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EFFECT OF THE LEACHING OF CALCIUM HYDROXIDE FROM CEMENT PASTE ON MECHANICAL AND PHYSICAL PROPERTIES

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ABSTRACT

This paper deals with the effect of the leaching process of cement based materials on their mechanical and physical properties. In order to characterize this effect, we have performed experiments on cement paste samples. The leaching process was achieved by the use of a 50% concentrate solution of ammonium nitrate. Both compression tests and water porosity tests were conducted on micro-cylinder samples (10, 12, 14 and 20 mm of diameter) because of the slow kinetics of degradation due to the leaching. The deterioration of the cement paste and the mortar exposed to the action of the ammonium nitrate was manifested by a peripheral zone of less resistance. This process induces mainly a total leaching of $Ca(OH)_2$ and a progressive decalcification of C-S-H which leads to a gradient of C/S ratio in the leaching zone. Both mechanical tests and water porosity tests show that there is a linear variation of the loss of strength and the increase in porosity in relation to the ratio of degraded area over total area of the sample A_d/A_t. It means that both compressive resistance and water porosity of the leaching zone are constant whatever the size of the degraded zone and then whatever the time of exposure to the chemical attack. So we could venture the hypothesis that the dissolution of calcium hydroxide is the essential parameter governing both decrease in strength and increase in porosity. © *1997 Elsevier Science Ltd*

Introduction

The research program in progress tries to characterize the deterioration of the mechanical properties of the concrete surrounding radioactive wastes, due to the water flow during storage. The chemical attack of this small amount of ionized water is essentially a leaching of the calcium hydroxide and a progressive decalcification of the C-S-H [1]. The slow kinetics of these chemical reactions leads us to increase the agressivity of the environment by using a solution of NH_4NO_3 (the chemical attack due to NH_4NO_3 is also a leaching but quicker than those obtained with the water). The similarity of this two leaching processes has been established chemically, mineralogically and mechanically by Carde [2].

TABLE 1

Chemical Composition (weight %)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O
20.2	4.9	3	63.4	0.67	3.2	0.25

In this paper, the results of an investigation carried out in order to better understand the mechanisms of deterioration of cement pastes in contact with an aggressive solution of NH_4NO_3 are presented. The test program was designed in order to obtain information on both the alteration of mechanical properties and porosity in relation to time and to determine the influence of the dissolution of calcium hydroxide and the decalcification of the C-S-H.

Experimental Program

Materials. The cement used to make the sample of paste is an OPC cement (CEM I 42.5) whose chemical composition is given in Table 1. The mixtures were poured into cylindrical moulds (11 × 22 cm). The demoulding was done after 24 hours, then the samples were cured for 27 days immersed in water saturated in lime at 20°C (1 °C).

Samples. Because of the slow kinetics of leaching, we have been obliged to work with samples of small sizes. The samples used are cylinders whose diameters are 10, 12, 14 and 20 mm with a ratio $h/\phi = 2$ (h height of the sample). After curing, the samples are extracted from the test pieces by means of a diamond tipped core lubricated with water. For each sample dimension, two series of samples have been made, the first one which has been immersed in the aggressive solution (treated series), the other one which has been kept in an endogenous environment (control series).

Leaching Process. The aggressive environment used is an ammonium nitrate solution. The ammonium nitrate NH_4NO_3 is very soluble in water, and reacts in the first time with the cement paste by reactions which lead to the appearance of a very soluble salt of calcium $Ca(NO_3)_2$ and an emanation of gaseous ammoniac NH_3. In a second time, an expansive calcium nitro-aluminate, empirical formula $3CaO.Al_2O_3.Ca(NO_3)_2.10H_2O$, is formed by reaction to the calcium nitrate with the hydrated aluminates from the cement paste [3]. Lea [4] has shown that this compound forms like the "climbing salts" that are transported by the water from an humid surface to a dry surface. Then, in a wet environment or if the concrete remains totally immersed, the lime leaching is the only deterioration. On the other hand, an environment submitted to humid and dry cycles has to favor the increase of ions concentration and the development of internal tensions which cause microcracking.

In this study, the calcium nitro-aluminate formation is essentially disturbing for the mechanical tests. As a result, the presence of a microcracks system can notably modify measured parameters during the test. Thus, samples are kept in water between their removal of the aggressive solution and the mechanical loading whose short duration does not allow the appearance of this expansive compound [2].

