

Thermal characterization of hydrated eco-friendly clinkers produced from pulp and paper mill waste

(Caracterização térmica de ecoclínqueres hidratados produzidos a partir de resíduos da indústria de papel e celulose)

L. Simão^{1*}, N. J. Lóh¹, D. Hotza², F. Raupp-Pereira^{1,3}, J. A. Labrincha⁴, O. R. K. Montedo¹

¹University of Southernmost Santa Catarina, Graduate Program in Materials Science and Engineering, VALORA Research Group, Av. Universitária 1105, 88806-000, P.O. Box 3167, Criciúma, SC, Brazil

²Federal University of Santa Catarina, Department of Chemical Engineering, Florianópolis, SC, Brazil

³Federal University of Santa Catarina, Department of Mechanical Engineering, Florianópolis, SC, Brazil

⁴University of Aveiro, Department of Ceramic and Materials Engineering, Aveiro, Portugal

Abstract

Industrial wastes from pulp and paper mills are potentially useful materials to use as alternative materials in clinker production. In this study, eco-friendly clinkers were obtained using only waste as feedstock. Eco-friendly clinker with different C_3S and C_2S contents were produced and hydrated for 7 days at 40 °C, or for 28 and 90 days at room temperature. The potentialities of these waste and the products obtained were revealed through chemical (XRF), thermal (DTA/TG) and surface area (BET) analysis. For comparison, a common ordinary Portland cement (OPC) was tested. As expected, the hydration rate of formulations presenting higher C_3S content was higher, generating higher amounts of $Ca(OH)_2$. Furthermore, the amount of Portlandite formed was lower when compared to OPC.

Keywords: pulp and paper mill waste, clinker, hydration, portlandite.

Resumo

Os resíduos do setor de papel e celulose são potenciais para serem usados como materiais alternativos na produção de clínqueres. Neste estudo, ecoclínqueres foram obtidos utilizando apenas resíduos como matéria-prima. Ecoclínqueres com diferentes teores de C_3S e C_2S foram produzidos e hidratados por 7 dias a 40 °C, ou por 28 e 90 dias em temperatura ambiente. As potencialidades destes resíduos e dos produtos obtidos foram reveladas através de análise química (FRX), térmica (ATD/TG) e de área superficial (BET). Para comparação, um cimento Portland comercial (OPC) foi testado. Como esperado, a taxa de hidratação das formulações apresentando maior teor de C_3S foi maior, gerando maiores quantidades de $Ca(OH)_2$. Além disso, a quantidade de portlandita formada foi menor quando comparada ao OPC.

Palavras-chave: resíduos da indústria de papel e celulose, clínquer, hidratação, portlandita.

INTRODUCTION

Industrial wastes from pulp and paper mills are potential replacements for raw materials (e.g. limestone and clay) used in clinker production [1, 2]. This is mainly due to the high concentration of major oxides (CaO [3-6], SiO_2 [7-10], and Al_2O_3 [1, 2]) present in such wastes, which are required for the formation of desirable crystalline phases in the clinker (C_3S , C_2S , C_3A and C_4AF) [11]. Works [12] demonstrated that this method of waste recovery is technically and environmentally feasible, and reported that high alkali content ($Na_2O + K_2O$) is a major issue in the end product. Those alkalis found in the waste, and consequently in the clinkers produced from the waste, arise from chemicals used in the digestion and separation of cellulose and lignin [13].

Those alkalis may cause some problems in the durability of the final concrete. Literature reports indicate that high alkali content is harmful to concrete, causing alkali-aggregate reactions that result in delayed expansion and rupture of the material with time [14]. According to regulatory standards, the acceptable alkali content in concrete is less than 0.6% [15], while it is typically between 2 and 3% in cement produced with waste from pulp and paper mills [16].

