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Chemistry of cement hydration in polymer-modified pastes containing lead compounds

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Abstract

The role of polymeric additives on the hydration process of cement pastes admixed with a lead compound (Pb_3O_4) was investigated. Three series of pastes were prepared: the reference series, mixing water with Ordinary Portland Cement (OPC), and two series in which whether a styrene–butadiene rubber latex or a superplasticiser based on acrylic-modified polymer was added to the pastes. For each series, 5 and 10 wt% of Pb were mixed with the pastes. Phase analysis and microstructural characterisation were carried out by means of X-ray powder diffraction and SEM–EDX. Thermogravimetric analysis was performed to monitor the hydration degree of the three pastes; indeed, quantitative determination of portlandite and calcite was performed.

Dynamic leach tests were performed on solidified monoliths to evaluate the effective immobilisation of Pb_3O_4. After 384 h leaching, excellent results were obtained by pastes mixed with superplasticiser that showed a cumulative release of Pb equal to 0.62 mg/l for samples containing 5 wt% of Pb, and equal to 0.84 mg/l for samples bearing 10 wt% of Pb.

Keywords: Microstructure-final; X-ray methods; Chemical properties; Cement paste

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1. Introduction

Cement-based solidification/stabilisation processes (S/S) represent one of the most widely used technology in the treatment of hazardous inorganic waste (e.g. heavy metals) before landfilling. Due to the chemical properties of cement, the S/S processes allow both a physical entrapment of the waste and/or a chemical binding of the contaminant to the cement matrix.[1] The evaluation of the mobility of the hazardous species in the cement based solidified/stabilised waste is made by means of leach tests. However, the knowledge of the leaching mechanisms and chemistry of the cement hydration reactions is helpful for interpreting the leach tests results and for reliable prediction of long-term stability.[2,3] In particular for Pb contaminated wastes, it has been reported that calcium silicate hydrates (C–S–H) and calcium sulfoaluminate hydrates, such as ettringite and monosulfate, are largely responsible for the retention of Pb.[4] Generally, compounds of Pb cause a retardation of the hydration reaction of cement. In order to improve the retention capability of the cement matrix and, eventually, prevent the negative effects of the contaminant on the hydration properties, polymeric additives may be added during the preparation of the pastes. Although this route has not been deeply studied, it looks promising to reduce the release of Pb.[5,6]

The purpose of this work is to investigate the role of two different additives (i.e. a styrene–butadiene rubber latex and a superplasticiser based on acrylic-modified polymer) on the hydration process of cement pastes admixed with a lead compound (Pb_3O_4) and their effectiveness in the retention of the contaminant, compared to an additive-free matrix. Dynamic leach tests were performed on solidified monoliths to evaluate the effective immobilisation of Pb_3O_4 in compli-

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Table 1
Average composition of cement CEM I 52.5 R (according to the cement chemistry notation: C = CaO, A = Al_2O_3, S = SiO_2, F = Fe_2O_3)

Chemical composition	Percentage	Mineralogical composition	Percentage
SiO_2	24.43	C_3S	41.6
Al_2O_3	4.37	C_2S	38.7
Fe_2O_3	1.69	C_3A	8.7
CaO	63.65	C_4AF	5.1
MgO	1.72		
K_2O	0.75		
Na_2O	0.18		
SO_3	3.11		

ance with a recent Italian regulation about the reuse of waste materials.[7] Phase analysis and microstructural characterisation were carried out by means of X-ray powder diffraction and combined scanning electron microscopy and energy dispersive X-ray spectrometry (SEM–EDX). Thermal analysis (TGA and DTA) was performed to estimate the hydration degree of the pastes.

2. Experimental

2.1. Sample preparation

Cement pastes were prepared using an Ordinary Portland Cement (OPC) Type I 52.5 R (Cementi Rossi, Piacenza, Italy), whose average composition is reported in Table 1; the OPC was mixed with deionised water, admixtures for concrete, in particular a styrene–butadiene rubber latex (GRANIRAPID, Component B, Mapei, Italy) and a superplasticiser, based on acrylic modified polymer (DYNAMON SP1, Mapei, Italy). The former additive is a solution whose solid content is 21%, while the superplasticiser is a solution whose acrylic modified polymer content is 30.5%. The model lead-containing hazardous compound was Pb_3O_4 (98% purity). Two concentrations of Pb_3O_4 were added to the pastes, containing 5 and 10 wt% of Pb.

