



Burning wastes as an industrial resource Their effect on Portland cement clinker

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Received 30 March 1999; accepted 12 October 1999

Abstract

The use of industrial wastes as an alternative fuel in the cement industry is a reality in several countries because wastes are removed and economic incomes are obtained preserving non-renewable energy resources. In the present work, the effect of the addition of small amounts of ashes from pyrolysis of used oil from cars in the clinkering process of Portland cement is studied. The study simulates the burning process in an industrial furnace that uses up to 30% of this kind of waste fuel. The different behaviours of the clinker so obtained (clinkering, milling, phases, hydration, etc.) are discussed and these behaviours are compared with those of a clinker obtained without additions. Chemical analysis, X-ray diffraction, Blaine specific surface, calorimetry, Differential thermal analysis-thermal gravimetry (DTA-TG), pyrometric cone equivalent, porosimetry and mechanical strength were used as the main evaluation techniques. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Clinker; Waste management; X-ray diffraction; Hydration products; Thermal analysis

1. Introduction

Companies that recycle combustible wastes receive liquid wastes, solid or pasty (contaminated muds) which are processed and transformed into a trade marked product. This product may be used as a partial substitute for traditional fuel in specially designed cement furnaces. It is expected that high temperature, chemical conditions and the long period of time of gas retention completely destroys organic compounds [1].

Contaminants present in wastes, basically inorganic materials and heavy metals, are combined with silicates formed in the cement kiln. The recycling process used by these companies assures no effluents or secondary wastes. However, some research has studied the influence of the addition of heavy metals on the characteristics and properties of Portland cement. These works ensure that the more volatile metals (mercury, selenium, thallium, cadmium, lead, antimony) are concentrated in cement kiln dust, while those more refractory (chromium, nickel, beryllium, barium, arsenic, silver) are concentrated in the cement [2].

Silicate and calcium aluminate networks retain large amounts of Cd [3], Pb, Cr and Zn, but modify their behaviour during hydration [4]; Cd and Zn delay setting and diminish strength [5,6], while Cr shortens setting time and increases early strength [7].

Odler and Schmidt [8] performed a careful study on the effect of ZnO on the Portland cement structure. They found that the amount of C_3S and $C_2(AF)$ formed increases significantly, while βC_2S and C_3A decrease due to this addition. [Cement nomenclature are used: C:CaO, S:SiO₂, A:Al₂O₃, F:Fe₂O₃, $C_3S:3CaO.SiO_2$, $C_2S: 2CaO.SiO_2$, CSH: CaO.SiO₂.nH₂O and so on.]

The influence of oxides of Mo [9], Nb, W and Zr [10] was also studied and it was found that they affect the microstructure and properties of clinker. For instance, the Mo and the W produce a viscosity decrease of molten product formed during clinkering; consequently there is an increase of diffusion rate of solids and bigger alite crystals were obtained.

Results must be interpreted with caution and it is important to consider the magnitude of addition, because the fixation efficiency depends on the addition level compared with saturation level and with the thermal effect (calcination temperature, residence time, partial gas pressure, etc.) [7]. The type of process used (dry or wet) and the presence or absence of preheats should be taken into account.

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Published papers refer almost exclusively to the synthetic additivity of pure compounds added in amounts larger than the ones incorporated through alternative fuels in real situations. In our work, ashes from used oils of cars were used as additives taking into account the replacement limit accepted in industrial plants.

2. Materials and methods

2.1. Raw materials and characterization

Several fractions of used oils from cars were transformed into ashes by calcination at 1000°C in order to be used as impurities in this test. Chemical analysis of these ashes is shown in Table 1. Table 2 shows chemical analysis of the crude dust used as a Portland cement raw material and its potential composition as clinker.

The mixing of crude dust (raw material mixture for feeding a clinker furnace) with the adequate amounts of ashes was performed in a rotating cylinder, with alumina balls to help mixing. The balls were then separated by sieving. Samples so obtained were transformed into pellets and clinkered.