High proportions of alkalis may also negatively influence the ultimate strength of cementitious materials, even in the absence of alkali-aggregate reactions [16]. Depending on how alkalis are present in cementitious binders, hydration and properties of the cement may be affected. In typical cements, alkalis may be incorporated into the clinker phases or in the form of sulfates [16]. Some works [17] showed that alkalis in the form of sulfates do not alter the hydration of cement, but significantly reduce its tensile strength. In similar

*lisandrosimao@gmail.com

works [18], the increase of the amount of alkaline oxides in hardened cement pastes (from 0.15 to 2.8 wt%) reduced the compressive strength by ~56%. Smaoui *et al.* [16] reported cases of loss of strength at any curing age, whereas Jawed and Skalny [19] reported that this attenuation occurs only at ages later than 28 days, having no effect during early curing.

The proportion of the crystalline phases C_3S (alite) and C_2S (belite) is another factor that directly influences the hydration of cement. Alite hydrates much faster than belite. After 28 days of hydration, 70 wt% of C_3S reacted (hydrated), while only 30 wt% of C_2S completed hydration [20]. The main hydration compounds of typical cements are calcium silicate hydrate (C-S-H) and portlandite [$Ca(OH)_2$], being the last expectably more abundant when C_3S/C_2S ratio is higher. When subjected to thermal characterization by differential thermal analysis and thermogravimetry (DTA/TG), those hydrated compounds suffer dehydration between 120 and 400 °C (C-S-H), and between 400 and 520 °C [$Ca(OH)_2$] [11]. The subsequent mass loss of $Ca(OH)_2$ dissociation might be used to quantify its amount [21]. In the present work, hydrated samples of eco-friendly clinker were analyzed thermally to quantify the amount of portlandite present.

EXPERIMENTAL

Materials: the materials used in the present work were ashes from biomass combustion, wastewater treatment plant (WWTP) sludge, and lime mud from pulp and paper mills from Brazilian plants. Ordinary Portland cement (purchased in the Brazilian market) was used as a hydraulic binder reference (HBR).

Characterization: particle size distribution was determined by laser diffraction (Cilas 1064) for lime mud and WWTP sludge, and by sieving (5-0.03 mm) for biomass ashes. The chemical analysis was performed by X-ray fluorescence spectrometry (XRF, WDXRF Axios^{max}, PANalytical), while thermal analyses (DTA/TG, differential thermal analysis/thermogravimetry) were performed in a simultaneous thermal analyzer (SDT Q600, TA Instruments). The heating was conducted in synthetic air atmosphere at temperatures up to 1400 °C, at a heating rate of 10 °C.min⁻¹, and with samples of 15 mg mass in an alumina crucible. The hydrated eco-friendly clinkers were analyzed in nitrogen to ensure an inert and dry atmosphere, and at a heating rate of 5 °C.min⁻¹ up to 600 °C. Eq. A was used to estimate the portlandite (CH) content in hydrated eco-friendly clinkers from the mass loss (ML_{CH}) associated with its dihydroxylation [21]:

$$CH(\%) = ML_{CH}(\%) \times \frac{MM_{CH}}{MM_{H_2O}} \quad (A)$$

wherein MM_{CH} and MM_{H_2O} are the molar masses of portlandite and water, respectively. Specific surface area (BET Quantachrome Nova 1200e) measurements were conducted using nitrogen gas as adsorbate, for both eco-friendly clinkers and HBR. The mineralogical compositions

were analyzed by X-ray powder diffraction (XRD, Shimadzu XRD-6000; $CuK\alpha$ radiation, 0.02° 2 θ step-scan and 10 s.step⁻¹) and phase quantification was performed by Rietveld refinement using GSAS (general structure analysis system) with EXPGUI software. The internal standard was refined as a crystalline phase and used to determine the amorphous fraction of samples. The evaluation of the quality of refinement was based on least squares (χ^2) and the graph.