Three series were prepared using the mixes shown in Table 2. The water/cement (w/c) weight ratio was equal to 0.4 in the reference (series E) and in the latex (series F) pastes, but 0.25 in the superplasticiser (series G) pastes; whereas the latex (solid)/cement and SP1 (solid)/cement weight ratios were 0.11 and 0.02, respectively. Pb_3O_4 and OPC were stirred for few minutes until a homogeneous powder was obtained; then, water, latex or superplasticiser solution were added, hand-mixed for about 10 min to a smooth paste, and then transferred in a mortar mixer (CONTROLS, 65-L0005) to obtain a homogeneous paste. Following the same procedure as in previous experiments [8], the pastes obtained were cast into cylindrical PE moulds (2.2 cm diameter, 3.2 cm height) and shaken for few minutes to remove air bubbles. Then, the partially filled moulds were sealed with an impervious plastic film. The sealed moulds were stocked for 28 days in a room where temperature (23 ± 1 °C) and relative humidity (50% RH) were controlled. Several replicates for each recipe were prepared; one sample for each series was demoulded after 28 days and dried up to constant weight (at 105 °C) in order to stop hydration. Samples weighing at each stage allowed a precise determination of free water. Then the solidified monolith was cut: a fraction of the sample was ground in a grinding mill to obtain the powders used for the analytical measures, i.e. X-ray diffraction and thermogravimetric analysis; while some fragments were used for the scanning electron microscopy (SEM–EDX) analysis. A second monolith was demoulded after 28 days and used to perform the dynamic leach test.

Table 2
Formulations of the cement-based pastes

Series	E0	E5	E10	F0	F5	F10	G0	G5	G10
w/c	0.4	0.4	0.4	0.4[a]	0.4[a]	0.4[a]	0.25	0.25	0.25
Pb wt%	–	5	10	–	5	10	–	5	10
Latex/cement	–	–	–	0.11	0.11	0.11	–	–	–
SP1/cement	–	–	–	–	–	–	0.02	0.02	0.02

[a] Total amount of water, including that contained in the polymeric emulsion.

Table 3
Phase composition of 28 days hydrated cement pastes (++ = large amount, + = small amount)

Sample	Pb_3O_4	β-Ca_2SiO_4	Ca_3SiO_5	$Ca_3Al_2O_6$	$Ca(OH)_2$	$CaCO_3$	$CaMg(CO_3)_2$	SiO_2	$C_4A\mathit{C}H_{11}$[a]
E0	–	++	++	++	++	++	+	+	++
E5	++	++	++	++	++	++	+	+	++
E10	++	++	++	++	++	++	+	+	++
F0	–	++	++	++	++	++	+	+	++
F5	++	++	++	++	++	++	+	+	++
F10	++	++	++	++	++	++	+	+	++
G0	–	++	++	++	++	++	+	+	–
G5	++	++	++	++	++	++	+	+	–
G10	++	++	++	++	++	++	+	+	–

[a] $Ca_4Al_2O_6CO_3 \cdot 11H_2O$: monocarboaluminate hydrate.

