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Clinkers and cements obtained from raw mix containing ceramic waste as a raw material. Characterization, hydration and leaching studies

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ABSTRACT

A clinker and a cement obtained from a raw mix containing ceramic waste as an alternative raw material were characterized in the present study. Their hydration, physical–chemical properties and leaching behaviour in different acid media were also explored. The findings showed that both the clinker and the cement met all the requirements set out in European standards EN 197-1 [1], although they had higher ZnO, ZrO_2, and B_2O_3 contents than an industrially produced reference product.

According to the hydration studies, initial hydration was somewhat retarded in the new cement, which exhibited longer initial and final setting times and lower 2-day mechanical strength. The SEM/BSE/EDS microstructural study showed, however, that morphologically and compositionally, the hydration products formed were comparable to unadditioned Portland cement paste products. While low concentrations of Zn and B were observed to leach in acid media, the biotoxicity trials conducted confirmed that these concentrations were not toxic. Zr was retained in the cement pastes.

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1. Introduction

Prior research [2] has indicated that the chemical and mineralogical composition of certain types of ceramic waste, red ceramic wall tile, white and combination of red and white ceramic wall tiles would make it suitable for possible use as an alternative raw material in cement raw mixes. The mixes containing such waste (at 11–14%) were also found to be comparable to cement manufactured with conventional raw materials in terms of both reactivity and burnability, providing the waste particles used were ground to under 90 μm [3]. While the mineralogical and morphological composition of the clinkers obtained was suitable, the enamel coating on this waste raised their ZnO, ZrO_2 and B_2O_3 contents by 100–350%, depending on waste particle size [3]. Another important conclusion was that reactivity was at least as high in the raw mix prepared with a blend of red and white fired material as in the raw mixes prepared with each type of waste separately.

The present article, a continuation of the technological feasibility study [3] conducted on the new raw mixes, reports on hydration, physical–mechanical behaviour and leaching in the cements made with raw mixes containing blended ceramic waste. The findings of the raw mix and clinker characterization studies are also discussed. A cement prepared in the laboratory from an industrial raw mix was used as a reference for comparison in all trials.

2. Experimental

2.1. Raw mix, clinker and cement preparation

Table 1 gives the chemical composition of the ceramic waste used to prepare the raw mix, found by X-ray fluorescence (XRF) spectrometry. This waste contained a blend of porous red and white fired tile. Based on prior research [3], the particle size distribution established for the ceramic waste was: 5% under 45 μm; 15%, 45–63 μm; 70%, 63–90 μm; and the remaining 10%, 90–125 μm.

Limestone (ground to under 125 μm) and (Merck) chemical reagent Fe_2O_3 were added to the ceramic waste to prepare the raw mix (see proportions in Table 2). The chemical composition of the limestone is also given in Table 1.

The raw materials used in the raw mix containing ceramic waste were proportioned by setting the lime saturation factor (LSF), silica modulus (M_S) and melting modulus (M_F) to the values given in Table 2.

The waste-containing raw mix was prepared as follows: the raw materials were dried at 100 °C, weighed and mixed, blended in a turbula for 5 h and then suspended in ethanol. The excess ethanol was eliminated by heating at 100 °C. The reference raw mix,

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Table 1
Chemical analysis of limestone and ceramic waste (% wt.).

	Limestone	Ceramic waste (CW)
LOI	40.59	0.43
SiO_2	5.8	66.0
Al_2O_3	1.1	14.2
Fe_2O_3	0.71	3.31
CaO	50.2	6.1
MgO	0.64	1.83
Na_2O	<0.01	0.93
K_2O	0.30	3.36
TiO_2	0.07	0.57
MnO	0.02	0.04
P_2O_5	0.07	0.14
ZnO	<0.0020	0.74
ZrO_2	<0.0020	0.53
B_2O_3	<0.0020	0.42
SO_3	–	0.04
Cr_2O_3	<0.0020	0.0056

LOI: loss on ignition at 1000 °C.

Table 2
Ceramic waste-containing and reference raw mix moduli and proportions.

	Modulus			Proportion (% wt.)		
	LSF (%)	M_S	M_F	Limestone	CW	Fe_2O_3
RM-REF	102	2.37	1.45	–	–	–
RM-CW	98	2.70	1.26	84.84	13.86	1.30

Table 3
Chemical composition of raw mix and clinker (% wt.).

	Raw mix-REF RM-REF	Raw mix-CW RM-CW	Cinker-REF Cl-REF	Clinker-CW Cl-CW
LOI	35.0	34.4	–	–
SiO_2	13.1	14.6	20.6	22.2
Al_2O_3	3.3	3.5	5.1	5.0
Fe_2O_3	2.25	2.22	3.41	3.43
CaO	43.0	43.0	67.1	66.5
MgO	1.24	0.77	1.99	1.20
Na_2O	0.19	0.10	0.17	0.19
K_2O	1.01	0.69	0.38	0.29
TiO_2	0.17	0.15	0.25	0.25
MnO	0.02	0.02	0.03	0.02
P_2O_5	0.06	0.07	0.10	0.11
ZnO	0.02	0.08	0.03	0.12
ZrO_2	<0.0020	0.06	0.01	0.07
B_2O_3	<0.0020	0.06	0.05	0.09
SO_3	0.42	0.02	0.03	0.01
Cr_2O_3	<0.0020	<0.0020	<0.0020	<0.0002
Na_2O eq.	–	–	0.49	0.42

LOI: loss on ignition at 1000 °C.

RM-REF, was a conventional Cem Type manufactured at a Spanish cement plant. Table 2 also gives the moduli for the reference mix.

The chemical compositions of both the reference, RM-REF, and the ceramic waste-containing raw mix, RM-CW are given in Table 3. The proportions of the majority component were similar in the two raw mixes. Differences were observed in the minority elements, with MgO and K_2O higher in the reference than in the ceramic waste raw mix and the ZnO, ZrO_2 and B_2O_3 contents higher in the latter. The origin of the latter group of elements is the enamel coating on fired tile.

All the clinkers were prepared in the laboratory, forming pellets weighing about 4 g and measuring 30 mm in diameter that were fired at 1450 °C for 30 min and then cooled to laboratory temperature. The clinkers obtained were ground first in a small metallic grinder and then in an agate grinder to under 90 μm.

The reference cement, Cem-REF, and the ceramic waste cement, Cem-CW, were obtained by mixing the respective clinkers with mineralogically pure gypsum, Ca_2SO_4 in proportions that would ensure that the SO_3 content in the final cement would not exceed 3%. The clinker and gypsum were blended in a turbula for 24 h.

2.2. Tests conducted

2.2.1. Clinker and cement characterization

The following analyses and trials were conducted on the reference and experimental clinkers and cements.

2.2.1.1. Clinker chemical analysis. Clinker chemical composition was determined with a Panalytical PW2400 X-ray fluorescence (XRF) spectrometer fitted with an Rh tube and a PW 2540VCT automated sample changer. Samples were fused into beads for the XRF readings with a Panalytical PERL'X 3 bead maker. The flux used was a 50:50 blend of Johnson-Matthey $LiBO_2/Li_2B_4O_7$, while the anti-adherent treatment was 0.5 ml of a 250 mg l^{-1} solution of Merck LiI. Measurements were validated and calibrated with suitably proportioned reference materials and blends [4,5].

Boron content was found with UV–Vis spectroscopy on a Shimadzu UV 116A spectrophotometer.

2.2.1.2. Clinker mineralogical analysis. The crystalline phases were identified on a Bruker Theta-Theta D8 Advance X-ray diffractometer (XRD) from samples mounted horizontally on methacrylate slides. The X-ray tube was set to 30 kV and 40 mA and readings were taken at 2θ diffraction angles ranging from 5° to 70°, with a step size of 0.02° and a contact time of 5 s. TOPAS software was used to find the Rietveld [6] quantification values for the clinker crystalline phases.

