Study of dehydration and rehydration processes of portlandite in mature and young cement pastes

Esperanza Menéndez · Carmen Andrade ·
Luis Vega

Abstract The hydration process of the cements induces the formation of different kinds of hydration products. The main products of hydration are C–S–H gel and portlandite [Ca(OH)$_2$]. The C–S–H gel is an amorphous compound that is discomposed progressivity with the temperature until approximately 1,000 °C, while the portlandite is discomposed between 450 and 550 °C. Also, calcium carbonate can be formed as a consequence of the portlandite carbonation. All of these processes can be analysed and quantified by simultaneous differential thermal analysis and thermogravimetric analysis. And by X-ray diffraction it is possible to identify the crystalline phases. Some authors have corroborated that the portlandite can be rehydrated, after dehydration processes due to thermal exposition of the cement paste. But all of these experiments have been made with young cement pastes or at temperatures lower than 650 °C. In this work the behaviour of young and mature cement pastes have been studied in relation with the portlandite decomposition and the possibility of the rehydration of it in water presence. We found that young pastes and old pastes, stored at laboratory conditions, and later burned, show a certain grade of rehydration, specially the pastes burned at 650 °C (with ≈ 80% of reformation of portlandite) with respect to the pastes burned at 1,000 °C (between 20

and 40%). It is corroborate that the rehydration process is directly related to the formation of CaO during the burning. Also, a formation of unstable portlandite is detected in young pastes burned at 650 °C, which can be rehydrated easily. Although, the mature pastes that have been burned initially and stored under laboratory conditions cannot be rehydrated, due to the formation of stable products during the storage.

Keywords Dehydration · Rehydration · Portlandite · Mature pastes · Young pastes

Introduction

The hydration of ordinary Portland cement produces the formation of different hydration products, which correspond mainly to hydrated calcium silicates, which evolve into amorphous structures and are known as C–S–H gel, crystalline calcium hydroxide, also known as portlandite, as well as other lesser compounds such as primary ettringite. Additionally, calcium carbonate can be formed, crystallised in the form of calcite or aragonite generally due to the carbonation mainly of the portlandite, brought about by the interaction with ambient CO$_2$ [1]. For its part, cements with the addition, for example, of fly ash or blast furnace slag, give rise to the formation of hydration products mainly similar to those of OPC [2, 3]. The evolution of hydration processes can be monitoring by thermal analysis, mainly calorimetry and thermogravimetry, this specially interesting when the new pozzolanic addictions are using [4–7].

The effect of temperature on the hydration products of the cement gives rise to alterations in it. Thus, it is possible to identify the temperature intervals in which the decomposition of certain compounds present in the cement paste takes place. Thus, the portlandite decomposes approximately

E. Menéndez (✉)
Institute Eduardo Torroja of Construction Science
(IETcc-CSIC), Madrid, Spain
e-mail: emm@ietcc.csic.es

C. Andrade
Centre of Investigation in Security and Durability of Structures
and Materials (CISDEM–CSIC–UPM), Madrid, Spain

L. Vega
Ministry of Development of Spain, Madrid, Spain

between 450 and 550 °C, calcium carbonate approximately between 700 and 900 °C, while the crystallisation water of the hydration products disappears gradually between 100 and 1,000 °C. It is considered that the total dehydration of the CSH comes about from the exposure of pastes to 1,000 °C for 15 min, in small-sized samples [1]. This behaviour of the pastes in the presence of temperature allows the monitoring of the existence of certain products, when these pastes are tested by means of simultaneous analysis by differential thermal analysis and thermogravimetry (DTA–TG). This technique also allows us to identify the presence of hydrated products. On the other hand, work has been carried out using DTA–TG techniques to determine the degree of hydration of cement pastes modified with polymers, through the determination of the amount of portlandite, carbonates, and hydration products, although in these cases the polymer pyrolysis is also determined by means of the quantification of the loss of weight that takes place between 390 and 450 °C [8]. Other thermal analysis techniques on hydrated products in cement are related to the determination of the approximate content of the cement in concrete with sand and siliceous gravel by quantifying the loss of weight that takes place between 100 and 750 °C in samples previously dried at 110 °C [9]. Another application of these techniques in the analysis of cement pastes is the use of TG curves to identify the presence of brucite, which is formed as a consequence of the reaction of dolomite additions with the portlandite that gives rise to the formation of brucite through ionic exchange [10]. Analysis through X-ray diffraction (XRD) also allows the crystalline phases present in the burnt or rehydrated reference pastes to be identified. The thermoanalytical technique is applied jointly with XRD for characterisation of burnt products. For example, it is observed that the temperature of decomposition of carbonates decrease until 500 to 800 °C due to the formation of complex compounds of amorphous forms of carbonate hydroxide hydrates (CCH) [11].

