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Long-term leaching test in concretes: An X-ray powder diffraction study

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ABSTRACT

Long-term leaching tests on concretes have been performed to investigate portlandite dissolution by means of X-ray powder diffraction and the Rietveld method, which reveals a promising approach to detect CH content in leached concrete. Several concrete samples have been prepared and immersed in deionised water for 0, 35, 99 and 150 days. The results have been compared with those obtained by DTA/TGA measurements. The Rietveld method provides quantitative determinations of $Ca(OH)_2$ in agreement with thermal analyses. Portlandite dissolution front in a concrete drifts inward upon increasing leaching duration. The distribution of portlandite as a function of the sample depth in the concretes treated for 0, 99 and 150 days show similar trends.

1. Introduction

The degradation phenomenon commonly called "leaching" in cement paste is due to pure water, or low-pH water with respect to the pH-value of pore fluid, promoting the hydrolysis of hydrates [1]. This transformation may be regarded as a diffusion–dissolution process, involving diffusion fronts that propagate through the concrete. Under the action of an aggressive solution, hydrolysis reactions propagate both from the surface into the bulk by a diffusion of the weathering agents, and from the inside to outside by a diffusion of dissolved products. In this view, leaching develops through a front of dissolution/precipitation [2]. Hydrolysis yields an important increase in cement paste porosity, owing to (i) the leaching of hydrate such as calcium hydroxide (i.e. portlandite, labelled CH) and (ii) the decalcification of the calcium silicate hydrates (hereafter C–S–H) [3,4]. Note that porosity provides a way of ingress to external solution, thus favouring degradation reactions [5,6].

Given that the leaching-rate is usually very slow [7], the degradation of cement paste due to dissolution rarely affects common concrete structures, but it grows relevant to hydraulic structures, such as dams and radioactive disposal facilities, wherein long-term stability must be guaranteed [7–9]. For instance, cementitious materials have been widely used as structural and filling components in nuclear waste; however, they are unstable in water, thus exhibiting properties that are a function of time [10]. Concrete long-term performance under the action of groundwater is a fundamental aspect in terms of safety, and an understanding of the dissolution phenomena plays a chief technical role for an effective maintenance planning.

Several tests have been designed so far to assess and predict leaching phenomena in concretes. In practice, two approaches are usually carried out: a "long-term test", based on days/months long chemical attack with deionised water on concretes [1,5,6]; an "accelerated test", using a more aggressive chemical attack with a NH_3NO_4 solution [11,12]. Similarities between these approaches have been pointed out by Carde [13].

The concrete degradation due to leaching is then usually assessed by physical and mechanical analyses [12,14], often resorting to thermal and chemical methods [15–17]. In particular, thermogravimetry (TG) is the most used and commonly accepted analytical technique to determine the phase content in hardened cementitious materials, and its limits are discussed by [17,18]. X-ray powder diffraction (XRPD) can be regarded as an alternative approach for quantitative phase analysis in cement industry. In particular, on the basis of a very small quantity of powdered sample XRPD allows a direct quantification of both hydrated and anhydrous phases; moreover, an accurate modelling of the diffraction pattern enables to get information about (i) strain and crystallite size, which are relatable to the development stage of degradation processes [19], and (ii) nature of the phases involved. Significant instrumental improvements of diffractometers (for instance the introduction of focusing geometry, development of fast detectors,

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etc. [20]) have attributed to XRPD a relevant role among the most widespread and promising characterisation techniques of polycrystalline materials, both in research and industrial laboratories. Note that studies on the use of XRPD for quantitative phase determination in cement paste have been reported by several authors, pointing out a good precision and accuracy of the attained results [21–26]. In such a view, a pilot study has been undertaken aimed at investigating the well-known leaching phenomenon on concretes by XRPD combined with the Rietveld method as a new approach for a direct quantification of portlandite dissolution. XRPD has been chiefly used to date for extracting qualitative information only [5,12]. In the present case, concrete samples have been leached by a *N*-days long ion-exchange treatment in water (*N* ranging from 1 to 150) and then characterised by X-ray diffraction and Rietveld method. Furthermore, measurements of calcium hydroxide in leached concretes have been performed by thermal analysis in order to cross-check the results from the Rietveld method.