All the raw mixes were thermally treated (clinkered) up to 1450°C (rate: 10°C/min and kept for 1 hour at 1450°C) in an electric furnace and cooled rapidly in air. Sintering and cooling conditions were similar to the ones used in industry. Table 3 shows the different synthesized clinkers and percentage of ashes added.

M5 (0.5%) and M6 (1%) samples were prepared to evaluate the possible formation of lower eutectic that could affect the production equipment, although in practice these concentrations are never reached.

Milling of different clinkers was performed in a batch oscillating laboratory mill at equal times and conditions; these parameters were selected in order to obtain specific surface areas within the range used in normal cements. The following tests were carried out on milled material: Blaine specific surface area, (ASTM C204); pyrometric cone equivalent (PCE), ASTM C24; free CaO (ASTM C114); DTA-TG; and X-ray diffraction (XRD).

On the other hand, the milled clinkers with w/c = 0.4 were hydrated. Hydration was followed through (XRD),

Table 1
Chemical analysis of ashes used as additives

Component	Weight	Component	Weight
SiO ₂	3.80%	Ba	158 ppm
Al ₂ O ₃	1.64%	Sr	214 ppm
Fe ₂ O ₃	2.32%	Pb	23632 ppm
MnO	0.18%	Zn	114483 ppm
MgO	13.35%	Mo	119.9 ppm
CaO	21.34%	Cu	1426 ppm
Na ₂ O	1.08%	Cr	737 ppm
K ₂ O	0.84%	Sn	390 ppm
TiO ₂	0.04%	S	5.11%
P ₂ O ₅	19.28%	Cl	0.01%

Table 2
Chemical analysis of crude dust used as Portland cement raw material (%w/w) and its potential composition as clinker (%w/w)

CaO	43.52	Na ₂ O	0.69	C ₃ S	70.7
SiO ₂	14.28	K ₂ O	0.03	C ₂ S	9.6
Al ₂ O ₃	3.12	SO ₃	0.49	C ₃ A	6.6
Fe ₂ O ₃	2.37	LOI	34.9	C ₄ AF	11.1

LOI = loss on ignition.

DTA-TG, differential calorimetry, mercury intrusion porosimetry and compressive strength.

3. Results and discussion

3.1. Crude dust and clinker

3.1.1. DTA-TG

Differential thermal analysis-thermal gravimetry (DTA-TG) analyses of M0 and M4 crude samples were carried out with the following temperature program:

From 20°C–1450°C → 10°C/min
 At 1450°C → permanence 30 min
 From 1450°C–1350°C → 40°C/min
 From 1350°C–1300°C → 20°C/min

In all cases the following changes were observed. As an example a complete description of those changes are shown for M0: a first endothermic peak between 860–890°C corresponding to limestone decomposition; then, the CaO reaction zone with silicates and aluminates as an endothermic band in the 950–1100°C zone was observed. This band is typical for reactions in solid state with diffusional control. Then, an endothermic peak was observed at 1340°C assigned to the formation of molten phase (clinkering). During cooling an intense exothermic peak at 1275°C was defined due to solidification of molten phases formed during heating. Table 4 shows the shifts in reaction temperatures corresponding to the added series.

The total weight loss and enthalpy of reaction measured for each peak did not vary significantly from one sample to the other (M0 to M6). However, in the clinkering zone 1272–1396°C a change in the shape of the endothermic peak was observed. This peak widened when the percentage of ash added increased. The non-definition of clinkering temperature when ash was added to the system may be produced by diffusional problems that widen the temperature range in which the reaction occurred.