Other works use thermal analysis techniques also combined with other tests to evaluate the situation of concrete exposed to fire, in such a way that the progression of the temperature in the interior of the material allows the concrete damaged by fire to be re-evaluated structurally [12]. Another evaluation application in the presence of high temperatures could be able to check the behaviour of cement with partial substitutions of fly ash and homra in the presence of fire by analysing the behaviour at different temperatures of between 200 and 800 °C, concluding that the use of additions improves the hydrated pastes resistance to fire. To do it, the water of a normal consistency and the amount of water chemically combined through DTA analysis is determined [13].

The analysis of the dehydration and rehydration of cement pastes through thermal analysis techniques or by other instrumental techniques has been tackled at different test temperatures and for different degrees of maturity of the hydrated test specimens, although generally dehydration and rehydration is analysed by using pastes or young materials, that is, with curing at less than 100 days. The hydration reaction in young pastes is still incomplete, although its evolution is fairly slow after these periods. On the other hand, the young pastes have not had sufficient time in contact with ambient conditions for there to have been ambient carbonation through atmospheric CO_2. However, the behaviour of the material in mature pastes, in those in which a stabilisation of the hydration products, together with a superficial carbonation through the action of ambient CO_2, will have to be checked.

Different authors have studied the dehydration and hydration of young pastes under different test conditions. The dehydration of portlandite has been studied using high-pressure DTA (a 17.8 ± 1 bars) observing that dehydration takes place at a higher temperature than at atmospheric pressure. Under these conditions a phase called portlandite II is formed, which is detected through XRD because at low 2θ angles the background of the film is very high, and reflections, if present, could not be observed. However, this phase cannot be detected by DTA as its transformation is very fast [14]. Other studies analyse the rehydration of pastes burnt at 450 and 750 °C, 2 h in cured pastes and stored for 70 days sealed at an ambient temperature. Under these test conditions a total decomposition of the portlandite does not take place not even with burning at 750 °C. And in the rehydration process, the recrystallisation of calcite, portlandite and ettringite and the CSH reformation from the new nesosilicate with a CaO/SiO_2 ratio close to the initial C–S–H gel and recovering its initial stoichiometry is not observed. The studies are carried out using a combination of DTA–TG with magnetic nuclear resonance (MNR) [15]. On the other hand, the reformation of portlandite in 'in situ' tests using neutron diffraction has also been observed in those tests that study pastes cured for 28 days and that have been burnt at 650 °C, cooling down in contact with water vapour which favours the reaction of the anhydrous phases formed to rehydrate the portlandite [16]. Also, in pastes cured under water for 28 days and burnt at temperatures higher than 500 °C the dehydration and decarbonation are irreversible. However, the rehydration of portlandite is reversible and occurs rapidly after heat treatment [17].

On the other hand, in mature pastes, stored for 7 years in sealed cylinders and treated at temperatures of between 80 and 300 °C a reversibility of dehydration is observed, when the restoration by direct water absorption and water vapour absorption is analysed. The modification of the porosity associating the collapse of the C–S–H gel microstructure with the increase in pores in the range of 0.02–0.2 μm in diameter, which occurs between 80 and 150 °C is also

analysed in a complementary manner. Although it is considered that some degree of reversibility exists for OPC pastes heated at temperatures of up to 300 °C this is associated with a rehydration of decomposed C–S–H or hydration of initially unhydrated cement grains [18].

In the present work the decomposition and rehydration of portlandite have been analysed in young and mature cement pastes, in 1- and 4-year-old samples. The young and mature pastes have been tested at different temperatures of calcinations (650 and 1000 °C). Also, the potential rehydration of the portlandite is analysed after the calcinations. The hydrated and non-hydrated phases have been determined using techniques of thermal analysis and XRD, analysing the relation between the crystalline compounds formed and the compounds identified by thermal analysis techniques.

