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Experimental study of accelerated leaching on hollow cylinders of mortar

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Abstract

Two mortars, differencing mainly in their initial porosity, were degraded by the use of a chemically accelerated process with ammonium nitrate solution. To specifically study the leached material, the chemical attack was undertaken on thin walled tubes. The leaching effects were evaluated by studying variations in mechanical and hydraulic properties. For both mortars tested, the kinetics of relative loss in strength, in elastic modulus and of increase in permeability were similar. For the same time of degradation, the increase in porosity and the loss in volumetric mass roughly depend on the estimated cement paste proportion of each mortar. The total process of degradation was carried out in three steps: 4, 8 and 16 days. Very sharp variations of all the studied properties were observed until 8 days of leaching followed by a plateau. These two phases are attributed to Portlandite dissolution first then to progressive C–S–H decalcification. At the end of the leaching test, a permeability increase of more than two orders of magnitude and a loss in strength and elastic modulus of more than 85% were observed for both mortars.

Keywords: Chemical degradation; Leaching; Porosity; Permeability; Mechanical effects; Mortars

1. Introduction

Among different possibilities, the isolation in France of high-level radioactive waste at about five hundred meter depth seems to be the most probable. Containers of waste would be placed into concrete rooms and tunnels drilled into rocks like Callovo Oxfordian Argillite. Despite a low water permeability (less than 10^{-20}m^2), these rocks are porous (around 10%) and their pores are filled with water which is not in chemical equilibrium with that of concrete. As a result there will be calcium concentration gradients leading to hydrate dissolution. This is due to Ca^{2+} diffusion toward the external surrounding of concrete. This typical leaching process leads to significant degeneration of cement based material properties that must be studied for structures designed for long term service. The dissolution of calcium bound in the cement matrix occurs first with leaching of Portlandite ($Ca(OH)_2$ or CH) and then a progressive decalcification of calcium–silicate–hydrates (C–S–H) [1]. This phenomenon takes place with a sharp dissolution front [2,3]. However, if carried out with deionized water or reconstituted argillite pore water, leaching is a very slow process that complicates experimental studies. This slow kinetics is a major issue which has made necessary the development of an accelerated test setting up. The kinetics can be either electrochemically [4] or chemically accelerated [5]. The second possibility was chosen with the use of a concentrated ammonium nitrate (NH_4NO_3) solution. The similarity of water and NH_4NO_3 leaching has been established chemically, mineralogically and mechanically by Carde [6]. Another difficulty often comes from the degraded sample geometry. Generally they are cylinders which are degraded radially. As a result, intact and more or less degraded zones are present in the same sample. This leads to difficulty in the study of properties of the degraded material alone. For example, mechanical tests performed on non-homogeneously degraded sample (i.e. non-homogeneous stiffness properties) lead to non-homogeneous stress distributions which are sometimes uneasy to interpret. Therefore the development of inverse numerical methods is most often required to deduce hydraulic and mechanical properties from samples which behave as structures [7]. To overcome this problem, tube samples were cored from mortar beams and then degraded. As

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Table 1
Mortar compositions

Components	Mortar05	Mortar08
Normalized sand (EN 196-1) 0/2 mm	1350 kg	1350 kg
Cement CEM II/B-M 32,5 R (EN 197-1)	450 kg	450 kg
Water	225 kg	360 kg
W/C ratio	0.5	0.8

the tube thickness is low, a quite homogeneous degradation was expected and, moreover, only degraded material was experimentally tested. This is a great advantage compared with most of the usual tests as this method will directly give the property variation of material at different stages of degradation. As reported in the literature, the Portlandite crystals CH are dissolved first [6,8] which leads to a large amount of created porosity. As a result, a significant increase in permeability and a decrease in mechanical properties will occur. The dissolution of calcium bound in the C–S–H follows that of Portlandite and is more progressive. This phenomenon would induce smoother changes in hydraulic and mechanical material properties.

The objective of this study is a better understanding of the sole degraded zone property variations which could be linked to the respective role of CH and C–S–H dissolution. This change in properties underlines the long term variation of strength, modulus, porosity and permeability of two kinds of mortar.