2. Sampling

2.1. Test samples

Concrete samples have been prepared by mixing Ordinary Portland Cement (OPC) with known contents of water (water to binder ratio ≈ 0.5) and aggregate (70% in volume), the latter constituted of dolomitic rock fragments ranging in size from 1 to 25 mm. Concrete prisms ($20 \times 30 \times 50$ mm) have been cast and cured at 20 °C for 28 days. Such samples have undergone the dissolution test described in the next paragraph.

2.2. Dissolution test

The concrete prisms have been placed in a sealed polyethylene container and immersed in deionised water (liquid/solid weight ratio is ≈ 50). At intervals of 0, 35, 99 and 150 days the samples have been extracted and rolled up by a waterproof film. Each concrete prism has then been lathed so as to obtain a section from the outermost (leached) to the innermost (un-weathered) layers (Fig. 1). Each layer has been labelled as DLT*x*_*y*, where *x* and *y* fix the leaching time (i.e. 0, 35, 99 and 150 days) and the layer position, respectively. The content of calcium hydroxide has been measured by XRPD and TG.

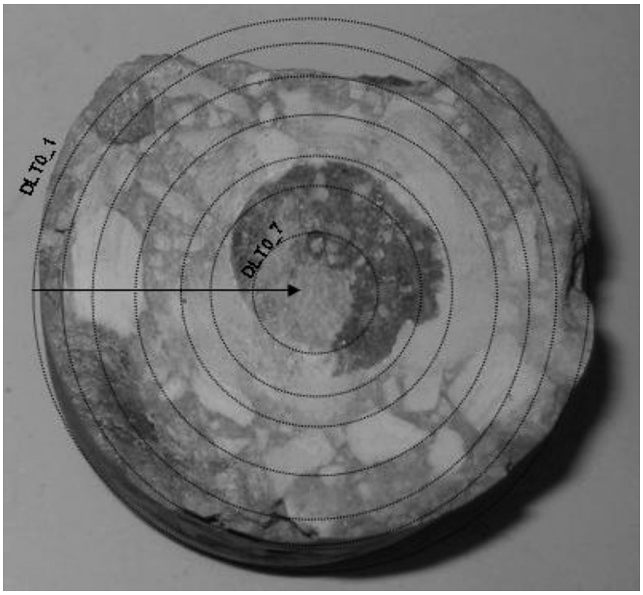

Fig. 1. Stratigraphic section of leached concrete (samples DLT0_1/7).

3. Experimental

3.1. Physical analysis: X-ray powder diffraction

The concrete samples have been side-loaded on a flat Al sample-holder, and measured by a Bragg-Brentano geometry PANALYTICAL X'Pert Diffractometer, using Cu Kα radiation (40 kV and 40 mA). Data collections have been carried out over the 5–90° 2θ-range, with counting time 15 s/step, a divergence slit of 1°, a receiving slit of 0.1 mm. A multi-channel detector (X'Celeretor) equipped with an anti-scatter shield has been used. Al_2O_3-NIST 67 has been added to the powdered samples (10 wt.%) and used as an internal standard to estimate the amorphous phase content [27]. Given that the cement hydraulic phases undergo rapid carbonation by air exposure, two X-ray diffraction patterns for each sample have been recorded sequentially to make us sure that no significant reaction has developed within the data collection time.

Quantitative phase analyses have been carried out on the collected diffraction patterns by the full profile Rietveld method [28–30] using the GSAS and EXPGUI packages [31,32]. We have adopted the following refinement strategy: (i) the observed patterns have been modelled by a pseudo-Voigt function, whose FWHM has been parameterised through one Gaussian (GW) and two Lorentzian coefficients (LY and LX); (ii) background has been fitted by 15 Chebyshev polynomials; (iii) preferred orientation has been accounted by the March-Dollase function, assuming (001) as a cleavage plane, in portlandite. The weight fraction, lattice parameters, and profile coefficients for each phase have been refined, along with the overall background coefficients. The starting models for the structure refinement have been taken from the International Crystal Structure Database (ICSD) [33].