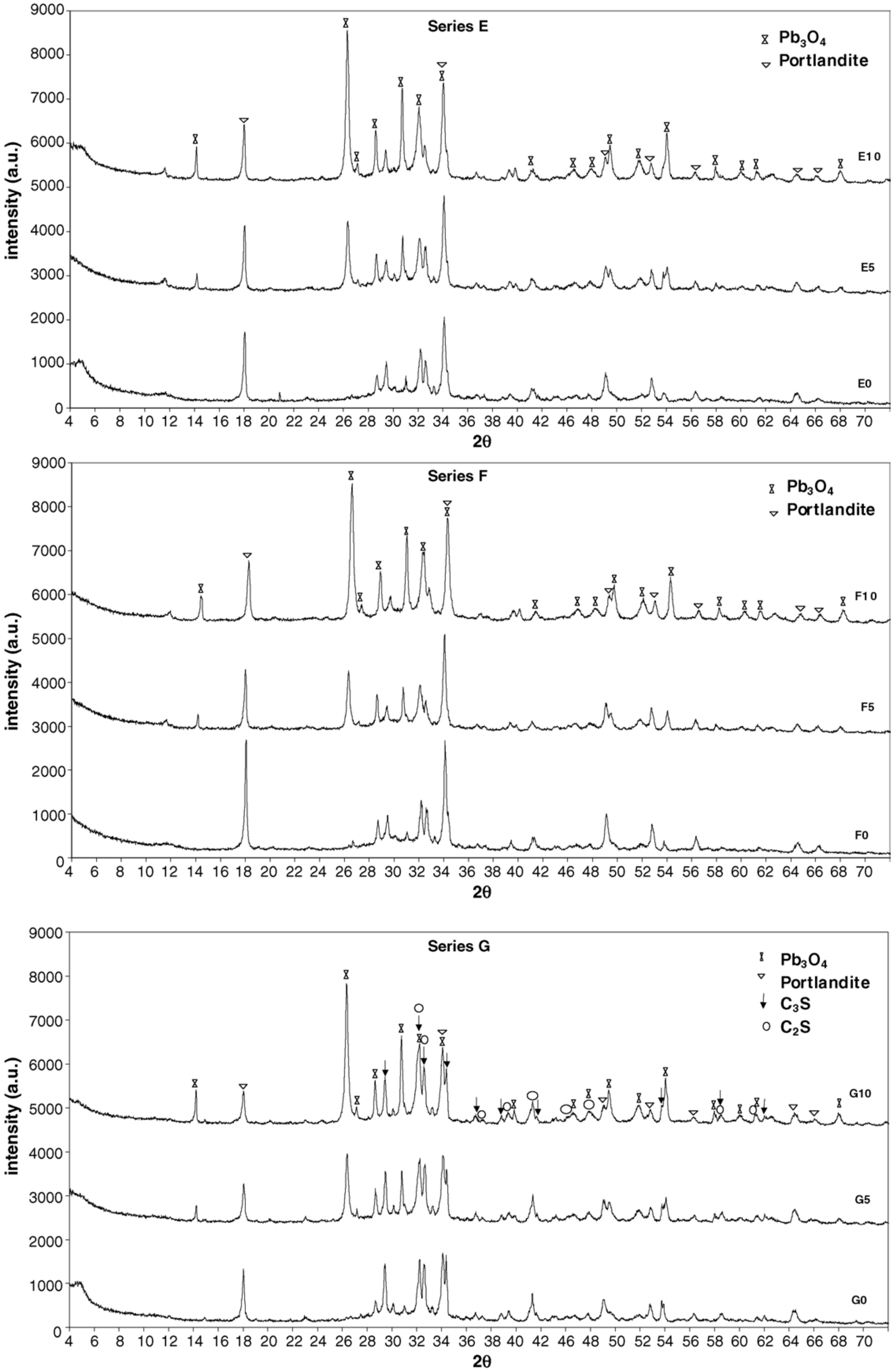

Fig. 1. XRD patterns for series E, F and G after 28 days of curing.