Preparation and hydration of eco-friendly clinkers: the formulations (Table I) of eco-friendly clinkers were prepared based on the lime saturation factor (LSF) and Bogue equations [10]. Compositional adjustments using the Bogue equations were performed in order to control the crystalline phases after thermal processing. In this sense, F1 and F5 had a greater tendency to form belite and alite phases, respectively [2]. The formulations were fired in a bottom loading furnace (ME 1700/V/Eg, Fortelab) in two steps (decarbonation and clinkering). In the first step, decarbonation was held at 1000 °C with 5 °C.min⁻¹ heating rate, and 120 min holding time. For clinkering, three different maximum temperatures were used: 1350, 1400 and 1455 °C, fixing the heating rate at 10 °C.min⁻¹, and the holding time at 90 min. These temperatures were chosen from the ternary diagram of CaO-SiO₂-Al₂O₃ and of a similar procedure related in the literature [12, 22]. At the end of the firing cycle, the samples were rapidly (>50 °C.min⁻¹) cooled down to room temperature. After processing, the clinkers were ground and sieved (<45 μ m) and 1 g mass was mixed with distilled water (w/c= 0.48) to form cementitious pastes. The cement pastes were placed to a plastic film and, after 24 h in air, bodies were immersed in water. Some samples were hydrated for 7 days in a climate chamber at 40 °C, while another set of samples were cured for 28 and 90 days in room conditions (25 °C).

Table I - Investigated formulations (wt%).

[Tabela I - Formulações investigadas (m%).]

Formulation	Lime mud	Biomass ashes	WWTP sludge
F1	66	34	0
F2	66	31	3
F3	68	30	2
F4	69	29	2
F5	70	30	0

RESULTS AND DISCUSSION

Characterization of wastes and clinkers: the results obtained by XRF confirmed that the wastes considered in this work contained high levels of CaO, Al₂O₃ and SiO₂, and are potential substitutes for traditional raw materials used in clinker production [1]. The generation of these wastes would not provide a clinker production only with these materials, but their use could complement the raw commercial materials. However, considerable alkali contents were found in all three wastes, highlighting the high K₂O content

Table II - Chemical composition (wt%) of the wastes.
[Tabela II - Composição química (m%) dos resíduos.]

Component	Biomass ashes	WWTP sludge	Lime mud
Al ₂ O ₃	9.94	13.24	0.22
SiO ₂	49.65	5.24	1.06
Na ₂ O	0.33	0.67	1.06
K ₂ O	3.14	0.30	<0.05
CaO	2.10	2.14	53.55
MgO	1.25	0.32	0.91
Fe ₂ O ₃	4.07	0.75	0.16
MnO	0.24	0.29	0.10
P ₂ O ₅	0.65	1.83	0.65
TiO ₂	0.95	0.07	<0.05
^a LOI	26.97	74.84	42.25

^aLOI - loss on ignition at 1000 °C.

in biomass ashes (3.14 wt%) and Na₂O in lime mud (1.06 wt%), as listed in Table II. Mineralogical composition of the waste (Fig. 1) showed that WWTP sludge did not present intense crystal peaks. Lime mud and biomass ashes, in turn, showed crystal peaks of calcite and quartz, respectively. Particle size distributions [1] showed d₅₀ of 14.6, 20.7 and 80.0 μm for lime mud, WWTP sludge and biomass ashes, respectively. These values can be considered suitable for obtaining clinker.

All three wastes showed extensive mass losses (Fig. 2), either by burning of organic matter (in WWTP sludge -74%; and biomass ashes - 34%) or by decarbonation of compounds (in lime mud - 41%). The DTA and TG curves of lime sludge (Fig. 2a) clearly showed the endothermic peak at 745.9 °C corresponding to decarbonation of calcium carbonate. Thermography (DTA) of the ash sample

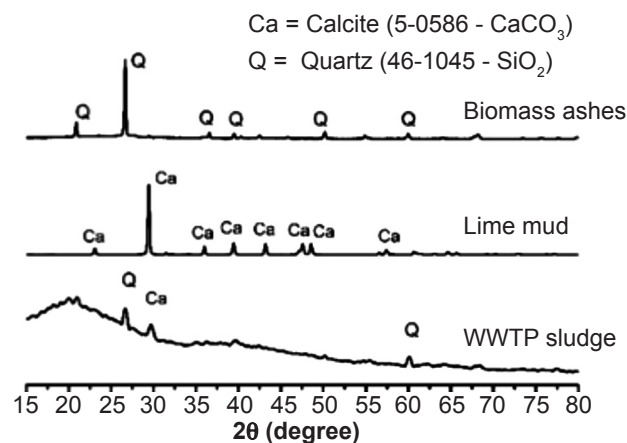


Figure 1: XRD patterns of biomass ashes, lime mud and WWTP sludge.