The kinetics of degradation is directly linked to the concentration of the aggressive solution. To increase significantly this kinetics, the concentration retained is equal to 437 grams

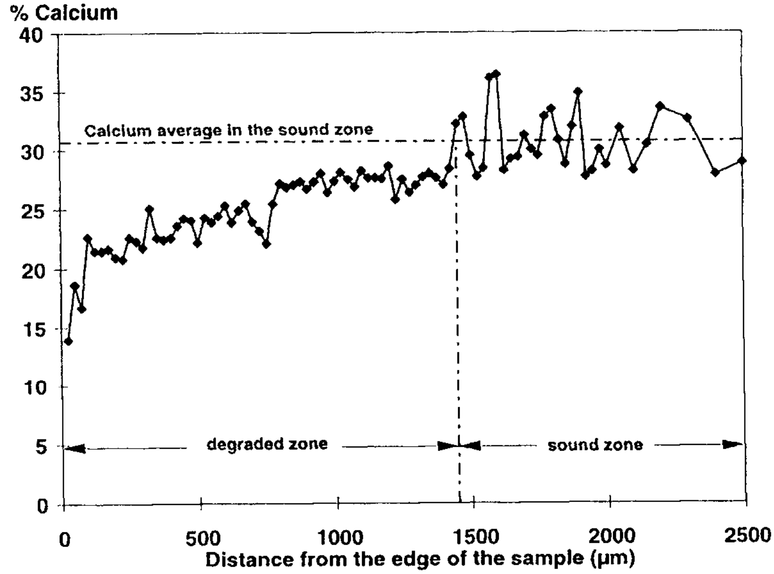

FIG. 1.

Variation of the dissolution of Ca in relation to the depth of a pure cement paste sample treated for 1 day in the ammonium nitrate solution (microprobe automatic analysis: depth step is 25 µm (±1 µm) and % calcium in mass (±0.3%)).

of ammonium nitrate per liter of solution, which corresponds to the half saturation. The environment is permanently shaken to favor the diffusion.

Since this process induces mainly a total leaching of the calcium hydroxide and a progressive decalcification of C-S-H, the removal of Ca ions is monitored by microprobe analysis which allows to plot the calcium profile along the samples (residual calcium content in solid phase), and the removal of $Ca(OH)_2$ is confirmed by the plot of XRD (Cobalt radiation) curves at different depths obtained by polish sequences. The results are presented on Figure 1 (sample of pure cement paste treated for 1 day in the ammonium nitrate solution) and Figure 2 (sample of pure cement paste treated for 2 days in the ammonium nitrate solution) respectively.

These results show that the peripheral degraded zone is delineated by the dissolution front of calcium hydroxide. The leaching process leads to a uniform degradation of the samples. Then, the peripheral degraded zone must be more porous than the bulk sample and also less resistant.

The degradation is governed by a diffusion mechanism and can be described by the Fick's law relating the degraded thickness to the square root of time $\sqrt{t}$. Figure 3 shows the linear variation of the degraded thickness, measured out with a microscope, and the loss of mass of the sample in relation to the square root of immersion time in the aggressive solution.

Mechanical Tests. Both the treated samples and the control samples have been subjected to a compressive load in order to measure their compressive resistance. The device used is a Hounsfield press with a maximal capacity of 50kN. The displacement speed is controlled during the load. The force applied on the sample and the longitudinal displacements are measured during the test. The displacement measured is the average of three displacements