2. Experimental device and program

2.1. Materials and samples

Two different mortars were investigated. They were made with 0/2 mm Leucate normalized sand. As indicated in Table 1, the difference between both materials is the water/cement ratio (W/C). In the following, mortar05 or mortar08 will respectively designate mortar with W/C = 0.5 or W/C = 0.8. As its W/C ratio is very high, mortar08 is considered a very low quality material. Porosity of both materials was measured by usual comparison of dry and saturated samples density. The main difference will be a high mortar08 porosity (24%) compared to that of mortar05 (15%), which leads to lower strength and elastic modulus. Moreover, as the effective diffusion coefficient increases with porosity [9] this property will be a key parameter in the leaching process which is mainly diffusive. The mixtures were cast in a beam formwork protected by a plastic cover to prevent local desiccation. The beam dimensions were 1 m in length and 150 × 150 mm^2 in section. Five days after casting, beams were immersed in lime saturated water at 20 °C for six months. Samples were cored from the beam with a core barrel especially designed for this study. The resulting sample is an 8 mm thick tube (with 37 mm external and 21 mm internal diameters) (Fig. 1). These tubes were used for mechanical, porosity and permeability measurements. The reasons for this choice of tube dimension are discussed below in Section 2.2.1.

Fig. 1. Photography of tube sample — intact sample is on the left and others are degraded.

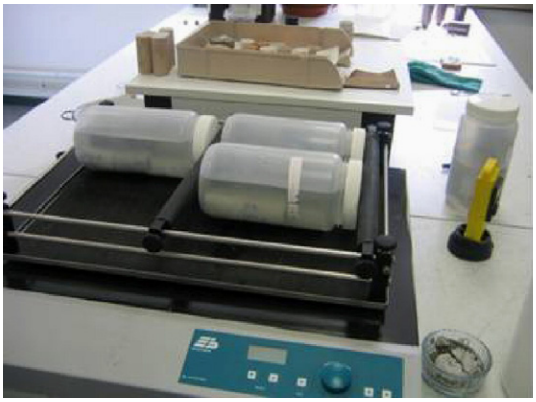

Fig. 2. “Ping Pong” table used to agitate the leaching solution.

2.2. Experimental program

Elastic modulus, compressive strength, porosity (and/or loss of mass) and gas permeability were the properties chosen to demonstrate leaching degradation effects. As ammonium nitrate leads to high leaching kinetics three short degradation periods were selected: four, eight and sixteen days. To ensure the significance and reliability of the results, five samples were used for the various tests: 2 samples for elastic modulus and strength determination; 3 samples for porosity and permeability determination. Thermogravimetry analysis (TGA) was also performed (as a preliminary test) on 3 samples: unleached and after 8 or 24 days of leaching. This method is useful to evaluate if

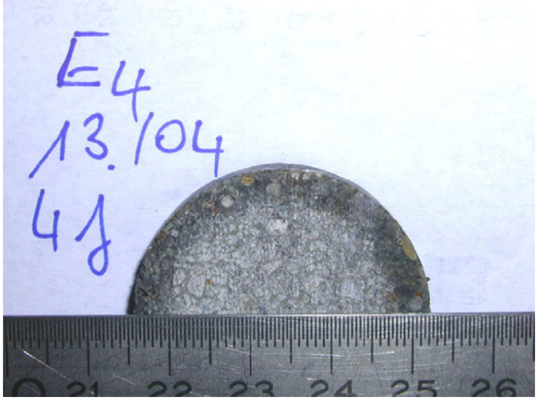

Fig. 3. Measurement of degraded thickness for a cylinder of diameter 38 mm.

