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Belite cements obtained from ceramic wastes and the mineral pair $CaF_2/CaSO_4$

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ABSTRACT

The cement industry is seeking alternative approaches to reduce the high energy and environmental costs of Portland cement manufacture. One such alternative is belite cement. In the present study clinkers with high (36–60%) belite contents were obtained at 1350 °C from raw mixes consisting of ceramic waste and the fluxing/mineralised pair $CaF_2/CaSO_4$. The factors found to affect the mineralogical composition and the clinker phase polymorphs obtained were the lime saturation factor (LSF), the presence of ceramic waste and the addition of CaF_2 and $CaSO_4$.

The reactivity of these belite clinkers with water was analysed with isothermal conduction calorimetry. A statistical study was then conducted on the findings to determine the effect of each variable when the response signals were peak heat flow rate and the time needed to reach that peak. The statistical analysis identified the optimal experimental conditions to be a LSF of 90%, a $CaSO_4$ content of 2.60%, and the absence of both ceramic waste and CaF_2.

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1. Introduction

Portland cement manufacture is characterised by a series of drawbacks such as high fossil fuel-based energy consumption, a heavy environmental impact due to the use of natural prime materials and substantial particle and GHG emissions [1–3]. Among the latter, CO_2 is the gas with the largest environmental footprint. Around 850 kg of CO_2 are emitted per tonne of cement manufactured [3–5], and the cement industry is responsible for 5–7% of all anthropogenic emissions world-wide [3–7].

In recent years the cement industry, in conjunction with the scientific community, has been seeking new avenues to minimise the adverse effects of the manufacture of this binder in an attempt to attain sustainable development and comply with the provisions of the Kyoto Protocol as well as other intergovernmental accords. One possible solution would be to produce cements with low lime saturation factors (LSF), which are associated with higher C_2S contents. The production of this type of cement is estimated to take from 15% to 20% less energy than Portland cement manufacture [5,8]. This, along with the lower $CaCO_3$ content involved, would reduce CO_2 emissions [5,8–10]. The environmental benefits of producing high C_2S content cement are offset, however, by its low hydraulicity and scant development of early age mechanical strength [8,9,11–13]. A number of procedures have been devised to raise early age strength in belite cements. One involves activating the C_2S by stabilising high temperature polymorphs with quick cooling or modifying their structure through the inclusion of ions [5,8,9,13–15]. Another consists of preparing cements in which initial strength development is due to the rapid hydration of other phases such as alite or C_4A_3s [16–19].

Different papers [14–29] have been published on belite cement production involving the thermal treatment of raw mixes with industrial waste or by-products (such as fly ash, phosphochalk, fluidised bed combustion, phosphogypsum, oil shale or sludge) as alternative prime materials. Raupp-Pereira et al. [25] studied the production of belite cements from sludge with a high aluminium content (anodising sludge), sludge from the filtration/treatment of potable water and from cutting marble. Their findings showed that clinkers obtained from sludge turned powdery as a result of the presence of calcium aluminium oxide sulphate and the stabilisation of the γ-C_2S polymorph. The long setting times (660 min) and low mechanical strength (3.22 MPa after 28 days of curing) in these cements were attributed to the presence of low hydraulicity phases such as gehlenite (C_2AS), mayenite ($C_{12}A_7$) and γ-C_2S, along with a low C_2S content.

Another by-product that has been used as a prime material is fly ash. Sahu et al. [19] synthesised sulfoaluminate belite cement at 1200 °C from limestone, fly ash (13–20%) and gypsum as prime materials. The cements obtained contained 43–58% C_2S and 13–18% C_4A_3S. These cements exhibited high 28-day compressive strength (36.6 MPa) and lower total porosity than conventional Portland cement.

Pimraksa et al. [28] obtained belite cement from fly ash and $CaCO_3$, with a Ca/Si ratio of 2.0, 2.5 and 3.0 via both clinkerisation reactions and hydrothermal treatments. The 28-day compressive

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strength was low (1.5–2.5 MPa) in the clinkerised cements with a Ca/Si ratio of 2.0, due partially to the presence of substantial amounts of gehlenite (C_2AS), a non-reactive compound. The cement obtained hydrothermally, by contrast, had mechanical strength values of 9.5 MPa. Arjunan et al. [21] used low calcium content fly ash, limestone powder and sludge as alternative prime materials to produce belite cement and observed the appearance of both calcium sulfoaluminate ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$) and dicalcium silicate ($2CaO{\cdot}SiO_2$). The formation temperature of these phases changed with the physical state of the prime materials: in nodules it was around 1250 °C, but declined to 1175 °C in powder. The compressive strength and microstructure of these sulfoaluminate belite cements made them apt for use as cementitious materials. Further to the findings reported by several authors [23,24], phosphogypsum waste can also be used as a prime material in sulfo-belite cement production. The findings showed that the clinker phases formed at 1250 °C. The 28-day mechanical strength, at 52 MPa, and the setting times were comparable to the values found in sulfo-belite cements made from conventional prime materials.

Previous studies conducted by the authors' research team proved that fired ceramic tile is a technologically viable alternative prime material for manufacturing Portland cement [30,31]. The chemical and mineralogical analyses of the clinkers and cements made with this waste were similar to the findings for the materials obtained with conventional prime materials. The former exhibited higher C_2S contents, however, confirming the stabilisation of the high temperature polymorph, α'_H-C_2S.

Fired tile waste has a high B_2O_3 content [32], which favours the stabilisation of potentially more reactive C_2S polymorphs [33]. Taking these premises as a starting point, a study was designed to ascertain the technological feasibility of using ceramic waste as an alternative prime material in raw mixes to obtain belite cement.