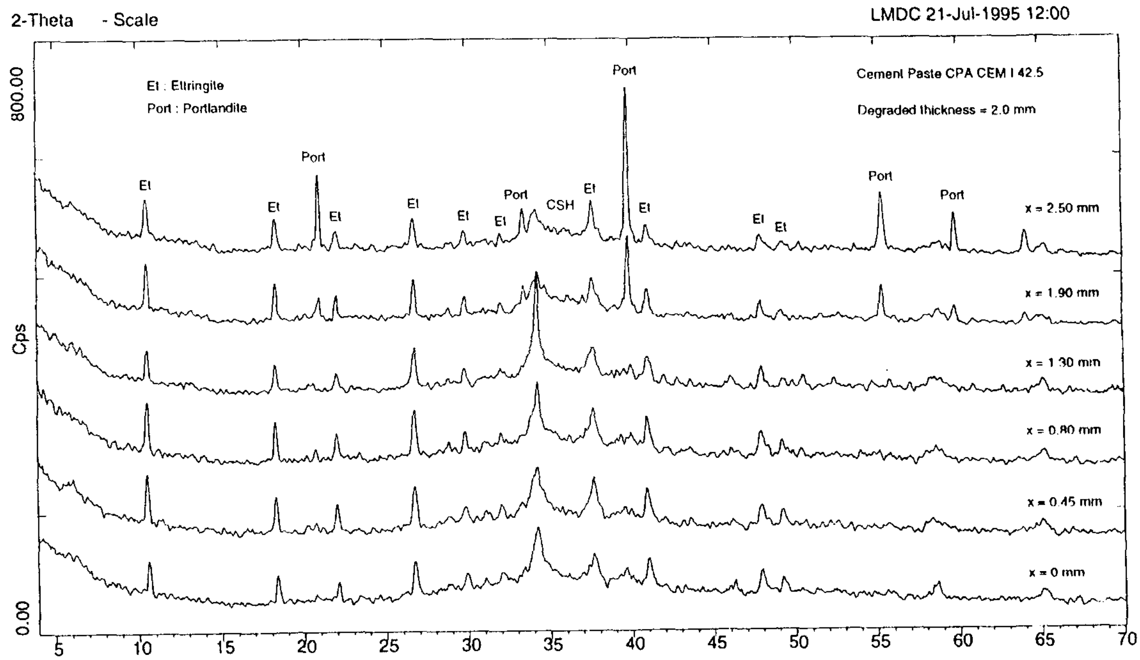

FIG. 2.

Variation of the dissolution of $Ca(OH)_2$ in relation to the depth of a pure cement paste sample treated for 2 days in the ammonium nitrate solution (SRD pictures: Cps in relation to 2θ scale with cobalt radiation.

recorded during the test by means of three transducers fixed on the clamping plate with an angular location of 120° (Fig. 4), so the bending effects cannot disturb the measure of the displacement.

The average longitudinal strain εl_{avr} is calculated using the three measured displacements.

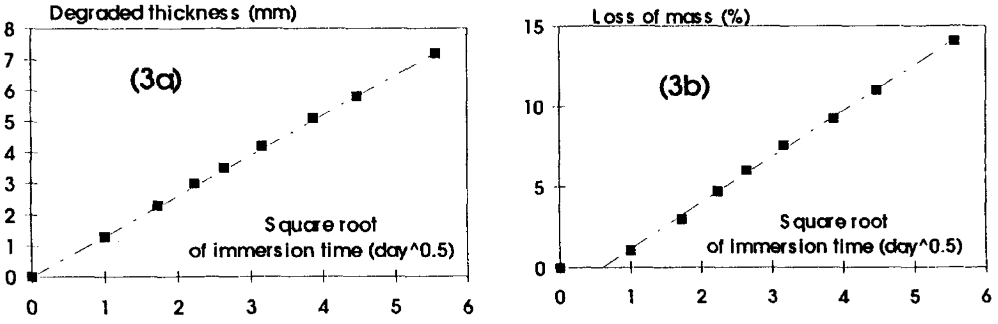

FIG. 3.

Variation of degraded thickness (3a) and the loss of mass (3b) in relation to the square root of immersion time in the solution of NH_4NO_3 (50%).

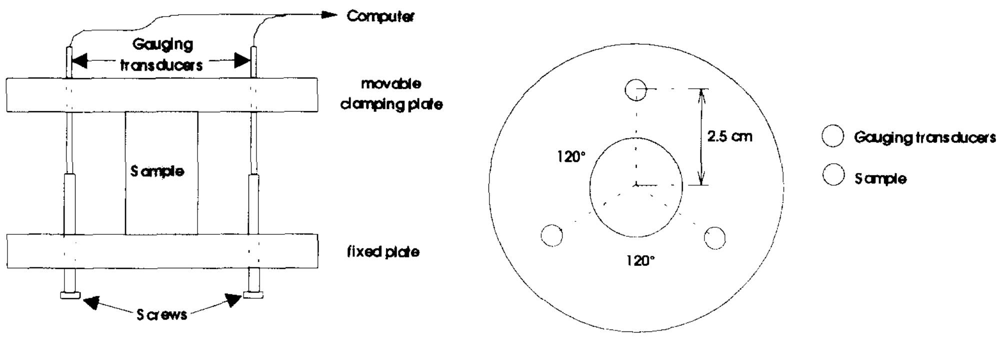

FIG. 4.
Experimental device for the compressive tests.