2.2.1.3. Clinker morphological analysis. The clinkers were packed in epoxy resin, sliced and polished for analysis under a Nikon Eclipse ME600 reflected light microscope to determine their morphology. The silicate phases were highlighted with a 1:1000 solution of Nital (HNO_3 and absolute ethanol).

2.2.1.4. Cement specific surface and particle size distribution. Cement specific surface (Blaine fineness) was found as specified in European standard EN196-6 [7]. Particle size distribution was determined for both clinkers and cements with a Sympatec helos 12 LA laser diffraction sensor.

2.2.1.5. Cement compressive and flexural strength, setting times and drying shrinkage. Cement setting times and volume stability were determined according to European standard EN 196-3 [8]. Mortar specimens (40 × 40 × 160 mm) were prepared with the two cements as specified in European standard EN 196-1 [9]. After storage in a moist cabinet for 24 h at 95% relative humidity and 20 °C, the specimens were removed from the moulds and stored in a water tank. Strength tests were conducted after 2, 7 and 28 days. EN 196-1 standard sand with a 99% quartz silicon content was used to prepare the mortars.

2.2.2. Hydration

2.2.2.1. Isothermal conduction calorimetry. The isothermal conduction calorimetry trials were conducted on a Thermometric TamAir facility. Distilled water was added to the cement at a water/cement ratio (w/c) of 0.35. After mixing with a spatula for 3 min, the 120 h calorimetry trial was conducted at a constant temperature of 25 °C.

Table 4
Clinker mineralogical composition (% wt.).

	Cl-REF	Cl-CW
C_3S	72.33	62.75
β-C_2S	8.29	13.24
α′-C_2S	–	7.09
C_4AF	12.72	8.28
C_3A	3.54	6.76
CaO	1.08	0.11
CH	2.00	1.76
Rwp	4.62	5.08

Rwp: weight profile *R*-factor.

2.2.2.2. Paste characterization. Hydration product studies were performed on cement paste specimens prepared with a w/c ratio of 0.35, suspending hydration with acetone and ethanol at 1, 2, 7 and 28 days. The following trials were run on the samples.

- Differential thermal and gravimetric analysis (DTA/TGA) on oven-dried (24 h, 40 °C) pastes with an SDT Q600 analyzer in a nitrogen atmosphere. The temperature was ramped to 80 °C at a rate of 10 °C/min, held for 60 min and then ramped to 1200 °C at a rate of 4 °C/min. The samples were subsequently cooled at 20 °C/min.
- X-ray diffraction (XRD) on the cement pastes with a Bruker Theta-Theta D8 Advance diffractometer using Cu Kα radiation and a 2θ angle range of 5°–60°.
- Fourier transform infrared spectroscopy (FTIR) on KBr pellets (1 mg of sample pressed into 300 mg of KBr), using a Nicolet 6700 spectrometer and a spectral range of 4000–400 cm^{-1}.
- Magic angle solid nuclear magnetic resonance (MAS NMR) with a Bruker MSL 400 spectrometer. The recording conditions for ^{29}Si were: resonance frequency, 79.49 MHz; number of signal acquisitions per sample, 800; relaxation time, 5 s; sample rotation frequency, 4 kHz. Chemical shifts were measured in ppm, using trimethyl silane (TMS) as the external standard. The ^{27}Al recording conditions were: resonance frequency, 104.2 MHz; number of signal acquisitions per sample, 200; relaxation time, 5 s; sample rotation frequency, 12 kHz. Chemical shifts were measured in ppm, using an aluminium trichloride solution as the external standard.
- Scanning electron microscopy (SEM and BSE) and energy dispersive analysis (EDS) on a JEOL 5400 microscope fitted with an OXFORD-LINK ISIS energy dispersive analyzer. The original solid samples were carbon coated for SEM analysis. For the BSE study, samples were packed in epoxy resin, cut, polished and carbon coated.

2.2.3. Leaching

The clinkers were exposed to acid solutions to determine whether Zn, Zr and B would leach and, as appropriate, to what extent. Leaching was performed on samples ground to a particle size of 63 μm or smaller with a wolfram carbide ring grinder. The medium used was acetic acid as specified in Spanish legislation [10], and more specifically Method 1, which is equivalent to the EP method described in US standards. Since the cement paste pH was highly basic, the pH values could not be brought down to 5–6, even after adding the maximum amount of acid allowed by

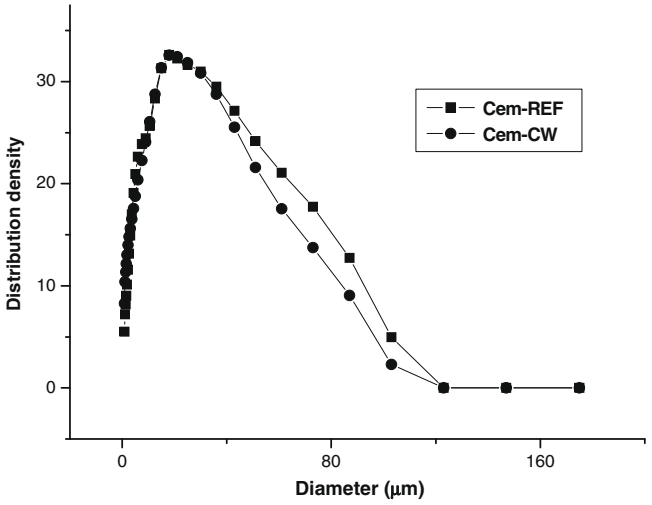
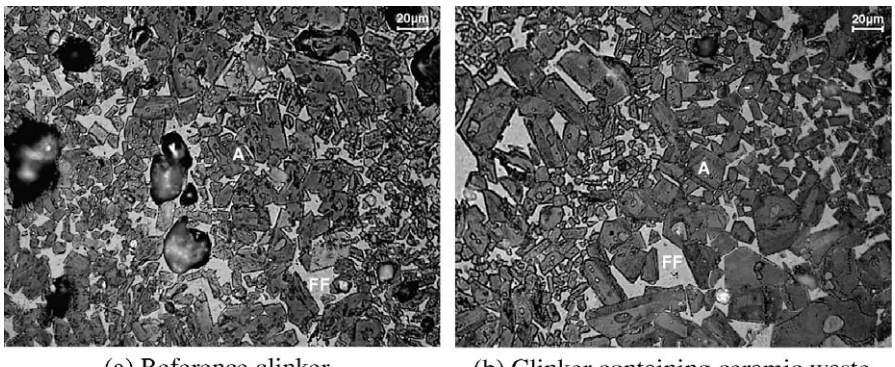


Fig. 2. Particle size distribution.

Table 5
Physical and mechanical properties of the reference cement and the cement made from a raw mix containing fired ceramic waste.

	Cem-REF	Cem-CW
Specific weight (kg/m^3)	3.137	3.168
Blaine fineness (m^2/kg)	331.3	294.3
Consistency at w/c ratio	0.25	0.25
Setting time (min)		
Initial	147	184
Final	207	277
Drying shrinkage (mm)	<10	<10
Flexural strength (N/mm^2)		
2 d	4.21 ± 0.07	4.00 ± 0.34
7 d	7.86 ± 0.19	7.39 ± 0.08
28 d	9.93 ± 0.21	10.42 ± 0.82
Compressive strength (N/mm^2)		
2 d	22.88 ± 0.74	19.21 ± 0.88
7 d	47.79 ± 1.23	40.27 ± 1.81
28 d	69.71 ± 1.80	68.99 ± 1.86



(a) Reference clinker (b) Clinker containing ceramic waste

Fig. 1. Micrographs of clinkers Cl-REF and Cl-CW A – alite; FF – interstitial phase.

