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LEACHING OF BOTH CALCIUM HYDROXIDE AND C-S-H FROM CEMENT PASTE: MODELING THE MECHANICAL BEHAVIOR

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ABSTRACT

This paper deals with the effect of the leaching process of cement based materials on their mechanical properties. 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. In a previous work, we venture the hypothesis that the dissolution of calcium hydroxide was the essential parameter governing both decrease in strength and increase in porosity in the case of a paste sample made with an OPC cement which leads to a 20% content of calcium. In order to quantify the effect of the decrease of C/S ratio in C-S-H, we have performed experiments on 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. The leaching process was achieved by the use of a 50% concentrate solution of ammonium nitrate. Compression tests were conducted on micro-cylinder samples (10, 12, 14, 20 and 30 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 indicated by a peripheral zone of less resistance. The experimental results allow the modeling of the mechanical behavior of cement pastes in relation to the ratio of degraded area over total area of the sample A_d/A_t. The model thus defined allows to separate the effect of calcium hydroxide leaching and C-S-H leaching, and shows the importance of the first one.

Introduction

The currrent research program 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. The slow kinetics of these chemical reactions leads us to increase the aggressivity 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 that obtained with water).

TABLE 1
Chemical Composition of the Cement

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 the alteration of mechanical properties in relation to time and to determine the influence of the dissolution of calcium hydroxide and the decalcification of the C-S-H. Experimental results allow to model the mechanical behavior of degraded cement pastes.

Experimental Program

Materials. Two different types of pastes were investigated. The first one is a pure paste of Portland cement and the second one a mixture of Portland cement and silica fume. The cement used to make the sample of paste is an OPC cement whose chemical composition is given in Table 1. The W/C ratio is 0.5 for the pure paste. The silica fume used is 30 % substituted of the weight of cement. The W/(C+SF) ratio is 0.45. The high content of silica fume used is to be sure to consume all the calcium hydroxide.

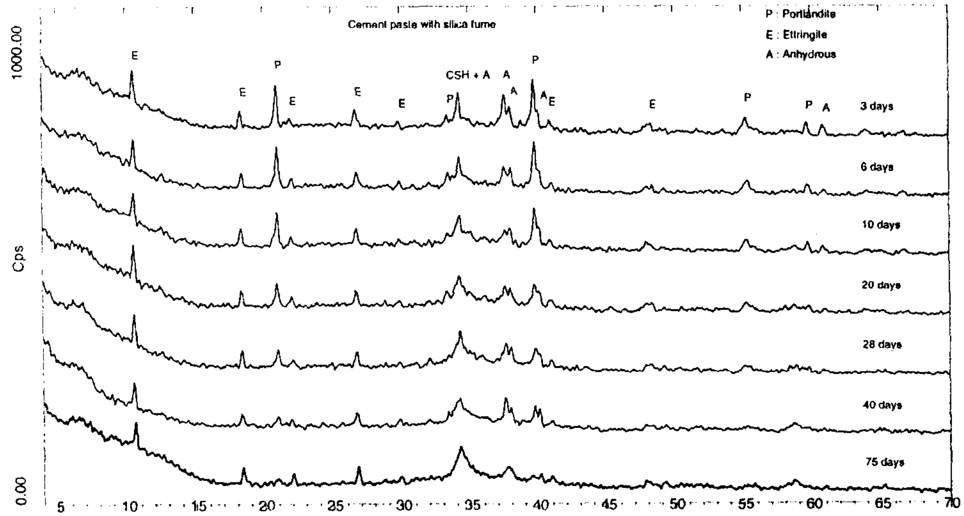

FIG. 1.
Evolution of the removal of the calcium hydroxide due to the pouzzolanic effect in relation to the curing time.

The mixtures were poured into cylindrical moulds (11 × 22 cm). The demoulding was done after 24 hours, then the pure paste samples were cured for 27 days immersed in water saturated in lime at 20°C (1 C). The paste samples with silica fume were cured during 75 days to achieve the complete pouzzolanic reaction (fig. 1).