In addition, the fluxing/mineralised pair $CaF_2/CaSO_4$ is known to have a dually beneficial effect on Portland cement clinker preparation, for it lowers the molten phase temperatures and accelerates alite formation [34–38].

The basic objective of the present study was to obtain cements with high belite content by combining favourable silicate phase formation kinetics and thermodynamics, as well as to analyse their reactivity with water and establish the effect of the variables studied in the process.

2. Experimental work

2.1. Prime materials

The following prime materials were used to prepare the raw mixes: limestone, sand, clay, ceramic waste (CW) and commercial Fe_2O_3 (Panreac) as a flux modulus regulator. Several percentages of CaF_2 and $CaSO_4{\cdot}2H_2O$ were used, both separately and jointly, as fluxes and mineralisers and a source of $CaSO_4$. The chemical composition of all the prime materials is given in Table 1. The particle size of the prime materials in the raw mix was monitored throughout. According to prior studies [30], in limestone the size was under 125 μm [39], in sand and clay under 63 μm [39], in the ceramic waste from 45 to 90 μm, and in the mineral pair (CaF_2 and $CaSO_4{\cdot}2H_2O$) under 45 μm.

2.2. Raw mix proportioning and preparation

The composition of the 36 raw mixes prepared is given in Table 2. The parameters varied in mix preparation were: lime saturation factor (LSF, see Eq. (1)), with values of 90 and 85%; the presence or absence of ceramic waste (CW), and the percentage of $CaSO_4$ and CaF_2.

Table 1
Chemical composition of the prime materials (wt%).

	Limestone	Sand	Clay	$CW_{(45<X<90\mu m)}$	CaF_2	$CaSO_4{\cdot}2H_2O$
LOI	40.50	2.09	9.20	0.15	1.04	21.32
SiO_2	5.60	89.40	52.0	63.0	1.00	1.40
Al_2O_3	1.30	3.90	15.1	16.3	0.16	0.36
Fe_2O_3	0.58	0.61	6.02	4.40	3.97	0.20
CaO	51.1	2.06	4.01	6.67	48.7	32.4
MgO	0.58	0.03	4.95	2.55	0.01	0.63
Na_2O	<0.01	0.07	0.58	0.81	–	–
K_2O	0.23	1.79	4.55	3.78	–	–
TiO_2	0.07	0.04	0.73	0.66	–	–
MnO_2	0.01	<0.01	0.10	0.04	0.02	–
P_2O_5	0.10	0.03	0.15	0.18	0.07	0.04
ZnO	–	–	–	0.31	–	–
ZrO_2	–	–	–	0.25	–	–
B_2O_3	–	–	–	0.13	–	–
SO_3	–	–	2.60	0.04	–	44.40
F^-	–	–	–	–	45.00	–

LOI = Loss on ignition (1000 °C) CW: ceramic waste.

Table 2
Raw mix composition (wt%) and LSF.

Sample	Limestone	Sand	Clay	Fe_2O_3	CW	CaF_2	$CaSO_4$	LSF
M_1	79.87	1.7	18.07	0.34	–	0	0	85
M_2	81.45	–	–	0.65	17.86	0	0	85
M_3	81.17	1.60	16.94	0.32	–	0	0	90
M_4	82.68	–	–	0.66	16.66	0	0	90
M_5	76.73	1.7	17.93	0.34	–	0	2.60	85
M_6	78.29	–	–	0.65	17.74	0	2.60	85
M_7	78.01	1.6	16.81	0.32	–	0	2.60	90
M_8	79.51	–	–	0.65	16.56	0	2.60	90
M_9	75.15	1.7	17.86	0.34	–	0	3.90	85
M_{10}	76.70	–	–	0.69	17.68	0	3.90	85
M_{11}	76.42	1.6	16.75	0.32	–	0	3.90	90
M_{12}	77.92	–	–	0.65	16.50	0	3.90	90
M_{13}	79.15	1.7	18.11	0.31	–	0.65	0	85
M_{14}	80.73	–	–	0.67	17.90	0.65	0	85
M_{15}	80.45	1.6	16.98	0.29	–	0.65	0	90
M_{16}	81.97	–	–	0.63	16.70	0.65	0	90
M_{17}	78.44	1.7	18.15	0.29	–	1.30	0	85
M_{18}	80.02	–	–	0.64	17.94	1.30	0	85
M_{19}	79.73	1.6	17.02	0.26	–	1.30	0	90
M_{20}	81.26	–	–	0.60	16.74	1.30	0	90
M_{21}	76.01	1.7	17.97	0.31	–	0.65	2.60	85
M_{22}	77.58	–	–	0.67	17.78	0.65	2.60	85
M_{23}	77.29	1.6	16.85	0.29	–	0.65	2.60	90
M_{24}	78.80	–	–	0.62	16.60	0.65	2.60	90
M_{25}	74.43	1.7	17.90	0.31	–	0.65	3.90	85
M_{26}	75.99	–	–	0.67	17.72	0.65	3.90	85
M_{27}	75.70	1.6	16.79	0.29	–	0.65	3.90	90
M_{28}	77.20	–	–	0.62	16.54	0.65	3.90	90
M_{29}	75.29	1.7	18.01	0.29	–	1.30	2.60	85
M_{30}	76.86	–	–	0.64	17.82	1.30	2.60	85
M_{31}	76.57	1.6	16.89	0.26	–	1.30	2.60	90
M_{32}	78.08	–	–	0.60	16.64	1.30	2.60	90
M_{33}	73.71	1.7	17.94	0.29	–	1.30	3.90	85
M_{34}	75.27	–	–	0.64	17.76	1.30	3.90	85
M_{35}	74.98	1.6	16.83	0.26	–	1.30	3.90	90
M_{36}	76.49	–	–	0.60	16.59	1.30	3.90	90

$$\mathrm{LSF} = (\mathrm{CaO}/2.8\mathrm{SiO_2} + 1.18\mathrm{Al_2O_3} + 0.65\mathrm{Fe_2O_3}) * 100 \tag{1}$$