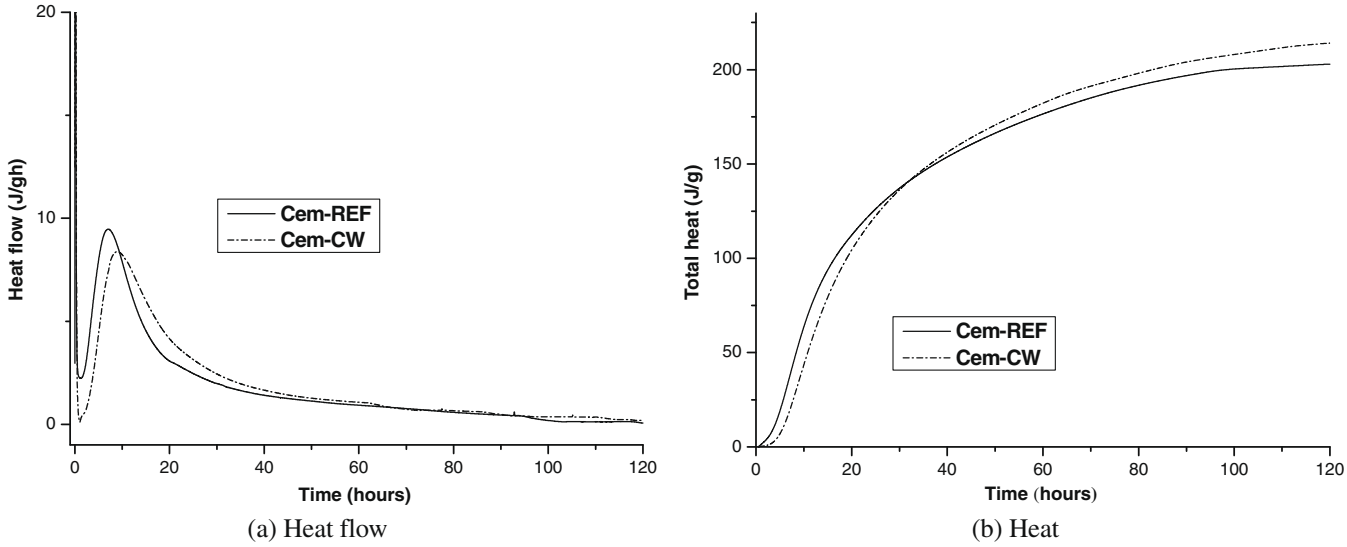


Fig. 3. Conduction calorimetry curves.

Table 6
Conduction calorimetry data.

	Cem-REF	Cem-CW
Start time (h)	1.27	1.05
Peak time (h)	7.04	9.02
Maximum release time (J/g h)	9.27	8.18
End time (h)	75.33	85.9
Peak duration (h)	74.06	84.85
Peak heat released (J/g)	187.06	201.56
Total heat released 120 h (J/g)	188.56	201.89

the method. Consequently, a second leaching trial was prepared using concentrate hydrochloric acid (HClcc) to control the pH values by gradually adding the amounts of acid required throughout the trial.

In light of the low leaching values, the experiments were conducted in a polypropylene reactor with a Teflon stirring rod to avoid contamination by other system elements. The stirring speed was 300 rpm. Samples were taken at different times throughout the leaching trial. The liquid samples were extracted with a 0.2 μm pore cellulose nitrate vacuum filter and analyzed to find the Zn, Zr and B concentrations. These elements were determined via inductively coupled plasma-optical emission spectrometry (ICP-OES) using a LEEMAN LABS INC. Direct Reading Echelle atomic emission spectrometer. The measurements were calibrated and validated with 1000 mg L^{-1} of Fluka and Merck standard solutions.

The biotoxicity tests were determined by the European standard EN 11348-2:1999 [11]. The bacteria used for the realization of the bioluminescence test were of the type Vibrio Fischeri, supplied by the firm HACH LANGE.

The bacterium was dissolved in a solution of 2% NaCl in distilled water. The measure of light emitted by the bacteria was performed with a luminometer GEM BIOMEDICAL model OPTOCOMP 1 with an incubator capable of maintaining the temperature at 15 ± 1 °C.

3. Results and discussion

3.1. Clinker and cement characterization

3.1.1. Clinker

Table 3 gives the chemical composition of the reference clinker, Cl-REF, and the clinker made with ceramic waste, Cl-CW. As expected, the two chemical compositions were similar. The most

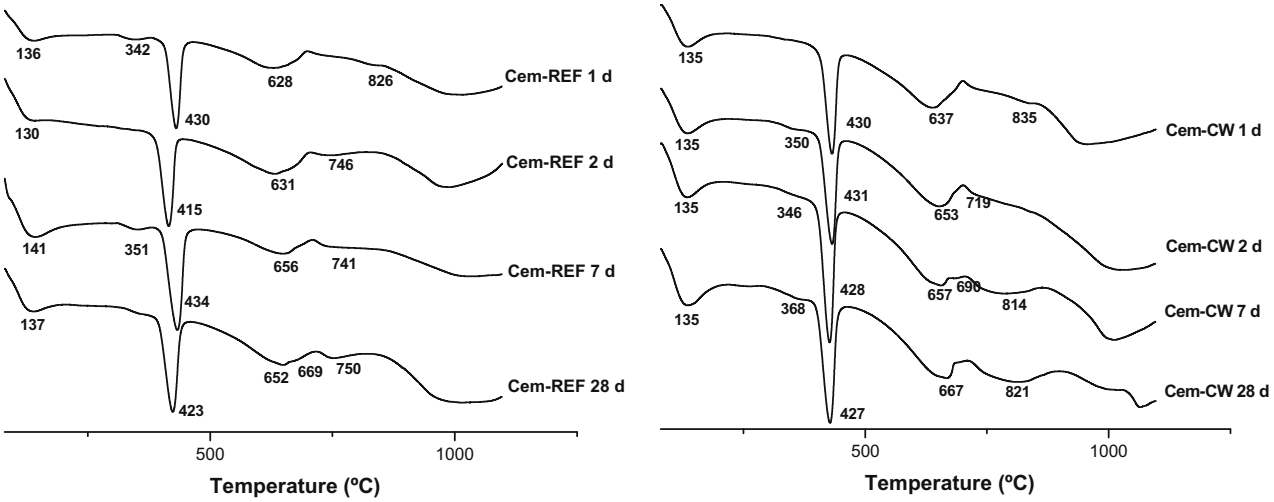


Fig. 4. 1-, 2-, 7- and 28-day DTAs for cements Cem-REF and Cem-CW.

prominent differences were found in the ZnO, ZrO_2 and B_2O_3, contents, which were higher in Cl-CW.

The results of Rietveld quantitative XRD mineralogical analysis on the clinkers are given in Table 4. The inclusion of the ceramic waste in the raw mix modified clinker mineralogical composition slightly. For example, the C_3S content was 13.24% lower in clinker Cl-CW than in Cl-REF. Cl-CW also had a higher C_2S (20%) content and the α'-C_2S polymorph was stabilized (7.09%). The differences observed in the silicate phase contents may have been due to the higher ZnO, ZrO_2 and B_2O_3 concentrations in raw mix RM-CW [12,13].

Differences were also observed in the aluminate and ferrite phases. The C_4AF content in clinker Cl-CW was around 35% lower than in the reference clinker, while its C_3A content was higher.

The morphology of the two clinkers under an optical microscope is shown in the images in Fig. 1. The morphology of the two clinkers was found to be similar, with the phases evenly distributed in both. C_3S, the majority phase in the clinker, exhibited a heterogeneous crystal size. In both Cl-REF and Cl-CW, these crystals were found to measure 5–10 μm in some areas and 20–30 μm in others. While belite clusters were observed in both clinkers, they were more abundant in Cl-CW.

3.1.2. Cement

The particle size distribution of the two cements is shown in Fig. 2. Note that the Cem-CW particle size distribution is slightly finer than that of Cem-REF.