[Figura 1: Difratogramas de raios X das cinzas de biomassa, lama de cal e lama de ETE.]

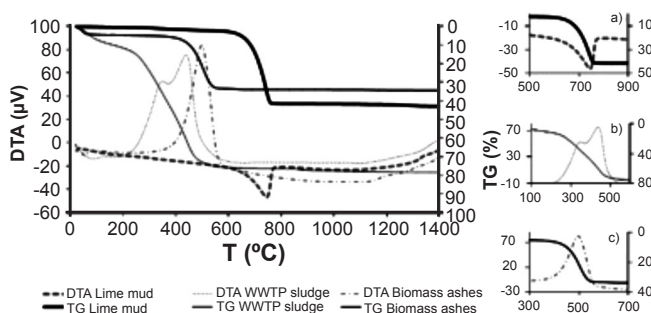


Figure 2: Thermograms (DTA/TG) of: (a) lime mud; (b) WWTP sludge; and (c) biomass ashes.

[Figura 2: Termogramas (ATD/TG) de: (a) lama de cal; (b) lama de ETE; e (c) cinzas de biomassa.]

(presented in detail in Fig. 2c) shows an exothermic peak at 499.2 °C, whereas the data for WWTP sludge shows peaks at 342.6 and 444.0 °C (Fig. 2b). These two exothermic peaks

Table III - Estimated chemical compositions (wt%) of the formulations.
[Tabela III - Composição química estimada (m%) das formulações.]

Component	F1	F2	F3	F4	F5	^a HBR
Al ₂ O ₃	4.88	6.02	5.38	5.24	4.35	3.46
SiO ₂	24.33	22.91	22.06	21.40	21.69	19.65
Na ₂ O	1.36	1.43	1.43	1.45	1.42	0.13
K ₂ O	1.52	1.43	1.37	1.33	1.35	0.84
CaO	62.11	62.28	64.02	64.92	65.70	66.30
MgO	1.62	1.61	1.61	1.61	1.62	4.74
Fe ₂ O ₃	2.08	2.00	1.92	1.87	1.87	3.65
MnO	0.23	0.25	0.24	0.24	0.22	0.10
P ₂ O ₅	1.04	1.23	1.17	1.18	1.05	0.12
TiO ₂	0.50	0.47	0.45	0.44	0.45	0.31
Na ₂ O+K ₂ O	2.88	2.85	2.81	2.78	2.77	0.97
^b Na ₂ O eq	2.36	2.37	2.34	2.32	2.31	-

^a - Real composition obtained by XRF; ^bNa₂O eq - Na₂O + 0.658xK₂O.

Table IV - Crystalline phases (wt%) determined by Rietveld method.

[Tabela IV - Fases cristalinas (m%) determinadas pelo método de Rietveld.]

Sample	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	χ ²	
HBR	-	59	26	4	11	4.264
1350	10	69	9	11	4.746	
F1	1400	31	49	3	17	4.692
1455	4	63	7	26	4.708	
1350	10	71	4	15	3.840	
F2	1400	22	46	16	16	6.529
1455	19	44	20	17	7.791	
1350	12	59	14	15	5.935	
F3	1400	49	31	6	14	7.102
1455	34	33	13	20	6.489	
1350	29	44	13	14	6.052	
F4	1400	39	37	8	16	5.772
1455	46	32	11	11	4.704	
1350	23	52	13	12	6.538	
F5	1400	36	35	6	23	5.502
1455	49	22	8	21	5.164	

Table V - Specific surface area (m².kg⁻¹) of the materials, after milling and sieving (<45 μm).

[Tabela V - Área de superfície específica (m².kg⁻¹) dos materiais, após moagem (<45 μm).]