Experimental

Materials

Cement pastes have been analysed to test the behaviour of hydrated cements. These pastes were subjected to different burning temperatures and rehydration processes. The pastes were manufactured with a CEM I 42.5 cement without additions. The chemical composition of the cement used is shown in Table 1.

Paste cubes were manufactured with a water/cement ratio equal to 0.5 and with dimensions of 3.5 cm³. They were cured for 24 h in a humidity chamber at 20 °C with a relative humidity greater than 95%. After the initial curing, the test specimens were left for 51 days in cured water, in order to avoid lixiviation. After the hydration period, burning and rehydration tests at different ages were carried out. Reference pastes that were not subject to heating processes were also analysed.

Burned and rehydration processes

Different burning and hydration processes were applied to the cement paste test specimens, testing them a different ages.

The burning process was carried out at two temperatures 650 and 1,000 °C. These temperatures were selected on the basis that at 650 °C the portlandite should decompose totally. On the other hand, at a temperature of 1,000 °C it

should give rise to a general decomposition of the cement paste and all of its hydration products. The burnings were carried out over a period of 48 h continuously to guarantee that all of the paste was subjected to a programmed temperature. After the burning, the test specimens were left to cool to ambient temperature in the furnace.

The rehydration was carried out over 14 days by exposing the test specimens to immersion in distilled water, in such a way that the burnt or reference test specimens were completely covered. This hydration period is considered sufficient to bring about a complete interaction between the material and the aqueous medium.

Methods

The test samples were analysed using different instrumental techniques after each test. The thermal behaviour of the cement pastes was analysed using simultaneous equipment for DTA–TG analysis with a Netzsch, STA 409 model. All of the tested cases were carried out under the following conditions: 50 mg sample, heating temperature 10 K/min, heating to 1,050 °C, platinum crucible, and ambient 100 cm³ of N_2. By means of this instrumental technique, the decomposition processes of the main hydration compounds were able to be identified: the dehydroxylation of the portlandite (approximately between 450 and 550 °C) and the loss of crystallisation water (which occurs gradually between 100 and 1,000 °C), together with the decomposition of the calcium carbonates, formed mainly through the carbonation of the portlandite, which is produced approximately between 700 and 850 °C. From the loss of hydroxyl ions (OH^-) it is possible to calculate the amount of portlandite ($Ca(OH)_2$) found in the sample. In the same way the amount of calcium carbonate ($Ca(CO_3)$) can also be calculated from the loss of CO_2.

On the other hand, the crystalline phases were analysed mainly by means of XRD, using the Bruker, D8 Advance model equipment. Finally a micro-structural analysis was carried out on the initial paste, both burnt and without burning by means of backscattered electronic microscopy (BSE), using the Jeol, 5400 model equipment.

Samples

Tests were carried out under different conditions of burning, rehydration and ambient exposure over different

Table 1 Chemical composition of the ordinary Portland cement CEM I 42.5

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	LOI	Cl^-
CEM I 42.5	20.5	5.19	2.20	62.04	3.61	2.83	0.30	0.86	0.24	0.14	2.52	0.03

periods. The samples for testing were codified in accordance with the treatment process to which they were subjected. The different testing conditions and their associated codifications are listed below:

- Thermal treatment:

  - Ref: Non-burnt and initially tested pastes or after a certain period of time exposed to laboratory conditions (20 °C and 60% of relative humidity) over a testing period indicated in each case.
  - Ini: Burnt pastes, after a period of initial hydration (51 days) and exposed to laboratory conditions (20 °C and 60% of relative humidity) over a testing period indicated in each case.
  - 650: Pastes burnt at 650 °C, for 48 h, tested after this burning or after the calcinations process and later rehydration.
  - 1,000: Pastes burnt at 1,000 °C, for 48 h, tested after this burning or after the calcinations process and later rehydration.

- Testing period:

  - 1A: Pastes exposed to laboratory conditions (20 °C and 60% of relative humidity) for 1 year.
  - 4A: Pastes exposed to laboratory conditions (20 °C and 60% of relative humidity) for 4 years.

- Rehydration:

  - Reh: Rehydrated pastes, for 14 days in water.

In all of these cases the samples are codified to indicate the thermal treatment, the testing period and the rehydration as required.