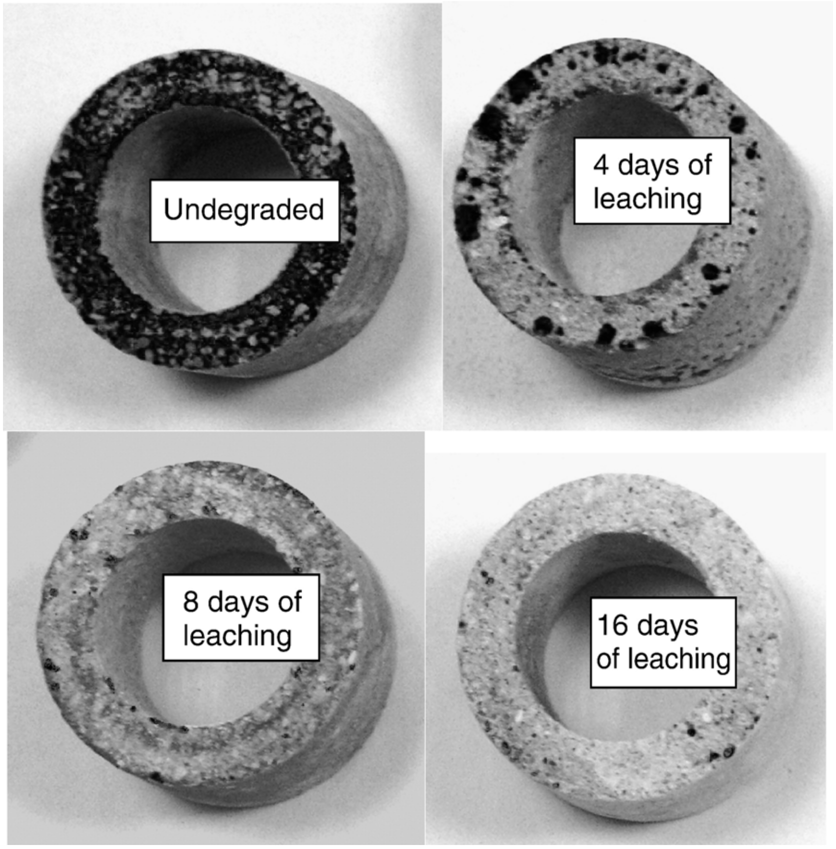

Fig. 4. Pictures of coloured samples with phenol–phtalein. Black zone or spots are pink colour in reality and obtained with pH higher than 9. Black (or pink) means no dissolution i.e. presence of CH.

Portlandite has been dissolved or not. In total 43 samples were tested of which 31 were degraded.

2.2.1. Leaching process

The aggressive solution was a 6-M ammonium nitrate solution (480 g/l). Such a solution leads to acceleration of the leaching process by 300 times compared with water [8]. This is obtained when the solution pH is lower than 9.25. Hence, the pH was regularly monitored to renew the solution as soon as its pH was between 8.5 and 9. Samples were immersed in the

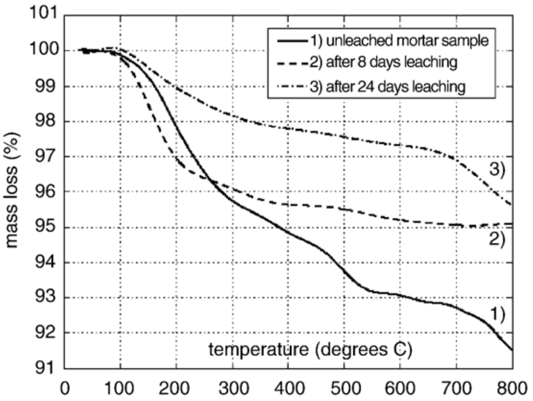

Fig. 5. Thermogravimetry analysis results. The change in slope of curve 1) that occurs around 500 °C is linked to CH dehydroxylation.

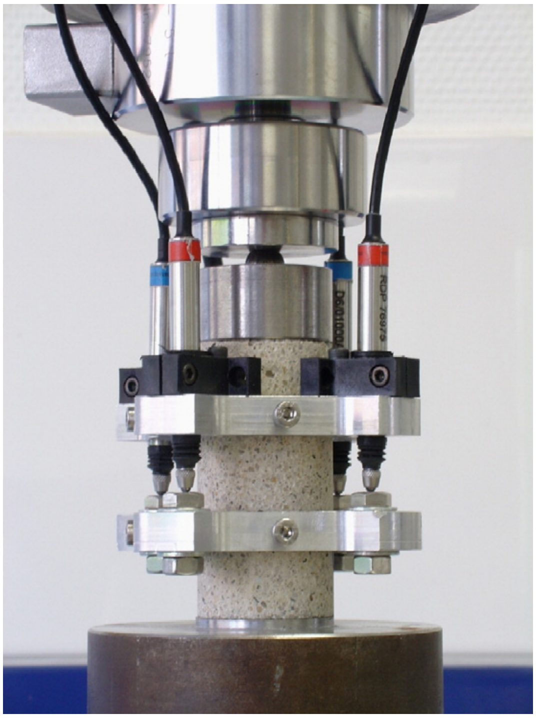

Fig. 6. LVDT rig and hinged device designed for displacement and strain measurements.

Fig. 7. Specific tube preparation for gas permeability measurements.

solution in tanks held on a slow oscillating table ("ping pong" table — see Fig. 2). Therefore, the bath was constantly agitated around the sample surface. As soon as the leaching duration is reached, the sample series considered is immersed in demineralised water for at least 10 days. This rinsing phase has proven to be very efficient to prevent the expansion of calcium nitro-aluminate produced by the chemical reaction [18]. Samples were then cut to remove the ends, which are more degraded, in order to get homogeneous 65 mm long specimens. Each series was finally dried in an oven at a moderate temperature of 60 °C and 10% relative humidity. This drying was stopped when constant weight was reached. Such drying is necessary to carry out gas permeability test as well as porosity and loss of mass measurements. Furthermore this operation allows mechanical testing to be performed at a known level of saturation (supposed here to be zero). On the other hand, heating leads to micro-cracking induced by shrinkage and differential strains between cement paste and aggregates. These effects have been evaluated in previous studies on the same mortar [10]. They are significant and cannot be neglected if accurate modelling is required. In the present case, the dried state is a reference state which was chosen in order to compare intact and leached material.