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, 20 and 30 mm with a ratio h/f = 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 a 50% concentrate solution of ammonium nitrate NH_4NO_3 (590g/l.). The chemical attack of the ammonium nitrate leads to the development of a soluble calcium nitrate, a not very soluble nitro-aluminate of calcium and an ammoniac emanating NH_3 [1]. This process induces mainly a total leaching of the lime and a progressive decalcification of C-S-H [2]. 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 immersion time in aggressive solution. The removal of Ca ions is monitored by microprobe analysis which allows to plot the calcium profile along the samples. The test is made in a controlled environment which prevents the carbonation samples. The calcium profile for the pure paste sample is shown on Fig. 2, while in the case of the admixture of silica fume, the profile is plotted on Fig. 3. The results show a difference between the two previous profiles: in absence of calcium hydroxide, the variation of Ca is an

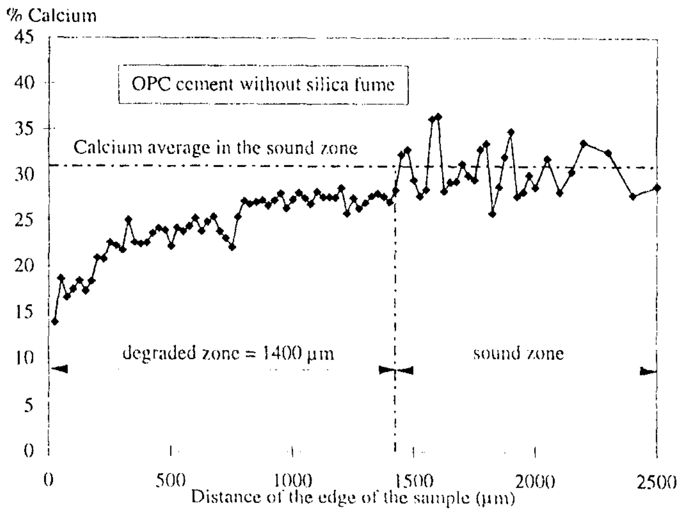

FIG. 2.
Variation of the dissolution of Ca in relation to the sample depth for the pure paste sample.

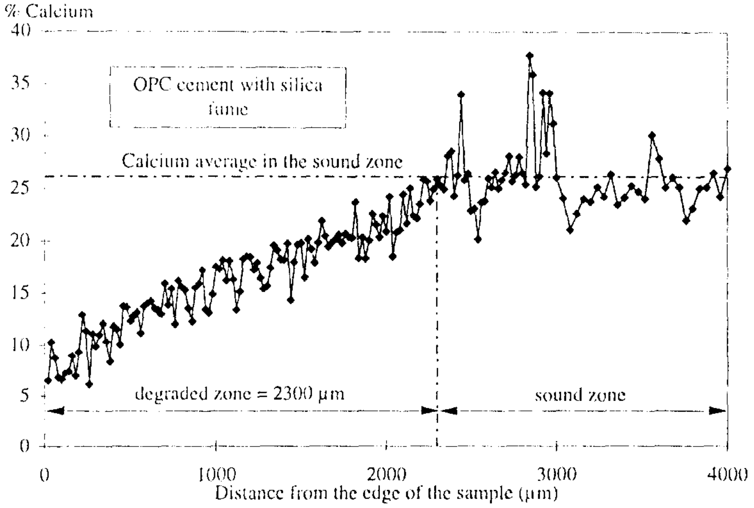

FIG. 3.
Variation of the dissolution of Ca in relation to the sample depth for the paste sample with silica fume.

almost linear function in relation to the depth of the degraded zone whereas in the presence of portlandite, the profile is linear only on half depth of the degraded zone and almost constant on the other half.

Mechanical Tests. Both treated samples and control samples have been subjected to a compressive load to measure their compressive resistance. The displacement rate 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 recorded during the test by means of three transducers fixed on the clamping plate with an

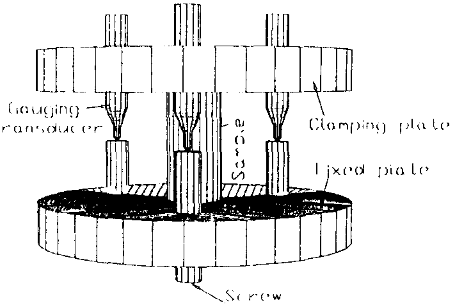

FIG. 4.
Experimental device for the compressive tests.

angular location of 120° (Fig. 4), so the bending effects cannot disturb the measure of the displacement. This device doesn't allow to evaluate the real strains in the sample because of the edge effect[3], but it is enough to describe the behavior up to the sample rupture.