Table 3
Percentage of ash addition and its clinker denomination

Denomination	% w/w of ashes
M0	0
M1	0.005
M2	0.010
M3	0.020
M4	0.040

Table 4
Reaction temperature comparison for different samples (extracted from DTG-TG data)

Sample	Decomposition temp. CaCO ₃ (°C)	Reaction temp. (°C)	Clinkerization temp. (°C) (heating)	Crystalization temp. (°C) (cooling)
M0	867.7 – 888.7	950–1100	1340.2	1275.7
M4	850.7 – 893.1	950–1100	1342.1	1275.0
M5	868.1 – 894.2	950–1100	1345.6	1270.5
M6	861.7 – 895.0	950–1100	1342.5	1268.4

For the same reason, the crystallization peak shifted during cooling toward lower temperatures with increase of addition percentage; that is, when the amount of added ashes increased, the sample solidified at lower temperatures maintaining its semi-molten aspect during more time than the M0 sample.

3.1.2. Milling

Equal portions of different clinkers were milled during equal periods of time with the equipment above mentioned. Fig. 1 shows results of milling test measured through specific surface according to Blaine method (m²/kg).

The increasing values of specific surface with the increase of addition percentage denoted a tendency to facilitate milling (presence of more fragile material), requiring less energy to obtain equal specific surface. Reference sample (M0) was out of the band determined for the series, indicating the presence of a clinkering product with different characteristics.

3.1.3. Pyrometric cone equivalent

Results of pyrometric cone equivalent (PCE) performed on different clinkers are shown in Table 5. M0 had a temperature of cone equivalent of 1512°C. The behaviour of series (M2-M4-M5-M6) shows that while the addition percentage increased, the equivalent temperature also increased.

At low concentrations of ash, they acted as flux, but in concentrations >0.5% they tended to form more refractory compounds. This higher softening temperature at higher addition percentage was related with the diffusional difficulty that will be further discussed. The M0 showed behaviour completely different from the one of added samples, indicating a clinkering mechanism different from the series.

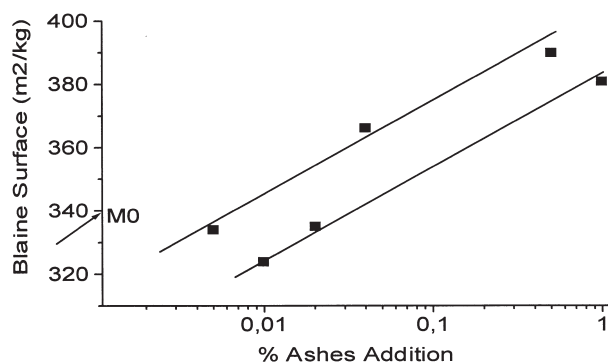


Fig. 1. Clinker Blaine surfaces (m²/kg) vs. % ash addition.

3.1.4. Free CaO

Results of free CaO obtained for different synthesized clinkers did not reveal differences between the reference sample and the added ones. At the final temperature and clinkering time used, the combination of calcium oxide with silica and alumina compounds was almost complete and adequate. The incorporation of ashes did not seem to influence the final content of free lime.

3.1.5. XRD

Diffraction patterns obtained for M0 clinkers and the added series are shown in Fig. 2 together with assignment of principal phases. Addition was not detected as new phases by this technique even on the samples with maximum percentage of ash.

A crystallinity increase of C₃S and C₂S phases may be observed when passing from M0 to M2. Although M2 had a variety of metals provided by ash additions, instead of contributing to increase the glassy phases at the expense of crystallinity, these produced the opposite effect. This may be interpreted as ash, in this percentage, acting as mineralizer in the system if we compare M0 with M2. But when the addition percentage increased in the series (passing from M2 to M4), a tendency to crystallinity decrease was observed while the addition percentage increased, that is to say the opposite effect with respect to the one observed between the M0 and M2 samples.

