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SCIENCE DIRECT
Cement and Concrete Research 35 (2005) 438–444
CEMENT AND CONCRETE RESEARCH

Waste fuels: their effect on Portland cement clinker

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Received 10 April 2003; accepted 27 May 2004

Abstract

Nowadays, different kinds of industrial wastes are increasingly used in the clinkering process by the cement industry, with the aim of taking advantage of their energy content or confining unsuitable substances. This work evaluates the physicochemical characteristics of the clinkers obtained after incorporating three different wastes in different proportions: two of them with energetic capacity—trade marked waste fuel and waste carbon of petroleum—and the third that would be confined—pyrolitic carbon.

The fusion temperature of the mixtures, the differential thermal analysis and the thermogravimetric analysis (DTA/TG) during clinkering and after hydration, the specific surface area at the same milling times, X-ray diffraction (XRD) and mechanical strength of the pastes elaborated with a water/cement 0.4 relation were analyzed. The results obtained were compared to those of the clinker obtained without additions.

Keywords: Portland cement; Clinker; Waste management; Hydration

1. Introduction

Cement companies are introducing the industrial waste coprocessing from a perspective that combines environmental policies with the interests of companies. Industrial wastes with residual energy and low content of chlorides and heavy metals can be appropriated to provide part of the energy required to make Portland cement.

These wastes can be used as alternative fuels for making Portland cement, as long as they fulfill the following requirements [1]:

- The emissions released by the cement plant must not increase when using alternative fuels.
- The cement quality and its compatibility with the environment must not decrease.
- The use of waste material as alternative fuel must not increase the costs; on the contrary, it must bring profits.

The materials frequently used with this purpose are the following: waste carbons from different industrial processes, used oils, solvents, tar muds, alcohols, etc. The high temperature processes, the cement kiln chemical conditions and the gas retention time inside it are supposed to destroy the organic compounds completely [2].

As regards inorganic compounds and heavy metals, which could be present in wastes, they would combine with the silicates or they would be trapped in the vitreous phase formed during clinkering, converting the toxic compounds into harmless ones [3]. The Portland cement matrix is built in a suitable place for the solidification/stabilization (S/S) of the dangerous wastes avoiding putting them under earth or burning with all the well-known consequences.

Different authors [4–13] concluded that the Portland cement matrix either normal or with some additions is suitable for the S/S of metals, such as Zn, Cu, Pb, Cd, among others. They also reported the formation of intermediate phases in the metallic oxide—$CaO–SiO_2–Al_2O_3$—system, which are stabilized during clinkering and/or Portland cement hydration [14–17].

Studies on different clinkers elaborated under laboratory conditions, with the addition of wastes in different levels replacing fuel partially, are presented in this paper. The replacement percentages were maintained within the limits accepted for industrial plants. The systems analyzed in this study come from the clinkering of crude dust in the presence of (a) waste carbon from a pyrolitic furnace, (b) waste carbon from petroleum with a high calorific power and (c) a trade

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doi:10.1016/j.cemconres.2004.05.045

Table 1
Raw material centesimal composition

CaO	43.52	K_2O	0.69
SiO_2	14.28	Na_2O	0.03
Al_2O_3	3.12	SO_3	0.49
Fe_2O_3	2.37	L.O.I.	34.9

marked fuel mixture nowadays used as alternative fuel in the cement industry. The first is incorporated to confine the waste, the last two to take advantage of their waste calorific power. Results will be compared to those corresponding to a clinker obtained without this kind of addition (called M0).

The following techniques were employed in this work: Blaine specific surface area, pyrometric cone equivalent (PCE) temperature, X-ray diffraction (XRD), differential thermal analysis and simultaneous thermogravimetric analysis, and mechanical strength to compression.

2. Experimental

2.1. Materials

The raw material used in this work corresponds to an industrial mixture provided by a local cement company. Its chemical analysis by X-ray fluorescence is presented in Table 1.

The material was characterized by XRD. $CaCO_3$ (calcite) and SiO_2 (quartz) were the majority crystalline phases observed. Muscovite [$KAl_2Si_3AlO_{10}(OH)_2$] was detected among the minority crystalline constituents.

