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Decalcification of activated paper sludge – Fly ash-Portland cement blended pastes in pure water

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ABSTRACT

Decalcification in pure water of ternary Portland cement (TPC) pastes, containing thermally activated paper sludge and fly ash, has been evaluated from the leaching of Ca^{2+} in pure water at the temperature of 20 °C during 90 days. Monitoring of calcium loss showed that the leaching kinetics are controlled by diffusion. The degradation of the material over time is estimated from the calcium effective diffusivity. A similar study of plain ordinary Portland cement (OPC) pastes was carried out for comparison. The results showed lower effective diffusion coefficients of calcium in the case of the TPC pastes. This behaviour is related to its microstructure, which is denser than that of OPC as a result of the pozzolanic activity of both additions.

1. Introduction

The replacement of cement clinker by pozzolanic additions represents one of the best solutions to mitigate CO_2 emissions caused by the cement industry. Further benefits to the environment can be achieved if the pozzolanic addition is a waste material [1–4]. However, any modification of the original cement matrix affects the calcium leaching (decalcification) of blended cementing matrix.

The decalcification of cement matrix is caused by the dissolution of hydrated compounds when it is exposed to pure water, or another aggressive environment. The leaching of ions (mainly calcium and hydroxide) from the pore solution to the external environment is responsible for the dissolution of these hydrates. This phenomenon typically affects structures which have been in contact with pure and acidic waters for long periods: dams, water pipes, radioactive waste disposal facilities, etc. Over the past two decades, it has been identified as a very relevant issue for nuclear waste storage. The consequences of ionic leaching are an increase of the porosity and permeability, and a loss of mechanical strength [5–17].

Therefore, knowledge about the leaching of calcium from new cement based materials, including the influence of new pozzolan blends is important due to its implications toward the durability and degradation of the material. It is also important on the estimations of the kinetic process [18].

This work is part of an extensive research on the durability of a specific ternary Portland cement (TPC), formed by an ordinary Portland cement (OPC), which was partially replaced by a pozzolan blend (thermally activated paper sludge (APS) and fly ash (FA)), at a rate of 21 wt.%. Both replacement materials are well known by their pozzolanic properties but have different reaction rates [5–9].

In this paper, the decalcification of TPC and plain OPC pastes has been investigated by means of leaching of Ca^{2+} caused by the immersion of pastes in pure water (conductivity <5 μOhms/cm) at the temperature of 20 °C during 90 days. The objective is to analyze the influence of this new blend of pozzolans on the calcium leaching with respect to the reference paste.

2. Experimental

2.1. Materials

A commercially available ordinary Portland cement (OPC) of high alkali content was used in this work. The cement is designed as CEM I 52.5N, according to the existing European standard [19], and was supplied by Financiera y Minera (Italcementi group).

The activated paper sludge (APS) was obtained by controlled calcination of paper sludge (PS) in a laboratory electric furnace at 700 °C for 2 h of retention, as described in previous work [20].

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The starting PS was provided by Holmen Paper Madrid Company, which uses 100% recycled paper as raw material.

A Spanish commercial fly ash (FA) from coal combustion, identified as V class in the European standard, according to its CaO content (below 10%) [21], was used in this work.

2.2. Blended cement pastes

APS–FA–OPC ternary blends were prepared by mixing APS and FA pozzolans with a ratio of 1:1 by weight and subsequently partial replacement of OPC by 21% of pozzolan blends. In Table 1 and Fig. 1 the corresponding chemical and mineralogical crystalline phase analyses of the raw materials are presented. More details of the characterization of raw materials can be consulted in [21].

Pastes of both TPC and OPC cements were prepared with pure deionized water at a water to binder ratio of 0.5. After mixing, different portions were moulded into 1 cm × 1 cm × 6 cm prismatic samples and compacted by vibration. After 1 day at 100% relative humidity (RH), samples were demoulded and cured by immersion in pure water at 20 °C for 27 days.

2.3. Aggressive dissolution and determinations

Pure deionised water with a conductivity <5 μOhms/cm and pH of 6 was used as decalcification agent. Series of six samples were immersed in individual plastic containers employing a ratio of 5 cm between the volume of the solutions and the external geometric surface area of samples: 26 cm^2 for one prismatic sample and 156 cm^2 for six prismatic samples.