The results of the cement chemical and physical characterization trials are given in Table 5. According to these findings, both cements (Cem-REF and Cem-CW) are European standard EN 197-1 [1] compliant. The two cements required the same amount of water, although the setting time was longer in Cem-CW than in

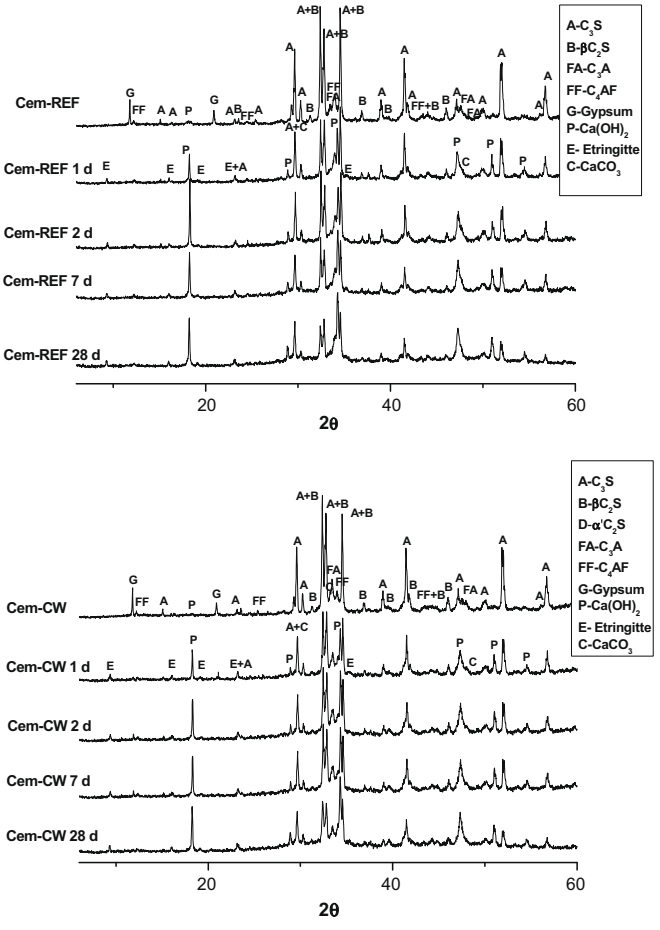


Fig. 5. XRD patterns for Cem-REF, Cem-CW and their pastes.

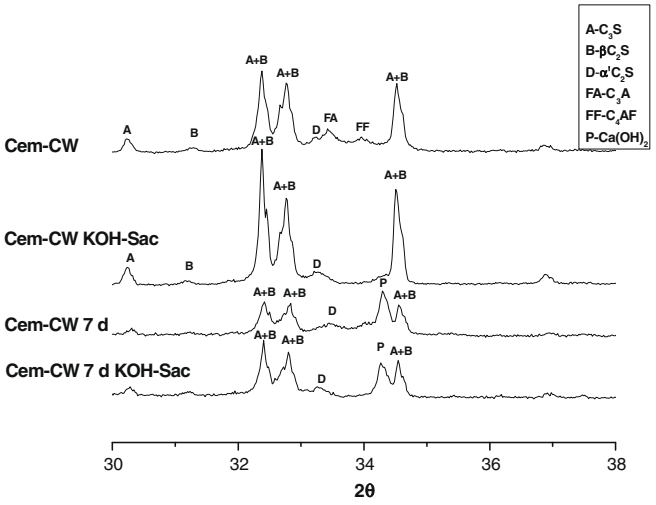


Fig. 6. XRD patterns for the solids obtained after KOH-sucrose treatment.

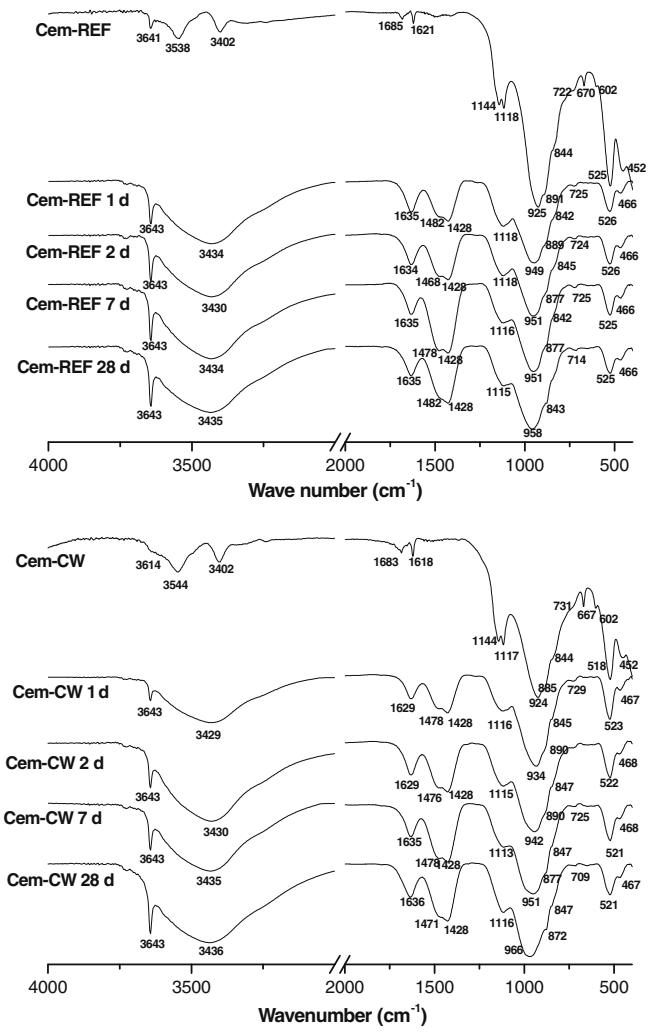


Fig. 7. FTIR spectra for Cem-REF and Cem-CW pastes.

the reference cement. This may have been due on the one hand to the lower C_3S content and on the other to the higher ZnO content in the ceramic waste-containing product. Some authors [14–17] have reported longer setting times in the presence of free ZnO in the clinker or cement, although the effect is less intense when the oxide is included in the clinker phases [18,19].

The data in Table 5 show that early age mechanical strength was slightly lower in Cem-CW than in the reference cement. This difference disappeared at later ages (28 days), however, at which point the flexural strength was slightly higher in Cem-CW. In any event, both cements met the strength requirements set out in European standard EN 196-1 [9].