2.2. Preparation of the samples

The alternative fuels can replace up to 20% of the traditional fuel in the cement industry in Argentina. For each 100 kg of clinker, the fuel equivalent to 10 kg of carbon is needed; therefore, these alternative fuels would be used up to the equivalent to 2 kg of carbon/100 kg of clinker. The substitution percentages change according to each country [18].

Following those parameters, different mixtures of raw material with different carbon addition levels were prepared for this work. Each sample denomination and the addition weight percentage in the pyrolitic carbon and in the petroleum carbon cases are shown in Table 2.

CR-20, the sample with petroleum waste carbon, was prepared with the maximum percentage of fuel replacement by waste carbon; it means 20% in weight. This replacement percentage involves the addition of 0.08% of ashes to the clinker (ashes 0.08 g/clinker 100 g). The other two samples, CR-10 and CR-5 were prepared with lower replacements, adding 0.04% and 0.02% of ashes.

Table 2
Addition percentage and denomination of the samples

Pyrolitic carbon clinker			Petroleum waste carbon clinker		
0.4%	0.6%	0.8%	5%	10%	20%
CP-04	CP-06	CP-08	CR-5	CR-10	CR-20

Table 3
Centesimal composition of the fuel mixture ashes

CaO	7.22%	Co	1100 ppm
SiO_2	49.13%	Cr	905 ppm
Al_2O_3	15.09%	Cu	6850 ppm
Fe_2O_3	12.44%	Pb	36,500 ppm
MgO	1.48%	Zn	25,700 ppm
Na_2O	2.48%	Mo	123 ppm
K_2O	2.77%	Ni	266 ppm
TiO_2	1.93%	Sb	152 ppm
MnO	0.12%	Sr	380 ppm
P_2O_5	1.67%	Mn	857 ppm
S	4510 ppm	Ti	10,400 ppm

The pyrolitic carbon does not have waste calorific power; consequently, percentages from 0.4% to 0.8% of raw materials were incorporated as loading. Because they practically do not burn during clinkering, they incorporate 0.48%, 0.72% and 0.96% of ashes (ashes g/clinker 100 g).

As regards the fuel mixture, the ashes that remained after the total combustion of fuel were directly incorporated to the raw mixture. The chemical analysis of the main compounds of ashes represented as oxides is shown in Table 3. The contents of the metals found are also included.

For this case—waste fuel—samples with three different addition levels, as it is shown in Table 4, were prepared. The MII sample was prepared taking into account that all the ashes, which remain when the traditional fuel was replaced by the maximum of alternative fuel, are incorporated to the clinker. MI had the half of addition and MIII had an excess in order to detect tendencies.

To prepare the different samples, the carbons or ashes and the raw material were quantitatively weighed and dry mixed. Samples so obtained were transformed into pellets and clinkered in a furnace muffle, with a heating rate of 10 °C/min up to 1450 °C and kept for 1 h at that temperature. Cooling rate was also controlled to ensure that the suitable hydraulic phases remain.

2.3. Analysis techniques

The different synthesized clinkers were milled in a Herzog HSM 100 oscillating mill with vanadium steel chamber. At equal times, equal quantities of each clinker were milled to make the measure test of the specific surface area obtained after milling comparative. The milling time was selected to maintain the specific surface area within the range used in normal cements.

Table 4
Percentage of ash addition from waste fuels and denomination of the different samples