Results and discussion

Young and mature reference pastes

Reference pastes, not subjected to burning but subjected to rehydration in the case of mature pastes, were analysed. The initial tests were carried out after a curing period of 51 days in water. The pastes were also tested after 1 and 4 years, exposed to ambient conditions in the laboratory, without rehydration and rehydrated. In order to carry out the rehydration process, samples were taken from the surface area of the specimen samples, since it is considered that any contribution of water to the material will be produced from the exterior surface. The surface of the samples exposed to ambient conditions (Ext.) and their internal parts (Int.) were analysed in the reference samples with the aim of evaluating the relationship between the portlandite and carbonates present.
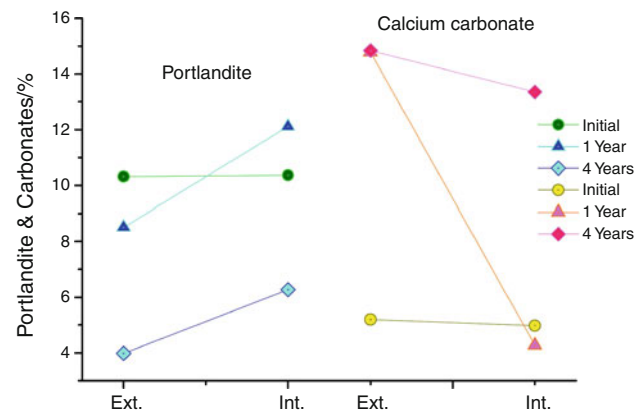

Fig. 1 Amounts of portlandite and calcium carbonates in the interior and on the surface of the samples obtained by DTA–TG analysis in reference pastes under different conditions
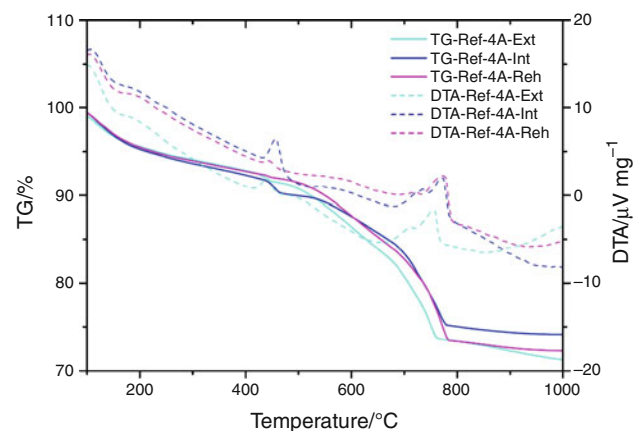

Fig. 2 DTA–TG curves of reference samples 4 years old in the interior and exterior of the samples and after the rehydration process

It was seen in the DTA–TG in all cases, that the surface has more carbonates than in the interior of the specimen samples due to the action of ambient CO_2. This is seen even in the test specimens initially analysed after 51 days' curing under water, even though it is more evident in the pastes situated in the laboratory for 1 and 4 years. The evolution of time indicates a progressive carbonation of the surface, under laboratory conditions, with the consequent reduction in the amount of portlandite, while in the interior there is an increase in the amount of portlandite, up to a year, with a later reduction in it, due to the progression of the carbonation towards the interior of the test specimen. Figure 1 details the amounts of portlandite and carbonates present in the cement pastes under the different test conditions. For its part, when the pastes exposed to ambient condition for 1 and 4 years are rehydrated, there is an increase in the calcium carbonates at the same time as a proportional reduction in the amount of portlandite, when there is predicted to be an increase in the amount of portlandite. This is because the presence of a certain amount of

Fig. 3 Microstructural aspect of the original pastes and after burned at 650 and 1,000 °C during 48 h

