

Use of industrial wastes for the synthesis of belite clinker

M.K. Enríquez^a, J.I. Tobón^b✉, J.H. Ramírez^a

a. Materials Catalysis & Environmental Group, Department of Chemical and Environmental Engineering,
Universidad Nacional de Colombia, (Bogota, Colombia)

b. Cement and Building Materials Research Group, Departamento de Materiales y Minerales,
Facultad de Minas, Universidad Nacional de Colombia, (Medellín, Colombia)

✉: jitobon@unal.edu.co

Received 18 October 2019
Accepted 30 March 2020
Available on line 26 June 2020

Abstract: The synthesis of belite clinker was studied using industrial wastes: paper sludge, cement kiln dust and rice husk ashes, as substitutes for natural raw materials. Wastes were characterized by XRF, XRD and TG analysis. Different formulations were prepared to produce clinker at 1300, 1350 and 1400 °C. The clinker obtained was characterized using optical microscopy, XRD and *f*-CaO content determined by ethylene glycol method. Finally, the hydration of prepared cements with the clinkers was evaluated by isothermal microcalorimetry. It was found that by mixing paper sludge, cement kiln dust and rice husk ashes, it is possible to obtain belite clinker with *f*-CaO content below 0.5%, in clinkering temperatures between 1350 °C and 1400 °C without the use of natural raw materials. It was found that these cements have a high hydration kinetic, far above the rate of Ordinary Portland Cement, due mainly by the amorphous phase content in clinkers obtained.

Keywords: Clinkering; Belite cement; Belite reactivity; Industrial waste; Cement hydration.

Citation/Citar como: Enríquez, M.K.; Tobón, J.I.; Ramírez, J.H. (2020) Use of industrial wastes for the synthesis of belite clinker. *Mater. Construcc.* 70 [339], e226 <https://doi.org/10.3989/mc.2020.14219>

RESUMEN: *Aprovechamiento de residuos industriales para la síntesis de clínker belítico.* En el presente trabajo se estudió la síntesis de clínker belítico usando residuos industriales: lodo papelerero, polvo de horno de cemento y ceniza de cascarilla de arroz, como sustitutos de las materias primas naturales. Los residuos se caracterizaron mediante FRX, DRX y TGA. Se prepararon formulaciones para producir clínker a 1300, 1350 y 1400 °C. El clínker se caracterizó usando microscopía óptica, DRX y *f*-CaO. Finalmente, se evaluó la hidratación de cementos preparados a partir de los clínkeres obtenidos. Se encontró que, con lodo papelerero, polvo de horno de cemento y ceniza de cascarilla de arroz, es posible obtener clínker belítico con contenidos de *f*-CaO ≤ 0,5%, a temperaturas entre 1350 y 1400 °C sin el uso de materias primas de origen natural. Se encontró una alta cinética de hidratación, muy por encima de la velocidad de hidratación de un cemento Portland convencional, principalmente debido al contenido de fase amorfa en los clínkeres obtenidos.

PALABRAS CLAVE: Clinkerización; Cemento belítico; Reactividad de la belita; Residuos industriales; Hidratación de cemento.

ORCID ID: M.K. Enríquez (<https://orcid.org/0000-0002-1697-0998>); J.I. Tobón (<https://orcid.org/0000-0002-1451-1309>); J.H. Ramírez (<https://orcid.org/0000-0003-1766-1174>)

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1. INTRODUCTION

Industrial activities contribute significantly to the generation of wastes; due to the lack of planning and ignorance of processes which they can be used, most of the wastes are destined for final disposal. For example, in the cement industry, a solid waste known as cement kiln dust (CKD) corresponds to 3-4% of the total cement produced, which by 2019 reached a world total production of 4.2 billion tons (1).

Recent research reports the use of CKD as a mineral addition to cement, finding satisfactory results (2-5). At the same time, research have been conducted with another type of wastes that are used in the manufacture of construction materials. An example of this, is the use of rice husk ash, which due to its high content of reactive silicon dioxide (SiO_2) provides satisfactory results on mechanical characteristics of the cement-base materials (5-7).

Other authors (8-11), reveal satisfactory results on the use of paper sludge as secondary material in clinker production. In this regard, it should be taken into account that in the production of clinker for Portland cement, the extraction of large quantities of raw materials (mainly limestone and clay) is required. It is estimated that 1.7 tons of raw materials are needed to produce 1 ton of clinker (11) and during the manufacturing process, for every ton of Portland cement, up to 0.97 tons of CO_2 are released; therefore, it is estimated that the cement industry is responsible for between 6 and 7% of the global anthropogenic CO_2 emission (12, 13).

The environmental impact associated with the extraction of raw materials, added to the important CO_2 emissions related mainly to the decarbonation of limestone and the high energy consumption, supplied mostly with fossil fuels, makes research in this sector to be oriented towards the design and manufacture of alternative cements which required less energy for their production. An alternative is replacing conventional fuels and raw materials in order to reduce CO_2 emissions (14).

In this regard, it has been investigated the possibility of producing cement with lower demands of calcium carbonate, for which low lime saturation factor (LSF) is handled, this is associated with the higher contents of belite phase in the clinker. It is estimated that the production of this type of belite cement requires 15 to 20% less energy compared to the production of alite cement, what is beneficial due to the cost of energy and the reduction of CO_2 emissions (15, 16).

Consequently, the environmental benefit of belite cements over OPC cements mainly are the increase in energy savings, the reduction in the burning temperature and the decrease in CO_2 and NO_x emission levels (17).

However, compared to the use of OPC cements, belite cements generally have less

hydraulic activity during the first hours of hydration, so that research focuses on the use of additives that improve hydraulic activation, the use of "remelting reaction" and the "sol-gel method". Nevertheless, these methods are not widely used on an industrial scale (18).