0.03%	0.06%	0.24%
MI	MII	MIII

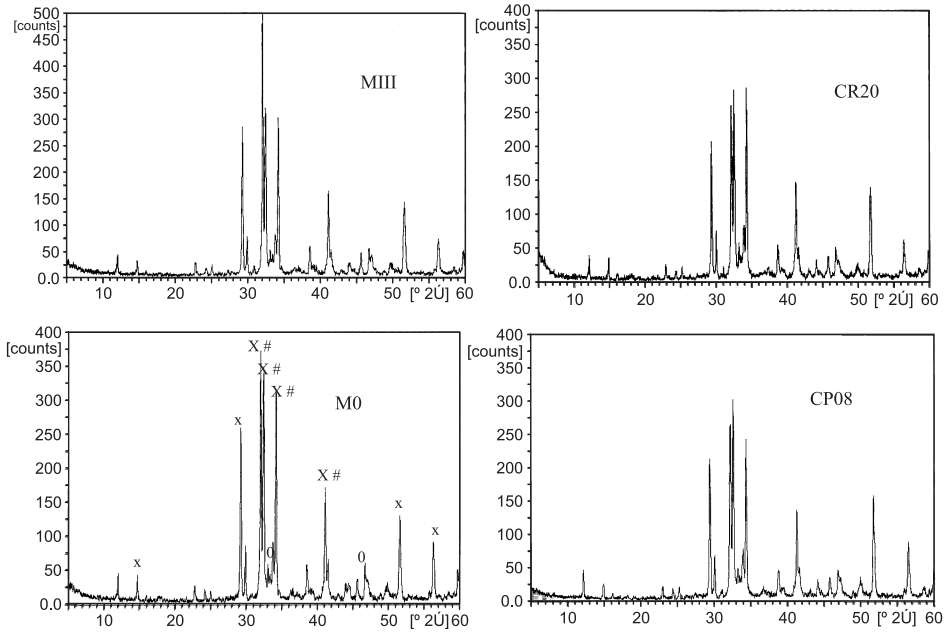

Fig. 1. DRX clinkers: Reference (M0), CR-20, MIII and CP-08 X = C_3S, # = C_2S, 0 = C_3A.

The milled clinkers were characterized using the following techniques: Blaine specific surface area (ASTM C204); PCE, ASTM C24; and X-ray diffraction (XRD). Clinkering reaction progress and hydration were followed through DTA/TG. Compressive strength tests on hydrated pastes with water/cement = 0.4 at different ages (3, 7 and 28 days) were made too. Thermal studies were carried out using a NETZCH STA 409 equipment, X-ray diffractograms by a PHILIPS PW 3710 diffractometer and mechanical tests using a modified JJ INSTRUMENTS machine.

3. Analysis, results and discussion

3.1. Clinkers

3.1.1. Analysis by XRD

Diffractograms corresponding to M0, CP-08, CR-20 and MIII clinkers are shown in Fig. 1, where all the typical Portland clinker phases, such as C_3S, C_2S and C_3A among others, can be identified.[1]

The pyrolitic carbon addition produces changes in the crystalline net. The crystallinity obtained was lower than that of the reference sample and similar at every addition percentage. At the maximum addition percentage, 0.8%, an inversion of the intensity of the main peaks takes place, as shown in Fig. 1.

In these samples (CP series) a slight shift of 2θ to higher values can be observed. This effect reaches its maximum when 0.6% of pyrolitic carbon is added and it would indicate a structural modification due to the addition of impurities during clinkering. This is shown in Table 5.

The diffractograms corresponding to the CR series show a lower crystallinity of the silicate phases compared to that of the reference sample, except for CR10 that is equivalent. The CR-20 also showed inversion of the intensities of the main peaks and lower crystallinity than all the series. There was no shift of DRX peaks observed for these samples.

The diffractograms obtained for the synthesized clinkers in presence of ashes from the fuel mixture in the specified proportions show a higher crystallinity of the phases when the incorporation is the maximum one (0.24%—MIII), being bigger than that of the reference sample and than that of all the previous samples. Remaining clinkers with 0.03% (MI) and 0.06% (MII) of ashes showed crystallinities similar to those of the reference sample, suggesting that the addition of mineralizing elements does not follow a rule proportional to the amount of doping agent.

3.2. Specific surface area

The specific surface area of milled clinkers was measured with a Blaine permeabilimeter, for it is suitable for this kind

Table 5
Shift of the main silicate peaks

Reference		CP-06	
2θ	d	2θ	d
32.035	2.7916	32.220	2.776
32.465	2.7556	32.665	2.7392
34.200	2.6197	34.345	2.6090

[1] Cement nomenclature are used, C: CaO, S: SiO_2, A: Al_2O_3, C_3S: $3CaO{\cdot}SiO_2$, C_2S: $2CaO{\cdot}SiO_2$,C_3A: $3CaO{\cdot}Al_2O_3$.

of materials and widely used in the cement industry. Taking into account the conditions under which clinkers were milled, this method also allowed to obtain information about their relative hardness and consequently about their difficulty to be milled.

The clinker behavior during milling is closely related with the texture and structure of the crystals formed during clinkering [19] and with the vitreous phases present. Results obtained for the different samples are shown in Table 6.