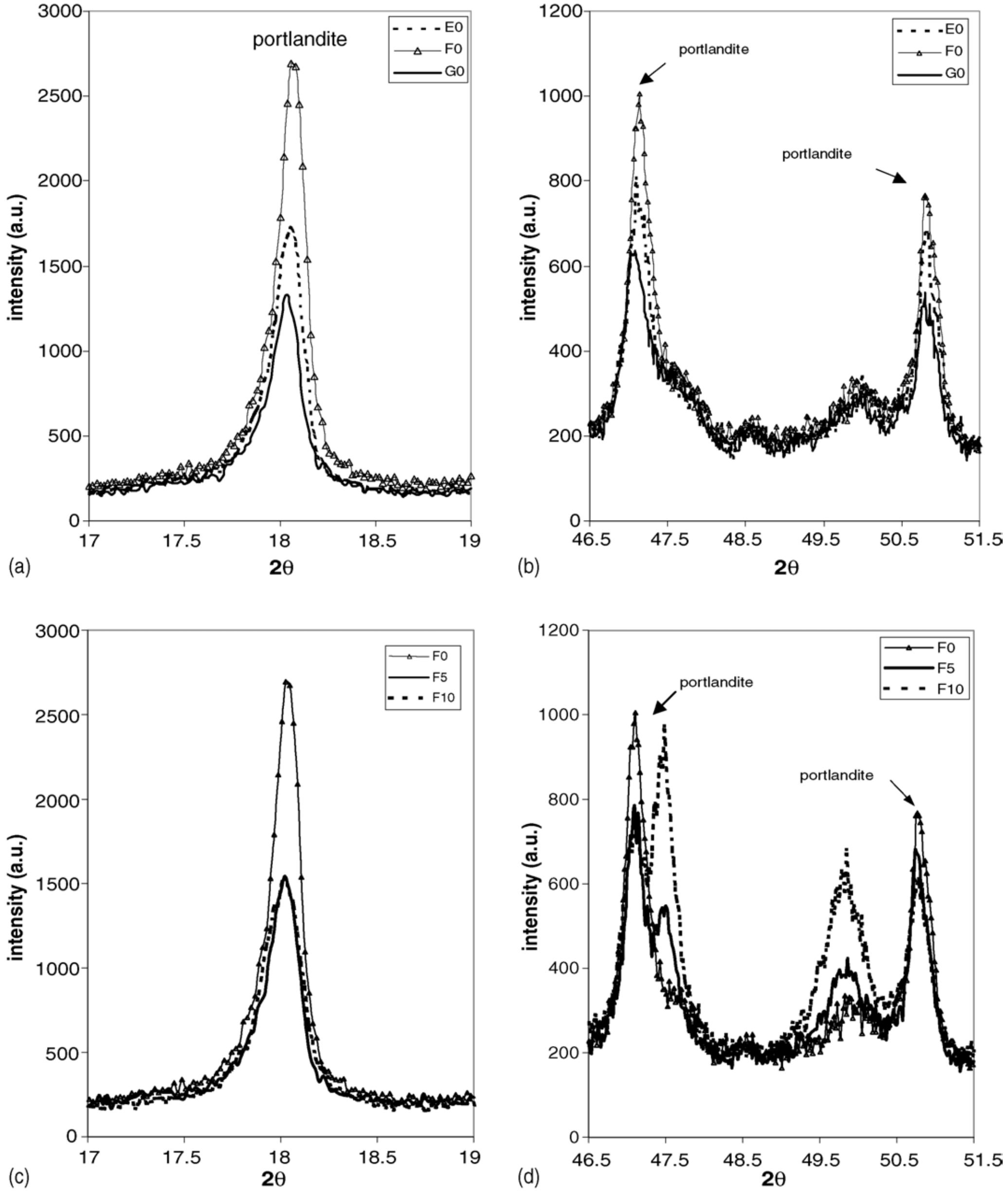

Fig. 2. XRD patterns, in the range (a) 17–19° 2*θ* and (b) 46.5–51.5° 2*θ*, for samples E0, F0 and G0 and in the range (c) 17–19° 2*θ* and (d) 46.5–51.5° 2*θ*, for samples F0, F5 and F10.

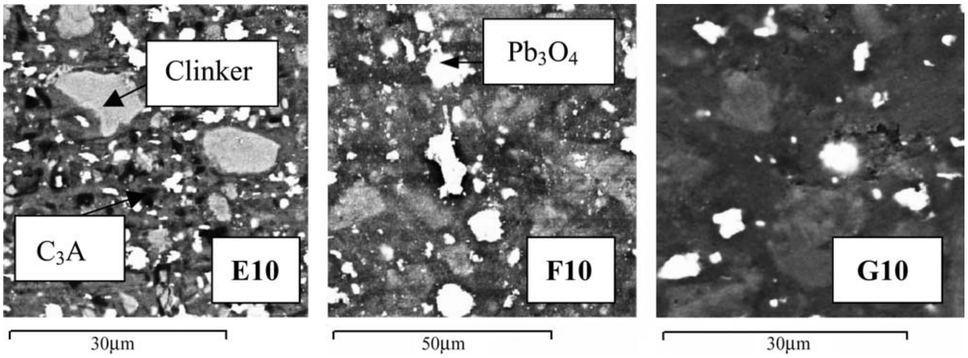

Fig. 3. BSE-SEM images for samples E10, F10 and G10.

2.2. X-ray diffraction analysis

X-ray diffraction (XRD) data were collected at room temperature with a Philips diffractometer, using graphite monochromated Cu-Kα radiation. The step scan was 0.02° 2θ and the measurement time 10 s/step. The samples were first roughly ground in a grinding mill and then finely ground in an agate mortar. The phase analysis was performed using the Diffrac Plus Evaluation software (Bruker AXS).

2.3. SEM–EDX

A scanning electron microscope (SEM) equipped with a Link energy X-ray dispersive spectrometer (EDS) was used for the morphological and chemical analysis of the hydrated sample. SEM–EDX analyses were carried out on both polished and fractured samples. All the samples were gold coated to prevent charging effects.

2.4. Thermal analysis

Thermal measurements were performed with a DTA–TG SEIKO 6300; TG and DTA analyses were carried out in nitrogen from room temperature up to 1000 °C, at 10 °C/min rate. Powdered samples, previously dried to stop hydration, were about 20 mg. The amounts of bound water, portlandite, $Ca(OH)_2$ and calcite, $CaCO_3$, were determined by TGA curves through the weight-losses between 105 and 650 °C, 400 and 600 °C and 600 and 800 °C, respectively.[9,10] All values are reported as grams per grams of cement powder, as the use of the ignited residue (or of the fresh cement paste) as a reference would also include the weight of Pb_3O_4 (totally o partially) giving misleading results about the actual hydration degree. For the same reasons, the amounts of bound water, calcite and portlandite were corrected for the weight losses of cement powder, latex and Pb_3O_4. All data here reported refer to 28-day samples. For the sake of comparison, free water data were also reported as grams per grams of cement