In the same way, there are studies in which some methodologies are implemented, by which raw materials required in the manufacture of cement are partially replaced (11, 19-21). For these replacements, waste from the thermoelectric, steel, paper and ceramic industries, among others, are implemented (22).

In accordance with this, in the present research work, it is of interest the evaluation of the total substitution of raw materials required in the production of belite clinker by using three types of industrial waste: paper sludge (PS), cement kiln dust (CKD) and rice husk ash (RHA). The objective of this research is the reduction of primary resources, energy demand and CO_2 emission in the clinker production, providing value of this type of by-products, that is currently not widely used. On the other hand, with the obtaining of the belite clinker, lower consumption of CaCO_3 will be obtained and lower temperatures will be required, which results in lower energy consumption and a decrease in CO_2 emissions.

2. MATERIALS AND METHODS

2.1. Materials

For clinker preparation, the mixture of three wastes generated in different industries was used: (i) paper sludge (PS); (ii) cement kiln dust (CKD) and (iii) rice husk ashes (RHA). The PS comes from the tissue paper industry; in this process, limestone (CaCO_3) and kaolin are added to fulfill the filler function, which are concentrated in the paper sludge. The CKD is generated in the production of cement, where part of the limestone has an incomplete reaction and the finest dust is carried by the air stream (23). The RHA comes from burning the rice husk.

The paper sludge was previously calcined at 800 °C, the CKD and RHA were dried at 105 °C. The residues were milled and sieved (< 90 μm) individually.

2.2. Clinker preparation

Using the tool Solver, the mixing ratios of the residues were calculated, in order to prepare three formulations (Table 1) with the following objectives: (i) replacing 100% of natural raw materials and (ii) achieving a belite clinker composition with a high content of alite. This, from the chemical composition of the residues, using the Bogue equations and

TABLE 1. Mixtures composition (wt. %).

Formulation	PS	CKD	RHA	LSF	SM	AM
F1	20.27	68.79	10.94	95	2.20	2.13
F2	26.17	63.90	9.92	100	2.10	2.32
F3	25.37	65.65	8.98	104	2.00	2.28

TABLE 2. Chemical composition of residues determined by XRF.

(wt %)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	Cl	SO ₃	LOI*
PS	29.28	13.50	3.37	0.38	0.60	0.59	0.06	0.11	0.16	0.04	0.16	51.69
CKD	59.48	9.76	5.18	3.73	0.69	0.24	0.88	0.35	0.29	0.22	0.87	18.12
RHA	0.87	88.28	0.07	0.09	0.72	0.04	3.11	2.04	---	0.54	0.86	3.15

* LOI: loss on Ignition at 800 °C

the lime saturation factor (LSF; Equation [1]) in a range between 95 and 104, so that the contribution of calcium oxide (CaO) was enough for the reactions to occur, without large amounts of CaO remaining in excess. On the other hand, the variation in the proportion of waste was taken into account and thus maintain appropriate values for the Silicon Module (SM; Equation [2]) and the Aluminum Module (AM; Equation [3]) (19).

$$LSF = \frac{100 * C - 0.7SO_3}{2.8 * S + 1.18 * A + 0.65 * F} \quad [1]$$

$$SM = \frac{S}{A + F} \quad [2]$$

$$AM = \frac{A}{F} \quad [3]$$

Each formulation was burned in a fixed bed electric oven (Carbolite model BLF 17/3). The heating ramp to obtain the clinker involved the following stages: (i) heating at 10 °C/min up to 800 °C; (ii) residence time for 30 minutes at 800 °C to promote complete decarbonation; (iii) heating at 10 °C/min to the maximum temperature: 1300, 1350 or 1400 °C; (iv) remain 45 minutes at the maximum temperature to promote complete clinkering and (v) forced convection cooling.

2.3. Residues characterization

The by-products were characterized in terms of moisture content and ignition losses (EN12880:2001) (24). In the case of the paper sludge (PS), the mass changes were analyzed as a function of temperature using a TGA equipment (TGA 1 START System Mettler Toledo). This analysis was performed in the temperature range of 25 to 1000 °C, using an

alumina crucible without lid of 70 µL volume. During the experiments, the Air-Nitrogen gas mixture was used to ensure an inert atmosphere. The gas flow was set at 50.0 mL/min and a heating ramp of 10 °C/min was programmed.

The chemical composition of the residues, presented in Table 2, was determined by X-ray fluorescence spectrometer (MagixProw PW-2240 Philips). The mineralogical composition of the wastes was determined by X-ray diffraction using the equipment PANalytical Xpert-Pro vs 1.9 with a copper X-ray tube, which operates at a voltage of 45 kV and a current of 40 mA. Data were collected in the 2θ range from 5° to 90°. In order to determine the content of amorphous material, quantification was performed by the Rietveld method, using a 25% internal standard of zinc oxide (ZnO) of high purity. The data obtained were analyzed by the software X'pert HighScore Plus (PDF-2 Release 2004 database; COD_2013 223339).

2.4. Clinker characterization

The chemical and mineralogical composition were studied as described above for the residues. The content of free lime (f-CaO) in clinker samples was determined by means of the ethylene glycol method (25). In order to identify the formed phases, polished sections were prepared to be observed under the conventional polarized light optical microscope and with the reflected light method. The polished sections were attacked with 1% of Nital and observed in an Olympus microscope, model BX41. Likewise, the distribution of the phases and the microstructure of the clinker were analyzed by SEM/EDS. With this purpose, the polished sections were coated with graphite and subsequently observed in a scanning electron microscope FEI-ESEM-Quanta 200.