3.2. Clinker hydration

3.2.1. XRD

For this study, samples of different clinkers were hydrated with w/c = 0.4 and were kept in sealed flasks during 1 hour, and 1, 7, and 28 days. Then, the flasks were opened, the samples were milled with abundant acetone to stop the hydration reaction and X-ray diffraction patterns were obtained. It must be concluded that these samples, observed with this technique, generated equal hydration products, indepen-

Table 5
Pyrometric cone equivalent for different samples and their corresponding temperatures

Sample	% Addition	PCE	Equivalent temperature
M0	0	17	1512
M2	0.01	15	1430
M4	0.04	15	1430
M5	0.5	16	1491
M6	1.0	18	1520

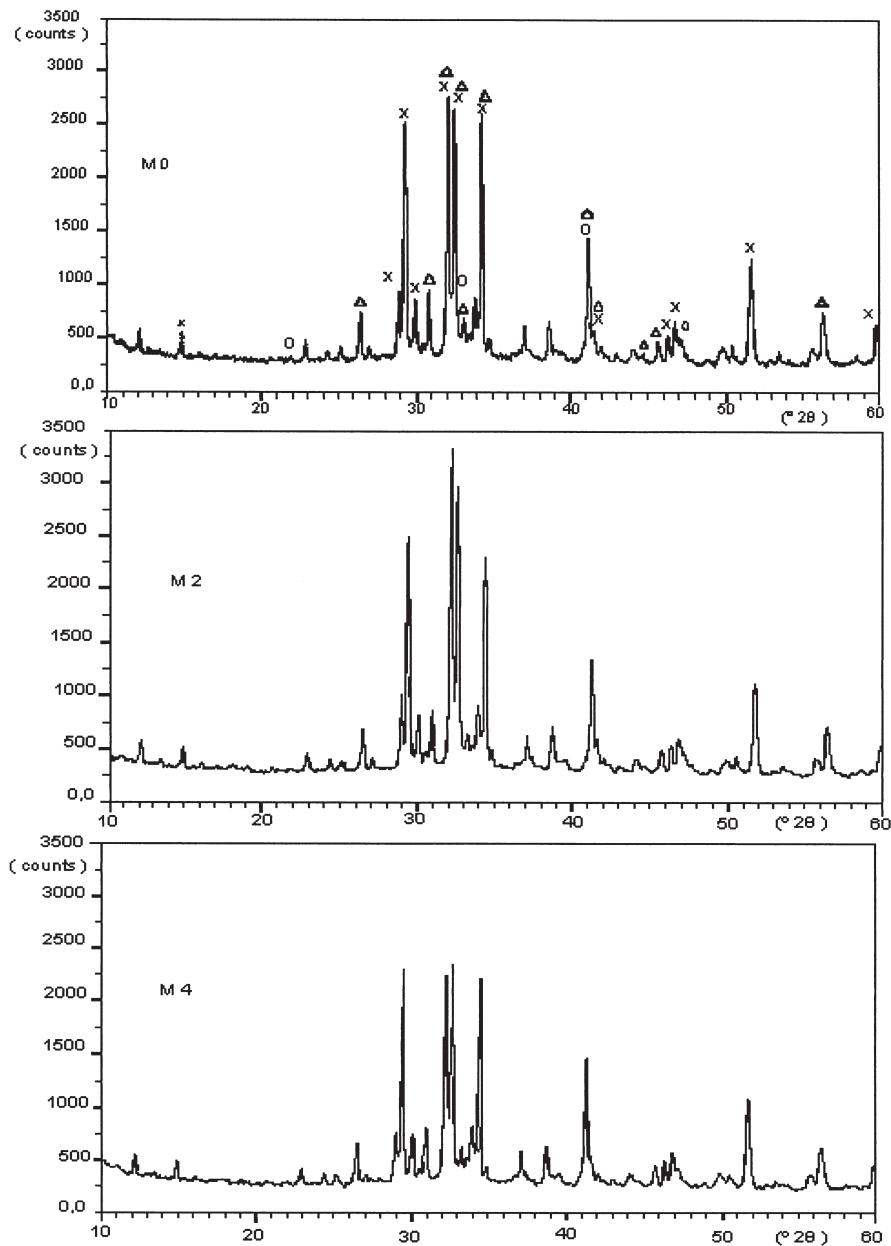


Fig. 2. XRD diffractograms for M0, M2 and M4 clinkers. Δ = C_2S , X = C_3S , O = C_3A .

dently of the amount of addition, and the only slight differences observed were a function of time.