The Ca^{2+} and pH were analyzed after intervals of static leaching, for cumulative leaching times up to 90 days. The temperature was 20 °C during the leaching process. The analyses of the leachates were carried out in duplicate samples leached.

The concentration of calcium was determined by titration against 0.01 N EDTA by means of a Mettler DL40RC automatic memotitrator, with potentiometer determination of the end point. Porosity and pore-size distribution were investigated by mercury intrusion porosimetry carried out with a Micromeritics Auto Pore IV 9500 v1.05. X-ray diffraction patterns were recorded on a BRUKER D8 ADANCE diffractometer operating at a wavelength of 1.5404 (λCu kα) and at 2θ interval of 5–60°. SEM analysis was performed with a Jeol 5400 instrument equipped with an Oxford ISIS model energy dispersive X-ray spectroscopy module (EDX). The samples were covered with carbon by sputtering. The samples were prepared by traversal fracturing the respective small pieces with a hammer and chisel.

3. Results

In Fig. 2, the cumulative Ca^{2+} leached of the TPC and OPC pastes is presented. The concentration of Ca leached is low in the two cases and mainly for the TPC paste: significantly lower than typical values of 21 mM for solubility of portlandite at 20 °C [22]. It is well known that portlandite ($Ca(OH)_2$) is the first hydrated compound which will dissolve, because it is the most soluble hydrated compound, but its solubility decreases as pH increases: in the presence of NaOH 1 M and pH of 14 the concentration of Ca^{2+} decreased down to 0.36 mM at the temperature of 20 °C [22].

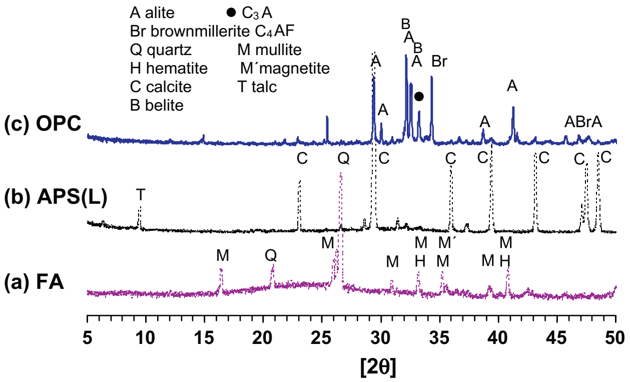

Fig. 1. XRD patterns of raw FA, APS(L) and OPC.

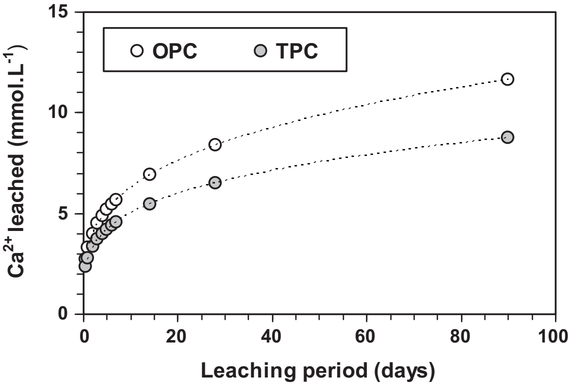

Fig. 2. Cumulative concentration of Ca^{2+} leached. OPC and TPC pastes.

So, the reason for the low values, aforementioned, is the high alkali content of the cement (see Table 1) (1.82% of Na_2O equivalent). According to this alkali concentration and the water/binder ratio of 0.5 used, the Na^+ concentration in the pore solution would be 1.2 M, with the same concentration of OH^- (considering the total dissociation of the NaOH and the total dissolution of alkalis in the pore-solution). In fact, pH values of 14 and 13 were reached in the water used after 28 days of curing of OPC and TPC pastes, respectively.

In the case of the TPC pastes, the amount of Ca^{2+} leached is lower than that of OPC pastes. This could be due to (i) the dilution effect of the additions on the cement content and (ii) the pozzolanic reaction of additions, which consumes portlandite.