Diffraction patterns have also been collected in transmission mode by the BM08-GILDA beamline at the European Synchrotron Radiation Facilities (Grenoble, F) on untreated samples as a cross-check, using an instrumental collection geometry much less sensitive to preferred orientation than Bragg-Brentano's. Diameter glass capillaries (0.7 mm) were filled with the powder samples. The diffractions were collected with a Fuji imaging plate detector, using a wavelength of 0.682527 Å, calibrated by means of metal foil absorption and with a sample-detector distance of 230.2 mm, determined with diffraction standard LaB6 (SRM 660a). The XRPD images have been integrated and turned into intensity-2θ patterns by the Fit2D software.

3.2. Chemical analysis: differential thermal analysis/thermogravimetric analysis (DTA/TGA)

Thermal analyses have been performed by a NETZSCH Simultaneous Thermal Analyser 409c equipped with a differential scanning calorimeter and a thermogravimetric system. A heating rate of 10 °C min^{-1} under nitrogen flush or chromatographic air (65 mL min^{-1}) has been operated in the temperature range 25–1200 °C, using 40–50 mg samples and Pt/Rh crucibles. The weight loss revealed by DTA/TGA over the 450–500 °C temperature range is attributed to dehydroxylation of $Ca(OH)_2$, leading to a $Ca(OH)_2$-free concrete [16].

4. Results and discussion

In Fig. 2a and b the XRPD patterns of 0-days treated concretes recorded by our laboratory Bragg-Brentano diffractometer and on GILDA beamline at ESRF are shown, respectively. A full agreement

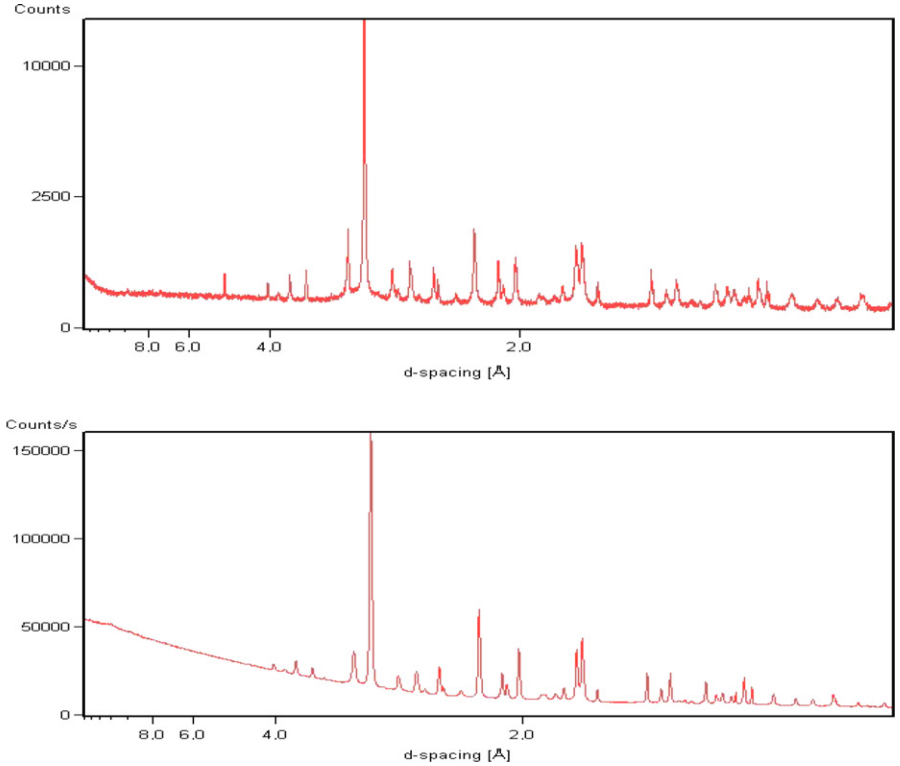

Fig. 2. X-ray diffraction patterns of the un-weathered concrete collected (1) by our laboratory diffractometer with a Bragg-Brentano geometry and (2) on GILDA beamline in transmission mode (ESRF, Grenoble) (sample DLT0_2).

in terms of mineralogical phases between the results provided by the two laboratories is visible. All the samples consist of dolomite, calcite and portlandite. The bump appearing between 2.5 and 4 Å *d*-spacing may be attributed to non-crystalline hydrated phases, such as C–S–H gel and ettringite, due to the cement paste hydration. No evidences of residual clinker cement phases (alite, belite ferrite phases, etc.) are observable.