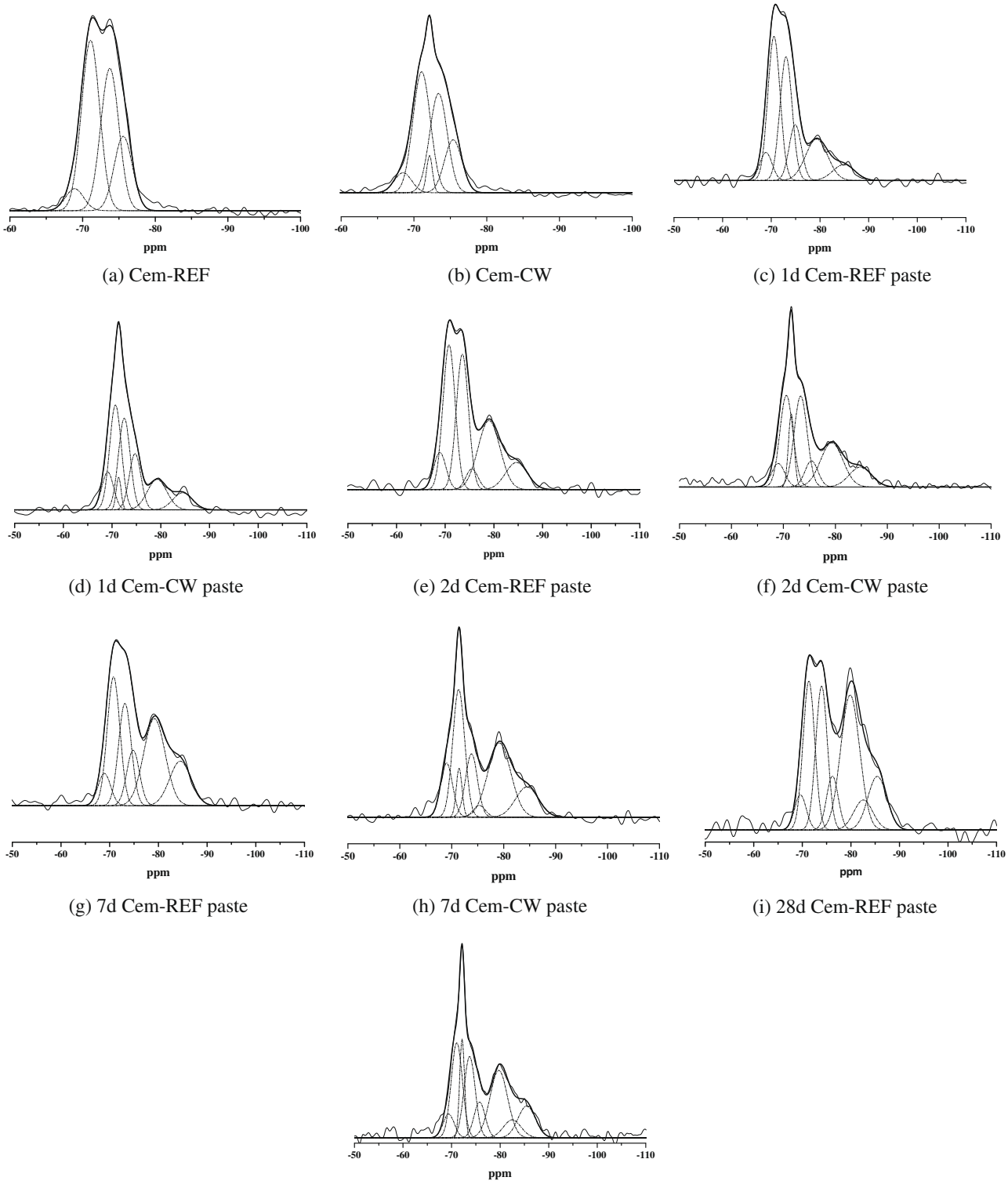


Fig. 8. ^{29}Si NMR spectra for anhydrous and cement pastes.

3.2. Hydration

Fig. 3 shows the heat flow and heat release rate curves for the cements studied. The calorimetric values obtained for the two cement pastes are given in Table 6.

The calorimetric findings showed that the calorimetric curve peak generated by the mass precipitation of reaction products was wider and less intense in the cement containing ceramic waste. This signal peaked at 9.0 h in cement Cem-CW and at 7.0 h in cement Cem-REF. Signal duration was also longer (by 10 h) in Cem-CW. These findings indicate that while Cem-CW hydration was initially less intense than in cement Cem-REF, its duration was longer. The total heat released after 120 h was greater in Cem-CW than in the reference, an indication that, although retarded, the reaction processes did take place.

This delay may have been due, on the one hand, to the lower C_3S content in cement Cem-CW and the higher proportion of the C_2S form, which reacts more slowly in cement hydration, and on the other, to the higher ZnO content in this cement, for this compound may inhibit the initial hydration reactions [15–19]. These results are consistent with the setting times and initial strength values found (see Table 5).

The DTA curves for all the pastes analyzed are shown in Fig. 4. Three zones can be differentiated on these curves. The first, up to 300 °C, exhibits a wide endothermic band covering a series of signals at 110–120 °C and two or three peaks at 200–400 °C associated with water loss in the C–S–H gel and ettringite. All these peaks overlap as a result of dynamic heat ramping [20]. The second area contains an endothermic signal at 400–450 °C corresponding to portlandite ($Ca(OH)_2$) dehydroxylation, while the endothermic signals in the third, from 580 to 900 °C, are attributed to the decomposition of calcium carbonate [21]. According to the literature [22], in the 580–900 °C area, a first signal at around 600 °C may be due to the decarbonation of amorphous calcium carbonate, and a second at 800 °C to the decarbonation of crystalline $CaCO_3$.

The DTA curves showed that the decomposition temperatures of the reaction products in the reference (Cem-REF) and ceramic residue-containing (Cem-CW) cement pastes were very similar.

Fig. 5 shows the XRD patterns for Cem-REF and Cem-CW and the 1-, 2-, 7- and 28 day hydrated pastes. Diffraction lines attributed to the anhydrous (C_3S, C_2S, C_3A, C_4AF and $Ca_2SO_42H_2O$) and hydrated (CH, $C_6As_3H_{32}$) crystalline phases in the cement pastes analyzed can be observed in these diffractograms.

The findings indicated a similar behaviour in the two cements, i.e., a decline in the anhydrous phases and a rise in the hydrated phases, portlandite and ettringite, with curing time.

The diffraction lines attributed to C_3A disappeared in the pattern for the 7-day reference cement paste, which also showed ettringite formation. By contrast, the XRD traces for Cem-CW at all ages contained a line in the $2\theta = 33.27–33.30$ range, which could be attributed to C_3A or α'-C_2S. The presence of ettringite on the Cem-CW cement paste diffractograms is proof of C_3A hydration, which is why this line was attributed to α'-C_2S. To confirm that attribution, cement Cem-CW and its 7-day paste were treated with KOH-sucrose [12] to selectively dissolve the aluminate (C_3A) and ferrite (C_4AF) phases, leaving the silicate phases (C_3S and C_2S) as the sole solid residue. The diffraction line in question remained on the XRD patterns for the solids obtained after selective dissolution (see Fig. 6), confirming its attribution to α'-C_2S.

Fig. 7 shows the 1-, 2-, 7- and 28-day FTIR spectra for the Cem-REF and Cem-CW pastes. The FTIR spectra for both types of cement pastes showed a series of signals attributed to the hydrated phases of the cement, portlandite, ettringite and C–S–H gel, along with the bands for the anhydrous phases, C_3S, C_2S, C_3A and C_4AF. The paste spectra also contained a series of bands attributed to $CaCO_3$, an indication of weathering also detected in the DTA and XRD analyses.

The shift to higher frequencies observed over time in the ν_3 (Si-O) stretching band at around 925 cm^{-1}, attributed to vibrations generated by the SiO_4 groups in the silicate phases present in anhydrous cement, denoted the formation of a hydrated calcium silicate. The findings showed that the shift in this band (925 cm^{-1}) was greater in cement Cem-REF than in the cement containing ceramic waste, Cem-CW, during the first 2 days, further confirming the initial retardation in the hydration reactions in the latter.

Fig. 8 shows the deconvolution of the NMR spectra for the anhydrous cements and their pastes at different curing ages. The signals appearing at –68 to –76 ppm were attributed to the Q^0 Si units found in anhydrous phases C_3S and C_2S. Another area on the cement spectra was attributed to the hydrated phases. The Q^1 units in Si tetrahedra bonded to the end hydroxyl groups in the C–S–H chain were detected at –76 and –80 ppm. This area also contained signals for the Q^2 units, which were separated into two components, one at around –85 ppm generated by Si tetrahedra bound to the calcium chain that forms the C–S–H gel, and the other with a shift value of –82 ppm, associated with bridge Si, Q^{2p} [23,24].

The differences between the ^{29}Si NMR spectra for the two cements appeared primarily in the anhydrous area (–68 and –76 ppm). In addition to the four C_3S signals, the deconvoluted spectrum for the ceramic waste cement, Cem-CW, contained new signal at –71.4 ppm, attributed to C_2S. This band overlapped the C_3S signals, however it is necessary to add it, due to the higher C_2S (β-C_2S + α'-C_2S) content (see Table 4).