So, for a more accurate comparison between the two types of pastes, it must take into account the cumulative fraction leached (CFL) of Ca^{2+}. CFL = c_n/C_0, where c_n is the concentration of Ca^{2+} of leachate (values of Fig. 2) and C_0 is the total amount of calcium ion from the cement and additions: 441 and 376 mM of Ca^{2+} for the OPC and TPC cements, respectively.

The evolution of the CFL with the square root of time (Fig. 3) is bilinear showing a change of the slope at 7 days. As the samples

Table 1
Chemical composition of raw materials (% by weight).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	Mn_2O_3	Cl^-	LOI[a]
FA	55.7	24.0	4.8	2.2	0.9	0.89	2.2	0.46	0.69	0.28	0.06	0	7.6
APS(L)	13.9	8.3	0.5	47.1	1.6	0	0.3	0.23	0.25	0.2	–	0.1	26.7
OPC	20.0	5.7	3.2	58.9	1.7	4.3	1.6	0.77	0.15	0.21	0.03	Traces	2.6

[a] LOI = loss on ignition.

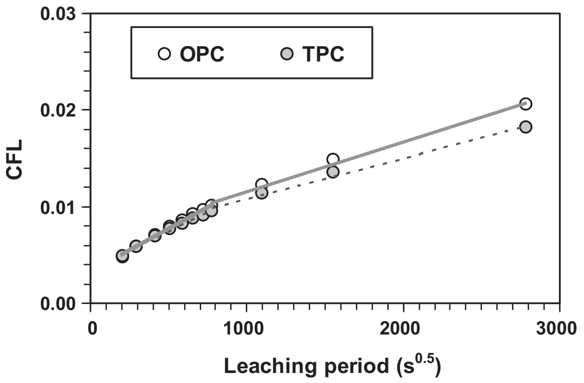

Fig. 3. Cumulative fraction leached (CFL) of Ca^{2+} versus the square root of time. TPC and OPC pastes.

maintained their dimensional integrity during leaching and taking into account the very low CFL values (lower than 20%), they may be considered as a semi-infinite medium, where the outer boundary is considered to be effectively at an infinite distance from the inner region during the experiment [11].

The leaching mechanism of Ca^{2+} is diffusion-controlled and the effective diffusion coefficients can be calculated according to Fick's second law, as follows [11],

$$\mathrm{CFL}(V/S) = 2(D_e/\pi)^{0.5}t^{0.5} \tag{1}$$

where CFL is the cumulative fraction leached (c_n/C_0); V/S is the volume to surface ratio of specimen (1.38 cm in our case), t is the leaching time in seconds.

The effective diffusion coefficients D_e values are calculated from the slopes of Fig. 3 as follows:

$$\mathrm{Slope} = (2(D_e/\pi)^{0.5})(V/S)^{-1} \tag{2}$$

As it can be seen in Fig. 4, the effective diffusion coefficient (D_e) of the TPC paste, calculated from the first 7 days of leaching ($9.7 \times 10^{-11}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$) is slightly lower than that of the OPC paste ($1.4 \times 10^{-10}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$). In the case of the second lineal zone, D_e values of both TPC and OPC pastes decreased almost one order of magnitude ($2.7 \times 10^{-11}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ and $5.4 \times 10^{-11}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$, respectively).

As it was aforementioned, in the case of the OPC paste, the high alkali content of the cement (1.82% Na_2O equivalent) is the responsible for the strong decrease of the solubility of portlandite (from 20.9 mM to 0.36 mM) justifying the low concentration of Ca^{2+} leached.

The thickness of the degradated zone, caused by the leaching of Ca, as a function of time and D_e value can be calculated by applying [23]:

$$x = 3.64(D_e t)^{0.5} \tag{3}$$

In Fig. 4 are included the two values of degradation thickness, obtained by applying Eq. (3), from the data of the first 7 days and after 7 days of leaching, for an estimated service life of 100 years.