2.5. Heat flow during hydration

Clinker samples were milled and sieved ($< 45 \mu\text{m}$). Cement samples were prepared in proportion 95% wt of each clinker obtained and 5% wt of calcium sulfate dihydrate. A water/cement ratio of 0.55 was used. Heat flow was evaluated during cement hydration by conduction micro calorimetry, using a TAM Air microcalorimeter with an isothermal method and an air thermostat fixed at 25 °C. The samples were filled in glass ampoules and placed inside the kit for 40 minutes to achieve thermal stability. Then, the water injection was performed with a mixing device (admix), it was homogenized for two minutes. Finally, data were collected for a period of 120 hours.

3. RESULTS AND DISCUSSION

3.1. Wastes characterization

The PS contains a humidity of 48.20%, while the CKD and RHA, due to their generation in thermal processes, have much lower contents; 0.65% and 1.65% respectively.

Table 2 shows the chemical composition of residues. The PS comes from the tissue paper industry; in this process, limestone (CaCO_3) and kaolin are added to fulfill the filler function, which are concentrated in the paper sludge. Consequently, the XRF analysis of the sludge shows that it mainly contains 29.28 wt% of CaO, 13.50 wt% of SiO_2 and 3.37 wt% of Al_2O_3 . The LOI value of 51.69 wt% (Table 2) is consistent with the value of the total mass loss which was found by means of the thermogravimetric analysis (TGA) (Figure 1), that associates the decarbonation of calcite and possible dehydroxylation of the clays present in the paper sludge. The XRD pattern of the PS (Figure 2a) shows the presence of the calcite as crystalline phase (C) in 64.3%. No other diffractable minerals

were identified and the amorphous phase was estimated at 35.7% (Rwp 9.1%).

The analysis of rice husk ash (RHA) shows that it is mainly composed of SiO_2 ; moreover, it contains 3.11 wt% of K_2O , which may come from traces of fertilizers applied in rice cultivation. In XRD pattern of RHA (Figure 2b) the crystalline cristobalite (CB) phase is present in 46.7% and an amorphous content of 53.3% (Rwp 8.6%).

The XRD pattern of the CKD (Figure 2c) is consistent with its detected chemical composition: 92.8% calcite (C), 4.1% quartz (Q) and 3.1% of amorphous content (Rwp 6.5%).

Because the PS have higher losses on ignition (LOI), the thermogravimetric behavior of this residue was studied. In Figure 1, two changes of slope are observed, which indicate two different thermogravimetric events, represented in the temperature ranges: 300-400 °C and 650-750 °C. These events are associated with different stages of mass loss. In the first interval, a mass loss of approximately 30% occurs. The variation of the curve in TG analysis in this interval is interpreted as an effect of decomposition of the clays present in the PS (26, 27) and organic matter. In the next interval, a mass loss of approximately 30 wt% is observed and it is interpreted as an effect of decarbonation of the material, given that during paper manufacture, calcium carbonate CaCO_3 is used as a filler to improve the quality.

3.2. Mixtures formulations

Table 3 shows the results of the analysis of the chemical composition of the formulations, prepared according to the mixing ratios presented in Table 1. Formulations contain mainly CKD (65-69%), paper sludge (20-25%), and to a lesser extent in the rice husk (10%), all percentages by weight. In general, the formulations had low alkali contents, being beneficial in the clinkering process (28, 29).

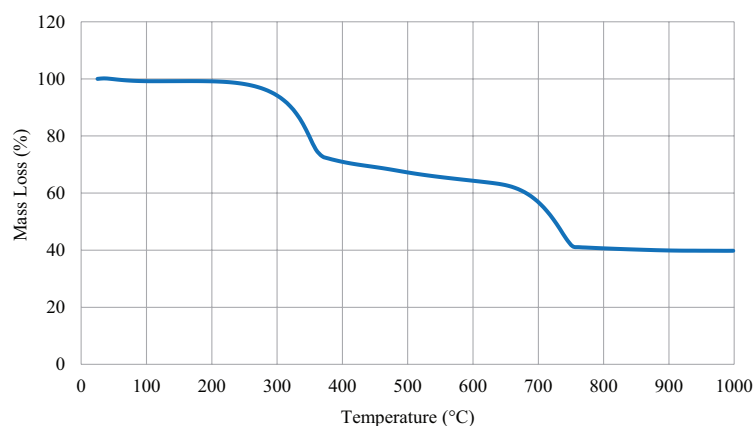


FIGURE 1. Result of the TG analysis of paper sludge (PS).