The silicate (M_S) and flux (M_F) moduli were constant in all the mixes, as shown below:

$$M_S = \mathrm{SiO_2}/\mathrm{Fe_2O_3} + \mathrm{Al_2O_3} = 2.00 \tag{2}$$

$$M_F = \mathrm{Al_2O_3}/\mathrm{Fe_2O_3} = 2.65 \tag{3}$$

The raw mixes containing ceramic waste as an alternative prime material had no clay or sand. Rather, they consisted solely of limestone, the ceramic waste (16–18 wt%) and Fe_2O_3.

The raw mixes were prepared as follows: the reagents were dried in an oven at 100 °C for 1 day, except the $CaSO_4{\cdot}2H_2O$ that was dried at 45 °C. The reagents were weighted in the adequate percentage for each raw mix, then the reagents were blended in a turbula for one hour and the liquid suspension was then homogenised in ethanol (99%) in an agate mortar for 30 min. The excess ethanol was removed by heating the mix under an infrared lamp.

2.3. Clinker preparation

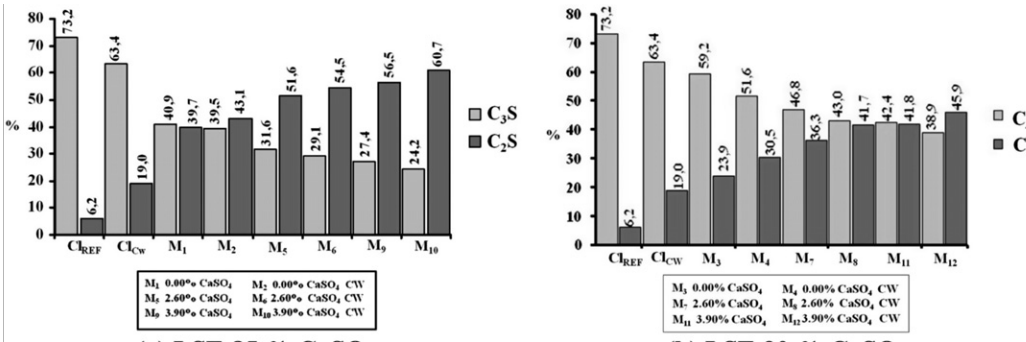
Wafers weighing around 4 g and measuring 3 cm in diameter were prepared from each mix. The clinkerisation temperature was 1350 °C. The wafers were placed in a kiln heated to temperature and fired for 45 min. The samples were cooled at ambient temperature and the resulting clinkers were ground in a small metallic grinder and then in an agate grinder in order to all the particles had the same size, under 45 μm.

The mineralogical composition of the clinkers obtained was compared to the composition of two Portland cement clinkers, CL_{REF} and CL_{CW} [31]. CL_{REF} was a clinker obtained from a raw mix provided by a cement plant, clinkerised in a laboratory kiln at 1450 °C for 30 min and subsequently cooled at ambient temperature; CL_{CW} was a clinker obtained from a raw mix containing limestone, ceramic waste and Fe_2O_3 and clinkerised under the same conditions as CL_{REF}.

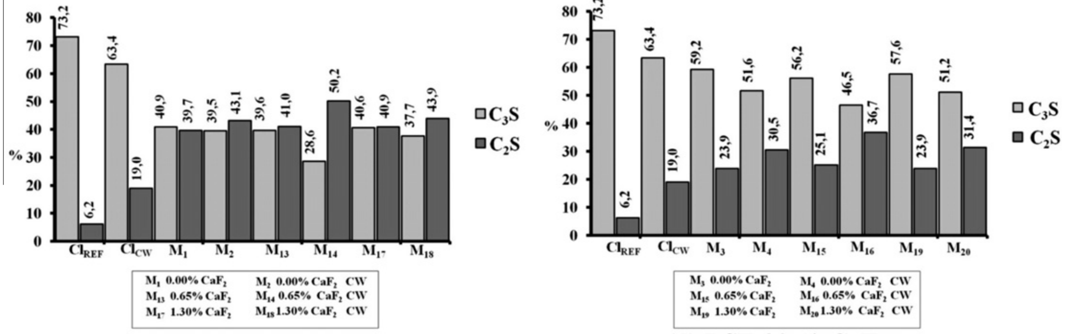
Belite clinker hydration was compared throughout to hydration in two Portland cements, PC_{REF} and PC_{CW}, prepared from clinkers CL_{REF} and CL_{CW} and the adequate proportion of gypsum.