Formulation	1350 °C	1400 °C	1455 °C
F1	1352	2499	2341
F2	1578	1575	2033
F3	2332	-	2391
F4	1668	1911	1196
F5	936	1964	1926
HBR		1107	

in the WWTP sludge may distinguish primary sludge from secondary sludge in the sample. The primary sludge has a high C:N ratio (150-250), while the secondary sludge has a low C:N ratio (5-30) [23]. These proportions suggested that the primary sludge had more complex molecules than the secondary sludge and that the two materials may, therefore, have different degradation temperatures. In this regard, it may be concluded that the higher temperature peak (444.0 °C) is due to the primary sludge, while the lower temperature peak (342.6 °C) corresponds to the burning of the secondary sludge. The energy released in these reactions is extremely interesting when clinker formulations are considered, since it may be used to reduce fuel consumption during clinkering.

Estimated chemical compositions of the formulations (Table III) indicate a higher CaO content in F5 than in F1,

mainly due to the more use of lime mud in F5. In general, the large amount of CaO in F5 resulted in a high C₃S content in

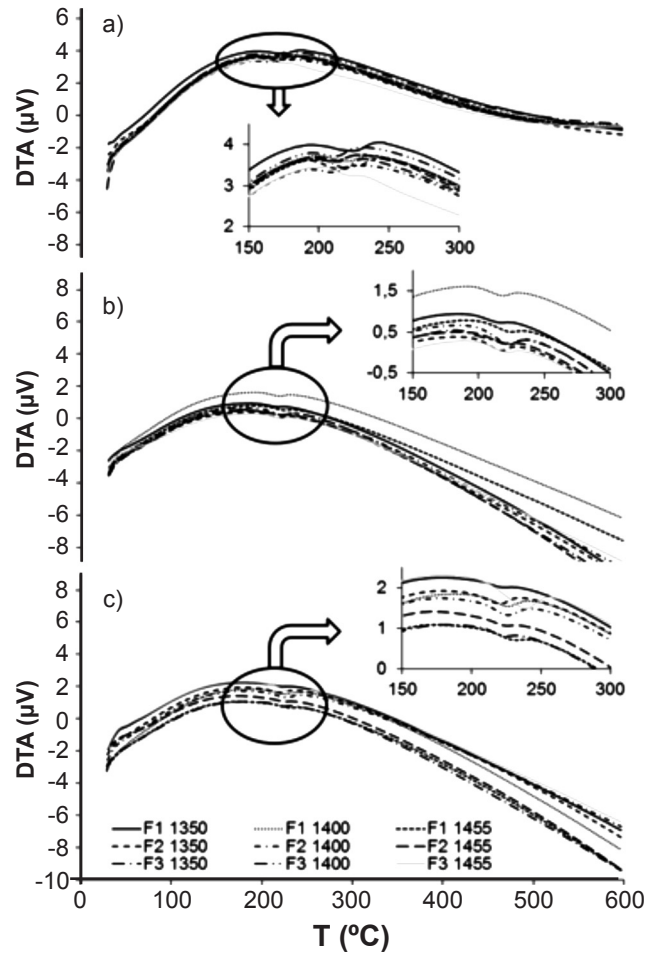


Figure 3: Thermograms (DTA) of formulations F1, F2 and F3 at: (a) 7, (b) 28 and (c) 90 days.

[Figura 3: Termogramas (ATD) das formulações F1, F2 e F3 em: (a) 7, (b) 28 e (c) 90 dias.]

Table VI - Dehydration temperatures (°C) of C-S-H identified in the thermograms of formulations F1, F2, F3 and F4.

[Tabela VI - Temperaturas de desidratação (°C) do C-S-H identificadas nos termogramas das formulações F1, F2, F3 e F4.]

Formulation	7 days	28 days	90 days	
F1	1350 °C	224.34	214.08	220.20
	1400 °C	219.57	218.11	225.38
	1455 °C	211.61	222.68	227.98
F2	1350 °C	209.73	217.18	219.70
	1400 °C	210.42	222.16	225.84
	1455 °C	214.20	217.67	223.34
F3	1350 °C	217.58	222.85	222.24
	1400 °C	212.67	-	-
	1455 °C	219.52	218.86	237.38
F4	1350 °C	216.21	216.98	220.82
	1400 °C	212.10	-	-