Table 7 gives the area percentages obtained after deconvolution of the NMR spectra. These values were used to calculate the degree of reaction, the C-S-H gel chain length (MCL) and the Q^2/Q^{2p} ratio.

The degree of reaction was similar in the two cement pastes, for the slight delays in initial hydration times detected with other techniques were not observed in the NMR spectra.

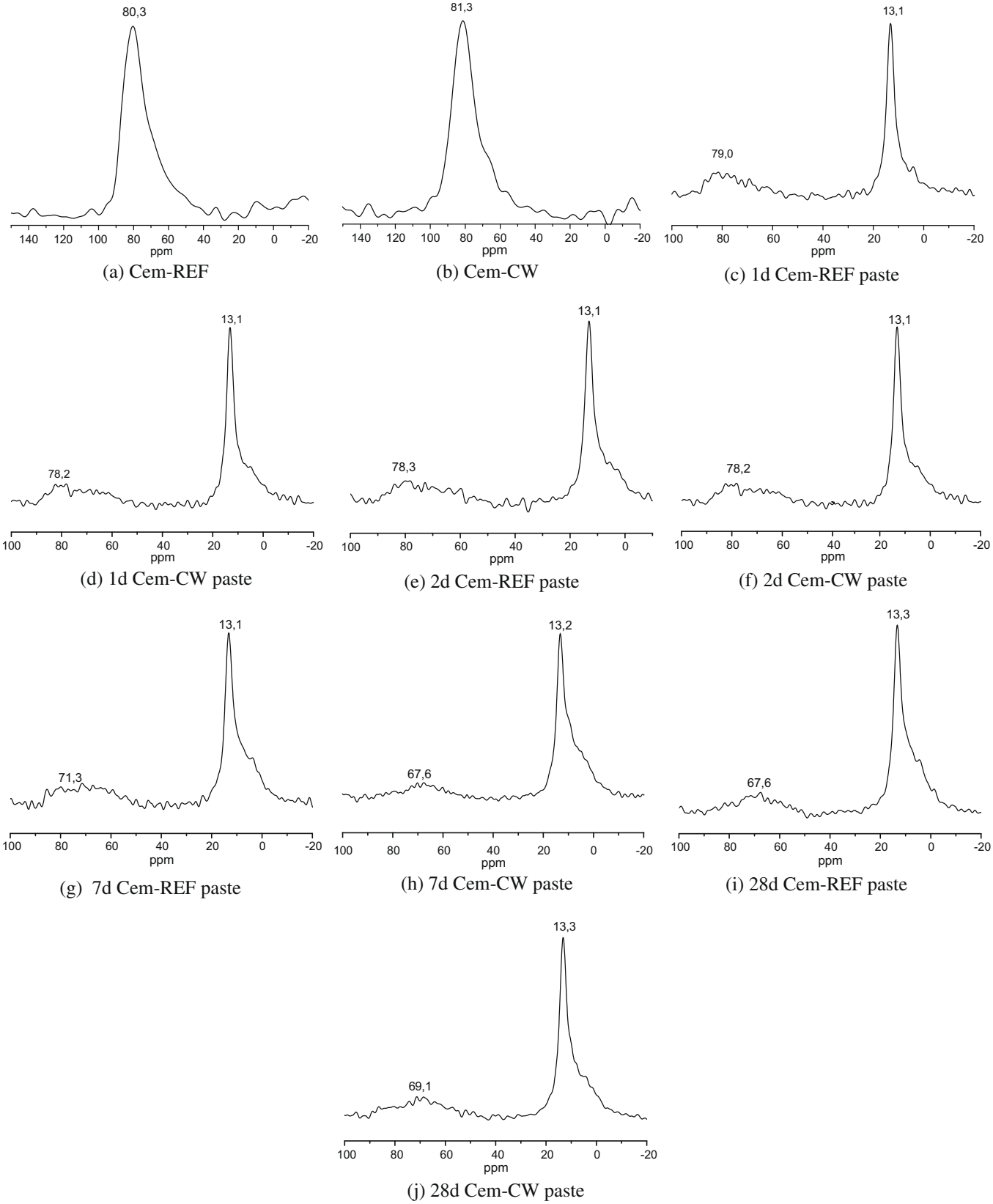
The mean chain length (MCL) of the C–S–H gel chain (see Table 7) was calculated from Eq. (1) [25]:

Table 7
Cement paste areas from NMR spectra (in %).

Sample	$Q^o(C_3S + C_2S)$ [Reaction degree, %]	Q^1	Q^{2p}	Q^2	MCL	Q^2/Q^{2p}
Cem-REF	100	–	–	–		–
Cem-REF 1 d	77.22 [22.78]	15.68	–	7.1	2.91	–
Cem-REF 2 d	66.87 [33.13]	23.34	–	9.79	2.84	–
Cem-REF 7 d	59.77 [40.23]	26.34	–	13.89	3.05	–
Cem-REF 28 d	52.1 [47.90]	29.09	6.25	12.56	3.29	2.01
Cem-WC	100	–	–	–		–
Cem-WC 1 d	78.85 [21.15]	13.56	–	7.59	3.11	–
Cem-WC 2 d	71.58 [28.41]	19.99	–	8.42	2.84	–
Cem-WC 7 d	58.57 [41.42]	28.6	–	12.82	2.89	–
Cem-WC 28 d	60.53 [39.48]	22.83	5.42	11.23	3.46	2.00

$$MCL = 2(Q^1 + Q^2(0A1) + Q^{2p}(0A1) + 3/2Q^2(1A1))/Q^1 \quad (1)$$

The MCL was nearly three units in the reference cement and in the cement containing ceramic waste and increased slightly in both in 28 day pastes. In these ^{29}Si NMR spectra Q^{2p} units appear, indicating the presence of longer silicate chains. The slight increase in MCL was confirmed by FTIR by the shift of the ν_3(Si–O) band at higher frequencies (960 cm^{-1}).



(a) Cem-REF (b) Cem-CW (c) 1d Cem-REF paste

(d) 1d Cem-CW paste (e) 2d Cem-REF paste (f) 2d Cem-CW paste

(g) 7d Cem-REF paste (h) 7d Cem-CW paste (i) 28d Cem-REF paste

(j) 28d Cem-CW paste

Fig. 9. ^{27}Al NMR spectra for anhydrous and cement pastes.

Fig. 9 shows the ^{27}Al spectra for the anhydrous cements and cement pastes at different curing times. The signals observed on the spectra at around 80 ppm were attributed to the tetrahedral Al in the C_3A present in the anhydrous cement. The signal attributed to the octahedral Al in ettringite appeared at 12.7 ppm [26].

The intensity of the 80 ppm signal, attributed to C_3A, was observed to decline with time and shift to lower values (75–67 ppm) on the ^{27}Al spectra for both cements. This signal was generated primarily by the tetrahedrally coordinated Al in C_4AF.

Cement paste microstructure was studied with scanning electron microscopic (SEM) methods. The micrographs in Fig. 10 show the general appearance of the 1- and 28-day Cem-REF and Cem-CW pastes. An analysis of the micrographs found the appearance of the pastes made from the two cements to be very similar. No morphological differences were observed in the C-S-H gel in the reference cement and the cement containing ceramic waste as the materials aged. The C–S–H gel was layered in the early ages, but grew more granular and compact as the paste matured.

Fig. 11 shows the 1- and 28-day BSE micrographs for Cem-REF and Cem-CW. The colour contrasts observed in the pastes are due to the differences in atomic weight of the elements present in the different phases. The lighter areas in the micrographs correspond to the anhydrous phases in the cement, namely the silicate phases (C_3S, C_2S), while the darker areas denote the presence of C–S–H gel. In both types of cement pastes, the anhydrous (light areas) phases were observed to decrease while the C–S–H gel (dark) areas grew over time. The pastes for the two cements, Cem-REF and Cem-CW, exhibited a similar appearance, and their anhydrous and C–S–H gel phase contents were similar (see Fig. 11).