In Table 1 the phase compositions estimated by the Rietveld method and calculated as the average of the results from the mentioned laboratories are displayed. As a whole, χ^2, R_{wp} and $R(F^2)$ [$\chi^2 < 3$, $R_{wp} < 0.10$ and $R(F^2) = 7.5\%$] resulting from quantitative phase analyses by the Rietveld method, along with satisfactory observed–calculated profile agreements, make us confident of the reliability of the results. Note that these results are also confirmed by measurements repetitions. Carbonate phases are due to concrete aggregate, consisting of dolomite (90 wt.%) and calcite (10 wt.%). A higher content of calcite is observed in the outer layer of the un-weathered samples; this might be ascribed to the carbonation process during preparation of the concrete prisms, and responsible of portlandite transformation into calcite. In Table 1 the portlandite weight percentage in leached concrete is also shown. The determination of the actual CH content in cement paste is carried out adopting two constraints: (1) the sum of all the weight fractions is set equal to 100% (i.e. normalization condition), (2) dolomite in leached concretes is entirely attributed to the aggregate fraction. This means that the actual CH value in cement paste is higher than the amount estimated by Rietveld method. This difficulty is overcome through a recalculation of the CH amount by subtracting the aggregate contribution and rescaling the cement phase fraction to 100%. For instance, the CH-fraction in un-weathered concrete obtained after rescaling corresponds to about 8 wt.% in cement paste, consistently with the $Ca(OH)_2$ amount commonly measured in fresh cement paste reported in the literature [34].

The determinations of portlandite by XRPD in leached concretes are then compared with those obtained by thermal analyses and the results are set out in Table 2. Fig. 3 reports a typical DTA/TGA scan: C–S–H dehydration corresponds to the linear portion of the TGA-trend up to 400 °C. The endothermic peak at 430 °C is attributed to the dehydroxylation of portlandite, whereas the two peaks in the range of 700–800 °C are associated to the decomposition of carbonates. The portlandite contents by XRPD and DTA/TGA have

Table 1
Average contents of main mineralogical phases in the un-weathered concretes (the values in brackets refer to the standard deviation value) (samples DLT0_1/7)

	Samples						
	DLT0_1	DLT0_2	DLT0_3	DLT0_4	DLT0_5	DLT0_6	DLT0_7
Dolomite	72.8(5)	73.0(2)	74.3(2)	73.0(2)	74.2(2)	72.3(2)	72.5(2)
Calcite	6.2(3)	4.8(3)	4.5(1)	4.6(2)	5.0(3)	4.5(3)	4.8(1)
Portlandite	1.1(1)	1.3(1)	1.3(2)	1.6(3)	1.8(2)	2.1(2)	2.2(1)
Amorphous	19.9(5)	20.7(3)	19.8(2)	20.7(1)	19.0(3)	21.0(2)	20.5(1)

Table 2
$Ca(OH)_2$ content in leached concretes detected by (1) X-ray powder diffraction and (2) thermal analysis, respectively (samples DLT99_1/9)

Sample	Portlandite (wt.%)	
	1	2
DLT99_1	–	–
DLT99_2	–	–
DLT99_3	–	–
DLT99_4	0.31(2)	–
DLT99_5	0.50(4)	0.60
DLT99_6	0.75(4)	0.81
DLT99_7	1.20(3)	1.30
DLT99_8	1.53(2)	1.65
DLT99_9	2.10(3)	2.20