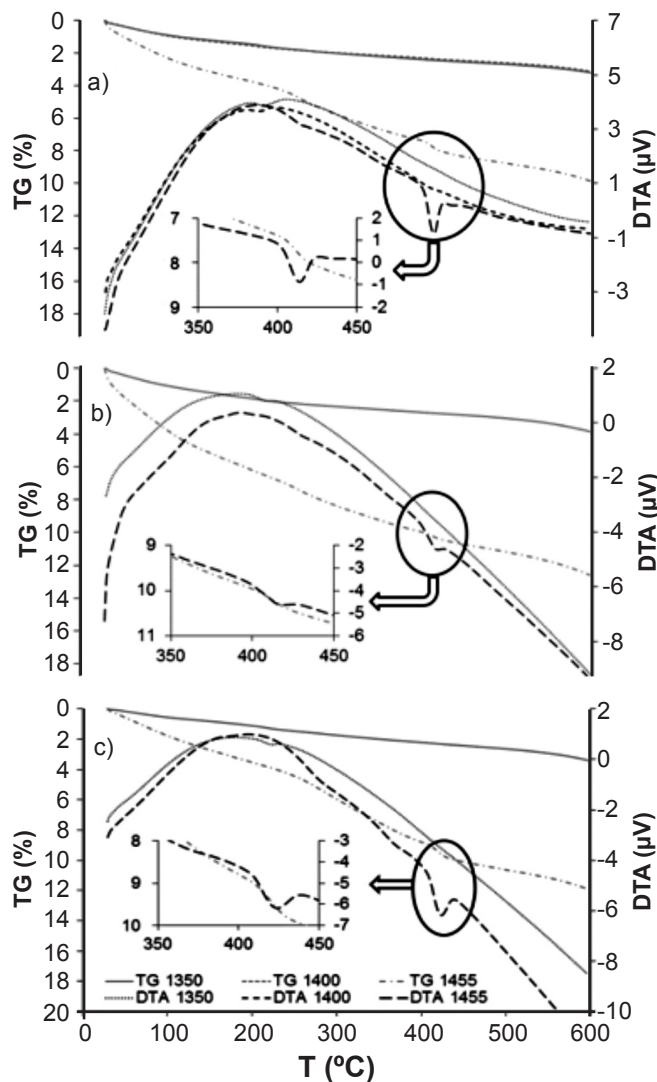


Figure 4: Thermograms (DTA/TG) of formulation F4 at: (a) 7, (b) 28 and (c) 90 days.

[Figura 4: Termogramas (ATD/TG) da formulação F4 em: (a) 7, (b) 28 e (c) 90 dias.]

the resultant clinkers, when compared with high C_2S content for F1 (Table IV), characterizing them as Portland and belite clinkers, respectively. The HBR sample showed an alkali (Na_2O+K_2O) content equal to 0.97 wt%. The eco-friendly clinker samples had alkali contents that were similar to each other (considering volatilization losses, $Na_2O+0.658 \times K_2O$), but much higher than HBR, ranging from 2.31 wt% in F5 to 2.37 wt% in F2.

Both the eco-friendly clinkers and the HBR were passed through a 45 μm mesh and show specific surface areas between 900 and 2500 $m^2.kg^{-1}$ (Table V). These results demonstrate that the samples had much higher specific surface areas than the required standards (240, 260, and 280 $m^2.kg^{-1}$ for cement classes 25, 32 and 40, respectively), according to NBR 05732 [24]. When compared with HBR, only F5 at 1350 °C had a lower specific surface area, but it was still higher than the NBR 05732 recommendation.

Estimation of portlandite content formed upon hydration: DTA and TG analyses of the hydrated F1, F2 and F3 pastes