The chemical composition of the outer C–S–H gel, the area of gel farthest from the anhydrous cement particles in both the reference cement, Cem-REF, and the cement containing ceramic waste, Cem-CW, was determined by EDS, with 20 analyses per sample. The findings are given in Table 8. C–S–H gel comprises primarily Ca, Si and Al. The gels from the reference and waste-containing cements exhibited a similar chemical composition. No differences in the Ca/Si ratios were observed in the two cements, which were stable at a value of around two at all of the ages studied. These findings indicate the absence of any substantial difference in the composition of the gel forming during hydration in the two cements.

3.3. Leaching

As noted in item Section 2.2.3, cement leachates were analyzed for Zn, Zr and B, since these elements were found in higher proportions in the clinker containing ceramic waste. The Zr concentration in the leachate obtained with the two treatments used in this study was constant and under the 0.2 mg L^{-1} detection threshold for both clinkers, Cl-REF and Cl-CW, indicating that Zr leached only minimally or not at all, and was largely retained in the clinker. Zn and B, by contrast, did leach out of the clinker. Zn and B concentrations in the leachate over time are show in Figs. 12 and 13.

In the two media used, the Zn and B concentrations were higher at all test times in the Cl-CW than in the Cl-REF leachates. The concentrations in the leachates were higher at all ages in the more aggressive HClcc medium than in the acetic acid medium.

The Zn concentration obtained after leaching with acetic acid for 0.5 h was 22% higher in Cl-CW than in Cl-REF, and by the end of the study (1344 h) the difference had risen to 292%. Nonetheless, the amount of Zn in the leachate after 1344 h was just 0.05% of all the Zn present in the clinker. The B concentration obtained after leaching with acetic acid for 0.5 h was 287% higher in the Cl-CW than in the Cl-REF leachate, and 672.73% higher after 1344 h.

From the outset, more Zn and B leached in the hydrochloric than the acetic acid medium. Their concentrations were respectively 420% and 383% higher in the Cl-CW than in the Cl-REF leachate. After 588 h the amounts of Zn and B leached were 363% and 425% higher, respectively, in the waste-containing than in the reference clinker. The more intense leaching in this medium would be justified by the fact that both the hydrated and anhydrous phases of the cement are more soluble at acid pH values.

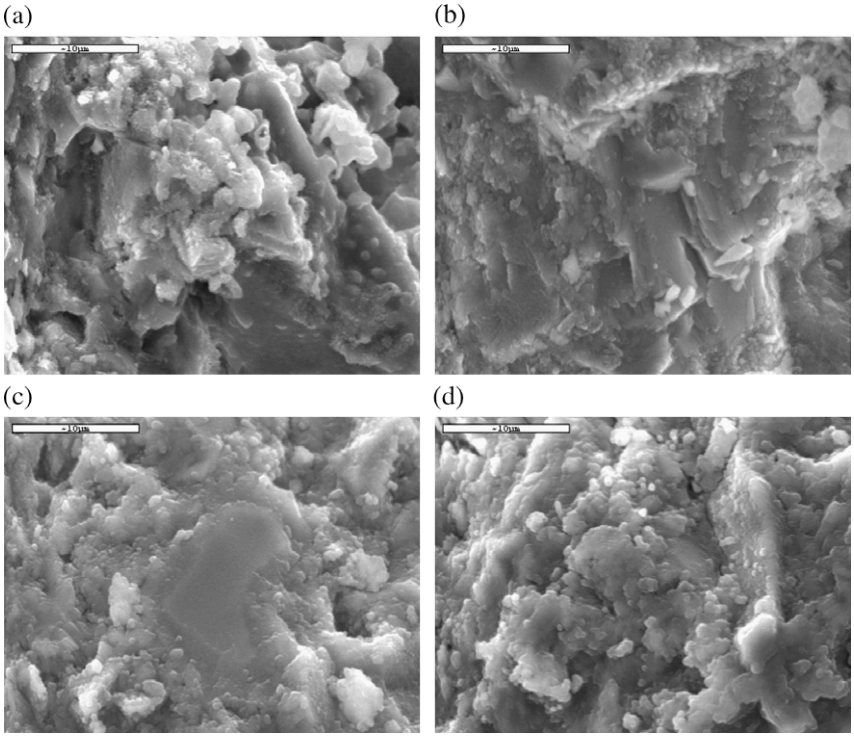


Fig. 10. SEM images of cement pastes. (a) 1-day Cem-REF; (b) 1-day Cem-CW; (c) 28-day Cem-REF; (d) 28-day Cem-CW.

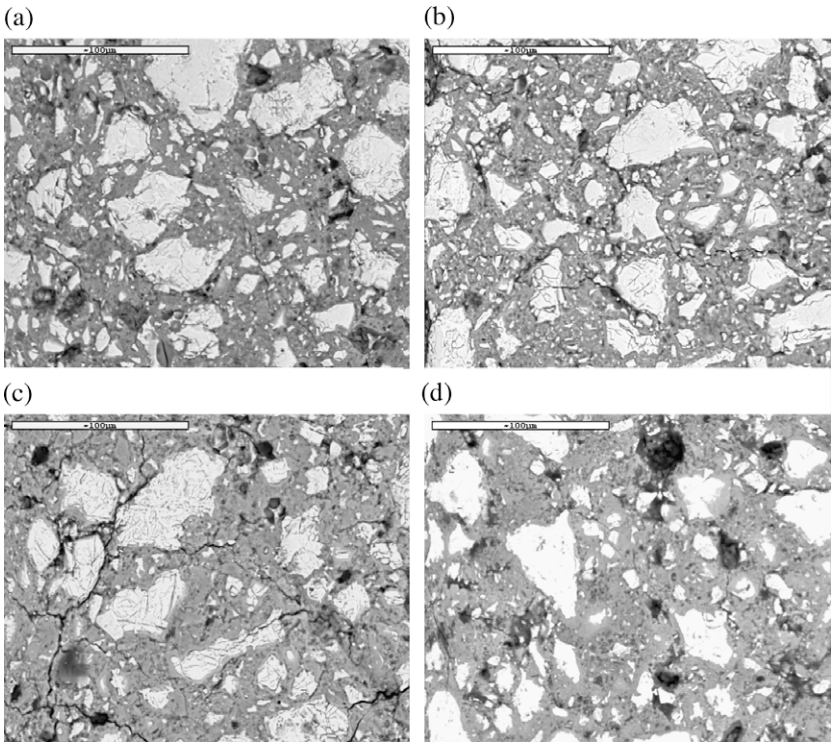


Fig. 11. Cement paste BSE micrographs. (a) 1-day Cem-REF; (b) 1-day Cem-CW; (c) 28-day Cem-REF; (d) 28-day Cem-CW.

Table 8
Chemical composition of outer C–S–H gel in the cement pastes (% wt.).