As a preliminary study the leaching process was undertaken on full cylinders made up with the same W/C = 0.5 and W/C = 0.8 mortars. This was mainly used to determine appropriate hollow tube thickness for which it could be assumed that tests are performed on materials with a uniform degree of degradation.

Table 2
Porosity and volumetric mass variations vs. leaching time: mean values

	Leaching time (days)	0	4	8	16
Mortar05	Volumetric mass (g/cm^3)	2.13 ± 0.01	1.95 ± 0.01	1.84 ± 0.02	1.80 ± 0.02
	Difference	0	0.18	0.29	0.33
	Porosity (%)	15 ± 0.1	21 ± 0.1	27 ± 0.5	29 ± 1
	Difference	0	6	12	14
Mortar08	Volumetric mass (g/cm^3)	1.88 ± 0.04	1.70 ± 0.02	1.62 ± 0.04	1.59 ± 0.04
	Difference	0	0.18	0.26	0.29
	Porosity (%)	24 ± 2	30 ± 1	34 ± 2	35 ± 2
	Difference	0	6	10	11

Three samples for each series.

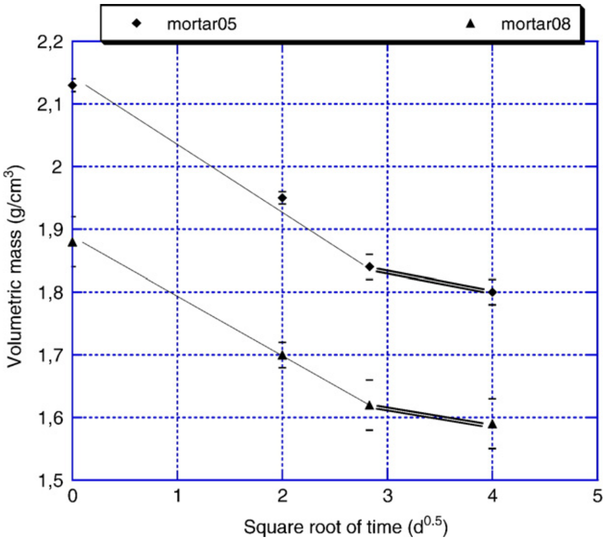

Fig. 8. Volumetric mass variations of both mortars versus square root of leaching time.

Following the process described above, 38 mm diameter full cylinders were leached for four days. They were then rinsed and cut in order to measure the thickness of the dissolution front (Fig. 3) which was found to be at least 4 mm. This measurement was made optically with the use of phenol–phtalein. This substance turns red–pink if applied on a material whose pH is higher than 9. Therefore, phenol–phtalein applied on a degraded zone will not coloured red. As Portlandite is reported to dissolve from pH 12 and lower [17], this technique can indicate its presence (or not). As a consequence, we chose to core 8 mm thickness tubes. Phenol–phtalein was also used on mortar05 tubes made of intact material and after each leaching time (4, 8 and 16 days). Results of this operation are given in Fig. 4. To allow better examination, red colour was transformed to black on these pictures. It clearly appears that intact sample is uniformly black (i.e. red). Over 8 days of leaching they are uniformly grey, which means that

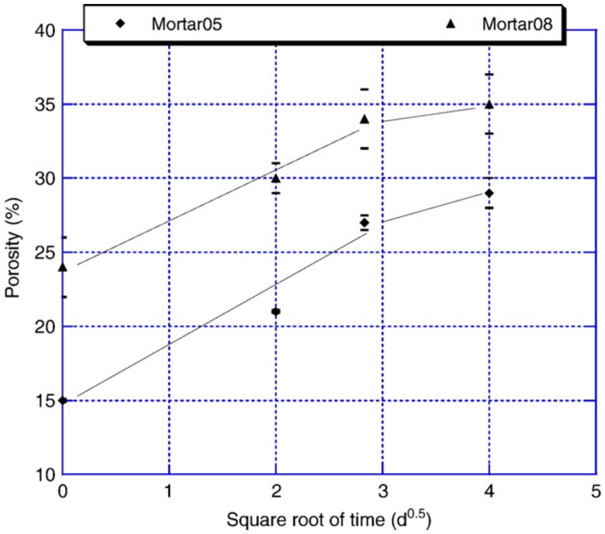

Fig. 9. Porosity variations of both mortars versus square root of leaching time.