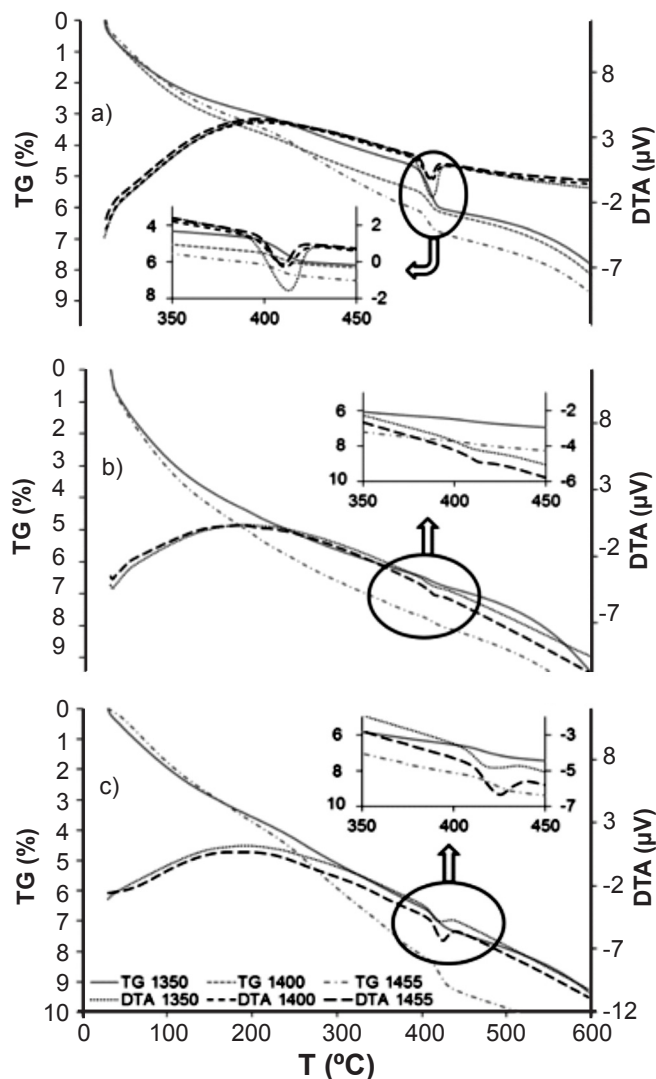


Figure 5: Thermograms (DTA/TG) of formulation F5 at: (a) 7, (b) 28 and (c) 90 days.

[Figura 5: Termogramas (ATD/TG) da formulação F5 em: (a) 7, (b) 28 e (c) 90 dias.]

at different ages and conditions showed the absence of dehydrating peaks of portlandite. Only decomposition of calcium silicate hydrates (C-S-H), between 120 and 400 °C, was evidenced by DTA (Fig. 3), as presented in Table VI. The same behavior was observed for pastes of F4 fired at 1350 and 1400 °C (Fig. 4). The absence of portlandite peaks in F1, F2 and F3 hydrated pastes may be explained by the relatively low amount of alite in such clinkers, as estimated by DRX (Rietveld method). In this sense, these formulations would take a longer time to hydrate. On the other hand, formulations F4 and F5 had higher alite content at 1455 °C, and therefore showed higher hydration rates and more expressive formation of portlandite as a by-product (see Figs. 4 and 5). The maximum amount of alite (and portlandite on hydrated paste) was observed for HBR (Fig. 6). Table VII gives estimations of portlandite (CH) contents formed in hydrated F4, F5 and HBR pastes, from TG analysis. In all cases, there was an increase in the portlandite amount formed with curing age due to a continuous