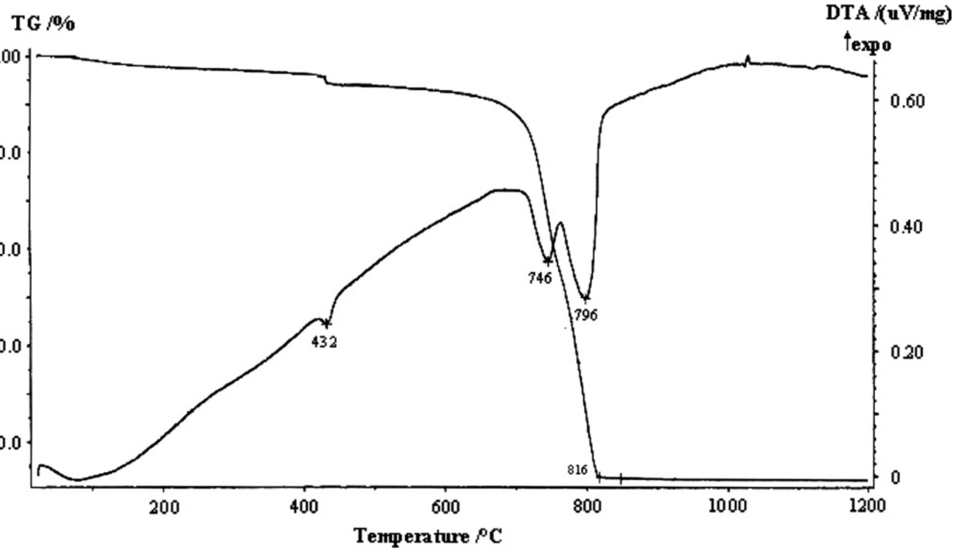

Fig. 3. DTA/TG scan of concrete sample leached for 99 days (sample DLT99_4).

been analysed by a linear regression, assuming that intercept and slope should be ideally zero and one, respectively. In so doing, one attains a correlation coefficient of 0.99, suggesting a good agreement between expectations and measurements. An inspection of Table 2 points out a discrepancy between the XRPD versus DTA/TGA issues in terms of a systematic underestimation of the former with respect to the latter. In particular, a 20% mismatch occurs in the layer wherein portlandite starts dissolving (i.e. DLT99_5). This might be related to a low degree of crystallinity of portlandite, often observed in cement materials, which yields a relevant broadening of the diffraction peaks. The LX profile parameter of CH implies a small crystalline size, hinting at an amorphous $Ca(OH)_2$ fraction occurrence, attributed to calcium hydrate by thermal analysis but not revealed as portlandite by X-ray diffraction [21,35]. Note that: (i) the discrepancies between XRPD and DTA/TGA lie within the uncertainties affecting the CH-fraction values attained by the Rietveld method; (ii) DTA/TGA does not bring to light CH in DLT99_4, whereas XRPD does.

In Fig. 4 the diffraction patterns collected on the layers of a 150-days treated concrete sample are reported. The $Ca(OH)_2$ content grows higher from the outer to the inner part of each sample, in keeping with the inwards propagation of the leaching process. Fig. 5 shows the content of $Ca(OH)_2$ as a function of the sampling depth after 0, 99 and 150-days leaching treatment. The reported trends are similar to each other and suggest that leaching is homothetic with respect to the reaction time. Portlandite chiefly decreases in the initial 15 mm depth, and keeps almost unchanged in the deeper layers, suggesting that the CH-loss due to dissolution is actually complete. The peripheral degradation zone is therefore encompassed by the dissolution front of calcium hydroxide [12]. Consistently with expectations one observes that the smaller the portlandite content, the longer the leaching time. For instance, in samples DLT99_8 and DLT150_5, which represent the concrete layers at 10 mm depth but leached for 99 and 150 days, respectively, $Ca(OH)_2$ occurs as abundant as 1.5 wt% and 1.2 wt%. The leaching trends as a function of the leaching time agree with the ones reported in literature, wherein the loss of Ca is supposed due to dissolution of portlandite and decalcification of C–S–H in cement paste [14,15]. All this further supports the reliability of the quantitative phase analysis by the Rietveld method in assessing concrete leaching.