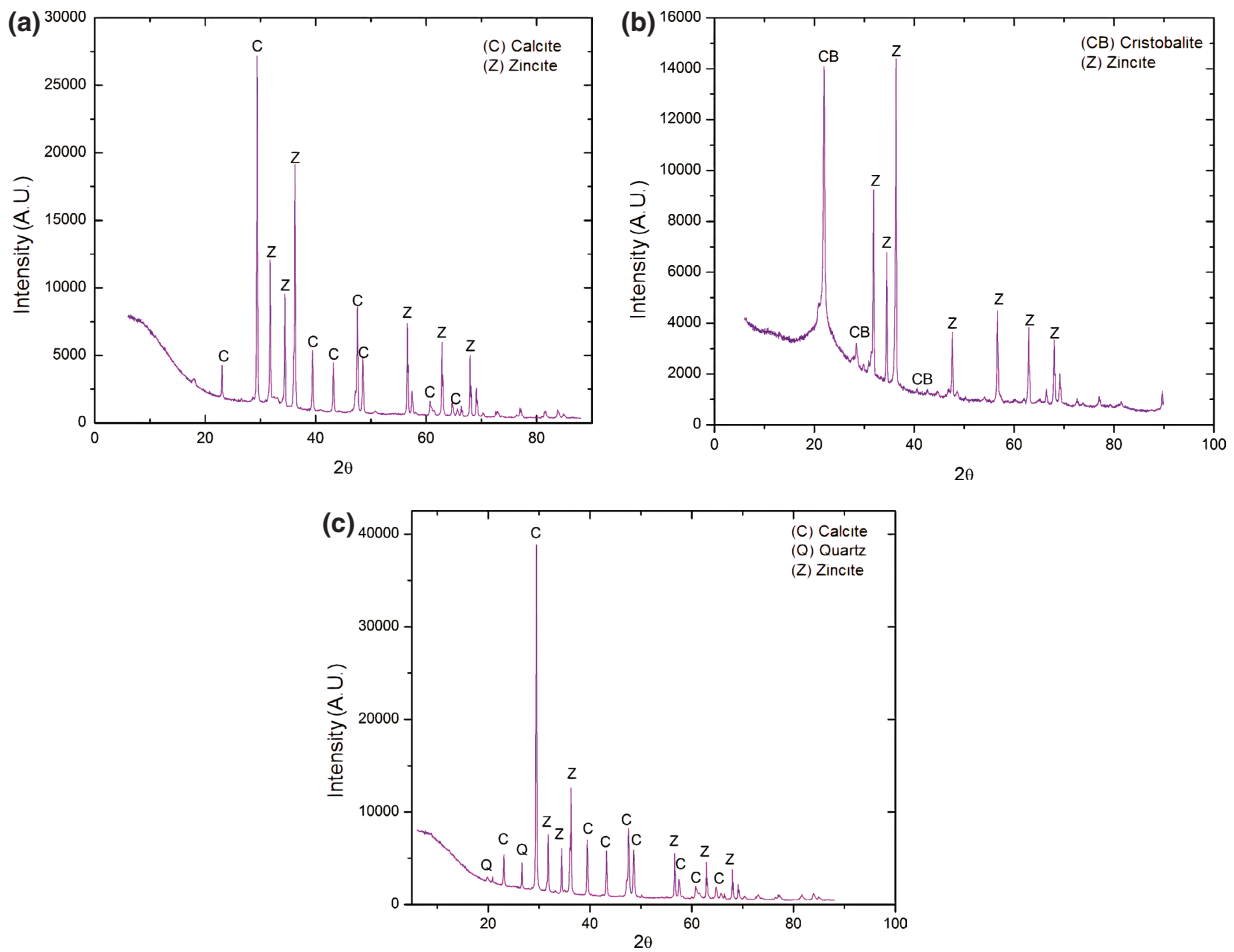


FIGURE 2. XRD patterns (a) paper sludge, (b) rice husk ash and (c) CKD.

TABLE 3. Chemical composition of each formulation XRF.

(wt%)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	Cl	SO ₃	LOI
F1	55.10	17.82	4.88	2.39	0.71	0.43	1.46	0.45	0.28	0.72	0.77	14.79
F2	53.22	16.33	5.10	2.44	0.71	0.35	1.14	0.36	0.30	0.65	0.76	18.42
F3	54.14	15.65	5.08	2.44	0.70	0.33	1.19	0.39	0.31	0.59	0.76	18.21

TABLE 4. *f*-CaO content in each obtained clinker.

	F1			F2			F3		
T (°C)	1300	1350	1400	1300	1350	1400	1300	1350	1400
% <i>f</i> -CaO	1.07	0.47	0.40	1.06	0.33	0.32	1.52	0.40	0.33

3.3. Clinker characterization

3.3.1. Quantification of free lime (*f*-CaO) in each clinker.

The percentage of free lime (*f*-CaO) was established as a response variable of clinkering

degree. According to the results in Table 4, lower *f*-CaO are observed at 1350 °C and 1400 °C. Moreover, at these temperatures, close values of *f*-CaO are found in formulations F2 and F3, which do not exceed 0.47%; this means that the CaO available in the mixtures reacts during clinkering.