Fig. 3 shows that M4 sample at 1-hour hydration presents peaks of C_3S and C_2S diminished respect to the ones of M0 under the same conditions, showing also a clear $Ca(OH)_2$ presence, indicating higher hydration than the M0 at earlier ages. This difference was clear during the first 24 hours. Following the hydration progress through peaks of $Ca(OH)_2$ at the ages of 7 and 28 days it was possible to observe a higher intensity of these peaks in all added samples than in M0.

3.2.2. Differential calorimetry

Calorimetric hydration curves in arbitrary units of temperature vs. time for the first 50 hours obtained for different

samples varied significantly. In Fig. 4 curves for M0 and M4 are shown in a comparative way as an example.

Indicators t_1 , t_2 , t_3 are the times in which maximum of each of the curves appear and they are shown in Table 6 for all samples.

When the clinker was in contact with water, there was a fast heat evolution that determined the maximum of the first exothermic peak corresponding to time t_1 . This stage corresponds to a surface solvation and formation of ions. These ions were formed on the surfaces of the silicate grains; it is a fast process and it is chemically controlled. Consequently, when the clinker specific surface is higher, the exposed surface is also higher and t_1 is lower. It was previously observed that when the addition percentage increased, there

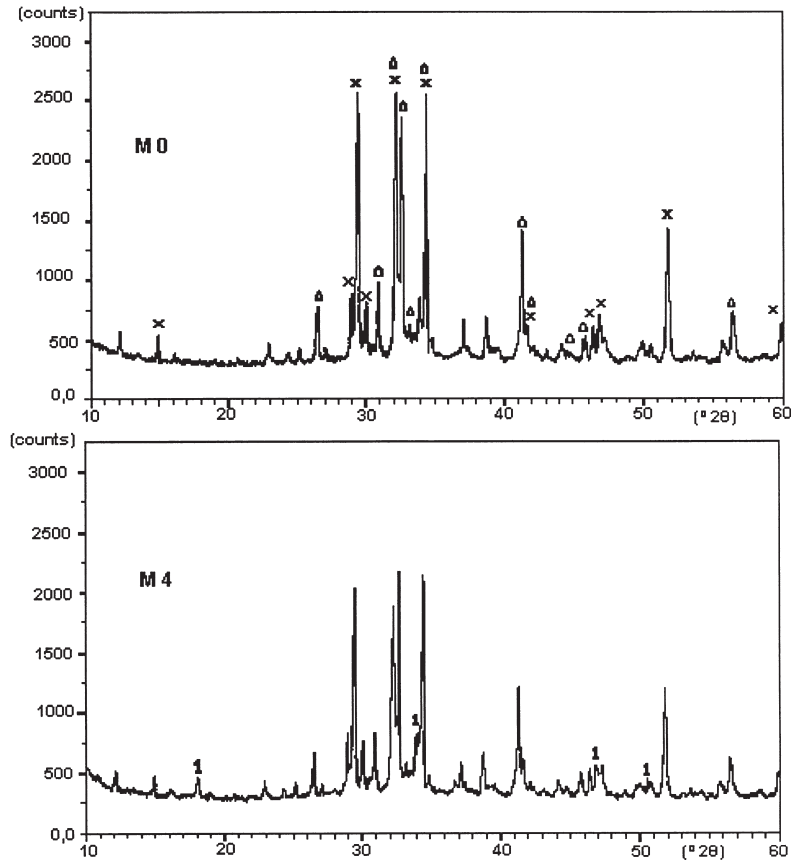


Fig. 3. XRD diffractograms for 1 hour hydrated M0 and M4 samples. (Ambient temperature, w/c = 0.4.) Δ = C₂S, X = C₃S, 1 = Ca(OH)₂.

was a tendency to increase the surface area of the material; for this reason, t₁ should be lower when increasing the Blaine surface area (as shown in Table 6).