2.4. Test conducted

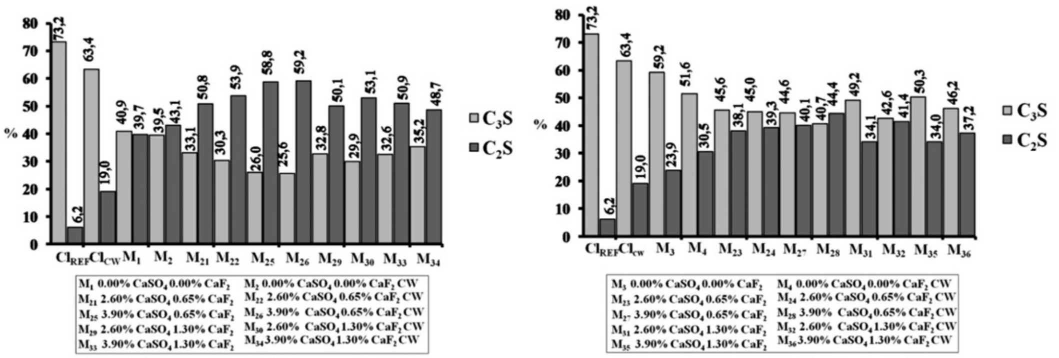
- The crystalline phases were analysed with XRD on a Bruker Theta-Theta D8 Advance X-ray diffractometer. Rietveld refinement [40], performed with GSAS software, was used in the quantitative analysis of the XRD patterns. No adjustment was made for the mineralogical phases representing less than 0.5% of the total.
- Clinker hydration was studied with isothermal conduction calorimetry performed on a Thermometric TAM Air analyser. The clinker pastes were mixed manually with water (w/c ratio,



(a) LSF-85 % $CaSO_4$ (b) LSF-90 % $CaSO_4$



(c) LSF-85 % CaF_2 (d) LSF-90 % CaF_2



(e) LSF-85 % $CaSO_4$ and CaF_2 (f) LSF-90 % $CaSO_4$ and CaF_2

Fig. 1. C_3S and C_2S contents in clinkers.

0.4) for 3 min, after which the calorimetric test was conducted at a constant temperature of 25 °C. Statgraphics software was used for the statistical study of the isothermal conduction calorimetric data.

3. Results and discussion

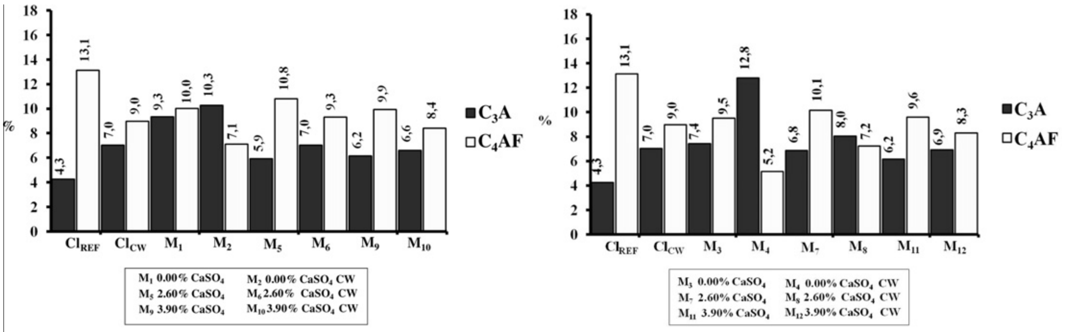
3.1. Clinker mineralogical composition

The mineralogical composition of the clinkers, found by Rietveld analysis of the XRD patterns, is shown in Figs. 1 and 2 and Table 3. Further to the findings, the four variables studied (LSF, % of ceramic waste, % of $CaSO_4$ and % of CaF_2) affected clinker phase content and polymorphism. As expected, the lime saturation factor, LSF, impacted the percentage of the silicate phases C_2S and C_3S (see Fig. 1). The C_2S content was higher in clinkers with LSF values of 85%. The presence of ceramic waste in the raw mixes likewise raised the percentage of C_2S. Moreover, the diffraction lines observed in clinkers M_2 and M_4 at 2θ values of 32.48° and 33.07° reflected α'_H polymorph stabilisation see Table 3 [31,33]. The percentage of this form of calcium silicate was higher in these clinkers than in clinkers M_1 and M_3, which also contained the polymorph.

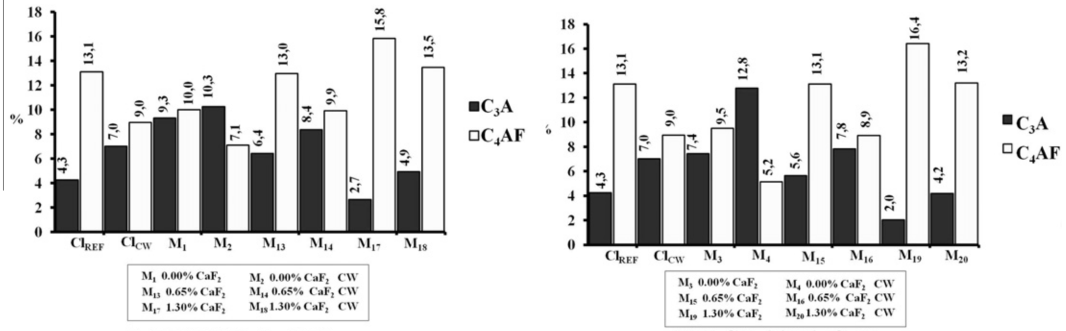
The results further showed that the addition of $CaSO_4$ likewise modified the silicate phase content and C_2S polymorphism. The C_2S content rose by 11–18% in clinkers M_5–M_{12}. The highest percentages were observed in clinkers obtained with 3.90% $CaSO_4$. This higher C_2S content was due to the enlargement of the C_2S stability field at the expense of the C_3S field [34,41,42]. The addition of $CaSO_4$ stabilised the β-C_2S polymorph, inhibiting the stabilising effect of the ceramic waste on the α'_H polymorph. In the clinkers obtained to the addition of $CaSO_4$ is not observed diffraction lines assigned to the Klein's salt.