$$\varepsilon 1_{avr} = \frac{d_1 + d_2 + d_3}{3} \cdot \frac{1}{h} \quad (\mu m / m)$$

where d1, d2, d3 are the displacements recorded by means of the transducers 1, 2 and 3 (μm) h is the height of the sample (m).

The compressive strength is evaluated by dividing the maximal load F_{ult} by the area of the sample S

$$\sigma_c = \frac{F_{ult}}{S} \quad (MPa)$$

The simultaneous recording of the force and the average displacement allow the plotting of the curve $\sigma = f(\varepsilon)$. Two loading methods are used.

The first one is a simple standard loading, the second one is an incremental cyclic loading (Fig. 5) which allows us to measure the degree of reversibility d_r of the materials [5]. This parameter characterized the irreversibilities due to the loading. The calculation of this parameter at the end of each cycle allows us to study the increase of the irreversibilities in relation to the % of the stress rupture σ_c, and then to compare the mechanical damage between the control samples and the degraded samples.

Physical Tests. Water porosity tests have been performed in order to characterize the microstructure of the degraded zone. The measure of the porosity is achieved by filling (the porous volume of the sample which was previously dried) with a given fluid. Nevertheless, the results obtained by different authors show a large dispersion which is due to the nature of the fluid used, to its ability to penetrate in the porous system and to the drying mode of the samples. For example, Feldman [6] has measured the porosity of different pastes samples (W/C respectively 0.4, 0.5, 0.6, 0.7) with different fluids and has shown that the use of helium (23.3%, 34.5%, 42.1%, 53.4%) leads to a lower porosity than the use of water (37.5%, 44.8%, 51%, 58.7%).

The experimental method used to measure the water porosity is to dry at 80°C a sample saturated in water until it reaches a constant mass. Then, we consider that the loss of mass corresponds to the volume of water stored in the porous system of the material, even if the results obtained by Taylor [7] show that some hydrates loss a part of their binding water at this temperature.

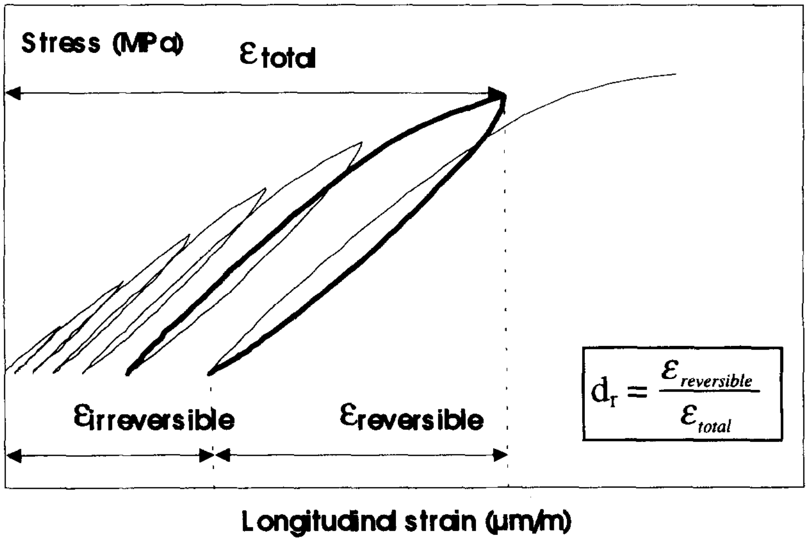

FIG. 5.
Incremental cycle loading to measure the degree of reversibility.