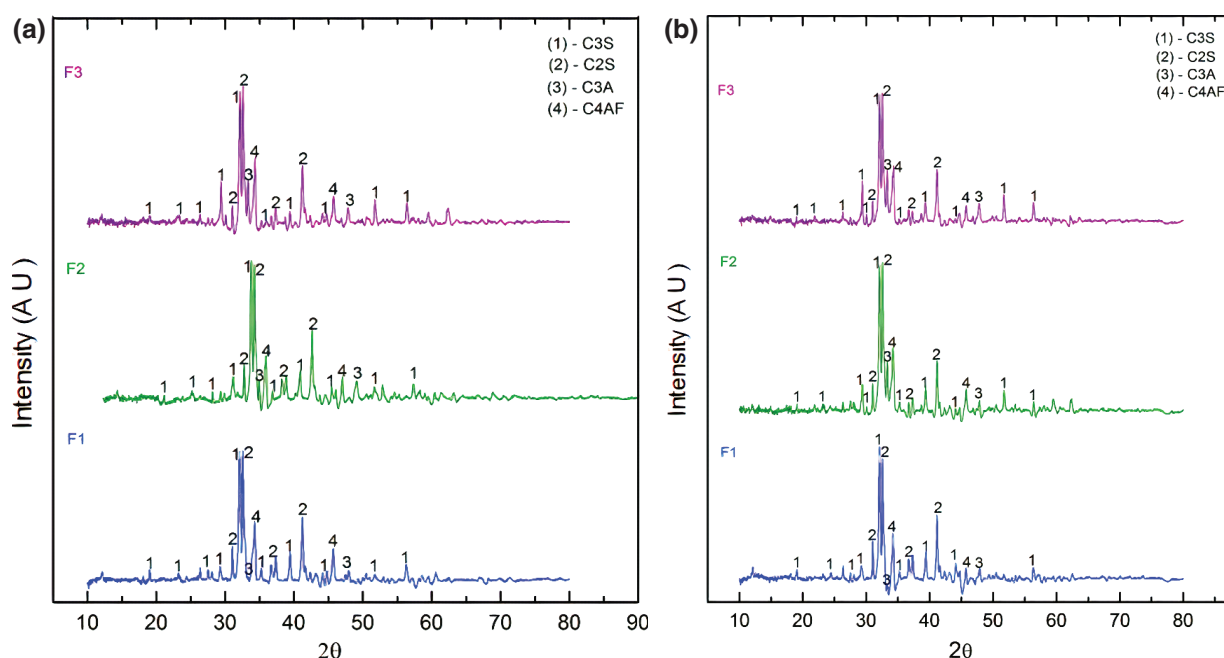


FIGURE 3. Clinker XRD. (a) Clanking temperature 1350 °C, (b) Clanking temperature 1400 °C. C₃S (ICDD 01-086-0402), C₂S (ICDD 01-077-0409), C₃A (COD 96-100-0040), C₄AF (COD 96-900-3337).

TABLE 5. Mineralogical analysis of clinker (% wt.) through Rietveld.

Temperature (°C)	Formulation	C ₃ S (Monoclinic)	C ₂ S (Beta)	C ₃ A (Cubic)	C ₄ AF	Amorphous	Rwp
1350	F1	8.7	50.9	4.3	3.9	32.2	9.0
1400	F1	10.3	29.5	0.5	1.3	58.4	9.3
1350	F2	9.5	46.7	8.0	3.3	32.5	8.4
1400	F2	10.3	27.7	2.6	1.4	58.0	8.9
1350	F3	9.3	43.5	14.4	2.9	29.9	8.9
1400	F3	12.5	24.0	3.0	1.8	58.7	8.6

3.3.2. Quantification of phases.

Through the Rietveld refinement it was identified and quantified the presence of the alite (C₃S), belite (C₂S), celite (C₃A) and felite (C₄AF) phases (30–32) in the obtained clinker at temperatures 1350 and 1400 °C. The diffractograms of each clinker are shown in Figure 3 and the quantitative analysis of phases is presented in Table 5. In general, it was found that belite phase predominates with percentages between 24.0 and 50.09%. There are also important contents of the amorphous phase between 29.9 and 58.4%, which may be a consequence of the content of the amorphous phase that was present in the raw materials; with what it is expected to have a high reactivity cement. The results also highlight that the content of belite decreases while increasing temperature. The increase in temperature favors the formation of alite phase, however, this phase is below 13% for all formulations and temperatures

that were evaluated. In order to verify this trend at higher temperatures, a clanking test was carried out at 1450 °C, encountering the problem that the clinker was completely melted compromising the integrity of the crucible. This was attributed to the large amount of amorphous material present in the waste used as raw materials.

3.3.3. Microscopic analysis

The formation of the mineralogical phases of clinker was confirmed by means of optical microscopy analysis (Figure 4). Mainly the formation of the belite phase was detected (Figure 4a), which corresponds to rounded granules with average sizes between 6.9–9.2 μm. Some grains of the alite phase that correspond to elongated crystals, whose size is in the range 8.8 – 18.6 μm, are also detected. The normal size of the alite phase is usually between 20–30 μm and the normal size of the belite is between