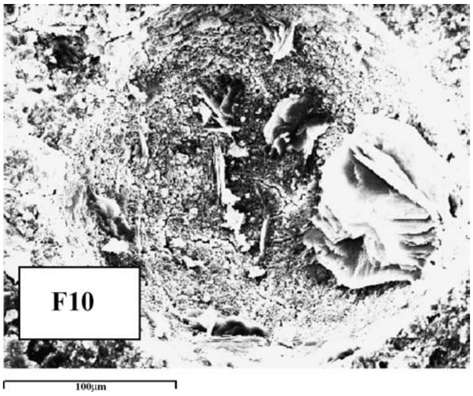

Fig. 4. SEM image of a macropore in sample F10. Portlandite crystals growing inside the pore are observable.

2.5. Dynamic leach test

The immobilisation was assessed by means of a dynamic leach test in compliance with a recent Italian regulation[7] about the reuse of waste materials. The prescribed procedure gives no indication about the size of samples to be tested, but simply about their mass, which should be larger than 100 mg. Moreover, solidified waste-forms have to be tested as monoliths after a proper time necessary for their stabilisation; then, before starting the leaching procedure, whose duration is 16 days, they have to be weighed and their volume measured. Deionised water is the prescribed leachant and the liquid-to-solid ratio has to be 5:1. The test is carried out renewing periodically deionised water at 2, 8, 24, 48, 72, 102, 168 and 384 h.

Each sample was hung with a cotton thread in a 100 ml polypropylene container, completely immersed and kept, without agitation, in 42 ml of deionised water (leachant solution). Before water-filling, the containers were washed with a 1 M HNO_3 solution. After each renewing pH was measured and finally the leachate was acidified to pH 2 with 1 M HNO_3 solution, in order to avoid precipitation of the metal ions prior to analysis. The leachate solutions were analysed by atomic absorption spectrometry.

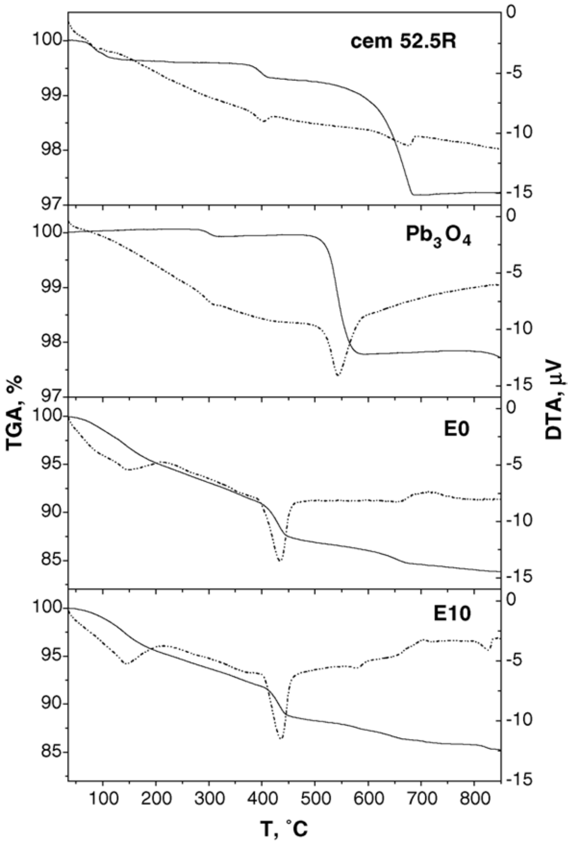

Fig. 5. TGA (solid line) and DTA (dashed line) curves of cement powder, lead oxide, samples E0 and E10 (from top to bottom).

3. Results and discussion

3.1. Mineralogical composition and microstructural characterisation

The mineralogical composition of hardened pastes was studied by means of XRD technique: the powder diffraction patterns of 28 days cured pastes of the three series E, F and G, are shown in Fig. 1 and the major crystalline phases are listed in Table 3. Tricalcium silicate (PDF # 49-0442), dicalcium silicate (PDF # 33-0302), tricalcium aluminate (PDF # 33-0251), portlandite (PDF # 04-0733), calcite (PDF # 05-0586), small amounts of dolomite (PDF # 71-1662) and quartz (PDF # 83-2465), and amorphous hydrated calcium silicate (C–S–H) were found in all pastes. The monocarboaluminate hydrate phase $Ca_4Al_2O_6CO_3 \cdot 11H_2O$ ($C_4A\mathit{C}H_{11}$, PDF # 41-0219) was detected only in samples of series E and F. The formation of the monocarbonate phase was probably due to the carbonation of calcium aluminate hydrate $Ca_4Al_2O_7 \cdot yH_2O$ (C_4AH_y), a product of cement hydration reactions. During the carbonation reactions the anion exchange $2OH^- \rightleftharpoons CO_3{}^{2-}$ produces the replacement of interlayer OH^- by $CO_3{}^{2-}$.[11] No evidence of new phases caused by the interaction of Pb_3O_4 with the cement was found. Crystalline ettringite was not detected as a consequence of the drying treatment performed to stop hydration reactions after 28 days curing, which might have damaged the crystallinity of ettringite.[12] This hypothesis was confirmed by XRD patterns collected from non-desiccated E5 and E10, cured for 5 months, that showed a significant content of ettringite.