TABLE 2

Compression Strength in MPa in Relation to the Degraded Ratio

φ (mm)	A_d/A_t	σ_c control (MPa)	Standard deviation (MPa)	σ_c degraded (MPa)	Standard deviation (MPa)
10	0.47	41.7	1.8	27.0	1.0
	0.64	41.7	1.8	18.8	1.3
	0.77	48.9	3.4	17.3	1.0
	0.94	48.9	3.4	12.4	1.5
	1.00	47.9	2.2	11.0	0.7
12	0.40	43.6	1.0	30.9	2.1
	0.64	48.7	1.6	23.9	1.4
	0.86	49.9	2.4	18.1	1.7
	0.97	55.2	2.5	14.0	1.6
	1.00	55.2	2.5	13.9	1.2
14	0.34	47.1	2.0	33.6	1.7
	0.57	47.1	2.0	25.9	1.9
	0.78	52.6	2.4	22.4	1.3
	0.87	52.6	2.4	18.5	1.0
	0.90	51.1	1.5	17.0	1.5
	0.97	51.1	1.5	14.8	1.1
20	0.40	48.3	1.9	35.3	1.5
	0.54	51.2	1.9	31.2	2.4
	0.65	56.9	2.6	31.3	2.1
	0.73	56.9	2.6	26.8	2.5
	1.00	55.2	1.1	13.1	1.4

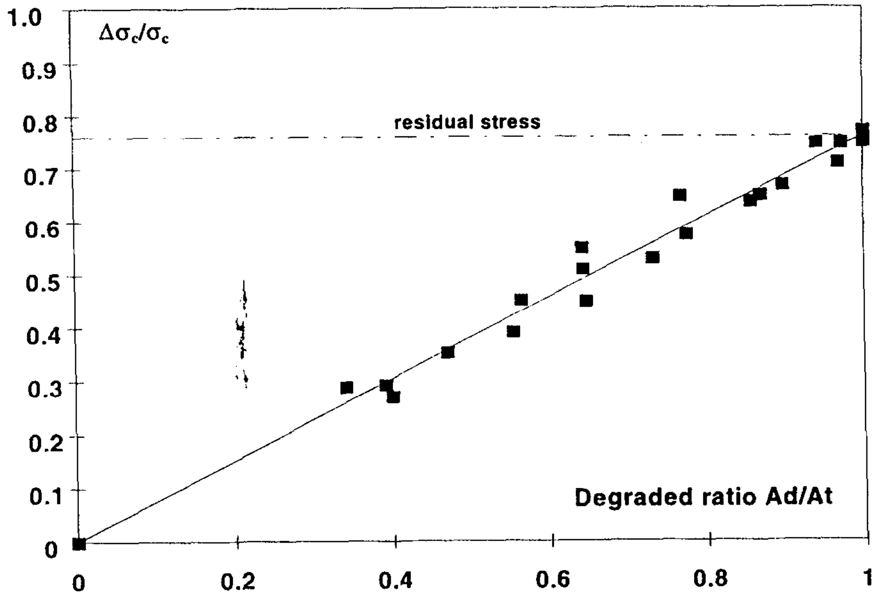

FIG. 6.
Variation of the loss of strength in relation to the degraded ratio.

Experimental Results

After treatment, the part of the base area which is degraded and would modify the displacement and the measured irreversibilities is eliminated from the samples.

The values of the compressive strength σ_c (average of 10 specimens) measured in the treated group and the control group are given in Table 2. The degradation level is assessed by the ratio of the peripheral degraded area (A_d) over the total area (A_t) of the sample.

To compare the results obtained with the different sizes of samples, the loss of strength is calculated using the following formula where σ_{ct} is the compressive strength of the control sample and σ_{cd} is the compressive strength of the degraded samples

$$\frac{\Delta\sigma_c}{\sigma_c} = \frac{\sigma_{ct} - \sigma_{cd}}{\sigma_{ct}}$$

The variation of the loss of strength in relation to the degraded ratio is presented Figure 6.

These results show that the decrease of stress $\Delta\sigma_c$ is independent of the size of the sample and is a linear function of the degraded ratio whose equation is:

$$\frac{\Delta\sigma_c}{\sigma_c} = 0.76 \cdot \frac{A_d}{A_t}$$

When the degradation is completely achieved, there is a residual strength representing about a quarter of the initial strength: $\sigma_{cd} = 0.24\sigma_{ct}$

The curves $\sigma = f(\varepsilon)$ corresponding to different levels of degradation for the 10 mm diameter samples are plotted on Figures 7a and 7b.