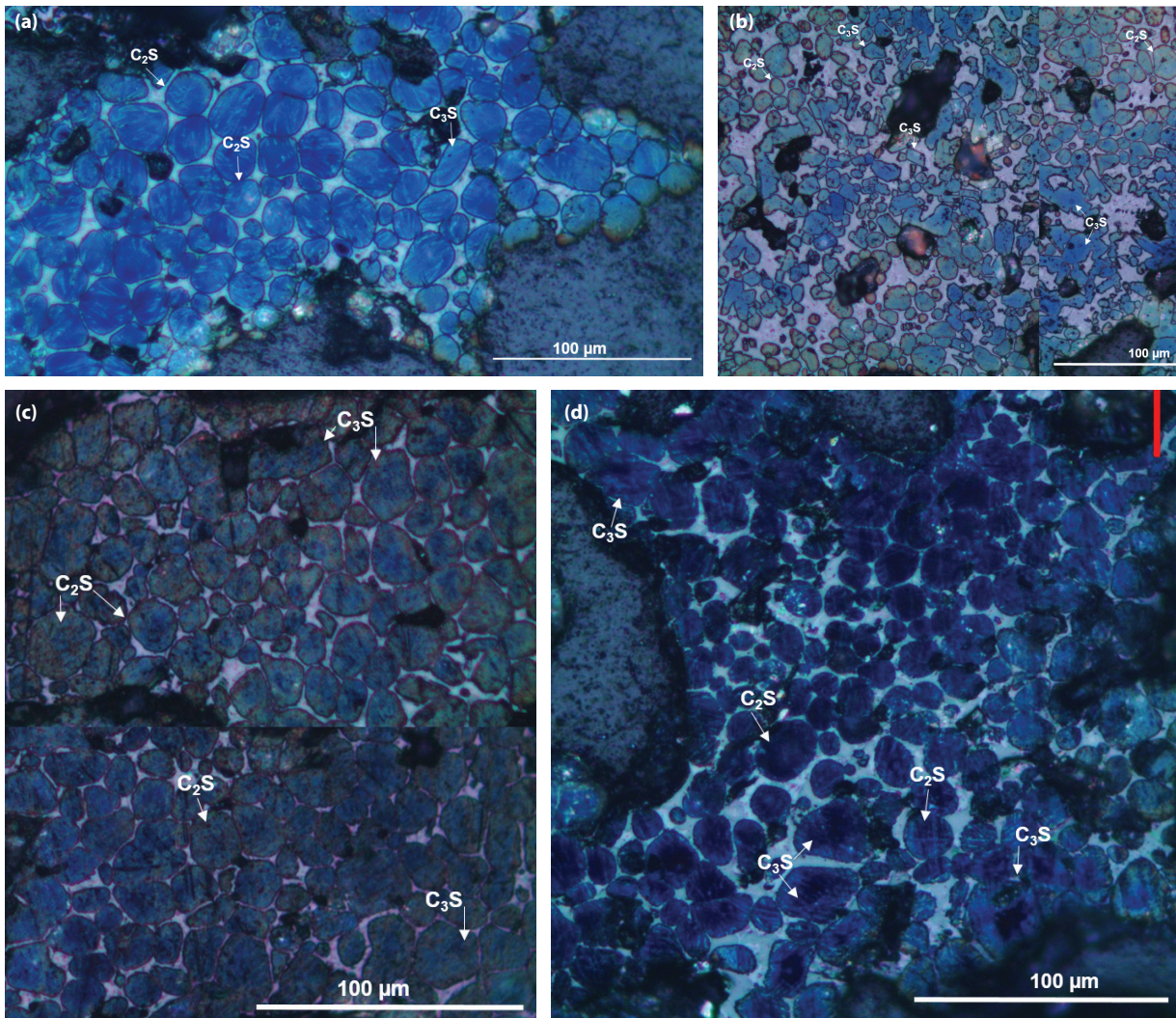


FIGURE 4. Clinker optical microscopy (a) Clinker F1 at 1350 °C, (b) Clinker F2 at 1350 °C, (c) Clinker F1 at 1400 °C and (d) Clinker F2 at 1400 °C.

TABLE 6. Average size of alite and belite in the obtained clinker.

Average size	F1		F2		F3	
	1350 °C	1400 °C	1350 °C	1400 °C	1350 °C	1400 °C
C ₃ S (µm)	10.0 ± 1.6	18.6 ± 2.3	8.8 ± 1.5	12.9 ± 1.4	12.6 ± 1.2	13.5 ± 3.1
C ₂ S (µm)	7.2 ± 2.3	7.8 ± 1.6	7.2 ± 1.4	6.9 ± 1.6	8.1 ± 1.1	9.2 ± 2.2

10 – 20 µm (25, 33). According to the data reported in Table 6, the average size of the crystals, calculated through the measurement of the diameter of 50 crystals, was found to be in a smaller range than normal size, even at the clinkering temperature of 1400 °C (Figure 4 c, d). In general, there is no presence of free lime and as for the interstitial phase, it is evenly distributed, surrounding all the crystals. There is no great crystallization of the celite and felite phases, which indicates proper cooling.

On the other hand, the polished clinker sections were coated with a graphite layer of 8 nm, and analyzed in a scanning electron microscope (SEM) equipped with an x-ray spectrometer (EDS). Figure 5 shows mainly the identification of the belite phase (C₂S). Likewise, it is possible to detail the rounded shape of C₂S, the distribution and size of the crystals. The crystals are surrounded by liquid (interstitial phase IP), which means that samples correspond to a clinker of good reactivity (34).