A general slight decrease in the amorphous content upon increasing leaching time is predicted by the XRPD with respect to

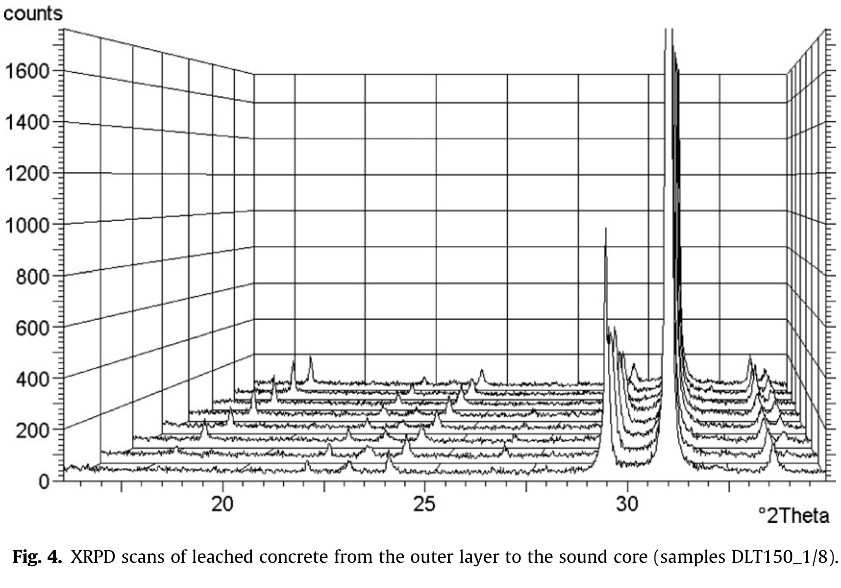

Fig. 4. XRPD scans of leached concrete from the outer layer to the sound core (samples DLT150_1/8).

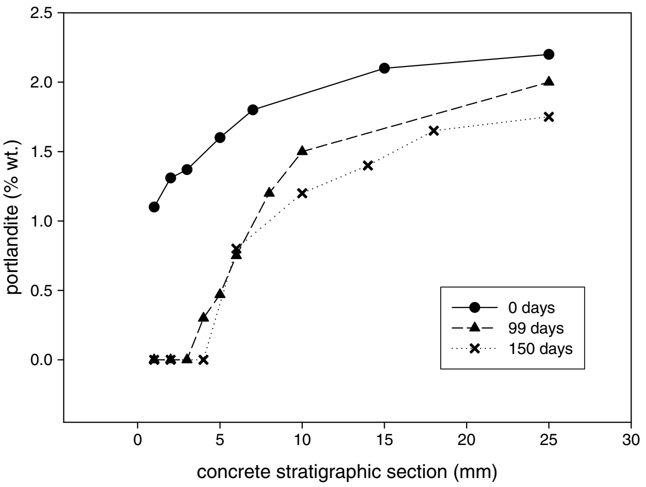

Fig. 5. Change of portlandite amounts from the outer to the inner layer in the cement paste of leached concretes at different leaching period (leaching time of 0, 99 and 150 days). Note that the reported CH weight fractions have been detected by XRPD.

DTA/TGA: in sample DLT0_3 the amorphous fraction related to the cement hydrated phases (C–S–H) is 20 wt.%, whereas in DLT150_5 it diminishes to 15 wt.%. This is in keeping with the fact that leaching develops through dissolution first of $Ca(OH)_2$, then of the C–S–H gel, thereby producing an amorphous content decrease. Earlier studies [3,4] have concluded that hydrolysis of C–S–H gel generates during the first step of leaching, leading to a decrease of the C–S–H content in weathered concretes. However, given that the dissolution of calcium hydroxide is the main reaction responsible of the loss of strength (70% of the initial strength), the C–S–H loss is negligible with respect to that of calcium hydroxide in terms of its effects on concrete performance [14].

5. Conclusion

Portlandite dissolution has been studied in weathered samples by XRPD using the Rietveld method. The results so obtained are compared with those from thermal analyses, in the case of 99 days long leaching. A general good agreement is revealed, though XRPD yields a systematic slight underestimation of $Ca(OH)_2$ with respect to DTA/TGA; this is presumably attributable to the formation of a calcium hydroxide amorphous phase. Moreover, XRPD has been able to detect portlandite even in those cases for which DTA/TGA has failed (sample DLT99_4).

XRPD indicates that portlandite hydrolysis processes at 0, 35, 99 and 150 days follow a homothetic behaviour as a function of depth, consistently with previous observations relying on thermal analyses.

In full, the results of the present investigation encourages the use of XRPD combined with the Rietveld method as an effective approach to reliably quantify the effects related to leaching in concretes.

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