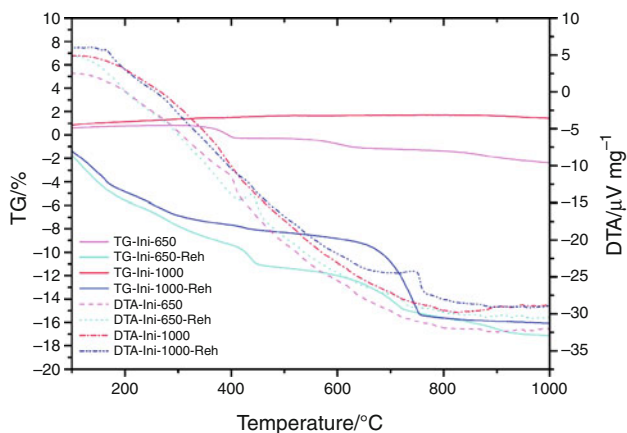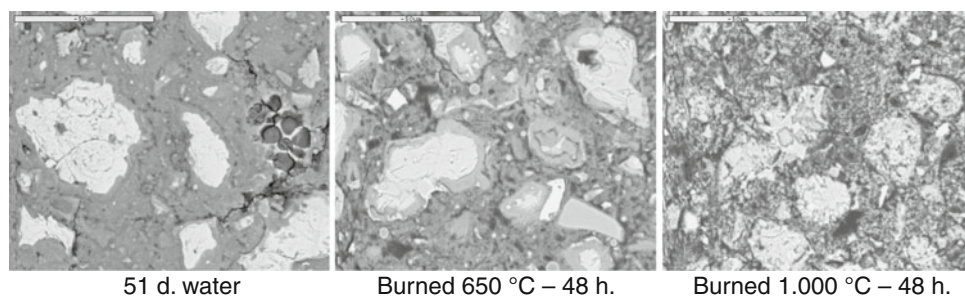51 d. water   Burned 650 °C – 48 h.   Burned 1.000 °C – 48 h.

Fig. 4 DTA–TG curves of young pastes burned at 650 and 1,000 °C and after their rehydration

water favours the carbonation of the cement pastes which would favour a rapid formation of calcium carbonates instead of stabilising the portlandite [19]. Figure 2 details the curves of the DTA and the TG of the exterior and interior reference pastes and rehydrated at 4 years, in which the relative evolution of the portlandite and the carbonates in each case are seen. For its part the analysis by means of DRX indicates that the carbonates formed correspond to the crystalline shapes of calcite and aragonite.

Pastes initially burned at 650 or 1,000 °C, stored and rehydrated

The behaviour of the pastes burnt at 650 and 1,000 °C is studied, just after the curing period, analysing its composition after the burning and after a period of 1 and 4 years under laboratory conditions. The potential rehydration of the pastes were also analysed at each of the test periods. The presence of portlandite and carbonates are studied by means of analysis through DTA–TG and the crystalline phases present, by means of analysis through DRX.

Additionally the micro-structure of the paste is analysed by means of BSE, both before and after the burning processes at 650 and 1,000 °C. It can be seen that initially the paste has a homogenous aspect in general and somewhat denser around the interfaces with the anhydrous cement particles. For its part, the paste burned at 650 °C shows degradation with an increase in porosity, while dense hydration products surrounding the anhydrous cement particles were still seen. Finally, the pastes burned at 1,000 °C show a much degraded aspect in the cement paste with a massive destruction of the hydration products together with a significant increase in porosity. In Fig. 3, the initial aspect of the paste can be seen, after burning at 650 and 1,000 °C.

In the young pastes burned at 650 °C the disappearance of the majority of the portlandite can be seen, while the remaining carbonates are maintained. And, in the rehydration process, a significant neo-formation of portlandite can be seen, rehydrating to approximately 80% of it. For its part, in the young paste burnt at 1,000 °C both the portlandite and the carbonates disappear. And there is a much more moderate neo-formation of portlandite in the rehydration process, around 20%. There also appear crystallised carbonates in the form of calcite and aragonite. Figure 4 details the DTA–TG graphs of the initial samples burnt at 650 and 1,000 °C and later rehydrated. In the analysis through XRD of the paste burnt at 650 °C and rehydrated, in which a neo-formation of portlandite can be appreciated, a double peak is seen in the area of 34° 2θ, where the portlandite reaches its maximum. This double peak disappears in the rehydrated sample, forming a characteristic single peak of the portlandite. Therefore, the simple rehydration of the portlandite in the young paste burnt at 650 °C is associated to a partial decomposition of it that tends to crystallise in the presence of water and with the formation of an unstable phase that can be rehydrated easily. In Fig. 5 the splitting into two of the portlandite peaks can be seen in the sample burnt at 650 °C, in relation to the reference and rehydrated samples.