By contrast, the addition of the CaF_2 to the raw mix affected the aluminate and ferrite phases in the clinker, with a substantial rise in the latter to the detriment of the tricalcium aluminate. This effect was more perceptible at the highest CaF_2 dose (1.30 wt%). The presence of CaF_2 raised the C_3S content due to the enlargement of its stability field [41].

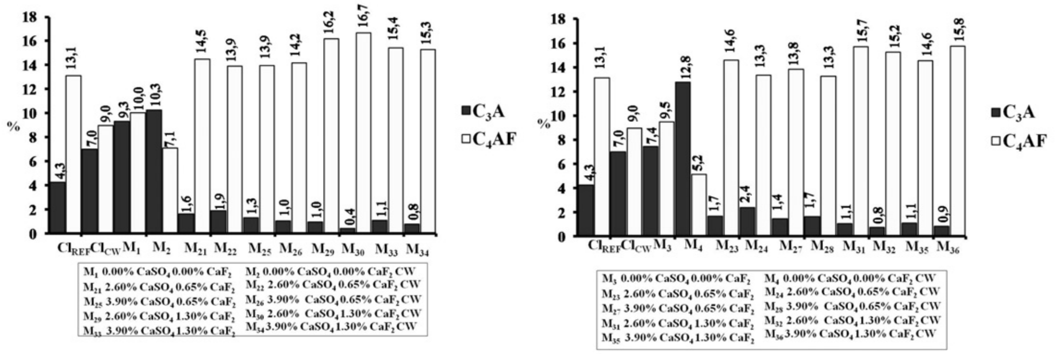
When the mineral pair CaF_2/$CaSO_4$ was added jointly to the raw mix, the mineralogical composition of the clinkers exhibited the combined effect of adding CaF_2 and $CaSO_4$ separately. In other words, the $CaSO_4$ raised the C_2S content and stabilised the β-C_2S



(a) LSF-85 % $CaSO_4$ **(b) LSF-90 % $CaSO_4$**



(c) LSF-85 % CaF_2 **(d) LSF-90 % CaF_2**



(e) LSF-85 % $CaSO_4$ and CaF_2 **(f) LSF-90 % $CaSO_4$ and CaF_2**

Fig. 2. C_3A and C_4AF contents in clinkers.

Table 3
Content of different C_2S polymorphs (%).

Muestra	LSF	β-C_2S	α'_H-C_2S	β-C_2S + α'_H-C_2S
CL_{REF}	102	6.21	–	–
CL_{CW}	98	12.65	6.11	18.76
M_1	85	4.64	35.07	39.71
M_2	85	4.38	38.74	43.12
M_3	90	4.66	19.22	23..8
M_4	90	3.17	27.32	30,49

Table 5
Variables and levels.

Variable	Symbol	Level		
		0	1	2
LSF	A	85%	90%	–
CW	B	Present	Absent	–
$CaSO_4$	C	0.00	2.60%	3.90%
CaF_2	D	0.00	0.65%	1.30%

polymorph, while the C_3A content declined and the C_4AF rose as a result of the presence of the CaF_2 in the mix.

Consequently, the mineralogical composition showed that high C_2S content clinkers can be obtained from fired ceramic waste as an alternative prime material and the fluxing/mineralised pair $CaF_2/CaSO_4$. The highest C_2S contents were found in clinkers with an LSF of 85%, ceramic waste and 3.90% $CaSO_4$.

3.2. Clinker hydration

While belite or high C_2S content cement production entails obvious environmental advantages, the hydration rate is slower in these materials than in Portland cement, a development that is associated with lower early age mechanical strength.

Hence the importance of determining the hydration rate of the new clinkers obtained in this study. Isothermal conduction calorimetry was used for this purpose. Hydration in these clinkers was compared to hydration in the control Portland cement, PC_{REF}, obtained from the reference clinker (CL_{REF}) and a Portland cement prepared from a clinker containing ceramic waste (CL_{CW}), PC_{CW}.

Table 4
Isothermal conduction calorimetry parameters and values T_M – signal peak time (h); V_M – peak heat flow rate (J/gh); C – total heat released at the theoretical end of hydration reactions (J/g).

Sample	T_M	V_M	C
PC_{REF}	7.04	9.27	226.57
PC_{CW}	9.02	8.18	213.81
M_1	18.71	7.13	295.22
M_2	19.65	5.06	263.45
M_3	11.71	8.04	291.12
M_4	15.27	7.29	309.52
M_5	8.58	10.47	244.50
M_6	10.02	8.72	252.47
M_7	4.86	22.59	288.35
M_8	10.09	9.57	265.80
M_9	7.99	10.13	233.89
M_{10}	11.47	7.81	253.81
M_{11}	3.39	20.53	270.25
M_{12}	5.82	10.49	281.38
M_{13}	21.32	6.55	269.08
M_{14}	36.17	4.15	278.44
M_{15}	20.27	8.73	333.22
M_{16}	21.44	7.13	309.45
M_{17}	62.37	6.27	290.78
M_{18}	58.26	4.98	253.59
M_{19}	46.4	8.33	323.89
M_{20}	42.73	5.41	299.55
M_{21}	19.32	7.56	234.52
M_{22}	15.84	7.66	206.92
M_{23}	12.68	11.19	200.93
M_{24}	18.77	8.91	279.81
M_{25}	15.38	7.55	192.92
M_{26}	23.98	5.66	200.37
M_{27}	21.3	9.45	255.10
M_{28}	25.62	7.25	266.76
M_{29}	25.79	8.04	238.41
M_{30}	40.16	6.48	250.70
M_{31}	22.76	12.35	276.53
M_{32}	31.63	8.77	258.75
M_{33}	23.37	6.58	220.92
M_{34}	24.51	6.97	214.80
M_{35}	27.35	11.92	238.11
M_{36}	19.43	11.63	245.38