Sample	Ca	Si	Al	Mg	Fe	Ca/Si	Al/Ca	Al/Si
Cem-REF 1 d	25.95 ± 0.83	10.58 ± 0.54	1.16 ± 0.47	1.13 ± 0.20	0.61 ± 0.22	2.44 ± 0.2	0.05 ± 0.019	0.11 ± 0.05
Cem-REF 2 d	23.46 ± 1.16	11.32 ± 1.45	1.87 ± 0.8	1.90 ± 0.60	0.76 ± 0.30	2.12 ± 0.45	0.08 ± 0.04	0.17 ± 0.09
Cem-REF 7 d	24.90 ± 1.01	11.89 ± 0.99	1.18 ± 0.73	1.15 ± 0.26	0.57 ± 0.25	2.11 ± 0.15	0.05 ± 0.03	0.10 ± 0.07
Cem-REF 28 d	23.90 ± 0.87	11.89 ± 1.18	1.49 ± 0.71	1.27 ± 0.24	0.69 ± 0.26	2.03 ± 0.21	0.06 ± 0.03	0.13 ± 0.07
Cem-CW 1 d	25.09 ± 0.85	11.64 ± 1.15	1.27 ± 0.62	0.86 ± 0.39	0.68 ± 0.24	2.15 ± 0.27	0.05 ± 0.025	0.11 ± 0.05
Cem-CW 2 d	24.06 ± 1.11	12.73 ± 0.92	1.20 + 0.66	0.87 ± 0.16	0.56 ± 0.27	1.90 ± 0.20	0.05 ± 0.03	0.10 ± 0.06
Cem-CW 7 d	23.50 ± 0.73	12.90 ± 0.75	1.29 ± 0.52	0.85 ± 0.16	0.61 ± 0.25	1.83 ± 0.12	0.06 ± 0.02	0.10 ± 0.04
Cem-CW 28 d	26.11 ± 0.52	11.81 ± 0.83	1.29 ± 0.31	0.40 ± 0.22	0.52 ± 0.16	2.22 ± 0.17	0.05 ± 0.01	0.11 ± 0.03

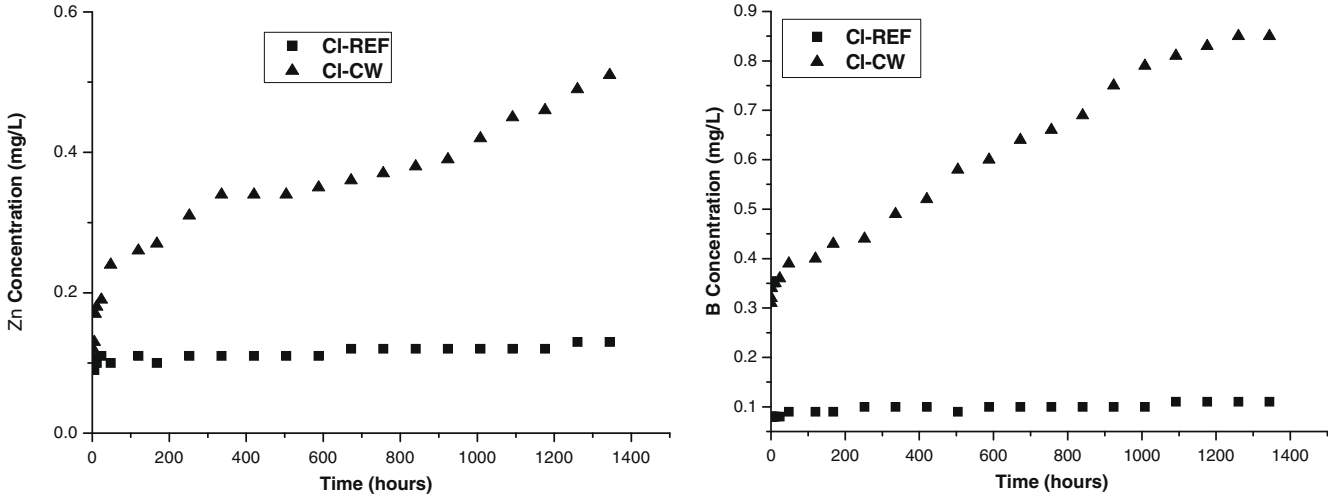


Fig. 12. Zn and B concentrations (mg l^{-1}) in the leachates obtained in acetic acid medium.

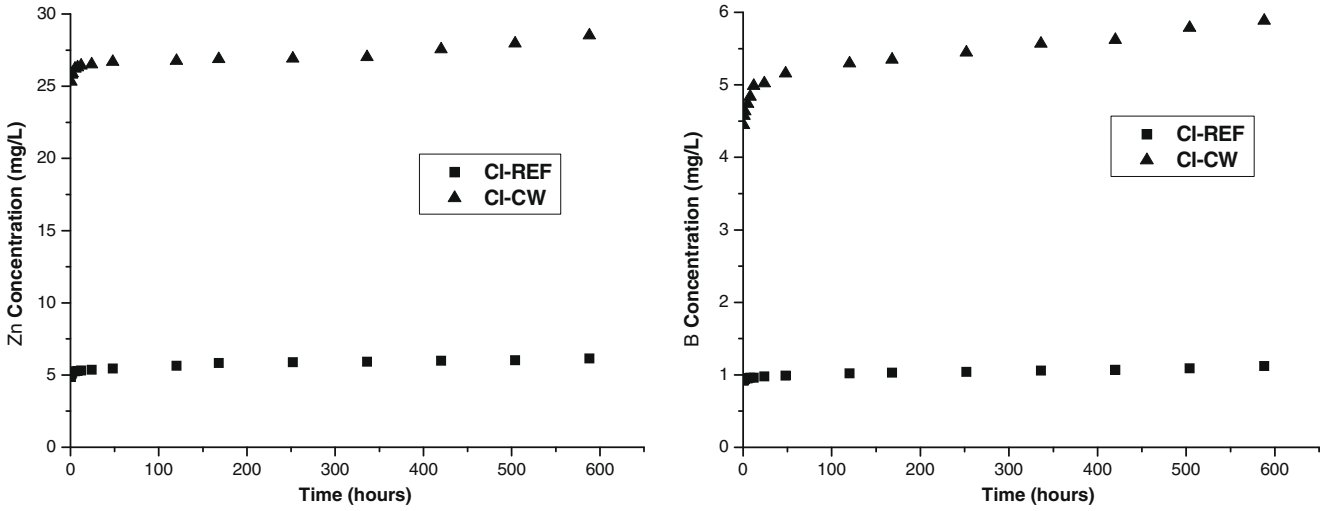


Fig. 13. Zn and B concentrations (mg l^{-1}) in the leachates obtained in HClcc medium.

The amounts leached were small for all three elements analyzed, due on the one hand to the low concentration at which they are found in the material, along, naturally, with their stabilization in the clinker phases, and on the other to the pH at which leaching took place, pH∼12.

The results of the biotoxicity tests have been expressed as the concentration of waste that reduces the intensity of initial light emitted by the bacteria by 50% after a contact of 15 min at 15 °C (value denominated EC_{50}). To evaluate the toxicity of the waste according to this test, the Spanish legislation provides that the waste is toxic when leaching residue has a value of $EC_{50} < 3 \times 10^{-3}$ mg l^{-1} [11]. The results showed that the concentrations of Zn and B leached were very low with a low or nil toxic effect, because EC_{50} value of the leachate was much higher than the 3×10^{-3} mg l^{-1} [11,27] threshold specified in the standard.

4. Conclusions

According to the results obtained in the present study it can be confirmed that the cement, obtained from a raw mix containing ceramic wastes tiles as an alternative raw material, provides all the technical conditions to be prepared and used as a Portland cement. Other conclusions to be drawn from the present study are the following:

1. The characterization studies conducted on the clinker (Cl-CW) and cement (Cem-CW) obtained with raw mixes containing ceramic waste as an alternative raw material met all the requirements and requisites set out in European cement standards (EN 197-1). Nonetheless, they have higher ZnO, ZrO_2, and B_2O_3 contents due to the enamel coating on this waste.
2. According to the hydration studies, initial hydration is somewhat retarded in Cem-CW, with longer initial and final setting times and lower 2-day mechanical strength.
3. The structure of the C-S-H gel determined by ^{29}Si NMR shows that it is similar in the two cements, with a mean chain length of three at early ages, increasing after 28 days.
4. Further to the SEM/BSE/EDS microstructural study, the hydration product morphology and composition are comparable in Cem-CW and reference Portland cement pastes.
5. The leaching studies showed that the Zr present in Cem-CW cement pastes is retained in the clinker, whereas Zn and B are leached out, the latter more intensely. In any event, the amounts leached are above the EC_{50} toxicity threshold specified in Spanish standards (3×10^{-3} mg l^{-1}).

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