Milled clinkers with pyrolitic carbon show a non-linear specific surface area in relation to the addition level used. Impurities added seem to modify their hardness, mainly when there is a low or a high concentration of them, needing in these cases a greater milling energy.

Waste carbon petroleum seems not to alter hardness, as the surface values obtained are not significantly different, nor differ from the reference sample as expected, because it does not incorporate a noticeable amount of unsuitable substances into the system as shown by the analysis methods used up to this moment.

It is worth observing what had happened when using the alternative fuel mixture. When increasing the percentage of ash addition, the specific surface area decreases, indicating a greater milling difficulty (harder material). The addition of impurities into the raw material affected the physicochemical properties of the liquid formed during clinkering, causing the formation of some phases in preference to others, and then affecting the clinker microstructure [8,20,21] as it could be observed by XRD. The greater amount of crystalline phases formed (specially C_3S) caused the greater milling difficulty.

3.3. Pyrometric cone equivalent temperature (PCET)

The test was carried out on the reference material with the addition of different carbons and fuel mixture in the test percentages. Results obtained are shown in Table 7. The temperature value of PCE obtained for the original sample (M0) was 1520 °C. From CP samples, we can infer that the pyrolitic carbon acts as flux at low addition percentage. The effect disappears at percentages equal to 0.8%.

When testing the material containing waste carbon, the value obtained decreased to 1500 °C, indicating that the material added acts by lowering 20 °C the flux temperature for every addition percentage. As it was observed, this is not due to the dopant addition but to the textural modification of the material. After the carbon burning, the material turned microporous, making the heat transfer to the inner mass of the cone easier, as the test furnace had a high convection of gases (the chamber volume was renewed around 60 times per second in that temperature range), and generating solid walls thinner than those of compact cones. For these reasons, the system finally collapsed some degrees before.

When the test was carried out with the fuel mixture ashes, it was observed that this addition increased the PCET as function of the impurity tenor and the values obtained were higher than those of the reference sample. This could indicate that the presence of them, unlike the previous cases, tends to form more refractory compounds. In addition, it is worth mentioning that the cones did not bend as usual at the temperature indicated but they violently melted, totally losing their shape. This indicates the formation of a fluid of much lower viscosity than that in the M0 case, which would cause problems in the industrial kiln and would damage the refractories if the melted liquid phases penetrated into them. However, during milling, the lower viscosity was good for the diffusional phenomena, helping the formation of greater crystals. The consequence in MIII was the formation of phases better crystallized and a greater resistance to the milling process.

Table 6
Blaine specific surface area in m^2/kg

Sample	m^2/kg
M0	363
CP-04	337
CP-06	359
CP-08	329
CR-5	359
CR-10	366
CR-20	353
MI	370
MII	347
MIII	316

Table 7
Equivalent temperature as function of impurity addition

Sample	Equivalent temperature (°C)
M0	1520
CP-04	1500
CP-06	1510
CP-08	1520–1510
CR-5	1500
CR-10	1500
CR-20	1500
MI	1530
MII	1540
MIII	1550

3.4. Thermal analyses

Differential thermal analyses and thermogravimetric analyses (DTA/TG) were performed in reverse order (heating–cooling) and under the same thermal conditions than those used for elaborating clinkers on the different crude dust samples with and without adding pyrolitic carbon, waste carbon and fuel mixture ashes within the percentages

indicated before. The following was the temperature program used:

From 20 to 1450 °C → rate 10 °C/min
At 1450 °C → permanence 1 h
From 1450 to 1350 °C → rate 30 °C/min
From 1350 °C to room temperature → 10 °C/min

During heating and after the system stabilization, the first endothermic peak of great magnitude corresponding to the limestone decomposition appears. This peak occurs at 922.3 °C and a TG mass loss was also observed. Once the decarbonation had been overcome and always during heating, the CaO reaction zone with the silicates and aluminosilicates showed an endothermic band in the 950–1100 °C zone. Because these reactions in solid state are mostly of diffusional control, this band is not defined as a peak. Then, flat and wide bands are generated instead of peaks. When the temperature went on increasing, an endothermic peak at 1345.6 °C was observed, caused by the semimolten phase formation (clinkering).

During cooling, only one exothermic sharp peak at 1285.1 °C, corresponding to the solidification of the liquid phase formed during clinkering, could be observed [22].