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

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

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

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

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

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

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.

TABLE 2

Compressive Strength in MPa in Relation to the Degraded Ratio for the Pure Paste Sample

ϕ (mm)	A_d/A_t	σ_T control (MPa)	Standard deviation (MPa)	σ_d 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
30	0.25	54.2	2.0	45.1	1.9
	0.39	54.2	2.0	38.1	1.7
	0.54	54.2	2.0	34.0	1.3
	0.72	56.5	1.5	28.3	1.3
	1.00	56.5	1.5	14.6	0.9

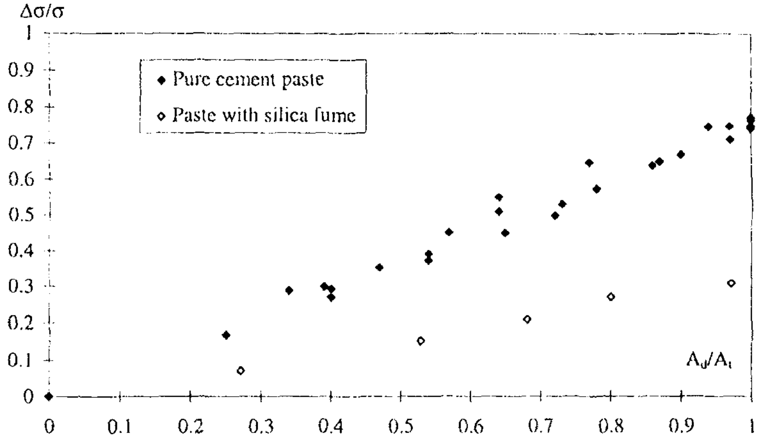

FIG. 5.
Variation of the strength loss in relation to the degraded ratio.

The values of the average compressive strength measured in the treated group (σ_d) and the control group (σ_T) are given in Table 2 for the pure cement paste. 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 strength loss is calculated using the following formula where σ_T is the compressive strength of the control sample and σ_d is the compressive strength of the degraded samples.

$$\frac{\Delta\sigma}{\sigma} = \frac{(\sigma_T - \sigma_d)}{\sigma_T}$$

The variation of the strength loss in relation to the degraded ratio is presented Figure 5.

These results show that the decrease of average stress $\Delta\sigma/\sigma$ is independent of the size of the sample. Because of these results, the experimental program, carried out to characterize the leaching of the paste with silica fume sample, mixes different sizes of samples with different degradation ratios. Results are presented in Table 3.

TABLE 3
Compressive Strength in MPa in Relation to the Degraded Ratio for the Paste Sample with 30% of Silica Fume

φ (mm)	A_d/A_t	σ_T control (MPa)	Standard deviation (MPa)	σ_d degraded (MPa)	Standard deviation (MPa)
10	0.68	54.4	2.6	43.1	2.3
	0.97	54.4	2.6	37.7	2.2
12	0.53	61.0	3.2	51.8	1.8
14	0.27	61.6	2.8	57.3	1.8
	0.80	62.3	3.1	45.5	2.4

Once the degradation is completely achieved ($A_d/A_t = 1$), there is a residual strength both in the case of pure paste samples representing about a quarter of the initial strength: $\sigma_d = 0.24\sigma_T$ and in the case of admixture of silica fume representing about 2/3 of the initial strength: $\sigma_d = 0.68\sigma_T$.

Modeling

Hypothesis. During the degradation process, the behavior of the material becomes more and more ductile when the degradation reaches the center of the sample, at this time there is still a residual resistance. During the leaching, the sample behavior is closed to a perfect elasto-plastic behavior when the strain increase is due to a constant load (fig. 6). This elasto-plastic property of the surrounded leaching zone leads to the conclusion that the global behavior of the sample is the sum of the behavior of both leaching and sound zone. This is the first hypothesis.