When these burnt pastes are studied by DTA–TG and DRX, after 1 and 4 years, having been kept under laboratory conditions, it is seen in all of the carbonate ones, but not in the portlandite. The calcium carbonates are crystallised mainly in the form of calcite and aragonite and in some cases little quantities in the form of vaterite. As regards the basic compounds, the presence of anhydrous calcium silicates is identified, but not CaO (which does
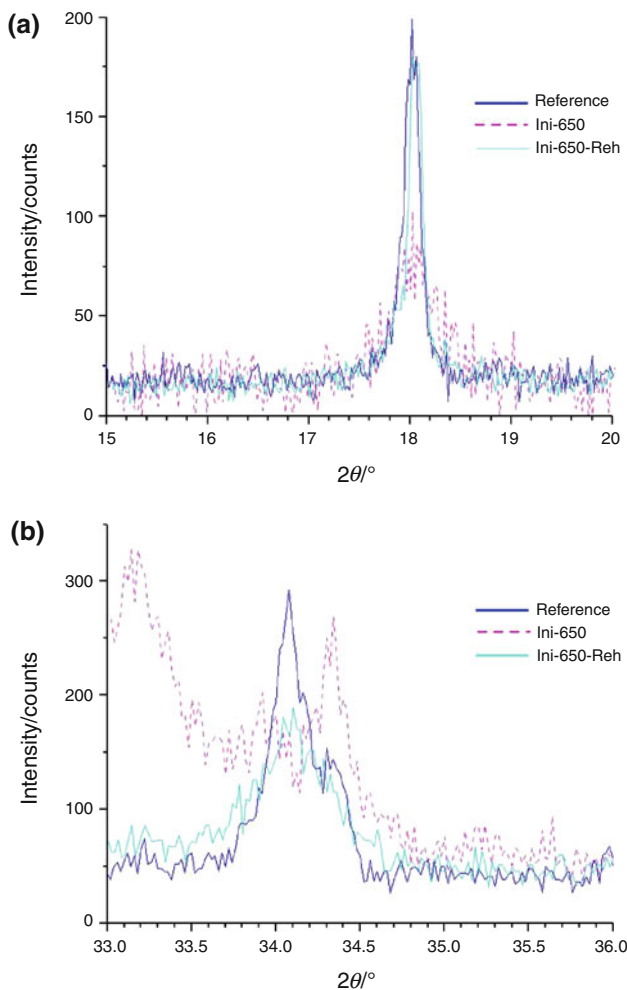
Fig. 6 DTA–TG curves of mature pastes, 4 years old, initially burned at 650 °C in which there is no reformation of portlandite due to the rehydration process

Fig. 5 Characteristic peaks of the portlandite in XRD in the areas 18° 2θ (a) and 34.1° 2θ (b), can be observe formation of unstable portlandite after the burned, forming a double peak in 34.1° 2θ area

appear in recently burnt pastes). When these pastes are subjected to a process of rehydration, a neo-formation of portlandite is not produced in the pastes stored under laboratory conditions for 1 and 4 years. Figure 6 details the DTA–TG graphs of the pastes after 4 years under laboratory conditions and after its rehydration. The presence of calcium carbonates can be seen but not portlandite.