Considering the first lineal zone, where Ca^{2+} leaching is controlled only by diffusion, the values of the degradation thickness extrapolated to 90 days from Eq. (3) would be 0.12 cm and 0.10 cm for the OPC and TPC pastes, respectively. These values concur fairly well with those previously obtained by Goñi et al. [13] and Revertegat and Glasser [24]: 0.11 cm and 0.12 cm, respectively. In the last case, the authors developed a corrosion model of Portland cement paste ($w/c = 0.4$) (discs of 70 mm of diameter and 4 mm of thickness) from leaching test data, which were obtained at 20 °C in deionised water as the corrosion solution. It should be noted the different dimensions of the sample employed by Revertegat and Glasser in comparison with the cylinder of 50 mm of diameter and 100 mm of height, employed by Goñi et al. and prismatic 10 × 10 × 60 mm used in the present work.

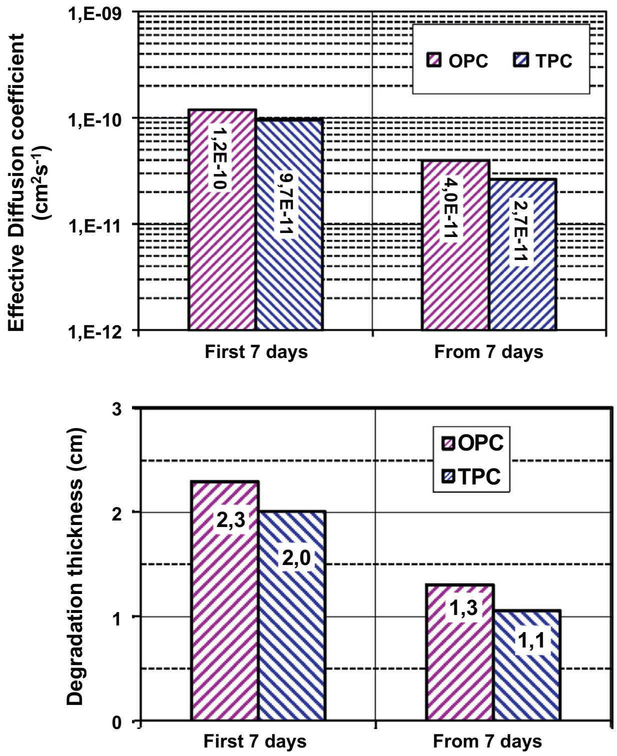

Fig. 4. Effective diffusion coefficients (D_e) and degradation thickness after 100 years of TPC and OPC pastes. Data obtained from the first 7 days and after 7 days of leaching attack. The degradation thickness data are obtained from Eq. (3).

The good agreement obtained among the different types of samples and dimensions and leaching test used by the cited authors validate the results presented here.

4. Discussion

The leaching of calcium is a coupled dissolution/diffusion process. Leaching by deionised pure water induces calcium and hydroxide concentration gradients which continuously decrease from the sound zone to the exposed surface of the material. This causes the diffusion of calcium and hydroxide ions from the pore solution to the aggressive solution, and thus lowers the amount of calcium concentration in the pore solution. Loss of calcium leads to the progressive dissolution of hydrated compounds according to their solubility products: $Ca(OH)_2$ > Afm > Friedel's salt > Aft > C–S–H gel [10].

In our case, the concentration of hydroxide ions leached has been determined from the pH values of the pure water (see Table 2), where a strong increase is produced after 1 day of leaching (from 6 to 12.0 and 10.5 in the case of OPC and TPC, respectively). After 90 days of leaching the pH values increased up to 12.5 for the two OPC and TPC pastes.

Table 2
pH of the leachate at different times of leaching attack.

	Leaching time (days)					
	0	1	7	14	28	90
OPC	6	12.0	12.0	12.0	12.0	12.5
TPC	6	10.5	11.5	12.0	12.0	12.5

It is known that the open porosity and specially the pore-size-distribution (PSD), among others, are microstructural parameters, which play an important role in the diffusion and contra-diffusion processes produced as a result of leaching attack in aggressive solutions [10,12,14–16]. Decalcification changes the bulk density and the pore structure of the hydrated cement paste, mainly through the dissolution of $Ca(OH)_2$ while the porosity created by C–S–H decalcification is negligible.

To verify the influence of the leaching of Ca^{2+} on the pore-structure of the pastes, the changes of the pore-size distribution (PSD) of the OPC and TPC pastes after 28 and 90 days of leaching time were measured by means of mercury intrusion porosimetry.