Fig. 2 shows DTG/TG diagrams for MIII. The other samples with different additions studied by DTA/TG show the same general aspect, with slight shifts of clinkering and crystallization temperatures, as shown in Table 8.

Samples calcined in the presence of pyrolitic carbon show a clinkering temperature similar to that of the reference sample and a slightly lower solidification. Samples with waste carbon show a greater clinkering temperature, which could be due to their lower thermal conductivity helped by the holes left by the carbon burned. Although this could contradict the foregoing PCET test, it must be taken into account that the atmosphere of this test remained almost stagnant whereas in the PCET test it was highly turbulent which increased the heat transfer phenomena. The solidification lowers to around 5 °C with respect to M0.

Clinkering temperature for samples of the M series show a similar tendency to that of the PCET tests, that is to say: MIII>MII>M0, with a ΔT of 5 °C between each of them.

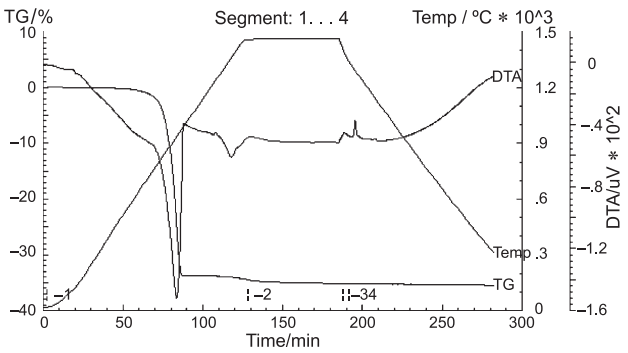

Fig. 2. DTA/TG diagrams for MIII.

Table 8
Reaction temperatures for different samples

Sample	Clinkering temperature (°C)	Solidification temperature (°C)
	Heating	Cooling
Reference	1345.6	1285.1
CP-08	1345.5	1282.6
CR-20	1350.0	1280.5
MII	1350.6	1284.5
MIII	1354.9	1290.0

The solidification temperatures are similar between MII and M0 but lower than that of MIII, coinciding with the sequence given for clinkering.

The slight increase of clinkering temperature and the solidification temperature variation observed in some cases, indicate a shift in the formation zone as well as in the remaining melted phase. Then, structural modifications were detected by XRD, different temperatures of PCE as well as different specific surface area between the milling material and the reference sample were observed.

3.5. Hydrated clinkers

3.5.1. XRD analyses

Samples were hydrated with w/c = 0.4 at early ages (from 1 to 28 days) and studied by XRD. There were no significant differences as regards the hydration type between the reference sample and the added ones, but small differences were detected at early ages taking into account the intensity (counts) of the main peak of $Ca(HO)_2$, showing lower intensities in those samples with additions.

In general, the hydration advance on the added samples was lower at early ages; however, from 28 days onwards, they reached (CP-08) and even slightly surpassed (CR-20 and MIII) the reference sample hydration. The samples with a greater impurity addition were in all cases those which show the better hydration advance at 28 days, within their respective series. This advance reached the maximum in MIII and consequently, greater values of compression strength at these ages could be expected.

3.5.2. Differential thermal analyses

The hydrated samples were analyzed by DTA/TGA for 45 days (with w/c = 0.4) with a heating rate of 10 °C/min up to 700 °C.

Two well-defined endothermic peaks corresponding to the dehydration of the C-S-H gels (first peak), and to the CH decomposition (second peak) were detected. The first one was observed in the 130–200 °C zone [23–25] as a wide band that shifts to higher temperatures when the hydration time increases according to references [26]. This peak round in shape is typical of substances that lose water without undergoing a significant structural change [27]. This change takes place with a great mass loss.

The second endothermic peak observed at around 540 °C is attributed to the decomposition of the crystalline CH

produced by the hydration of the silicate phases of the clinker [26,28]. The mass loss that takes place with this decomposition may be connected with the hydration increase.

Table 9 shows the results obtained for the different samples analyzed.

In Table 9, the temperatures of DTA peaks are slightly higher than those corresponding to TG because of the thermal inertia of the process.

Taking the M0 sample as comparative reference, for the CP-08, it was observed that, although both peaks of DTA do not show significant differences ($\Delta T \approx 0.2$ °C), the mass losses are slightly lower, as if the 45 days hydration did not progress in the same way.