Mature pastes burned at 650 and 1,000 °C and rehydrated

The behaviour of pastes recently burnt at 650 and 1,000 °C were also analysed, both in young pastes (after 51 days curing under water) and in mature pastes (kept under laboratory conditions for 4 years) and its behaviour in the face of rehydration. The reference pastes, stored 1 and 4 years, are burned after this period in the laboratory and after the rehydration of the pastes is studied.
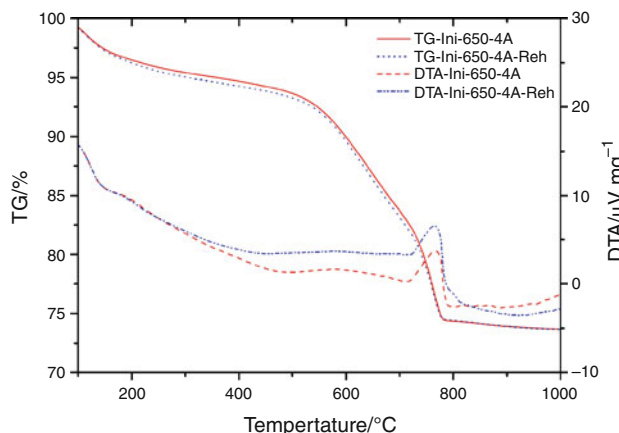
In the young paste recently burnt at 650 °C some portlandite can be seen, as well as calcium carbonate, which does not begin to disappear at this burning temperature. In the mature pastes burnt at 650 °C neither is there a complete decomposition of the portlandite, even though the amount of portlandite that remains unburnt is less. For its part, the amount of carbonates that does not decompose is similar in both the young and mature pastes, these carbonates are crystallised in the form of calcite and aragonite. In the analysis through DTA–TG of the pastes burnt at 1,000 °C the disappearance of the portlandite and the carbonates are seen both in young and mature pastes. However, in the analysis through XRD crystalline phases of calcium carbonate (calcite and aragonite) are identified, as well as the basic compounds (CaO and calcium silicates). This is associated with the re-crystallisation of small crystals of calcium carbonates when the burned pastes are in contact with CO_2 environmental. Figure 7 details the
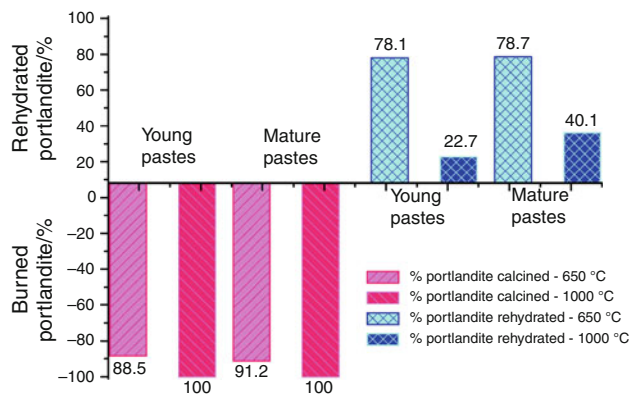

Fig. 7 Percentages of portlandite burned (at 650 and 1,000 °C) and rehydrated, with respect to the original ones, calculated from the DTA–TG analysis, in young and mature pastes
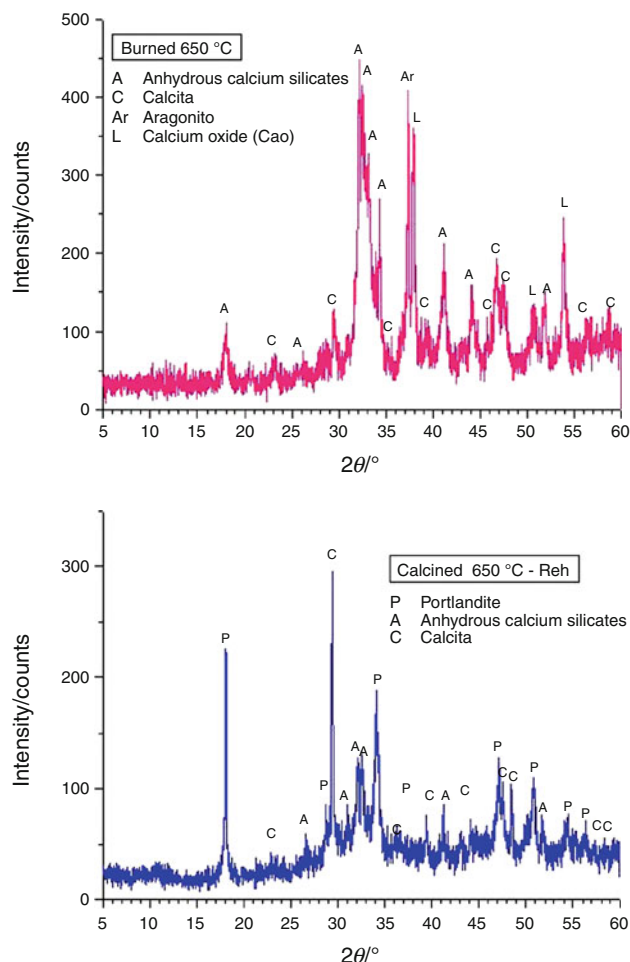
Fig. 8 X-ray spectra of pastes burnt after stored at 650 °C, with presence of CaO formed due to the calcinations (L) and later rehydrated, where the CaO has been disappeared due to the formation of portlandite (P)

percentages of burnt portlandite in relation to the reference sample at each age, in both the young and mature pastes for each burning temperature. It is observed that the portlandite have been completely burned when is exposed to temperatures of 1,000 °C. Although, when the pastes are burned at 650 °C a little quantities of portlandite remain, and there are not a big difference between the behaviour of young and mature pastes.