In light of the large quantity of data generated by running isothermal conduction calorimetry on the 36 clinkers obtained (see Table 4), a statistical analysis was conducted to determine the effect of each variable (LSF, CW, $CaSO_4$ and CaF_2) on the hydration reactions taking place in these new clinkers. In the experiments designed, two levels were assigned to LSF and ceramic waste and three to CaF_2 and $CaSO_4$. Table 5 lists all the variables and their respective levels.

On those grounds, the total number of experiments was: $2^2 \times 3^2 = 36$.

The response signals for the statistical analysis were time at the peak heat flow rate, T_M, and the value of the peak heat flow rate, V_M, which is associated with the mass precipitation of hydration products, primarily C-S-H gel and $Ca(OH)_2$ (see Fig. 3). The experimental T_M and V_M values for each clinker are given in Table 4.

The time at the calorimetric peak, T_M (Fig. 3), provides an indication of the time when most of the hydration reactions, and consequently hydration product precipitation, take place in the clinkers. Shorter times mean that the reactions began earlier and the hydration products precipitated sooner. The peak heat flow rate, V_M (Fig. 3), is related to the intensity of the hydration reactions and hydration product precipitation. High rates are an indication of intense hydration product precipitation. Consequently, the clinkers with the lowest T_M values and highest V_M values exhibit the highest reactivity with water.

The ANOVA technique was applied to the isothermal conduction calorimetry findings for each clinker studied (response signals T_M and V_M) to determine the statistically significant variables. Table 6 gives the P values at a 95% confidence interval. Variables and binary interactions were regarded to be statistically significant for the response chosen when their P values were under 0.05. Further to the results found when the response signal was the time at

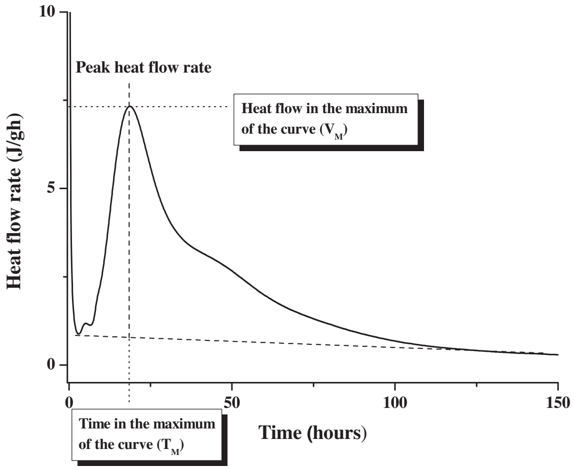


Fig. 3. Isothermal conduction calorimetric curve.

Table 6
Variable and binary interaction P-values.

Peak time (T_M)		1/peak time ($1/V_M$)	
Order of variables	Binary interaction	Order of variables	Binary interaction
$D^* > C^* > A^* > B^*$ 0.0000 = 0.0000 < 0.0079 < 0.0485	CD* 0.0004	$A^* > C^* > B^* > D^*$ 0.0000 = 0.0000 < 0.001 < 0.0040	CD 0.4159
	AD 0.3592		AD 0.8509
	BD 0.5834		BD 0.7677
	AC* 0.0611		AC 0.7053
	BC 0.5805		BC 0.2459
	AB 0.5319		AB 0.9935

Variables and binary interactions that are statistically significant at a 95% confidence level are flagged with an asterisk (*).

Table 7
Values of statistically significant variables by level when the response signals are T_M and $1/V_M$.

Variable	Symbol	T_M Level			$1/V_M$ Level		
		0	1	2	0	1	2
LSF	A	2.26	−2.26	–	0.020	−0.02	–
CW	B	−1.59	1.59	–	−0.01	0.01	–
$CaSO_4$	C	8.84	−3.97	−4.88	0.03	−0.02	-0.01
CaF_2	D	−11.71	−1.33	13.05	−0.01	0.01	0.006

the peak heat flow rate (T_M), all four variables studied (LSF (A), ceramic waste (B), the% of $CaSO_4$ (C) and the % of CaF_2 (D)) were statistically significant. Of the binary interactions, only two, $CaSO_4$–CaF_2 (CD) and LSF–$CaSO_4$ (AC) met the significance requirement.

The statistical model obtained when the response signal was the peak heat flow rate (V_M) did not appear to be assimilable in light of the behaviour of the ceramic waste. After testing a number of data transformations, reasonable results were found for an analysis of the inverse of V_M, $1/V_M$. As in the case of T_M, the four variables studied were statistically significant for $1/V_M$. None of the binary interactions among the variables proved to be statistically significant, however (see Table 6).