The loss of calcium in the degraded zone is linear in relation to the depth when there is no calcium hydroxide in the paste. In this phenomenon, the experimental results (fig. 2) show that minimal rate of calcium Ca_c is a constant in relation to the depth of the leaching zone. The progressive decalcification of the C-S-H in relation to the depth e is a linear function between Ca_T and Ca_c which are constant (fig. 7).

When the paste contains calcium hydroxide, experimental results (fig. 3) show that the calcium hydroxide has been totally removed from the degraded zone whereas the decalcification of the C-S-H is limited to half of this degraded zone. The progressive decalcification of the C-S-H in relation to the half depth e/2 is a linear function between Ca_p and Ca_{cp} which are constant (fig. 8).

The second hypothesis of the model proposed is that the evolution of the compressive stress in the sample in relation to the depth is similar to the evolution of the calcium content which means that the removal of the calcium hydroxide leads to a brutal loss of stress and the pro-

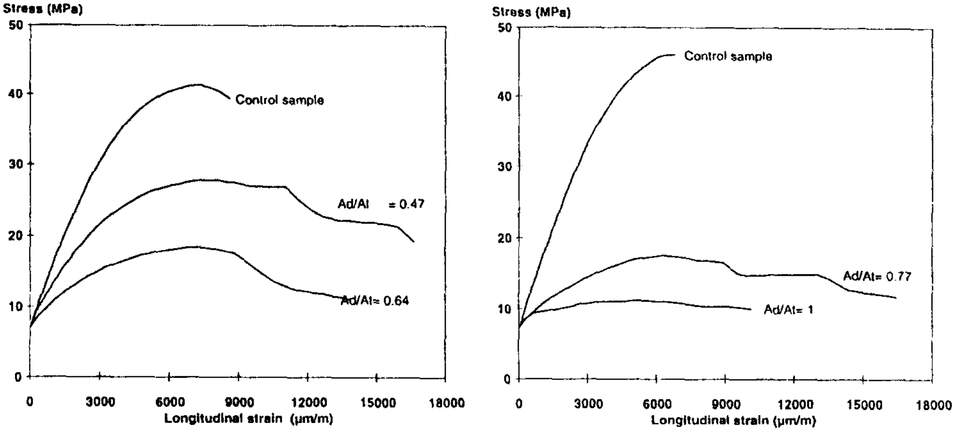

FIG. 6.
Curves $\sigma = f(\varepsilon)$ for different levels of degradation (samples $\phi = 10$ mm).

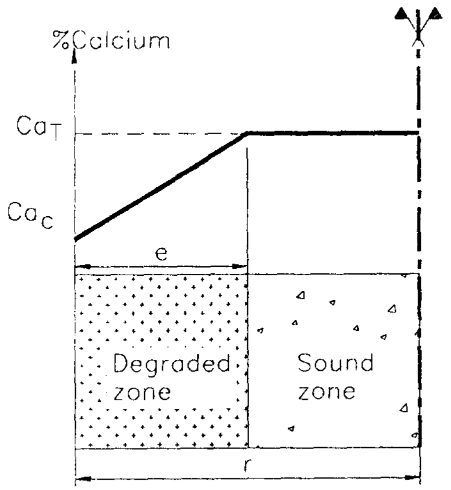

FIG. 7.
Decalcification shape for a paste without calcium hydroxide.