Table 3
Permeability variations vs. leaching time: mean values

Leaching time (days)	0	4	8	16
Mortar05 permeability (m^2)	2.2 (±0.1) 10^{-18}	6.3 (±0.1) 10^{-17}	1.7 (±0.5) 10^{-16}	2.3 (±0.5) 10^{-16}
Mortar08 permeability (m^2)	1.9 (±1) 10^{-17}	3.5 (±0.1) 10^{-16}	1.6 (±0.1) 10^{-15}	2.2 (±0.5) 10^{-15}

Three samples for each series.

they are degraded through the whole thickness. After 4 days of degradation, black spots may remain. This is the result of a degradation (and/or Portlandite dissolution) which is heterogeneous or not completely achieved. However, there are only slight variations of material composition through the 8 mm thickness. Hence, homogeneity can be considered as a reasonable hypothesis particularly over a period of four leaching days.

2.2.2. Thermogravimetry analysis

To complete the observations made with phenol–phtalein and to obtain complementary information, thermogravimetry analysis (TGA) [15,16] was performed on mortar samples weighing between 300 and 600 mg and previously maintained at 60 °C and 10% humidity for several days. Samples were subjected to a heating rate of 10 °C/min up to 800 °C in a Ugine-Eyraud thermobalance (Setaram, Lyon, France) which magnetically hinders any sample movement. This feature avoids the sample being subjected to any temperature gradient in the oven. Furthermore, the sample is surrounded by a closed silica glass tube in order not to be subjected to any hot air flux. The balance mass loss ouput signal is carefully calibrated in the range 0 to 240 mg. Mass loss Δm is expressed in percentage of the initial sample mass. Its initial value is taken as 100% (no mass loss). Temperature is recorded in the vicinity of the sample (at about 5 mm distance) using a K-type thermocouple protected in a stainless steel sheath.

Preliminary results of mass loss versus temperature are given in Fig. 5 for three samples at different leaching states: 1) unleached, 2) after 8 days leaching and 3) after 24 days leaching.

Total mass loss at 800 °C decreases with leaching duration. At 800 °C, Δm is 91.5% before leaching, 95.1% after 8 days leaching and 95.5% after 24 days leaching. Less than 0.1% is lost below 100 °C. Free water had indeed been removed from the samples before TGA. Above 100 °C and up to 200 °C is the typical C–S–H dehydration range, whereas Portlandite dehydroxylation is in the range 400 °C to 600 °C [15,16]. Below 400 °C, mass loss decreases notably with leaching duration. It is 94.9% before leaching, 95.6% after 8 days leaching and 97.9% after 24 days leaching. This is attributed to less C–S–H present in the samples after leaching. We interpret that leaching induces C–S–H dehydration. The unleached sample exhibits a marked mass loss around 500 °C which is attributed to Portlandite dehydroxylation. None is so clearly noticed for the 8-days and 24-days leaching samples. Therefore, leaching, even of only 8 days, induces Portlandite dissolution and gradual disappearance. Theses results are confirmation of the phenol–phtalein test i.e. no more Portlandite remains in the material after 8 days leaching. The mass loss, observed over a period of 8 leaching days, is only due to C–S–H dissolution whereas at early stages of leaching (i.e. below 4 days) CH dissolution is the main cause of mass loss.

2.2.3. Sample preparation for mechanical testing

A mechanical 300 kN Instron press was used to carry out strength and Young's modulus measurements. The displacement velocity was set at 0.12 mm/mn. An original rig was designed for measuring longitudinal strains. It is indeed very difficult to glue strain gauges on the degraded surface which is very porous. A specific surface preparation can be made with resin but preliminary tests have shown that resin leads to local increase in rigidity. Hence strain gauges measurements are inaccurate. It was therefore decided to design a support ring, equipped with LVDT sensors (Fig. 6). Displacement accuracy is improved by the use of four LVDT diametrally opposed and by a hinged device (to avoid bending effects due to eccentric loading) placed between the upper plate of the press and the sample (Fig. 6). The reference measurement length, used to derive strains, was 30 mm. The displacement was deduced from the average value of the four LVDT measurements. This has the advantage of compensating for any bending effects which may be present despite the hinged device. In the results presented below, Young's modulus is measured as the slope when the material is unloaded from 25% of the stress peak.

2.2.4. Sample preparation for permeability testing

To measure gas permeability, the experimental procedure was designed to obtain a steady axial flow through the sample placed in a confining cell. The complete procedure is detailed in

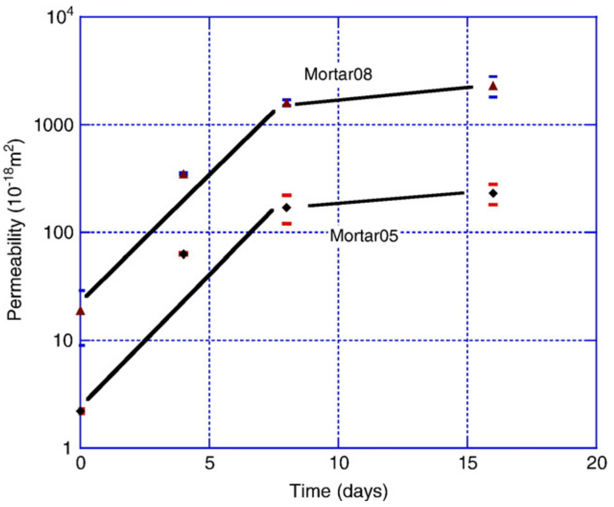

Fig. 10. Comparison of changes in permeability versus leaching time.