As it can be seen in Fig. 5, before leaching (after 28 days of curing, 0 days in the figure), in the case of the plain OPC paste, the PSD is bimodal with two populations of pores of 0.065 µm and 0.04 µm of diameter. The main difference of the TPC paste is the displacement of the pores of 0.04 µm of diameter to 0.02 µm, together with the increase of the intensity of this peak centred at 0.02 µm. After 28 days of leaching, the PSD of OPC pastes almost does not vary, whereas the PSD of the TPC paste shifts to lower values, compared to both that of OPC and that of TPC at 0 days. After 90 days the PSD of both OPC and TPC shifted to lower pore diameter values.

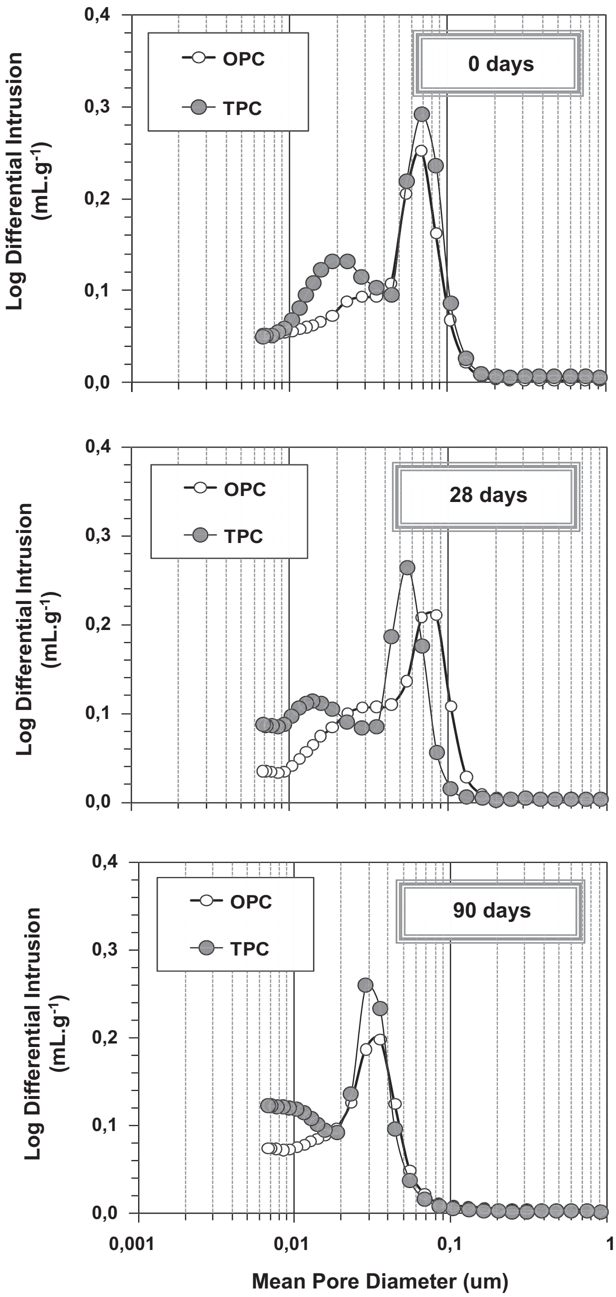

Fig. 5. Pore-size distribution of OPC and TPC pastes before and after 28 days and 90 days of leaching.

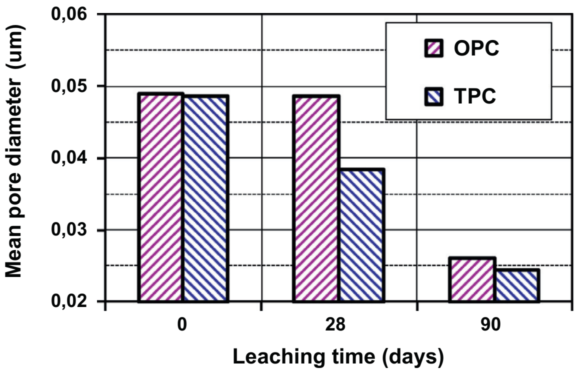

Fig. 6. Mean-pore-diameter of the TPC and OPC pastes before and after 28 and 90 days of leaching.