The influence of Pb_3O_4 and the additives (i.e. latex and superplasticiser) on the hydration process was evaluated by comparing the integrated intensities of portlandite diffraction peaks. The 17–19° 2θ and 46.5–51.5° 2θ ranges of the XRD patterns of E0, F0 and G0 are shown in Fig. 2a and b. The XRD patterns show three non-overlapping peaks of

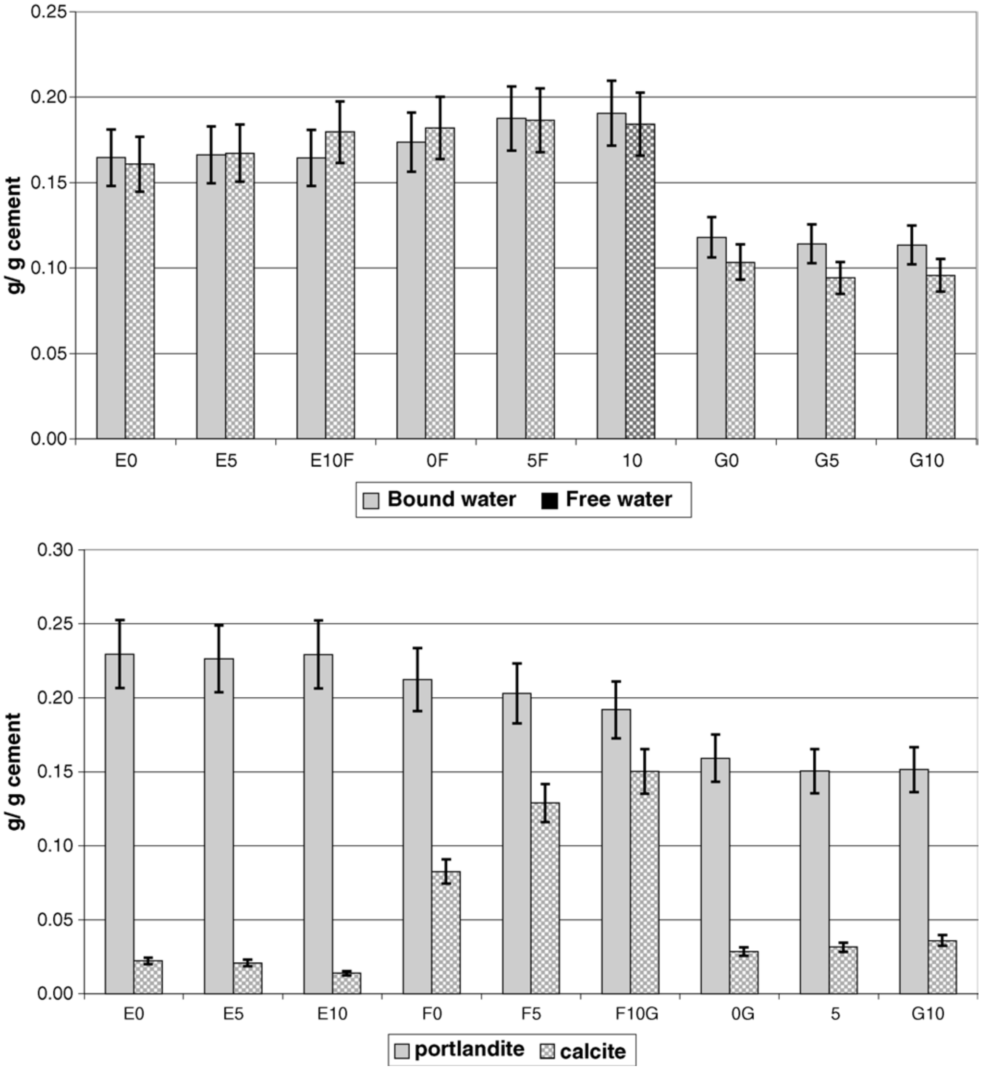

Fig. 6. Bound and free water (above), portlandite and calcite (below) amounts in the three series of samples as determined by thermogravimetric losses; all data are referred to 1 g of cement powder.

portlandite. These results indicate that the OPC hydration of F0 was faster than the equivalent control paste E0, while the OPC hydration of G0 was slower. The presence of Pb_3O_4 in the cement pastes slightly retards the hydration process in series E and G, whereas in samples F5 and F10 the delay is large (Fig. 2c and d).