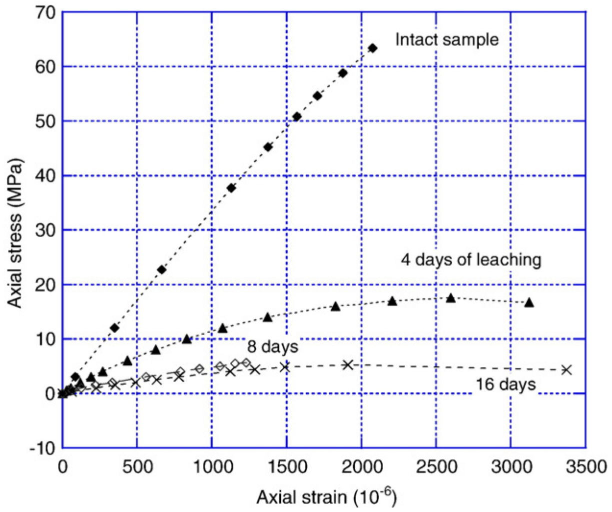

Fig. 11. Example of behaviour evolution occurring with leaching. This example is given for a mortar05 sample. It is nevertheless representative of behaviour evolution for both mortars.

Ref. [11] where experimental device description and measurement analyses are also given. In the present case, both sample sides were subjected to an inert gas pressure of $P_1 = 1.5$ MPa on the downstream side and freely drained at atmospheric pressure on the other side. The external surface was sealed with a Vitton membrane. P_c was limited to 3 MPa. As the hollow part of the tube was filled with araldite resin (which is gastight), gas flow occurred axially in the annular zone (Fig. 7). The gas used was pure Argon gas which viscosity is $2.2\ 10^{-5}$ Pa s at 20 °C. The sole difference, compared to what is described in Ref. [11], lies in the surface of the sample being that of the annular zone.

3. Results and discussion

3.1. Volumetric mass and porosity variations

All the results presented on mass and porosity variations are mean values obtained on at least three samples. Though results were found to be very homogeneous for each series of samples, scatter values are given. Porosity was deduced from the difference between saturated and dried sample weight and sample volume was calculated from accurate sample dimension measurements. The saturated weight of leached samples was measured after rinsing for ten days. It is possible that a low proportion of calcium nitro-aluminate was still present in porosity voids. However, several (2 or 3) rinsing tests carried out for longer periods did not reveal significant weight variations after ten days. On the other hand, variations between intact and leached material are sufficiently high to be considered as unambiguous. The whole set of mean results is presented in Table 2. Figs. 8 and 9respectively show changes in volumetric mass and porosity versus time. More precisely, mass variation is plotted versus the square root of time as proportionality between the two variables has been often reported. The conditions required to obtain proportionality to the square root of time are an unaltered zone in the sample and an aggressive solution with a constant composition [9]. In the present case, previous and preliminary results, exposed in Section 2.2.1 and Section 2.2.2, have clearly shown that, between 4 and 8 days leaching (and over), the whole sample is degraded. It means that an unaltered zone is unlikely to remain in the tube after more than four to five days of degradation. Hence it seems logical not to obtain the proportionality mentioned above as Figs. 8 and 9 show. Two phases can be observed: a first and almost linear phase (until eight leaching days) followed by what could be a “plateau” i.e. a significant drop in the leaching kinetics. We interpret these two phases as evidence of an important macroscopic effect of leaching, linked with the rapid decalcification of Portlandite (CH) followed by a delayed and progressive decalcification of the C–S–H hydrates. C–S–H decalcification leads to microporosity since CH decalcification produces macro-porosity [12]. The slopes of porosity and mass variations for the two mortars, observed in Figs. 8 and 9, are almost parallel but it is difficult to draw definitive conclusion about the impact of W/C ratio on the kinetics of leaching. A simple calculation shows 20% more paste is present in mortar05 than in mortar08. This would theoretically lead to a ratio of 1.2 of mass leached from mortar05 compared to mortar08 [9] when the material is totally degraded. This is roughly the case after 16 days of leaching — see Table 2. At early degraded states (i.e. 4 days leaching), the changes in volumetric mass for both mortars are similar. This may be due to higher porosity for mortar08 which would lead to faster initial kinetics of dissolution (due to a higher diffusion coefficient and a lesser cement paste quality [1]). Although not investigated, the specific surface of both mortars porosity probably also induces kinetics effects at the beginning of leaching.