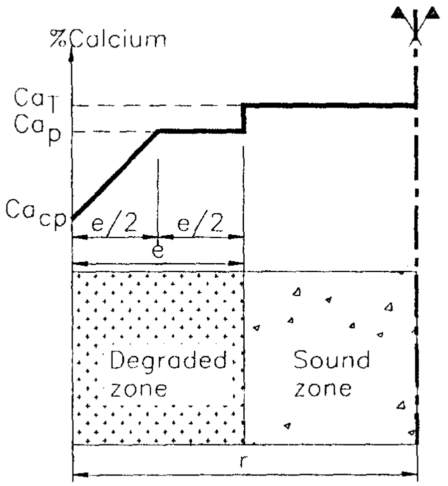

FIG. 8.
Decalcification shape for a paste containing calcium hydroxide.

gressive decalcification of the C-S-H leads to a progressive loss of strength. Because experimental results show that there is a residual strength after total degradation and because the calcium content remains constant at the edge of the sample, the minimal stresses achieved in the leaching zone $\sigma_{T\text{-}c}$ (fig. 9) or $\sigma_{T\text{-}p}$ and $\sigma_{T\text{-}cp}$ (fig. 10) are assumed to be constant.

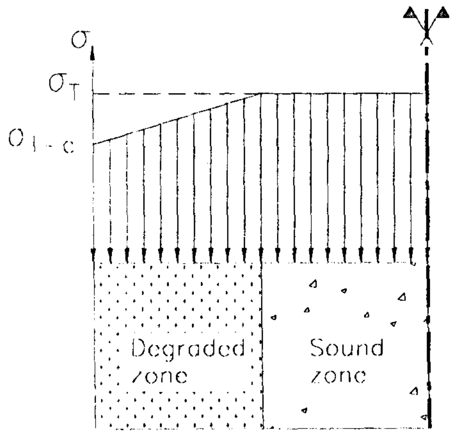

FIG. 9.
Modeling of the stress distribution for both sound and leaching zone for a paste without calcium hydroxide.

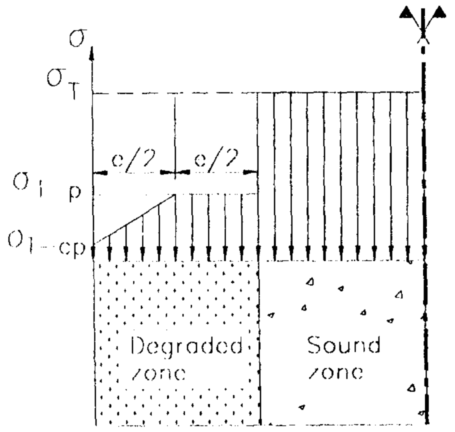

FIG. 10.
Modeling of the stress distribution for both sound and leaching zone for a paste containing calcium hydroxide.

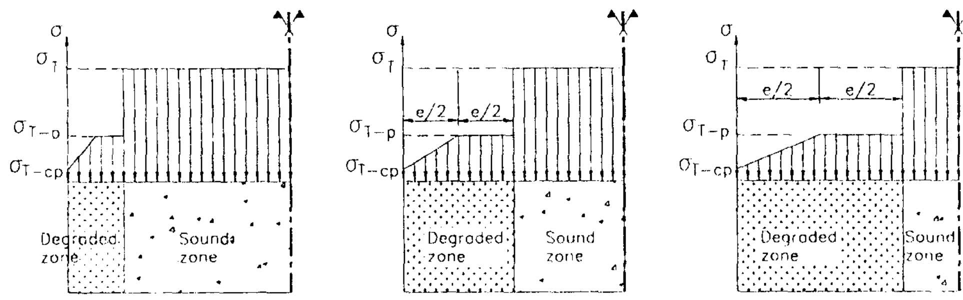

FIG. 11.
Shape of the stress distribution for different degraded ratio.

The increase of the leaching process in relation to time leads to an increase of the degraded zone depth e but the different stresses $\sigma_{T\text{-}cp}$ at the beginning of the leaching zone and $\sigma_{T\text{-}p}$ at the middle of the leaching zone, remain constant (Fig. 11).