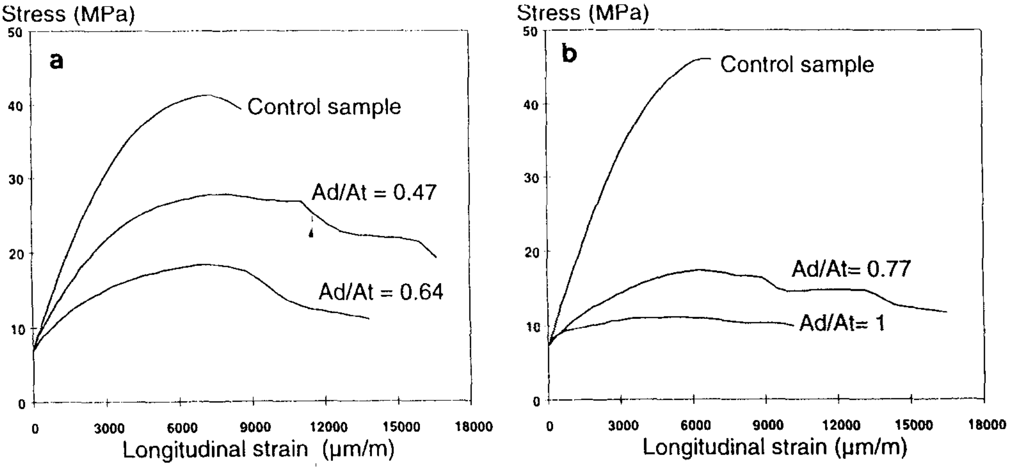

FIG. 7(a), (b).
Curves $\sigma = F(\varepsilon)$ for different levels of degradation (samples $\phi = 10$ mm).

These curves show that the behavior of the material become more plastic in relation to the degradation process. Only a small part of the curve corresponds to a reversible behavior and in the second part the increase of the strain is almost due to a constant stress. In this second part, the strains measured are irreversible and correspond to the development of microcracks in the paste. The increase of the degraded ratio corresponds to an increase of the ductile behavior of the sample submitted to a compressive tests. In the case of the control sample, the rupture energy is very important and corresponds to the development of a large amount of cracks, whereas in the case of the degraded sample, energy is spent even at the beginning of the load to develop the damage of the degraded zone.

The variation of the degree of reversibility leads to the same conclusion. Fig. 8 shows that the degree of reversibility decrease in relation to the degraded ratio even for a small value of the compressive stress.

If we suppose that the chemical attack leads to the development of two separated zones, a peripheral one which is degraded and the bulk which is sound, we can model (in a simplified way) the distribution of stresses in the sample. We can venture the hypothesis that the stress at rupture is the same in the degraded zone whatever this thickness, then the knowledge of the mechanical parameters of the sound zone (the same than a control sample) and the degraded zone (the same than a totally degraded sample) allows us to model the distribution of the compressive stress at the moment of the rupture for a partially degraded sample.

The compressive rupture strength of a totally degraded sample is

$$F_d = 0.24\ \sigma_{ct} A_t$$

where A_t is the total area of the sample and σ_{ct} the compressive rupture stress of the control sample; then $F_t = \sigma_{ct}$ At is the rupture strength of the control sample.

For a partially degraded sample, the stress in the degraded zone is assumed to be 24% of the stress in the sound zone, so the compressive rupture strength is:

$$F = 0.24\sigma_{ct} A_d + \sigma_{ct} (A_t - A_d)$$

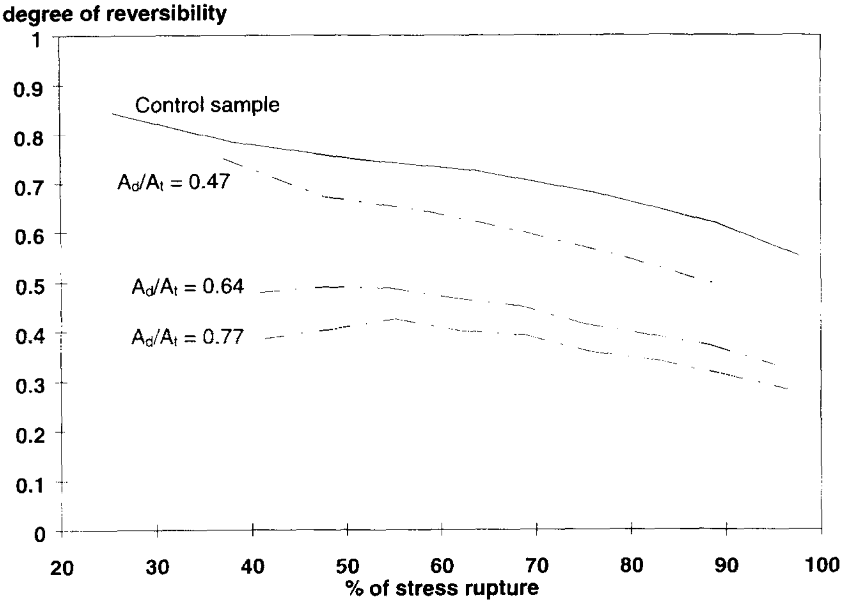

FIG. 8.

Variation of the degree of reversibility in relation to the compressive stress for different degraded ratio (samples $\phi = 10$ mm).

so the average compressive stress is

$$\sigma_c = \frac{0.24\sigma_{ct}A_d + \sigma_{ct}\left(A_t - A_d\right)}{A_t}$$

then the loss of stress is

$$\frac{\Delta\sigma_c}{\sigma_c} = \frac{\sigma_{ct} - \sigma_{cd}}{\sigma_{ct}}$$

$$\frac{\Delta\sigma_c}{\sigma_c} = \frac{\sigma_{ct}}{\sigma_{ct}} - \frac{0.24\sigma_{ct}A_d}{\sigma_{ct}\cdot A_t} - \frac{\sigma_{ct}\left(A_t - A_d\right)}{\sigma_{ct}\cdot A_t}$$

$$\frac{\Delta\sigma_c}{\sigma_c} = 0.76\cdot\frac{A_d}{A_t}$$

This model of stress distribution between the sound zone and the degraded zone at the rupture seems to be a good description of the phenomenon because the calculations lead to the same formula as the experimental one. Fig. 9 describes the principle of the modeling.

Because the chemical attack due to NH_4NO_3 leads to the total leaching of the lime and a progressive decalcification of C-S-H, the microstructure of the degraded zone is not uniform, there is a gradient of C/S ratio of C-S-H (Fig. 1). The good approach of the mechanical

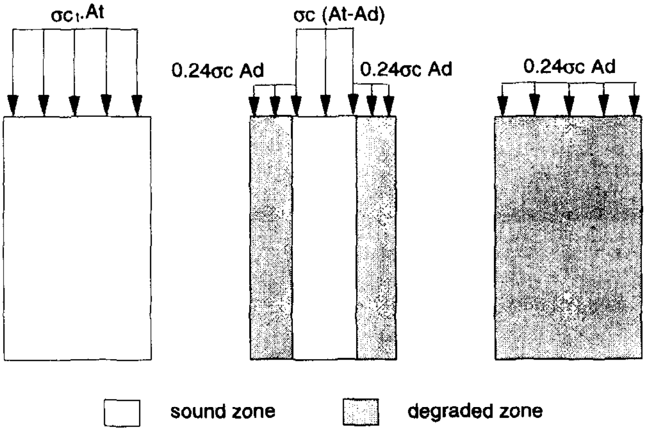

FIG. 9.
Distribution of stresses at the rupture for a sound sample, a partially degraded sample and a totally degraded sample.

results with a constant stress in the leaching zone assumes that the loss of stress is essentially due to the removal of $Ca(OH)_2$.

The water porosity has been measured on the control group, on partially degraded samples and totally degraded samples.

The results are presented in Table 3, where P_t is the total porosity of control samples and P_d is the total porosity of partially degraded samples.

The average (in relation to the size of the sample) increase in porosity due to the total leaching is 19.3% (Fig. 10). This result is almost the same as the percentage of calcium hydroxide in the paste. We can make the hypothesis that the increase in porosity is due to the total removal of the calcium hydroxide and then the decrease of C/S ratio of the C-S-H has a very small effect on the measurement of the porosity.