3.2. Permeability variations

As mentioned above, permeability was measured on dried samples. The results obtained are reported in Table 3 as mean values (calculated from three samples) for each series tested.

Table 4
Strength and modulus variation vs. leaching time

	Leaching time (days)	0	4	8	16
Mortar05	Modulus E (MPa)	36830 (±1000)	16400(±1000)	8100(±500)	6650(±1000)
	Strength Rc (MPa)	60 (±6)	17.8 (±0.4)	6.4 (±1.5)	5.8 (±0.5)
Mortar08	Modulus E (MPa)	18000 (±2000)	8600(±500)	2850(±250)	2500(±100)
	Strength Rc (MPa)	26 (±0.5)	5.9 (±0.6)	2.1 (±0.1)	2.0 (±0.1)

Three samples for intact series (0 day) and two for each degraded sample series.

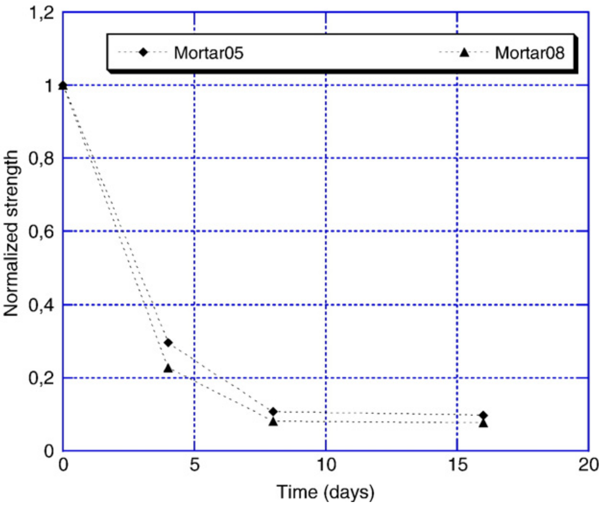

Fig. 12. Normalized strength variations versus leaching time.

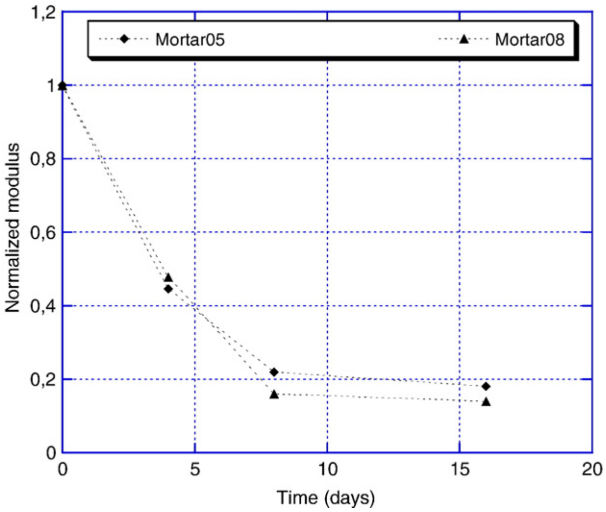

Fig. 13. Normalized modulus variations versus leaching time.

Several injection pressures were applied ($P_1 = 1.5$, 1 or 0.5 MPa) in order to evaluate possible influence of the Klinkenberg effect [13]. This effect was present but appeared to be negligible at the chosen pressure of $P_1 = 1.5$ MPa. It will therefore be assumed that the intrinsic permeability is measured.

Changes in permeability are plotted in Fig. 10 on a logarithmic scale. As for porosity measurements, two phases can be observed for both mortars. In the first phase, until eight degradation days, there are sharp permeability increases (by one order of magnitude) between two successive measurement steps. After eight days, there is a kind of "plateau" corresponding to a second phase during which permeability is still increasing but with a considerably reduced slope. Such phenomena can be examined in parallel with mass and porosity evolutions as the consistency is remarkable. This strengthens the hypothesis of a first leaching and degradation phase of Portlandite (i.e. sharp increase in permeability) since the following step, due to C–S–H leaching, leads to micro-porosity occurrence only (i.e. low permeability increase).