Backscattered SEM images combined with EDX microanalysis was used to characterise desiccated and polished 28 days old pastes (Fig. 3). The EDX analysis indicated that the white areas consisted of Pb_3O_4, the light grey areas consisted of β-Ca_2SiO_4 and Ca_3SiO_5. The dark grey regions corresponded to the matrix in which the unreacted clinker phases were embedded and mainly consisted of hydration products. Small black areas, well visible in E10, are mainly $Ca_3Al_2O_6$. In all pastes, backscattered SEM images highlighted a homogenous distribution of Pb_3O_4 in the form of small aggregates inside the hardened cement matrix.

Secondary electron SEM images of the fracture surface of non-desiccated 3 months old samples were taken in order to characterise the morphology of the pastes. For each series Pb_3O_4 containing samples did not show microstructural differences compared to the reference sample. The samples of series G have a very compact matrix, while the presence of microcavities was more frequent in series F than in E and G: in the microcavities ettringite needles were detected. Macropores having a diameter >100 μm were observed in samples of series F; this may be a consequence of a lack of anti-foaming agents in the commercial latex here used. As shown in Fig. 4, the inner part of these pores is characterised by the growth of euhedral crystals of portlandite.

3.2. Thermal analysis

Typical TGA and DTA curves are shown in Fig. 5: the reference (E0), a contaminated sample (E10) and, for comparison, the cement powder and Pb_3O_4. The cement powder has a loss of about 2.8%, mostly due to carbonates decomposition, while Pb_3O_4 loses weight mainly around 550 °C (∼2.1%). These losses, as well as that of latex, have been taken into account when calculating the bound water, the portlandite and the calcite amounts in the hardened pastes.

In accordance with XRD analyses, thermal data on samples cured for 28 days confirmed that the presence of red lead powder did not interfere with the hydration process of the cement. As reported in Fig. 6, the comparison between the amount of bound water in the reference and in the samples with 5 and 10 wt% of Pb for the series E, as well as for the series with the latex (F) and the superplasticiser (G), did not show any substantial difference. Indeed, the bound water amounts to about 0.166 g/g of cement in E0, E5 and E10, 0.180 g/g of cement in F0, F5 and F10, and 0.115 g/g of cement in G0, G5 and G10. Of course, the difference between the series E or F and G is due to the water-to-cement ratio, much lower in the G series (0.25) than in the other two (0.40). Similar considerations apply to the portlandite content (Fig. 6): about 0.230 and 0.150 g/g of cement in all the samples of the E and G series, respectively. Apparent differences in portlandite content between the reference (0.21 g/g of cement) and the contaminated samples (0.20 and 0.19 g/g of cement) in the series with latex (F) are probably within the experimental errors, even though the greater amount of portlandite observed in F0 with respect to contaminated samples is also suggested by XRD analysis.

The amounts of calcite are quite low in all the samples (below 3%) apart from F0, F5 and F10 (8, 12 and 15%, respectively. This anomaly could be explained by the anomalous porosity observed in the SEM micrographs of these samples and confirmed by the larger values of free water (0.185 g/g of cement); indeed, it is well known that a porous matrix favours carbon dioxide diffusion into the monolith.

3.3. Leaching behaviour

The leach tests carried out on the monoliths showed the ability of the cement matrices admixed with polymeric additives to stabilise Pb_3O_4. The cumulative release (mg/l) and the percentage cumulative release of lead during the leach tests on 28 day old monolithic samples are shown in Figs. 7 and 8. The cumulative release of lead was very low for the pastes prepared with superplasticiser, 0.62 and 0.84 mg/l for G5 and G10, respectively, which correspond to an excellent retention of lead, equal to 99.997% for G5 and 99.998% for G10. The