As regards the rehydration processes a certain degree of rehydration is seen in all of the cases, young and mature pastes burnt after storage at 650 and 1,000 °C. This rehydration is associated with the reactivity of the CaO, which is formed as a consequence of the burning. In the analysis through XRD of the recently burnt young and mature pastes, CaO is formed among other products, disappearing in the rehydrated pastes. Therefore, the neo-formation of the portlandite can be associated directly with the reaction of the CaO in the presence of water to form the portlandite. In this case we can observe that the pastes recently burned

are rehydrated, while the pastes burned 1 or 4 years ago cannot be rehydrated. This is associated with the carbonation and forming of stables compounds after the burned during the time stored at laboratory conditions. Figure 8 details, as an example, the XRD spectra of the paste recently burnt at 650 °C and then rehydrated (in which the CaO disappears in the rehydration to form portlandite) and of the paste burnt at 650 °C and kept under laboratory conditions for 4 years and then rehydrated (where neither the presence of CaO, nor the formation of portlandite in the rehydration is seen). On the other hand, the amount of rehydrated portlandite is quantified, in recently burnt pastes, in relation to the percentage of portlandite in the reference paste corrected with the amount remaining after the burning, in the case of there being some. In Fig. 7 it is seen that the percentage of the rehydration of the portlandite, after recently burning at 650 °C is around 80% for young and mature pastes. With respect to the rehydration processes and the reformation of the portlandite, the behaviour between pastes burned at 650 and 1,000 °C are very different. While in the pastes recently burnt at 1,000 °C the percentage of rehydration is less, even though a greater neo-formation of portlandite in mature pastes is seen. There is a clear relationship between the formation of crystalline CaO due to the calcinations process and the rehydration of the portlandite. In the first case, the reformation of portlandite is about an 80% of the original. But the pastes burned at 1,000 °C shown a rehydration degree much smaller than the others (between 20 and 40%). In this case, the mature pastes have shown approximately the double of the reformation of portlandite than the young ones. This is associated with the quantity of CaO formed during the carbonation.

Conclusions

The unburnt reference pastes carbonate superficially over time, while in the interior the hydration continues, making the proportional amount of portlandite increase even in the pastes exposed to ambient conditions until a year. However, over longer periods of exposure under laboratory conditions the carbonation progresses to the interior of the test specimen, making the proportional amount of portlandite decrease.

The rehydration of mature unburnt pastes, stored for 1 and 4 years under laboratory conditions, produces an increase in the relative proportion of calcium carbonates instead of producing an increase in the portlandite, as humidity favours carbonation in the paste, making it form calcium carbonates rapidly.

The micro-structural analysis of young pastes burnt at 650 and 1,000 °C in relation to the reference, indicates that

those burnt at 650 °C suffer an increase in porosity and a partial decomposition of the hydration products, with only dense hydration products remaining around the anhydrous cement; while those burnt at 1,000 °C suffer a massive destruction of the hydration products.

The burning of pastes at 650 °C over periods of 48 h produces a very significant, but not total, decomposition of the portlandite. The formation of an unstable portlandite is produced which tends to rehydrate easily, as well as CaO. Neither is there a total decarbonation. For its part, the burning of the pastes at 1,000 °C for 48 h produces a total decomposition of the portlandite and the carbonates, even though the analysis through XRD reveals the existence of some crystalline calcite and aragonite.

In the young and mature pastes there is a partial rehydration of the portlandite when it is carried out immediately after the burning. This rehydration is greater in pastes burnt at 650 °C rather than 1,000 °C, due to the presence of CaO and unstable portlandite formed during the burning process.

However, the mature pastes stored after their burning for 1 and 4 years under laboratory conditions do not present a neo-formation of portlandite when it is rehydrated. This is because during the period of storing, the CaO reacts with the ambient CO_2 stabilising it and forming calcium carbonate.

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