3.3. Compressive strength and Young's modulus variations

From a general point of view the leaching effect is similar for both mortars. Fig. 11 gives an example of the evolution of behaviour with leaching time for mortar05. This is representative of changes which occur to the behaviour of all samples tested. As clearly indicated in Fig. 11, the mechanical behaviour evolves from brittle (intact samples) behaviour to more and more ductile behaviour with leaching duration. This phenomenon has already been reported for mortar and cement paste [5]. As ductility gets more pronounced, the strength loss is very spectacular finally decreasing by 90 to 95% after only eight days of leaching. Such drops were also described by Heucamp et al. [8] and were attributed to a chemical decohesion of the leached cement paste. In parallel, Heucamp et al reported a bulk modulus which strongly decreased due to concomitant porosity growth within the paste. This is seen here from a sharp drop of Young's modulus which is about 80% for the two mortars. The complete set of data is given in Table 4. Evolutions of strength and modulus are depicted respectively in Figs. 12 and 13. To avoid scale representation problems, the plotted properties are normalized i.e. divided by the initial (or intact) property value. It can then be observed that, with such a representation, the two materials exhibit virtually the same behaviour: identical relative amplitude of degradation with common kinetics. This was not the case with, for example, relative porosity variations (see Fig. 14).

Concerning the phenomenon linked to CH and C–S–H decalcification, it is clear that between 8 and 16 days of leaching there are only slight changes of strength and modulus. On the one hand, this is an evidence that C–S–H dissolution induces a very slow process of mechanical property variations as well as permeability changes (see also Refs. [5,14]). On the other hand, this demonstrates the interest in studying mortar or concrete (like high performance concrete) with lower proportion of CH which is clearly the weakest point when leaching occurs.

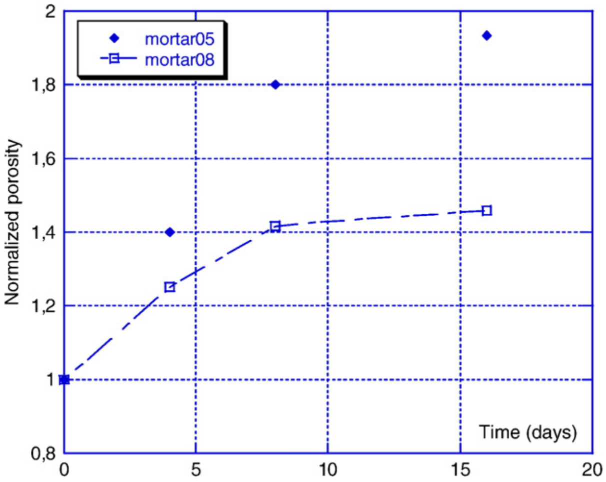

Fig. 14. Normalized porosity variations for both mortars versus leaching time.

4. Conclusion

Tube samples were cored in order to produce a homogeneous leaching phenomenon by the use of an ammonium nitrate solution. Preliminary studies showed that after 4 days of leaching, the depth of degraded material was at least four millimetres on plain cylindrical samples. On mortar05 tubes, impregnation with phenol–phtalein and thermogravimetry analysis both showed that Portlandite was dissolved between 4 and 8 days of leaching. This indicates that, after 8 days of leaching, the changes in properties are mainly due to progressive C–S–H dissolution. Moreover, testing hollow cylinders had the advantage, in comparison with other geometries, to allow the study of interesting property variations such as porosity, permeability, strength and elastic modulus on a quasi homogeneously degraded material i.e. with no need for inverse methods. Three leaching times were investigated: 4, 8 and 16 days. Two mortars, with a normal W/C = 0.5 ratio (mortar05) or with a very high W/C = 0.8 ratio (mortar08), were tested in order to evaluate the influence of a high initial porosity (24% for mortar08) and as a consequence a lower cement paste proportion in mortar08. For all variations in property measured, two stages were present for both materials. The first stage was characterised by rapid decrease in volumetric mass leading to sharp increase in porosity and in permeability or to spectacular decrease in strength and in elastic modulus. This typical step, associated with Portlandite decalcification, occurred for the first eight days of leaching. After this period, there was a second stage in which property variations were very limited. This is commonly attributed to calcium dissolution from C–S–H hydrates, dissolution that occurs more slowly. However for both mortars tested, major variations of properties are obviously linked to Portlandite decalcification which led to increase in permeability by two orders of magnitude and to loss in strength and modulus of 80 to 90%.

The W/C ratio had a predictable effect on the total quantity of leached calcium. The loss in mass and increase in porosity were higher for mortar05 than for mortar08. This occurred in proportion which, at the end of the leaching tests (i.e. 16 days), roughly corresponded to the cement paste proportion of both mortars. However, relative variations of permeability, strength and elastic modulus were found to be virtually identical and, as a result, independent of W/C ratio. Higher mortar08 initial porosity, being the consequence of higher effective diffusivity coefficient, should have induced more rapid calcium dissolution. Over four leaching days, period for which dissolution kinetics seemed higher, had there been no obvious evidence of an accelerated effect due to this initial porosity.

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