This hypothesis is confirmed by the mechanical result because the decrease of C/S ratio in relation to time and the degraded ratio does not lead to a decrease of the degraded area resistance which is constant at 24% of the control group resistance. So the loss of compressive strength could be linked to the increase of porosity due to the dissolution of the calcium hydroxide.

Conclusion

The deterioration of the cement paste and the mortar exposed to the action of the ammonium nitrate was manifested by a peripheral zone of less resistance. Because of the progressive decalcification of the C-S-H, there is a gradient of C/S ratio in the leaching zone. On the other hand, there is a complete dissolution of calcium hydroxide. Both mechanical tests and water porosity tests show that there is a linear variation of the loss of strength and the increase in porosity in relation to the degraded ratio A_d/A_t. It means that both compressive resistance and water porosity of the leaching zone are constant whatever the size of the degraded zone and then whatever the time of exposure to the chemical attack. So in the case of a paste sample made with CEM I cement which leads to a 20% content of calcium

TABLE 3

Water Porosity of Partially Degraded Sample (P_d), of the Control Group (P_t) and Their Differences (P_d - P_t). Average of 3 Measures

φ (mm)	A_d/A_t	P_t (%)	P_d (%)	P_d - P_t (%)
10	0.47	43.9	51.4	7.5
	0.64	43.9	57.4	13.5
	0.77	41.3	59.0	17.7
	0.94	41.3	61.9	20.6
	1.00	42.1	63.1	21
12	0.40	44.2	50.7	6.5
	0.64	43.7	55.3	11.6
	0.86	41.9	59.2	17.3
	0.97	43.0	61.7	18.7
	1.00	43.0	63.5	20.5
14	0.34	43.2	49.3	6.1
	0.57	43.2	52.5	9.3
	0.78	41.8	56.5	14.7
	0.87	41.8	58.3	16.5
	0.90	41.8	59.2	17.4
	0.97	41.8	59.4	17.6
20	0.40	40.5	49.1	8.6
	0.54	40.5	50.8	10.3
	0.65	39.7	55.4	15.7
	0.73	39.7	53.8	14.1
	1.00	40.0	59.8	19.8

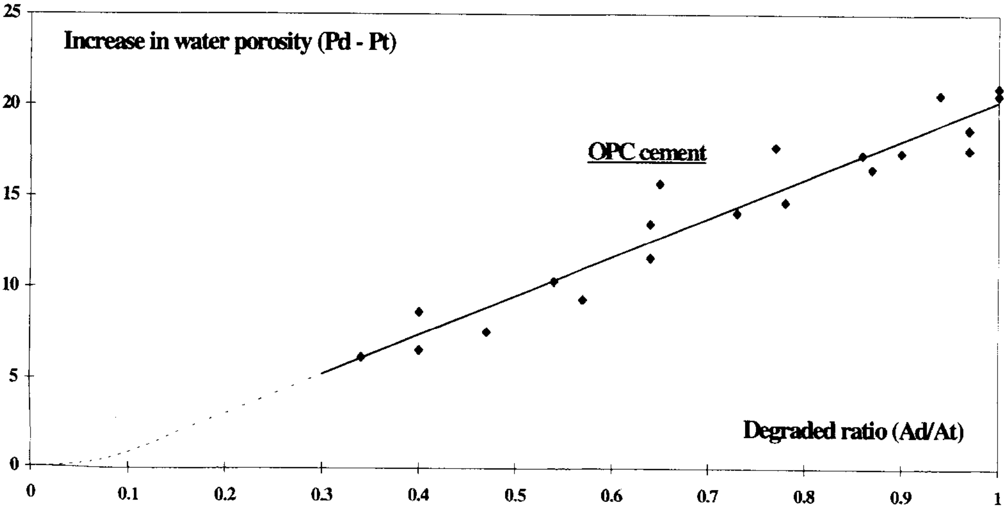

FIG. 10.
Increase in porosity in relation to the degraded ratio.

hydroxide, the dissolution of this calcium hydroxide is the essential parameter governing both decrease in strength and increase in porosity.

The next step of this research will be to use paste sample with the admixture of silica fume to reduce the content of calcium hydroxide and thus emphasize the effect of C/S ratio decrease of the C-S-H.

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