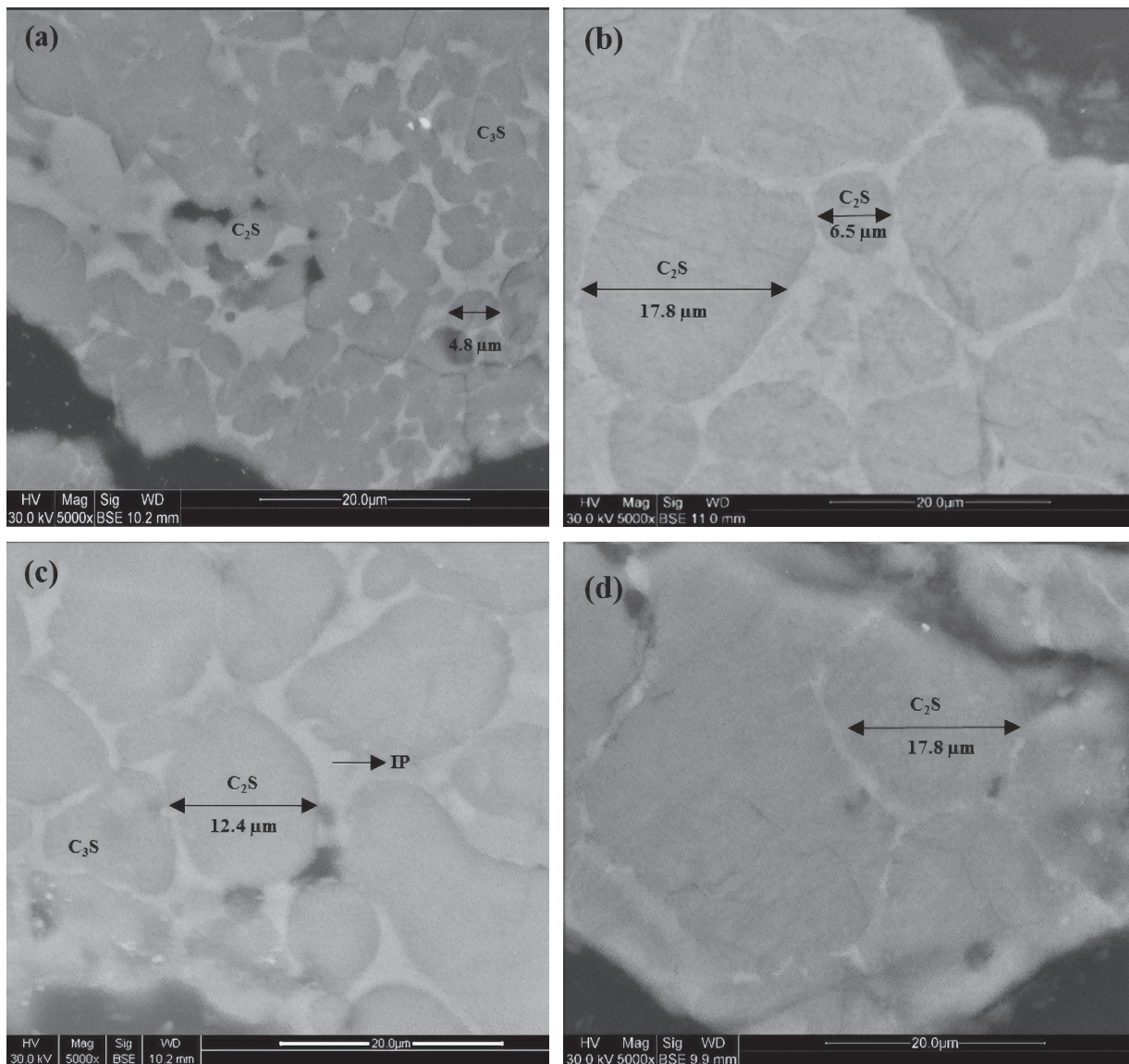


FIGURE 5. Clinker electron microscopy (a) Clinker F1 at 1350 °C, (b) Clinker F2 at 1400 °C, (c) Clinker F3 at 1350 °C and (d) Clinker F3 at 1400 °C.

In Table 7, the chemical composition of the phases alite, belite and interstitial phase is presented. It is highlighted that mainly for the F1 formulation, in the case of the belite phase, potassium (K) contents are identified in a proportion greater than 0.75%; at this content negative effects on the alite phase formation are observed according to Kolovos et al (28). This is due to the increase in the viscosity of the liquid phase, which negatively affects the reaction of belite (C_2S) with CaO to form alite (C_3S) (35). Similarly, sulfur (S) contents are greater than 0.5% in the belite phase, what causes an effect of stabilization in the belite phase, preventing conversion to alite phase (36). This reaffirms the reason why the clinkers obtained are of the belite type.

3.4. Microcalorimetric evaluation

Figure 6 shows the heat evolution curves for the hydration of cements prepared from the clinker obtained at 1350 °C with a w/c ratio of 0.55. The microcalorimetric response indicates two peaks: the first peak (Figure 6a) is caused by the release of heat associated with the dissolution of cement in water; the second peak (Figure 6b) is related to the formation of C-S-H and $Ca(OH)_2$ through the hydration of calcium silicates (37, 38).

Among the heat flow curves corresponding to the first peak, it is found that in the case of C2 cement, more heat is released in the first minutes of hydration. In addition, for C2, a second peak is not found,

TABLE 7. Chemical composition of the alite (C_3S), belite (C_2S) and interstitial phases (IP), by means of de SEM/EDS (wt%).

Element	Formulation F1						Formulation F3					
	1350 °C			1400 °C			1350 °C			1400 °C		
	C_3S	C_2S	IP	C_3S	C_2S	IP	C_3S	C_2S	IP	C_3S	C_2S	IP
Ca	65.07	63.82	63.35	58.59	60.92	50.45	63.44	65.86	62.50	68.57	46.08	66.66
Si	16.01	15.77	3.81	16.86	13.81	7.84	14.98	17.62	12.81	16.43	16.61	14.63
Al	1.67	1.86	3.11	1.74	1.92	10.36	3.43	2.17	5.36	1.65	6.95	2.20
Fe	1.63	1.14	17.04	1.67	0.00	12.20	2.23	1.49	3.74	0.00	2.88	2.09
P	0.59	1.52	0.81	1.13	1.60	0.97	0.83	0.88	0.59	0.56	0.90	1.07
Mg	1.05	0.24	0.55	1.06	0.33	2.89	1.15	0.00	0.48	0.00	1.59	0.57
K	0.60	0.79	0.88	0.91	0.49	0.68	0.61	0.00	0.69	0.81	1.30	0.54
S	0.56	0.94	0.47	0.74	0.82	0.98	0.57	0.00	0.00	0.56	1.38	0.54
Na	0.53	0.00	0.00	0.73	0.00	0.67	0.57	0.00	0.00	0.00	1.05	0.00