The second stage is a period of apparent inactivity, known as the dormant period, which determined that the cement remained in plastic state for some hours. From a chemical point of view, during this stage ions remained in solution to acquire necessary concentrations to start precipi-

tation of hydration products. The final phase of the dormant period determined the start of setting of Portland cement.

Time t₂ indicates the moment in which aluminate precipitation reactions start, and will depend on concentrations reached by ions in solution. The fact that t₂ first increased with addition increase was directly related with the higher rate of previous stages and corresponded to same causes. The value of t₂ for the M0 sample remained out of the sequence.

Previous to the t₃ maximum, an acceleration period was observed (Fig. 4), determining by its maximum point the ending of the formation processes of nuclei of hydrates and the beginning of paste strength gain due to increase and the crosslinking of these hydrates formed. This process controlled chemically and diffusively was started by forma-

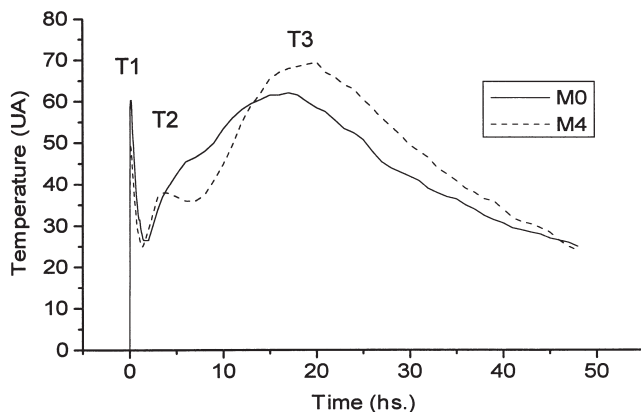


Fig. 4. Hydration calorimetric curves for M0 and M4.

Table 6

Times of the different hydration stages for samples M0–M4 according to calorimetric curves

Sample	Ash addition %	Blaine (m ² /kg)	t ₁ (min.)	t ₂ (hs.)	t ₃ (hs.)
M0	0	340	9	6.11	16.8
M1	0.005	334	7	8.03	17.6
M2	0.01	324	9	7.04	16.5
M3	0.02	335	8	7.04	17.1
M4	0.04	366	6	3.58	19.9