The C-S-H of a Portland cement is not the same as the C-S-H with silica fume. As a result, their chemical composition and more particularly their C/S ratio (1.7 for the pure cement paste [4] and about 1.1 for the paste with silica fume [5]), their porosity, their microtexture are different. But Carde [6] has measured similary increases in porosity for the two C-S-H degraded in the ammonium nitrate solution. Thus, the third hypothesis of the model proposed is that the alterations of the mechanical properties of the C-S-H due to the leaching process are the same for both C-S-H in the pure paste and in the paste with silica fume. This last hypothesis leads to:

$$\frac{\sigma_{T\text{-}c}}{\sigma_T} = \frac{\sigma_{T\text{-}cp}}{\sigma_{T\text{-}p}}$$

Calculation

The ratios RT, RC, RP et RCP are defined as following:

$$R_T = \frac{\sigma_T}{\sigma_T} = 1; \quad R_p = \frac{\sigma_{T\text{-}p}}{\sigma_T}; \quad R_{cp} = \frac{\sigma_{T\text{-}cp}}{\sigma_T}; \quad R_c = \frac{\sigma_{T\text{-}c}}{\sigma_T}$$

The hypothesis 2 leads to: $\frac{\sigma_{T\text{-}c}}{\sigma_T} = \frac{\sigma_{T\text{-}cp}}{\sigma_{T\text{-}p}} \Rightarrow R_{cp} = R_c \,.\, R_p$

Paste with Silica Fume. The total strength F_d resulting from this integration of the stress distribution plotted fig. 8 is:

$$\frac{F_d}{\sigma_T} = \int_0^e \left(\frac{1 - R_c}{e}\right).x.2\pi.(r - x)dx + \int_0^e R_c.2\pi.(r - x)dx + \int_e^r R_T.2\pi.(r - x)dx$$

Then $F_d = \pi\sigma_T.\left[\left(\frac{1 - R_c}{3}\right).e^2 + r.(R_c - 1).e + r^2\right]$

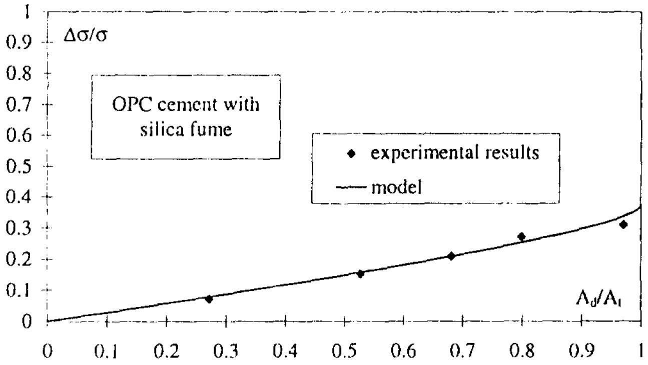

FIG. 12.
Comparison between the model and the experimental results for paste with 30% of silica fume.

The loss of total strength is then

$$\frac{\Delta F}{F} = \frac{F_T - F_d}{F_T} = \frac{\pi r^2 \sigma_T - \pi \sigma_T \left[\left(\frac{1 - R_c}{3}\right).e^2 + r.(R_c - 1).e + r^2\right]}{\pi r^2 \sigma_T}$$

$$\frac{\Delta F}{F} = 1 - \frac{1}{r^2}.\left[\left(\frac{1 - R_c}{3}\right).e^2 + r.(R_c - 1).e + r^2\right]$$

ΔF/F is the same as the relative loss of average stress Δσ/σ which is experimentaly recorded

The comparison of ΔF/F with the experimental results (fig. 12) allows the calculation of the parameter $R_c = 0.44$.

Pure Cement Portland Paste. The total strength F_d resulting from this integration of the stress distribution plotted fig. 9 is:

$$\frac{F_d}{\sigma_T} = \int_0^{e/2} \left(\frac{1 - R_c}{\frac{e}{2}}\right).R_p.x.2\pi.(r - x)\,dx + \int_0^{e/2} R_c.R_p.2\pi.(r - x)\,dx$$

$$+ \int_{e/2}^{e} R_p.2\pi.(r - x)\,dx + \int_e^r R_T.2\pi.(r - x)\,dx$$

Then $F_d = \pi\sigma_T.\left[\left(1 - \frac{R_c.R_p}{12} - \frac{11R_p}{12}\right).e^2 + \left(\frac{3r.R_p}{2} + \frac{r.R_c.R_p}{2} - 2r\right).e + r^2\right]$