The isothermal conduction calorimetry data were used to calculate the equations that described the effect of the statistically significant variables on T_M (see Eq. (4)) and $1/V_M$ (see Eq. (5)), as follows:

$$T_{M(ijkl)} = 22.34 + A_i + B_j + C_k + D_l + (CD)_{kl} + (AC)_{ik} + E \quad \sigma_2 = 20.01 \tag{4}$$

$$1/V_{M(ijkl)} = 0.13 + A_i + B_j + C_k + D_l + E \quad \sigma_2 = 0.00 \tag{5}$$

where A_i is the increment above or below the mean generated by variable A or LSF at level 0 (85%) or level 1 (90%); B_j is the increment above or below the mean generated by variable B or ceramic waste at level 0 (absence of ceramic waste) or level 1 (presence of ceramic waste); C_k is the increment above or below the mean generated by variable C or% of $CaSO_4$ at level 0 (0.00% $CaSO_4$), level 1 (2.60% $CaSO_4$) or level 2 (3.90% $CaSO_4$); D_l is the increment above or below the mean generated by variable D or % of CaF_2 at level 0 (0.00% CaF_2), level 1 (0.65% CaF_2) or level 2 (1.30% CaF_2); $(CD)_{kl}$ and $(AC)_{ik}$ are, respectively, the increments above or below the mean generated by the interactions between variables C and D (% of $CaSO_4$ and CaF_2, respectively) and variables A and C, LSF-$CaSO_4$; and E is the experimental error in distribution $N(0, \sigma_2)$.

Table 7 shows the values of each statistically significant variable as defined above, by level, when T_M is the response signal. Table 8 gives the values of the statistically significant binary interactions (see Table 6), by level.

As noted earlier, the time at which the calorimetric signal peaks is associated with the maximum precipitation of hydration products. If the hydration reactions take place quickly, the peak time should be short. Variable levels with negative values obviously have a favourable effect on the time at the peak heat flow rate (T_M), which is shortened. Further to that logic and the values of the variables and levels in Table 7, an LSF of 90% (level 1), the absence of ceramic waste (level 0), the addition of both percentages of $CaSO_4$ to the mix (levels 1 and 2) and the absence of CaF_2 (level 0) and ceramic waste (level 0) reduced the T_M value.

Eq. (4) and the values for the variables and levels were used to identify the 36 possible experimental conditions. The most favourable were found for clinkers M_7, M_{11} and M_9, as shown below.

M_7-CaF_2 = 0.00 (level 0), $CaSO_4$ = 2.60% (level 1), LSF = 90% (level 1) and no ceramic waste (level 0).
M_{11}-CaF_2 = 0.00 (level 0), $CaSO_4$ = 3.90% (level 2), LSF = 90% (level 1) and no ceramic waste (level 0).
M_9-CaF_2 = 0.00 (level 0), $CaSO_4$ = 3.90% (level 2), LSF = 85% (level 0) and no ceramic waste (level 0).

Table 7 also shows the values that each statistically significant variable may adopt (see Table 6) for $1/V_M$, depending on its level. The peak heat flow rate on the calorimetric curve is associated with the mass precipitation of hydration products. The higher peak intensity, which is indicative of substantial precipitation of hydration products, the lower the $1/V_M$ value. Variable levels with negative values in the $1/V_M$ equation lower $1/V_M$ and raise the peak heat flow rate, V_M. Further to the values in Table 6, 90% LSF (level 1), the

Table 8
Values of binary interactions between statistically significant variables by level.

Level	Binary interaction value	
	CD	AC
00	−3.14	2.63
10	1.73	−2.63
20	1.41	–
01	−5.05	−0.68
11	−3.85	0.68
21	5.44	–
02	8.19	−1.94
12	−1.34	1.94
22	−6.85	–

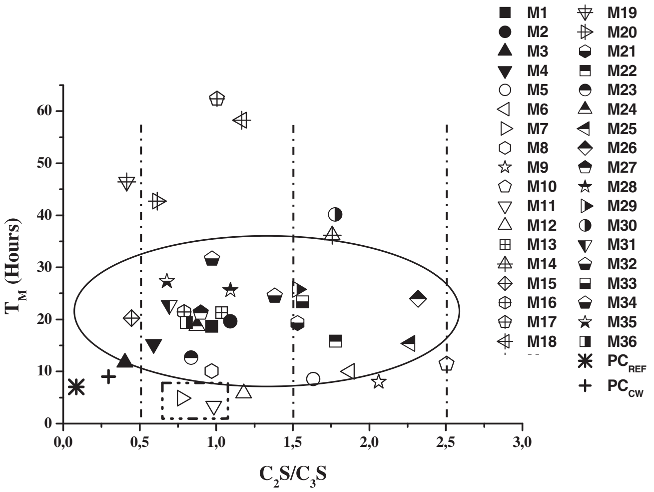


Fig. 4. T_M versus C_2S/C_3S.

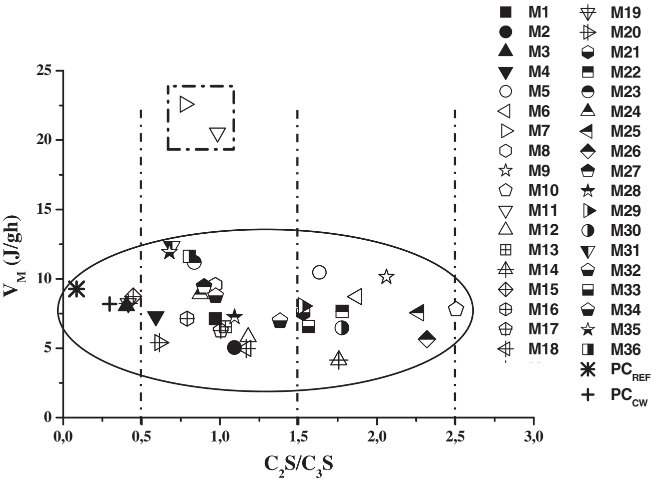


Fig. 5. V_M versus C_2S/C_3S.

absence of ceramic waste (level 0), the addition of $CaSO_4$ (levels 1 and 2) and the absence of CaF_2 (level 0), contributed to lowering $1/V_M$ and therefore to raising the peak heat flow rate.