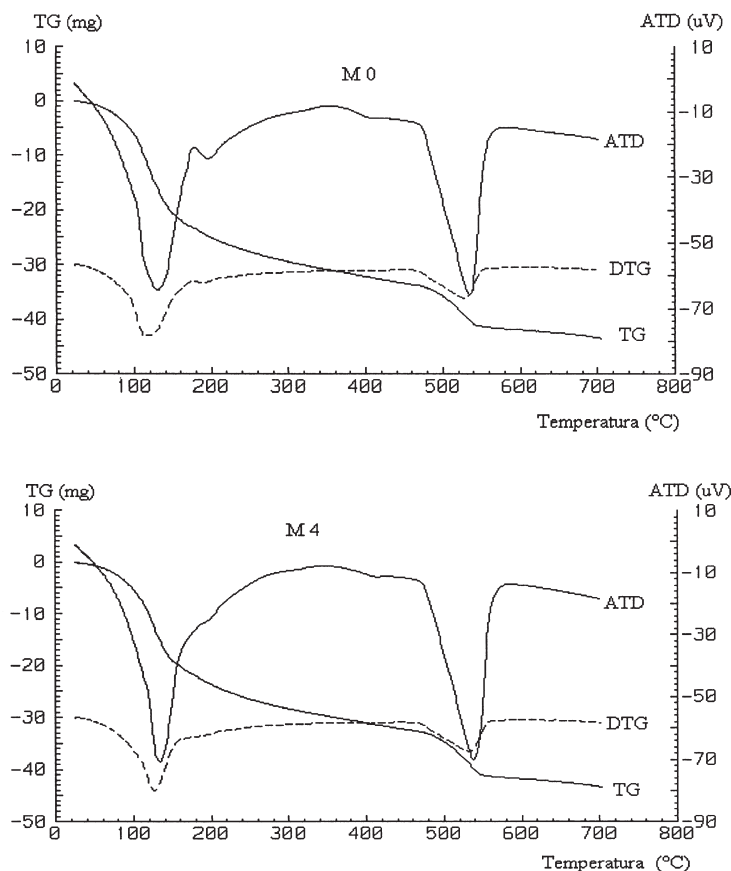


Fig. 5. DTA-TG diagrams for M0 and M4 hydrated for 28 days.

tion of hydration products from silicates. Consequently, in this stage, the kinetics depends on the water diffusion rate toward the hydrated material, and once there, on the hydration reaction (dissolution-diffusion-crystallization).

When the quantity of additives was increased, the system showed much more reactivity at the beginning; that is, in the stages controlled by chemical reactions. This process produces a large amount of gels, and consequently the water diffusion through these gels to reach the non-hydrated surface grain as well as the diffusion of ions to the external surface of hydrates (dissolution-re-crystallization process), both with diffusional control, were blocked and consequently t_3 increased with Blaine increase. Here, there is again a correspondence between added samples, while M0 remains out of this correspondence.

3.2.3. DTA-TG

Fig. 5 shows DTG/TG diagrams for M0 and M4 hydrated for 28 days. In M0 two endothermic peaks are observed at 130 and 200°C they are produced by dehydration of C-S-H [11–13]. The first endothermic peak was also observed in the added sample but at slightly higher temperatures, the second one was only insinuated and shifted to lower temperatures. This difference may be produced by the type of C-S-H

gel formed during hydration with respect to the Ca:Si ratio and to the number of adsorbed water molecules.

The third endothermic peak was observed at 530°C and was attributed to CH decomposition [14,15]. This peak appeared at the same temperature for all the clinkers tested.

Table 7 shows weight loss corresponding to each mentioned stage and the total weight up to 700°C for each analyzed sample. The total weight loss (20–700°C) showed a relation inversely proportional to the Blaine specific surface within the series. This is, at higher specific surface lower mass loss occurs, which makes us think that the hydration advance is not only related to the specific surface at this hydration age. Table 7 shows that the addition of ash in small

Table 7
TG weight loss measured on 28-day hydration samples

Sample	Blaine (m ² /kg)	Weight loss 20–450°C (%)	Weight loss 450–700°C (%)	Total weight loss 20–700°C (%)
M0	340	16.41	4.95	21.39
M1	334	18.31	5.40	23.71
M2	324	19.08	5.37	24.45
M3	335	17.57	5.18	22.75
M4	366	15.90	5.44	21.34

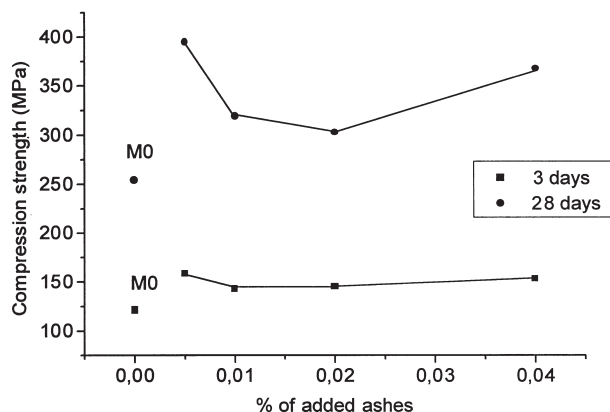


Fig. 6. Compression strength (Mpa) at 3 and 28 days vs. % w/w of ashes.

amounts generated a favourable effect on the hydration advance, exceeding the effect generated by the higher specific surface.

In the next section, it will be seen that the weight loss between 450–700°C could be related to the mechanical strength at equal age.