The loss of total strength is

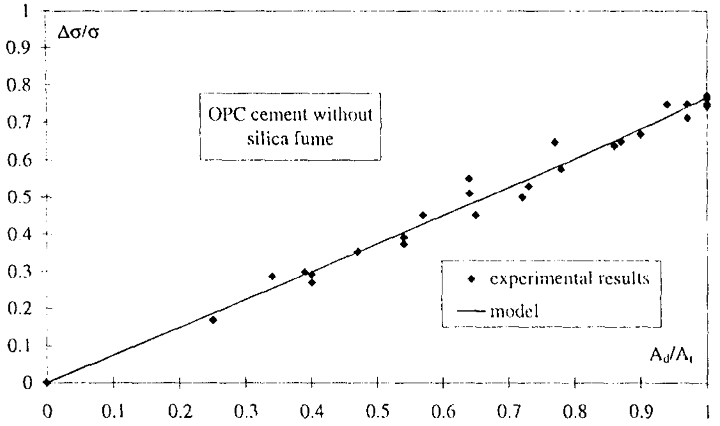

FIG. 13.
Comparison between the model and the experimental results for pure cement paste.

$$\frac{\Delta F}{F} = \frac{\pi r^2\sigma_T - \pi\sigma_T.\left[\left(1 - \frac{R_c.R_p}{12} - \frac{11R_p}{12}\right).e^2 + \left(\frac{3r.R_p}{2} + \frac{r.R_c.R_p}{2} - 2r\right).e + r^2\right]}{\pi r^2\sigma_T}$$

$$\frac{\Delta F}{F} = 1 - \frac{1}{r^2}.\left[\left(1 - \frac{R_c.R_p}{12} - \frac{11R_p}{12}\right).e^2 + \left(\frac{3r.R_p}{2} + \frac{r.R_c.R_p}{2} - 2r\right).e + r^2\right]$$

The comparison of ΔF/F with the experimental results (fig. 13) allows the calculation of the parameter $R_p = 0.3$. Then, $R_{cp} = R_c \,.\, R_p = 0.13$.

Discussion

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 evolution than the experimental one.

Pure OPC Samples. The modeling results show that the loss of strength due to the removal of the calcium hydroxide is 70% ($R_p = 0.3$). Then, the loss of strength due to the decalcification of C-S-H is only 6% because the residual average failure stress is $0.24\sigma_T$. This is due to the fact that the removal of the calcium hydroxide leads to the appearance of a macro-porosity whose size is about the same as the capillary porosity [7]. This macro-porosity leads to a drop in the strength of the sample. Whereas the removal of Ca in the C-S-H lead to the appearance of a micro-porosity which is a second order effect than the macro-porosity [8].

Mix OPC + Silica Fume. The modeling results show that the loss of strength due to the removal of the Ca from the C-S-H is 32% because the average residual failure stress is $0.68\sigma_T$. So, the micro-porosity created by the decalcification of C-S-H leads to a loss of strength higher (5 times) than the macro-porosity which appears in the case of the pure cement paste.

Then, the degradation of the mechanical properties due to the decalcification of C-S-H can be overlooked in comparison to the effect of the removal of the calcium hydroxide. But, on the contrary, the degradation of the mechanical properties due to the decalcification of the C-S-H is not overlooked when there is no calcium hydroxide.

Conclusion

The deterioration of the cement paste exposed to the action of the ammonium nitrate was indicated 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. The modeling of the mechanical effect of both removal of calcium hydroxide and decalcification of C-S-H allows to quantify their relative importance.

So in the case of a paste sample made with an OPC cement which leads to about 20% content of calcium hydroxide, the dissolution of this calcium hydroxide is the essential parameter governing both decrease in strength and increase in porosity. The loss of strength due to the decalcification of C-S-H is only 6% and can be neglected in relation to the global loss of strength due to the dissolution of $Ca(OH)_2$.

In the case of the use of a paste sample with the admixture of silica fume to consume all the calcium hydroxide, the effect of C/S ratio decrease of the C-S-H reduces the strength of about 30%. Then, the effect of the decalcification of C-S-H is not negligible but the residual strength of the material is important and the material could keep its mechanical functions.

Acknowledgment

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