The values in Table 7 and the equation obtained for $1/V_M$ (see Eq. (5)) can be used to obtain the most favourable experimental conditions, which were as shown below.

M_7-$CaF_2 = 0.00$ (level 0), $CaSO_4 = 2.60\%$ (level 1), LSF = 90% (level 1) and no ceramic waste (level 0).

M_{11}-$CaF_2 = 0.00$ (level 0), $CaSO_4 = 3.90\%$ (level 2), LSF = 90% (level 1) and no ceramic waste (level 0).

The T_M and V_M values obtained with isothermal conduction calorimetry (see Table 4) are compared to the silicate phase ratio (C_2S/C_3S) in the clinkers in Figs. 4 and 5.

Fig. 4 shows the relationship between T_M and the silicate phase content, C_2S/C_3S. According to these findings, the times at the peak calorimetric signal for clinkers made with $CaSO_4$ or the fluxing/mineralised pair and having a C_2S/C_3S ratio of 1.5–2.5, and a C_2S content of 35–60% (M_5, M_6, M_9, M_{10}, M_{14}, M_{21}, M_{22}, M_{25}, M_{26}, M_{29}, M_{30} and M_{33}) were comparable to the times for clinkers with lower C_2S contents (C_2S/C_3S of under 1.5) These shorter hydration times may be associated with the stabilisation of a more reactive β-C_2S polymorph due to the addition of $CaSO_4$ to the raw mix. Nonetheless, the clinkers obtained with 1.30% CaF_2 (M_{17}–M_{20}) that had a C_2S/C_3S ratio of 0.5–1.5 exhibited higher T_M values than the clinkers with a C_2S/C_3S ratio of 0.5–1.5, perhaps because the hydration reactions in these clinkers were initially inhibited.

Fig. 5 shows the relationship between V_M and the C_2S/C_3S ratio. V_M was not affected by clinker mineralogical composition, for the values were similar for all the clinkers, including PC_{REF} and PC_{CW}.

Clinkers M_7 and M_{11} had slightly lower T_M and V_M values than PC_{REF} ($C_2S = 3.6$) and PC_{CW} ($C_2S = 16.1$), despite the fact that their C_2S contents in the clinkers were much higher: 36.3% for M_7 and 41.9% for M_{11} (see Fig. 1). As noted earlier, this better performance in terms of hydration rate in both clinkers may be associated with the stabilisation of a more reactive form of β-C_2S resulting from the presence of $CaSO_4$ in the raw mix. The present findings show that belite clinkers (with C_2S contents of over 40%) can be obtained with hydration rates comparable to the rates in clinkers with C_2S contents of under 20%.

4. Conclusions

The main conclusions to be drawn from the present study are set out below.

1. Clinkers with a high C_2S content (36% and 60%) can be obtained at 1350 °C from raw mixes containing ceramic waste and the fluxing/mineralised pair $CaF_2/CaSO_4$. The highest percentages of C_2S were observed in clinkers obtained from raw mixes having a LSF of 85%, ceramic waste and 3.90% (wt. of raw mix) $CaSO_4$.
2. The variables studied (LSF, ceramic waste, % CaSO4 and % CaF_2) affected both clinker mineralogical composition and C_2S polymorphism:
   - The presence of ceramic waste in the raw mix raised the C_2S content by favouring the stabilisation of the α'_H-C_2S polymorph.
   - Adding (2.60 or 3.90 wt%) $CaSO_4$ to the raw mix increased the β-C_2S polymorph content, inhibiting C_3S formation. Moreover, the addition of $CaSO_4$ stabilised β-C_2S, inhibiting the stabilising effect of the ceramic waste on the α'_H-C_2S polymorph.
   - The presence of CaF_2 in the raw mix did not significantly modify the silicate phase content, although it did affect the aluminate and ferritic phase content in the clinker.
   - The addition of the fluxing/mineralised pair $CaF_2/CaSO_4$ revealed the joint effect of adding CaF_2 and $CaSO_4$ to the raw mix separately.
3. A statistical analysis of the isothermal conduction calorimetry data showed that when the response signal was the time at the peak signal on the heat flow rate curve, the statistically significant variables for a 95% confidence level were: CaF_2, $CaSO_4$, LSF and ceramic waste. The binary interactions CaF_2–$CaSO_4$ and $CaSO_4$-ceramic waste were likewise significant. When the response signal was the inverse of the peak heat flow rate, the statistically significant variables for a 95% confidence level were LSF, $CaSO_4$, ceramic waste and CaF_2. No binary interactions existed when the response signal was $1/V_M$.
4. The experimental conditions used to produce clinker M_7 led to the best results for the response signals T_M and $1/V_M$. The variable levels for this clinker, which contained 36.3% C_2S and 46.8% C_3S, were: $CaF_2 = 0.00$ (level 0); $CaSO_4 = 2.60\%$ (level 1); LSF = 90% (level 1) and no ceramic waste (level 0). Clinker M_{11} also exhibited low T_M values, although it had a lower peak heat flow rate than M_7. Here the variable levels were $CaF_2 = 0.00$ (level 0); $CaSO_4 = 3.90\%$ (level 1); and no ceramic waste (level 0). The C_2S and C_3S contents in this clinker were 41.9% and

42.5%, respectively. The T_M and V_M values in clinkers M_7 and M_{11} were observed to be comparable to the values for conventional Portland cement containing 3.6% C_2S.

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