The densification of the pore-structure of TPC pastes is reflected in the mean-pore diameter, as it can be seen in Fig. 6. The greatest decrease observed for the TPC pastes, mainly at later ages, could be explained as the extra effect of pozzolanic reaction of the blends (APS and FA).

The low slope value of the second lineal zone of the CFL for long leaching time (Fig. 3) and therefore, the decrease of D_e values could be explained by the strong decrease of the mean pore diameter (MPD), the formation of an external film, which seals the samples and the increase of pH of the surrounding medium.

The later phenomenon was observed previously by Serne [25], who made long-term leaching tests at different size scales. He

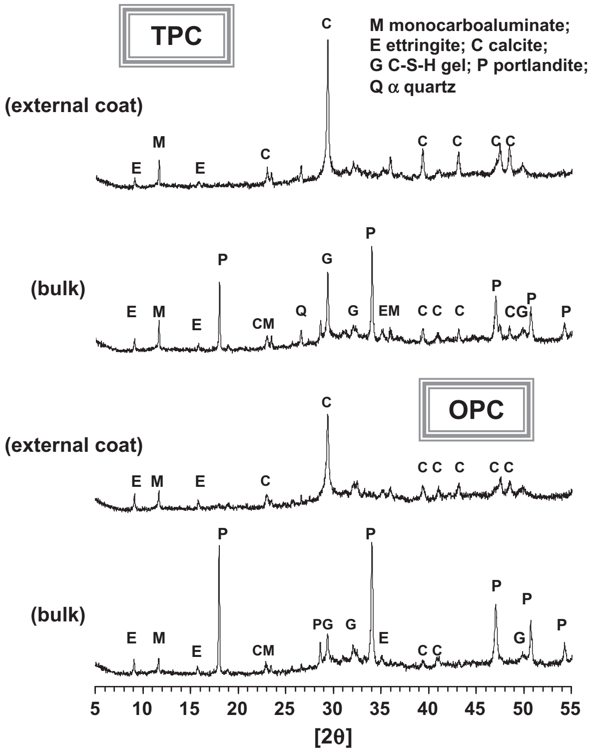

Fig. 7. XRD of the external coat and bulk of TPC and OPC pastes after 90 days of leaching.

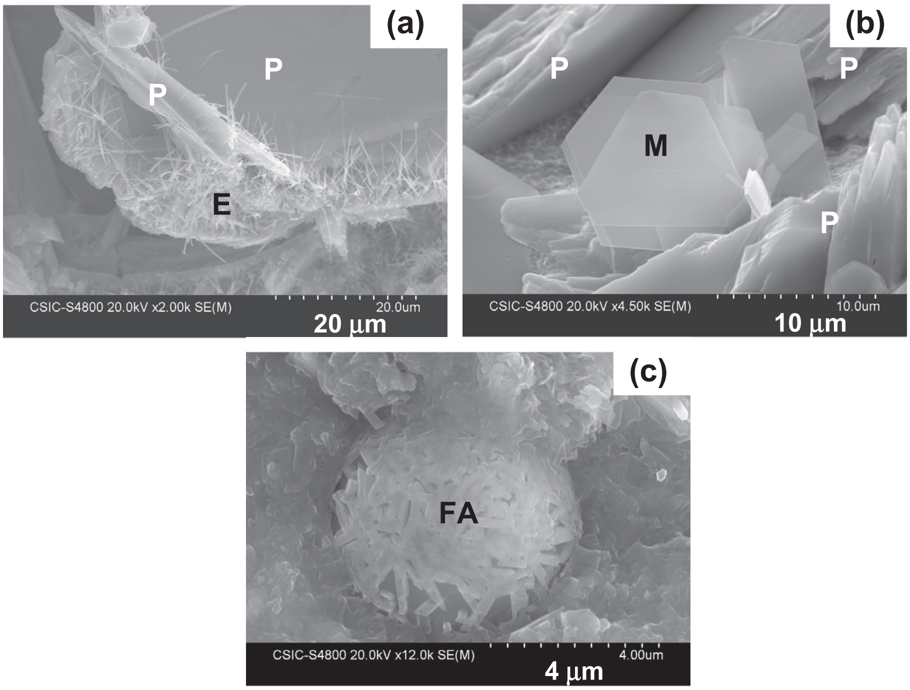

Fig. 8. SEM micrograps of OPC (a and b) and TPC (c) after 90 days of leaching in pure water. Details of needles of ettringite (E), dissolving plates of portlandite (P); hexagonal plates of monocarboaluminate (M) and cenosphere of fly ash with the surface covered by pozzolanic reaction products.