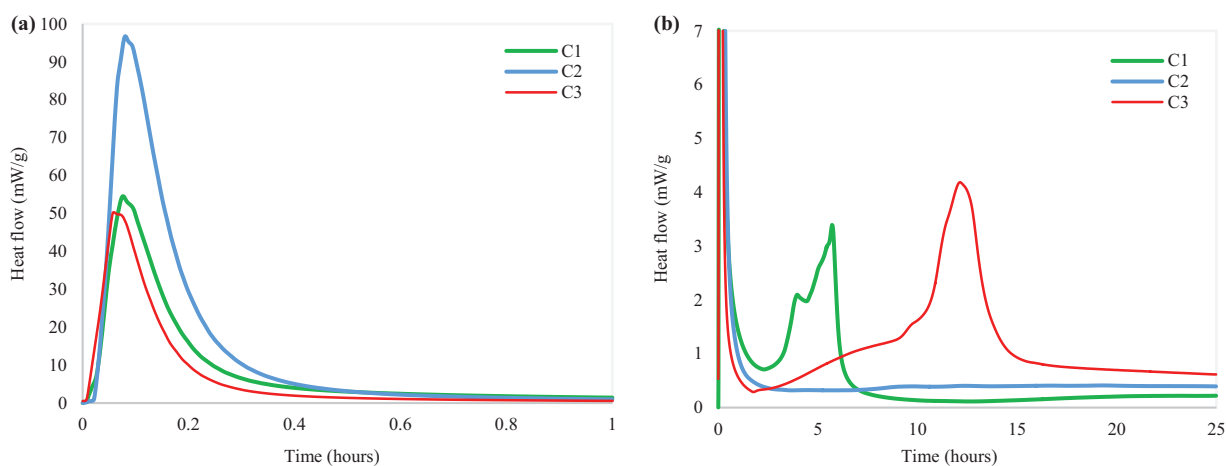


FIGURE 6. Microcalorimetry of cements prepared from clinker obtained at 1350 °C, (a) First peak; (b) Second peak.

TABLE 8. Heat flows in the hydration of prepared cements from each clinker formulation at 1350 °C.

ID	Formulation	First peak Area $t=0-0.99$ h	Second peak Area $t=1-25$ h	$Q_{\text{accum } t=2 \text{ h}}$ (J/g)	$Q_{\text{accum } t=100 \text{ h}}$ (J/g)
C1	F1	6.36	4.85	35.66	108.72
C2	F2	11.26	0.23	53.43	149.79
C3	F3	5.53	10.21	25.87	211.57

which means that the reactivity of C2 cement is greater and almost instantaneous. Despite having a C2 cement with an important content of the belite phase (46.7% by weight), the hydration reactions are carried out in the first minutes; this is associated with the high contents of amorphous phase in this cement (32.5% by weight), the content of celite phase (8% by weight) and the small size of belite (7.2 μm) that gives it a greater reactivity as has been suggested by some researchers (39).

On the other hand, the area under the heat flow curve was calculated in intervals of time between 0-0.99 hours and 1-25 hours, from which it is found

that during the first hour of hydration, the heat flow of the C2 cement is 43.5% higher than in C1 cement, and 50% higher than in C3 cement. When comparing the results presented in Table 8 with a commercial ordinary portland cement, which after 2 hours of hydration releases 15.81 J/g (40), it is found that all the produced cements have greater release of accumulated heat when 2 hours of hydration have elapsed; this is a very relevant aspect if it is considered that the produced cements are belitic. That is explained due to the high content of the amorphous phase in the obtained clinkers, which increases the speed of reaction of the cement that

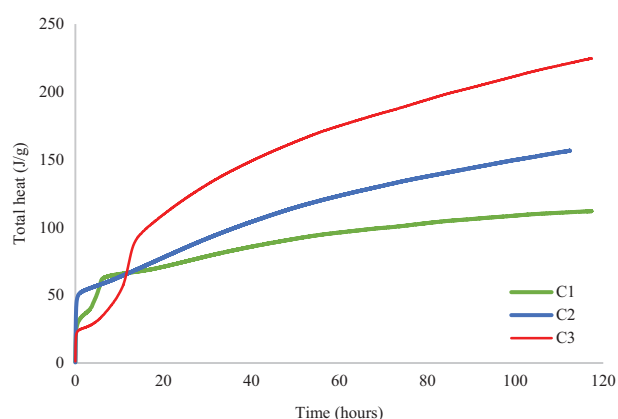


FIGURE 7. Cumulated heat microcalorimetry (Q_{accum}) in prepared cements obtained clinker at 1350°C .

is in accordance with what is proposed by other authors (41).

As observed in Figure 7 and the data in Table 8, in the first hours of hydration, C2 cement releases the greatest amount of heat compared to the other cements; while at times greater than 100 hours, C3 cement releases the greatest amount of heat, which corresponds to 30% more heat released by C2 cement and 48.6% more heat released by C1 cement; this is explained because C3 cement is the one with lowest content of amorphous (29.9 %) and larger crystals, which would reduce the reactivity at early stages compared to C1 and C2 cements. However, the hydration of belite phase (43.5% by weight) takes importance at times greater than 100 hours; therefore, C3 cement is the one with the highest accumulated heat at the last hours.

For the three cements, in the first 2 hours of hydration (induction period), the heat released is fundamentally controlled by the size of the alite and by the content of belite and amorphous material. It seems that for that initial period the content of C_3A is not so important. After 100 hours of hydration, the highest heat released is associated to the sample that has the highest percentage in the sum of all phases ($C_3S + C_2S + C_3A + C_4AF$), which corresponds to formulation 3.

4. CONCLUSIONS

The analyzed by-products have chemical compatibility with the raw materials traditionally used in the production of industrial clinker. The set of these residues, was composed mainly of CaO , SiO_2 , Al_2O_3 y Fe_2O_3 .

Belite clinker was obtained from the formulations in which 20-25% of paper sludge, 60-69% of CKD and 9-11% of rice husk ash were incorporated; consequently, 100% of the natural raw materials required in clinker production were replaced.

The increase in clinking temperature favored the formation of alite phase; however, the belite phase predominates, which may be due to the stabilization of belite when traces of elements such as potassium and sulfur are present, because they hinder the reaction of belite with CaO , preventing the formation of alite. It was also found that at higher temperatures than those presented in this research (1450°C) the clinker was melted completely.

Even when there are important contents of the belite phase, the prepared cements, with obtained clinkers at 1350°C , have great heat release at early ages, due to the amorphous content and the small size of the crystals.

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