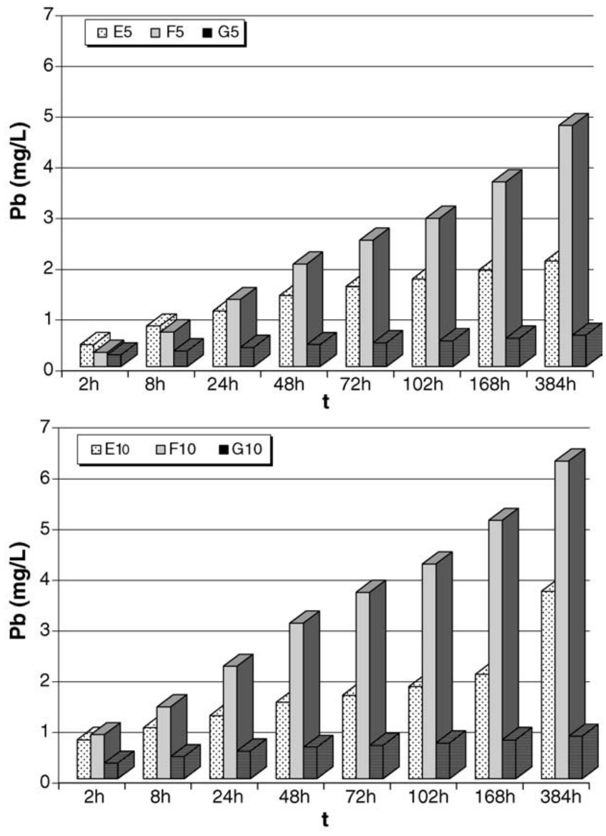

Fig. 7. Histograms showing the cumulative release of Pb for samples (a) E5, F5, G5 and (b) E10, F10, G10.

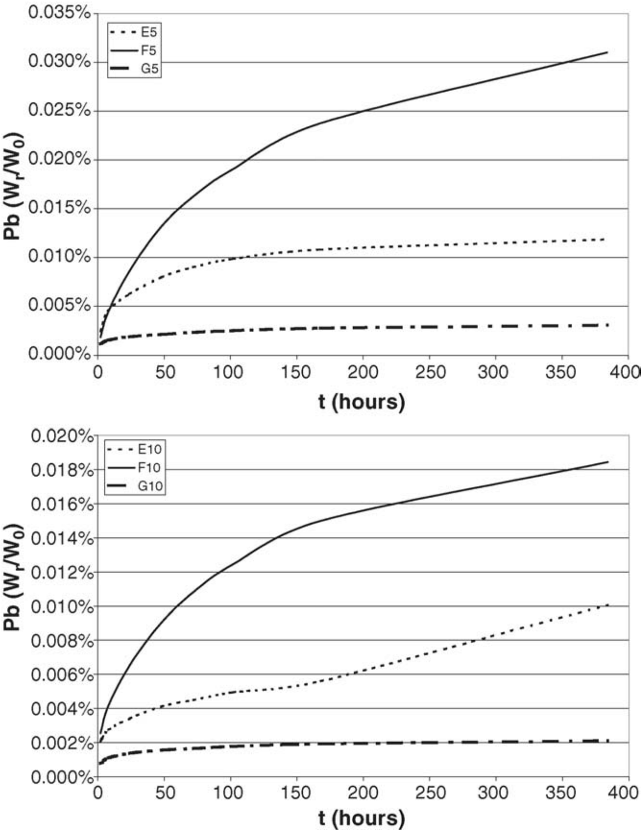

Fig. 8. Curves showing the cumulative percentage release (W_r = released Pb, W_0 = initial Pb) for samples (a) E5, F5, G5 and (b) E10, F10, G10.

amount of lead released by series G was well lower than that measured for other series, equal to 2.08 and 3.70 mg/l for E5 and E10, and 4.75 and 6.27 mg/l for F5 and F10. These results reflect the action of the polymeric additives: the addition of the synthetic rubber latex to the pastes caused the formation of a high porosity in the solidified monoliths; the presence of lots of cavities, increasing the area of the sample in contact with the leaching agent, justifies a higher release of Pb. The addition of superplasticiser, instead, improving the microstructural characteristics of the samples, leads to a better retention of Pb_3O_4.

4. Conclusions

This work investigates the influence of polymeric additives on the hydration process of cement pastes admixed with a lead compound (Pb_3O_4). XRD and TGA analyses showed the highest retard of the hydration process occurred in series G, while Pb_3O_4 most influenced hydration reactions in series F. Significant differences were highlighted by SEM–EDX analysis showing the presence of a large porosity in series F and a very compact matrix for series G. Dynamic leach tests were performed on solidified monoliths; the amount of lead released by series G was well lower than that measured for other series. Highest release was measured for series F: the addition of the synthetic rubber latex to the pastes, causing the formation of a high porosity in the solidified monoliths, increases the area of the sample in contact with the leaching agent, justifying a higher release of Pb. Very successful results, instead, were obtained by pastes belonging to series G: the addition of superplasticiser, improving the microstructural characteristics of the specimens, leads to an excellent retention of lead, larger than 99.99% for G5 and G10.

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