Something similar happened with the CR-20 as regards the position of the DTA peaks, but it seems to show a greater amount of gels (Δm of TG first peak).

The samples of the M series show a similar peak temperature of gel in DTA test to M0, except MIII, which is slightly higher (1.5 °C). The mass variation shows less quantity of gels in MIII than M0 and similar amount of CH (second peak TG).

Anyway, the results obtained by this technique—the differences between them—are not significant enough to suppose mechanical properties will be greatly different.

3.5.3. Mechanical strength

Results of compression strength obtained as an average of five tests, at 3, 7, 14 and 28 days for the M0, CP-08, CR-20 and MIII samples are shown in Fig. 3.

At an early age (3 days) the results show a greater hydration increase in the samples of the M series (although they were not all represented in order to obtain a clearer figure); however, the individual values of each test were greatly dispersed. The remaining samples revealed lower average values, and CR-20 had the smallest one.

At 7 and 14 days, the dispersion of individual values decreased and, with the exception of CR-20, all values approached, except for the reference that showed a value slightly higher at 14 days.

At 28 days, the samples of the M series and CP-08 show a homogenous behavior and values were similar to those of the reference. The sample calcined in presence of waste carbon at every age shows values lower than those of the rest of the samples; however, at 28 days, this difference was of only 3.5%. From these results, it could be concluded that the presence of additions, as those additions carried out in this study, did not significantly alter the cement compression strength.

Table 9
DTA/TG results for different clinkers pastes

Sample	Δm [%] (Total)	First peak	Second peak	First peak		Second peak	
		DTA (C-S-H)	DTA (CH)	TG (C-S-H)		TG (CH)	
		[°C]	[°C]	Δm [%]	T [°C]	Δm (%)	T [°C]
M0	26.3	147.0	540.4	18.6	133.7	6.9	534.1
CP-08	25.9	147.2	540.2	18.2	135.3	6.4	533.3
CR-20	26.5	147.3	538.2	19.0	135.1	6.5	531.9
MII	26.3	147.3	534.0	18.2	130.8	6.3	527.7
MIII	26.2	148.5	538.9	18.4	134.2	6.8	532.5

Δm = mass variation.

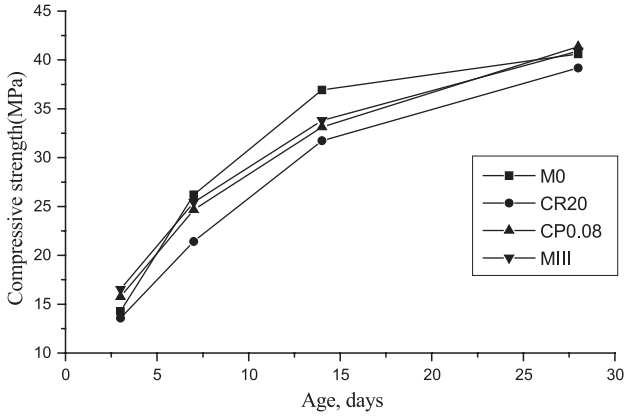

Fig. 3. Compressive strength, on paste in MPa.

4. Conclusions

4.1. Wastes that would be confined

4.1.1. Pyrolitic carbon

This waste would be suitable to be loaded with dust into the cement kiln, without altering the final mechanical strength. A slight increase of this value compared to the original one was observed at early ages (3 days).

4.2. Wastes that would be used for saving energy (fuel wastes)

4.2.1. Petroleum waste carbon

It would be suitable to take advantage of its energy; however, it has a slight tendency to damage the final mechanical properties.

4.2.2. Fuel mixture

It generates a greater crystallinity of the principal clinker phases and causes the greater energy requirement of the milling. The better crystallized C_3S presence determines the better values of compression strength at early ages.

The addition of this kind of wastes requires an excellent control of the temperature in the clinkering zone, because a slight excess of it over that temperature would excessively fluidize the clinker and might cause damages to the refractory lining of the furnace.

4.2.3. General

The addition of these wastes, within the percentages and under the conditions of this test, does not significantly alter the clinker properties.

Acknowledgements

The authors wish to thank Ms. María Eugenia Ghirimoldi for her contribution to this work.

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