). The evolution of this band was linked to that attributed to calcium hydroxide in the thermogravimetric diagrams (the 520–580°C region in Figure 7), which persisted after 90 d of curing and registered decreasing intensities with increasing TCW contents.

As explained by Lee and Li (2010), the bands that appeared at 1400–1500 cm^{-1}, together with that centred at 874–714 cm^{-1}, were associated with carbonate (CO_3^{-2}) asymmetric vibrations. In agreement with the XRD results, these bands did not appear in the raw material (TCW), but were clearly distinguished in all the hydrated pastes, being attributed to the calcium carbonate filler in the Portland cement used.
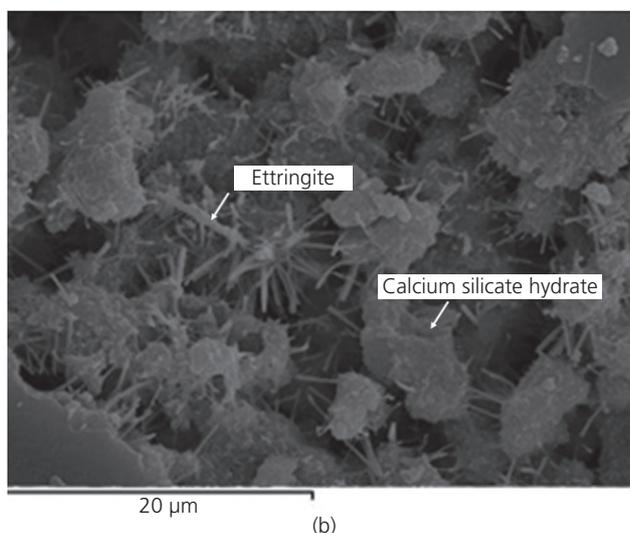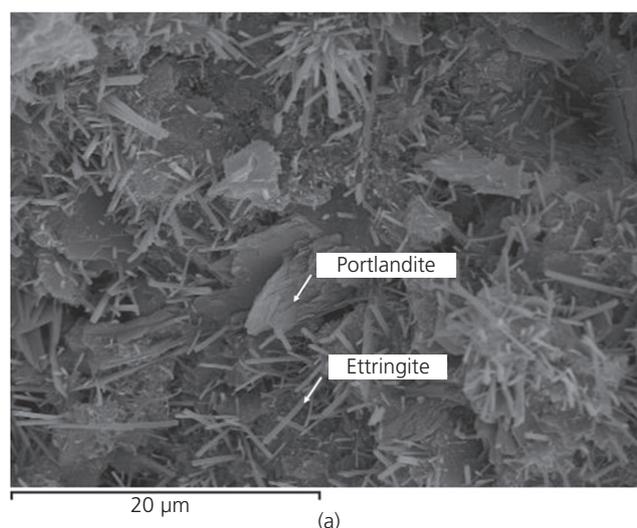

Figure 11. SEM images of pastes cured at 20°C for 28 d:
(a) 25 wt% TCW; (b) 50 wt% TCW

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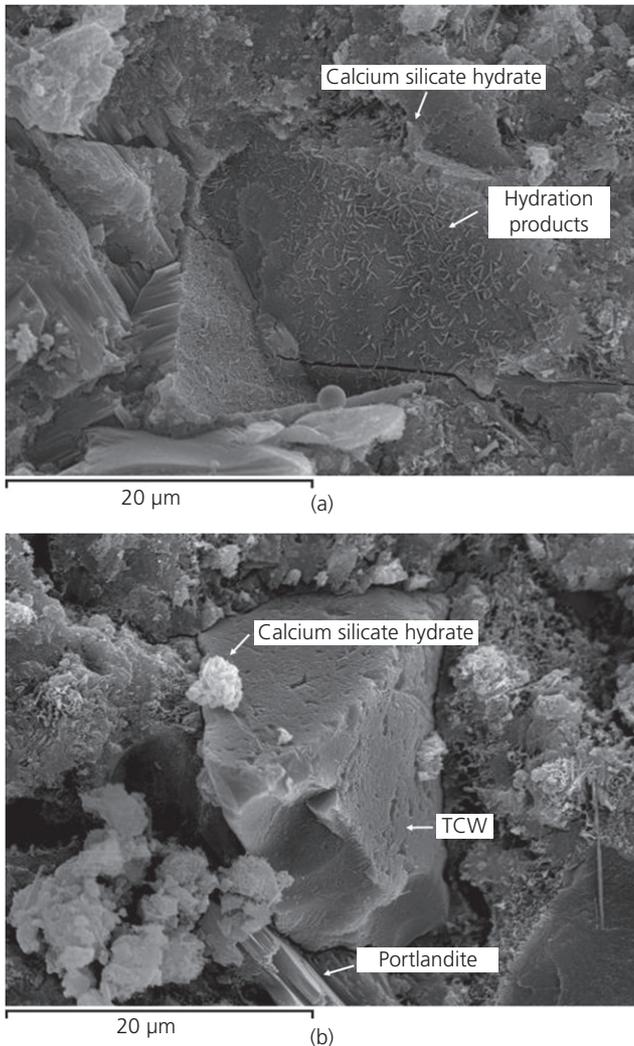
Figure 12. SEM images of pastes cured at 20°C for 90 d:
(a) 25 wt% TCW; (b) 50 wt% TCW

Scanning electron microscopy

The microstructures of the pastes containing 25 wt% and
50 wt% TCW as Portland cement substitute and cured for
28 d and 90 d are presented in Figures 11 and 12. The presence
of ettringite needles, hexagonal plates of portlandite and
calcium silicate hydrate amorphous products, previously iden-
tified by the XRD, FTIR and TGA, was corroborated by
SEM. Similarly, unreacted TCW particles slightly covered by
hydration products were observed (Figure 12).

Conclusions

This research has demonstrated the potential use of tile
ceramic waste (TCW) to produce pozzolanic cement. The
experimental study provided the following conclusions.

■ The TCW composition is appropriate for reacting with the
portlandite formed during Portland cement hydration to

form cementing compounds through the pozzolanic
reaction.
■ The negative fixed lime values obtained at short curing
ages denote an accelerated hydration process of Portland
cement due to the particle effect conferred by the pozzolan.
The positive values recorded after 90 d curing indicate that
the reactivity of TCW with the Portland cement hydration
products occurs mainly at long curing ages.
■ The workability of the mortars containing TCW was
similar to that presented by the control mortar without
TCW.
■ Additions within the range 15–35 wt% satisfy the strength
activity index established by fly ash regulations, and are
higher than 75% and 85% after 28 d and 90 d curing
respectively.

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