pointed out the formation of an alkaline-earth carbonate film, which covers the specimens impeding the leaching after 28 days.

Goñi et al. [13] stated a decrease of the effective diffusion coefficient of calcium by one order of magnitude (from 1.1×10^{-10} $cm^2\,s^{-1}$ to $1.6 \times 10^{-11}\,cm^2\,s^{-1}$), as due to the formation of a carbonated film of calcite composition.

In our case, the external coat after 90 days of leaching was identified by XRD (Fig. 7) as crystalline calcite ($CaCO_3$) for both TPA and OPC pastes. As it can be seen, the intensity of the XRD peaks of calcite is higher in the case of the TCP paste due to the contribution of calcite from the paper sludge.

The external coat together with the changes in the PSD changed the kinetic of leaching. In fact, the degradation thickness after 90 days of leaching, calculated by applying Eq. (3) and the second lineal zone of Fig 3, are: 0.07 cm and 0.05 cm for OPC and TPC, respectively. These low values were experimentally confirmed by the observation of samples by optical microscopic.

Details of the morphologies of the main hydrated crystalline phases detected by XRD in the bulk of samples (Fig. 7) can be seen in Fig. 8: needles of ettringite growing in pores (Fig. 8a); plates of portlandite Fig. 8a and b; big hexagonal crystal of monocarboaluminate (Fig. 8b) and a cenosphere of fly ash with the surface covered by products of the pozzolanic reaction (Fig. 8c).

Finally, it is interesting to note that although the porosity of the degraded outer layer increases as a result of the dissolution of portlandite, however, this is not reflected in our data of mean pore size, given the very slow kinetics of degradation, which does not alter the bulk parameters of pastes.

5. Conclusions

1. The results obtained here have demonstrated that the addition of a pozzolan blend (APS + FA, 50/50 in weight) within ternary Portland cements, together with the external coat that covers the samples, improve the stability against decalcification in pure water with respect to the control paste. This could be related to the combined effect of both pozzolans, which show different pozzolanic reaction rate. In the case of APS the pozzolanic reaction predominates during the first 28 days of reaction, while for the fly ash mainly acts at longer ages.
2. The decalcification of both TPC and OPC pastes in pure water is produced according to kinetics governed by diffusion in a semi-infinite medium. The effective diffusion coefficients (D_e) of Ca^{2+}, calculated by applying Fick's second law, decreased almost one order of magnitude after 7 days of leaching.
3. Consequently, the thickness of the degradation layer after 90 days of leaching, estimated from the D_e values of the first 7 days of leaching, was 0.12 cm and 0.10 cm for the OPC and TPC pastes, respectively, and 0.07 cm and 0.05 cm in the case of D_e values calculated after 7 days of leaching. For a service life of 100 years the corresponding thicknesses would be 2.4 cm and 2.0 cm, based on D_e determined for the first 7 days of leaching and 1.5 cm and 1.1 cm for D_e values calculated after 7 days of leaching, for the OPC and TPC, respectively. Clearly, long-term estimations of degradation thickness should be based on measurements that account for potential changes in D_e over the exposure period.
4. The decalcification process of cementing matrices depends on the solubility of hydrated phases, on the Ca/Si ratio, the nature and type of the cement, the nature of the pozzolan, and also of the pozzolanic reaction rate. In this case, both the APS and FA pozzolans have different reaction rates due to their nature: the first based on metakaolin (which primarily reacts within 28 days), and the second for its pozzolanic reaction beyond 28 days. The end result is a continuous pozzolanic reaction, which may have advantages in the development of the microstructure of the cement mixture, compared to when the pozzolans are used separately.

Acknowledgements

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