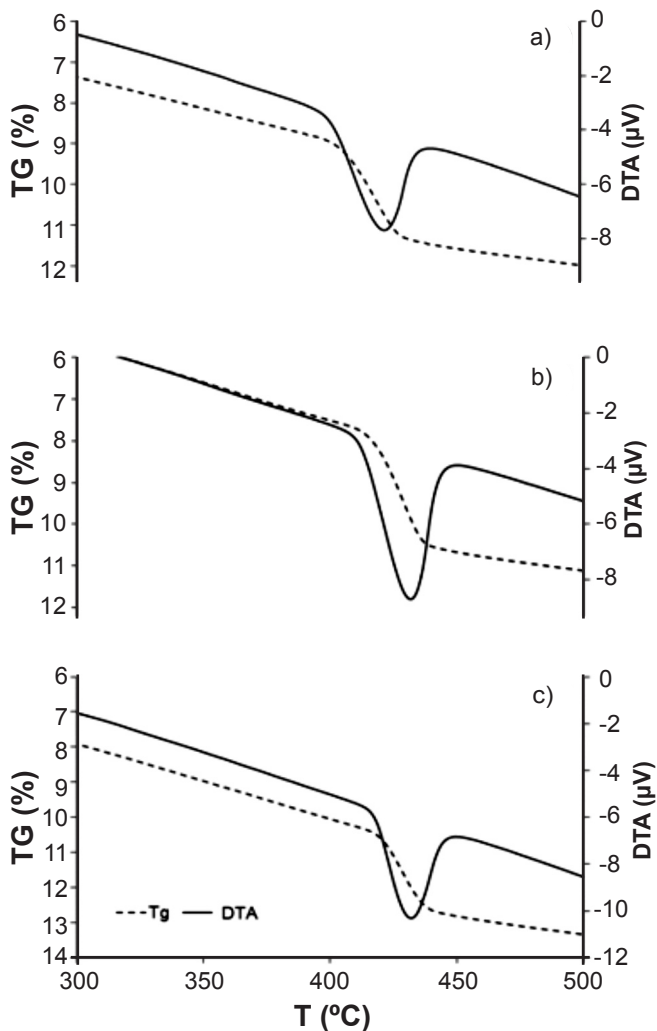


Figure 6: Thermograms (DTA/TG) of HBR at: (a) 7, (b) 28 and (c) 90 days.

[Figura 6: Termogramas (ATD/TG) de HBR em: (a) 7, (b) 28 e (c) 90 dias.]

hydration process (Table VII, Figs. 4 and 5). As expected, curing at 40 °C accelerates the hardening reactions, and F4 and F5 pastes tend to develop higher portlandite amounts, even when compared with samples cured for 90 days in room conditions. Estimations for HBR pastes (Table VII and Fig. 6) may be erroneous and difficult to interpret, probably because differences are within the experimental error of determination in such relatively portlandite-rich samples.

CONCLUSIONS

The results of this study showed that the thermal characterization of hydrated cements might be a useful technique for the study of cementitious materials. The major components (Al_2O_3 , SiO_2 and CaO) required for clinkerization were identified in lime mud waste, WWTP sludge, and biomass ashes, which were used for the formation of clinker compounds (C_3S and C_2S). F1-F3 formulations had lower CaO contents and, as a consequence, the respective clinkers were belite-richer and had relatively small amounts of alite. Their hydration was slower and the formation of portlandite was incipient, being undetectable by DTA-TG. By contrast, F4 and F5 clinkers predictably showed alite as the main phase, as well as the reference material (HBR). Hydration reactions were faster, as proved by the stronger dehydration portlandite peaks. Major concerns regarding the eco-clinkers now processed are related to the higher amount of alkalis. Thus, this issue deserves a future characterization of the alkali phases formed and potential measures for mitigating their potentially harmful effects.

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Table VII - Quantification of portlandite (CH) from DTA-TG curves.

[Tabela VII - Quantificação de portlandita (CH) a partir de curvas de ATD-TG.]

Formulation	Day	Wi (mg)	Peak (°C)	TG (mg)	CH (mg)	CH (wt%)
HBR		15.9670	421.49	0.4290	1.7637	11.05
F4	1455	19.7990	413.68	0.1511	0.6212	3.14
	1350	16.6930	412.59	0.2478	1.0187	6.10
F5	1400	16.9530	410.95	0.1300	0.5344	3.15
	1455	15.0000	409.53	0.1141	0.4691	3.13
HBR		16.6540	431.31	0.5072	2.0852	12.52
F4	1455	16.8490	415.30	0.1096	0.4506	2.67
	1350	17.2550	410.11	0.0652	0.2680	1.55
F5	1455	17.7140	413.51	0.0510	0.2095	1.18
HBR		15.4430	431.75	0.3710	1.5252	9.88
F4	1455	18.7680	422.29	0.2011	0.8267	4.41
	1350	16.4310	418.15	0.1153	0.4740	2.88
F5	1455	15.9870	424.32	0.1623	0.6672	4.17

Wi - initial weight; CH - calcium hydroxide (portlandite); ^a - in oven at 40 °C.

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