3.2.4. Compression strength

Results of compression strength at 3 and 28 days obtained by the added series with ashes and M0 as an average of four tests for each sample are presented in Fig. 6. In the figure it is possible to observe three phenomena. First, at 3 as well as at 28 days mechanical strengths of M0 had lower values than those obtained for the M1–M4 series, showing as well that M0 was out of the curves developed by the added series. Second, higher mechanical strengths at both ages corresponded to the sample with less addition (M1). This phenomenon may be interpreted from the point of view of a “mineralizer” for clinkering process; that is to say, small amounts of additives that promote or help the formation of the desired compounds, in this case hydraulically active phases. This effect disappeared or changed the mechanism at higher concentrations. Third, there was a correspondence between the 450–700°C TG weight loss and the mechanical strength of samples at 28 days and this correspondence was in agreement with the $\text{Ca}(\text{OH})_2$ generated during dehydration.

3.2.5. Porosimetry

M0 and the added series hydrated 28 days were tested by mercury intrusion porosimetry. In the macro-mesoporosity region (60000 up to 40Å) different microtextures were observed among M0 hydrated and added samples. Fig. 7 shows pore size distribution of M0 and M4. Between 50000 and 9000 Å (5 and 0.9 μm) the M4 sample showed a slightly higher porosity than M0, but from this last value and toward smaller pore radii M0 increased significantly notably its total pore volume, especially between 15000 and 5000 Å (1.5–0.5 μm). When the samples were analyzed in the macropore region (5–30 μm), M0 showed higher macropore volume than the other samples.

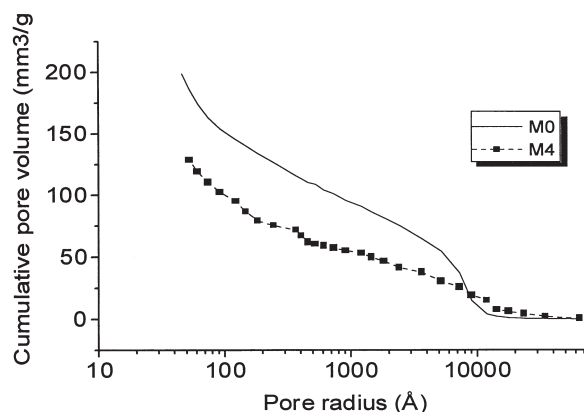


Fig. 7. Pore size distribution of M0 and M4 samples hydrated for 28 days.

For materials with similar compositions it is known from the existence of correlations between their microtexture (shape and distribution of pores) and their mechanical strength, that in this case this correspondence is fulfilled. That is to say, at higher porosity (mainly in macro and mesopores) the mechanical strength is lower, as it was observed between M0 and M4. On the other hand, a lower porosity will provide a material with lower permeability and consequently less susceptible to the attack of aggressive environment.

4. Conclusions

- Clinkers obtained by addition of small amounts of ash from used oils from cars showed different properties to the ones obtained without the addition of ash.
- The energy requirement to reach the same fineness in milling showed a tendency to decrease with the increase of additive concentration.
- The added system presented a higher initial reactivity during hydration with respect to M0 material.
- The mechanical strength at 3 and 28 days of pastes prepared with w/c = 0.4 and addition levels up to 0.04% showed a higher performance than that of the M0 sample.
- The hydrated added series showed lower porosity than the reference one and consequently these materials would be less susceptible to aggressive environments.
- Studies performed by differential calorimetry indicate that hydration stages controlled by chemical reactions are favoured by incorporation of ash, while the ones of diffusional control are notably blocked.
- In all the tests performed, the added series showed a typical behaviour, leaving the reference (M0) out of it.

The residues of metals and metallic oxides incorporated to the clinker during the clinkering process through an alternative fuel (used oils from cars) do not seem to alter detri-

mentally the characteristics of the material. But they do introduce technological improvement if the amounts and types of impurities added are similar to the ones described in this article.

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