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Modelling the loss of strength and porosity increase due to the leaching of cement pastes

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Abstract

Pure water leads to a progressive decalcification of hardened cement pastes. The physical and chemical processes of this degradation are relatively well defined today, but the consequences of the leaching on the porosity increase and the loss of strength have been only partially studied. Our work consists of correlating the alteration of these properties with the rate of degradation of the material. The leaching is achieved by an accelerated process. Compressive strength and water porosity are measured after different processing times in an aggressive solution. A physical phenomenon analysis leads us to propose a stress distribution model at rupture, and a calculation model of the porosity increase, taking into account the nature of the degraded hydrates (C–S–H).

Keywords: Cement pastes; Leaching; Strength; Porosity

1. Introduction

Our current research programme aims to characterize the deterioration of the mechanical and physical properties of the concrete surrounding radioactive waste, due to water flow during storage (small amounts of pure water). This chemical attack is one scenario of the degradation of the concrete barrier surrounding radionuclides during long term storage (300 years). At the cement paste contact, this pure water creates concentration gradients which lead to the diffusion of ions from the interstitial solution to these aggressive solutions. These transfers modify chemical balances and create a leaching of the calcium hydroxide and then a progressive decalcification of the hydrates (C–S–H) [1–3]. Because of the slow kinetics of deionized waters we decided to increase the aggressivity of the environment by using a concentrated ammonium nitrate solution. The chemical attack due to NH_4NO_3 also results in leaching of the cement paste but the kinetics is quicker than that obtained with water as reactant [2].

The consequence of this chemical attack is an increase in the material porosity and a global decrease in mechanical performance. In previous work [4], we showed that by using a global approach (the degraded zone has constant properties), both loss of strength and water porosity increase of pure paste samples were proportional to the degraded ratio.

In fact, the decalcification of cement hydrates is more complex: in particular, there is a gradient of calcium content in the degraded zone. The next step in the research was to compare a pure paste sample with a paste sample containing silica fume (to reduce the calcium hydroxide content) to separate the effect of C–S–H and $Ca(OH)_2$ decalcification on the loss of strength. The results [5] revealed that in the case of the pure paste sample containing both C–S–H and calcium hydroxide, the dissolution of the calcium hydroxide was the main parameter that governed the loss of strength (70% of the initial strength). The decalcification of C–S–H was only 6% in relation to the total loss of strength. However, in the case of a paste sample containing silica fume to consume all the calcium hydroxide, the decalcification of C–S–H reduced the strength by about 30%. Thus, the effect of C–S–H decalcification can be neglected in relation to the effect of $Ca(OH)_2$ dissolution, but is not negligible without calcium hydroxide. This could be due to the fact that the leaching of C–S–H and $Ca(OH)_2$ leads to two different porosities: a microporosity for the

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former and a macroporosity for the latter, whose separate and coupled effects could be totally different.

The object of the paper is to better understand the increase in porosity due to the leaching and to compare it with the resulting loss of strength. Modelling of the loss of strength in relation to the porosity increase is then proposed.

2. Materials and sampling

The cement used was an OPC cement (CEM I 42.5) with the chemical and mineral compositions presented in Tables 1 and 2, respectively. Since the degraded hydrates are calcium hydroxide and the C–S–H, two different cement pastes were studied: a pure paste (W/C = 0.5), and a paste (W/B = 0.45) in which 30% by mass of cement is replaced by silica fume (Sikacrete HD). In the latter case, all calcium hydroxide was consumed by pozzolanic reaction. Then, the chemical processing leads to a selective attack of the C–S–H.

The mixtures were poured into cylindrical moulds (110 × 220 mm). After 24 h, the pure paste samples were demoulded and cured by immersion for 27 days in water saturated in lime at 20°C (±1°C). The paste samples with silica fume were cured for 75 days to achieve the complete pozzolanic reaction (checked by X-ray diffraction [5]). The samples used were cylinders of diameters (ϕ) 10, 12, 14, 20 and 30 mm. The h/ϕ ratio is equal to 2 (h being the height of the sample). After curing, these samples were extracted from the test pieces by means of a diamond-tipped coring drill lubricated with water. Two series of tests were made for each sample size, the first for immersion in the aggressive solutions (treated series) and the second to be kept in an endogenous environment (control series).

3. Leaching process

The aggressive liquid used was a 50% concentrate solution of ammonium nitrate solution, NH_4NO_3 (590 g/l). The chemical attack of the cement paste by ammonium nitrate leads to the development of a soluble calcium nitrate, an expansive calcium nitro-aluminate and ammoniac emanating NH_3 [6]. Since the calcium nitro-aluminate forms only when the material is dried, the samples were kept in water after their removal from the aggressive solution and before the mechanical loading. Profiles of the concentration of calcium, silicon, aluminium and sulfur, obtained after the degradation of cement paste samples, were presented in a previous paper [2]. Examinations of these profiles showed that the chemical process mainly induces a total leaching of the calcium hydroxide and a progressive decalcification of the C–S–H. Other studies show that C–S–H withstands leaching and was characterized by very high cationic substitution rates [7].

Table 1
Chemical composition of OPC CEM I 42.5 cement

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3
% Mass	20.18	4.93	3.04	63.44	3.18

Table 2
Mineral composition of OPC CEM I 42.5 cement

	C_3S	C_2S	C_3A	C_4AF	$Ca(SO_4)_2$
% Mass	57.4	14.7	8.2	9.2	5.4

The removal of calcium ions from the two materials is monitored by microprobe analysis which shows the evolution of the loss of calcium in the solid phase according to the ratio between the distance from the edge of the sample and the degraded thickness. Figs. 1 and 2 present profiles of calcium concentration obtained on the pure paste of leaching and on the paste with silica fume after leaching in the aggressive solution. These diagrams are plotted for a unitary degraded thickness and Fig. 1 shows profiles obtained after 1 day and 3 days of leaching. As a result, Fig. 1 shows that the leaching is perfectly homothetic in relation to the leaching time.

The results indicate a difference between the two profiles: in the absence of calcium hydroxide, the variation of Ca is a linear function of the depth of the degraded zone, whereas in the presence of portlandite, the profile is linear only on the half depth of the degraded zone and almost constant on the other half.

4. Experimental programme

Both treated samples and control samples have been subjected to a compressive load order to measure their compressive strength (σ), which is evaluated by dividing the maximal load F_{ult} by the total cross-sectional area A_t of the sample. The displacement speed is controlled during the test. The force applied 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 angular location of 120° to suppress the bending effects. This device does not measure the strains in the sample because of the end-effects [8], but it is sufficient to describe the behaviour up to the sample rupture.

Measurement of water porosity were also carried out. The experimental procedure consists of drying, in a steamer, control samples, kept in the lime-saturated

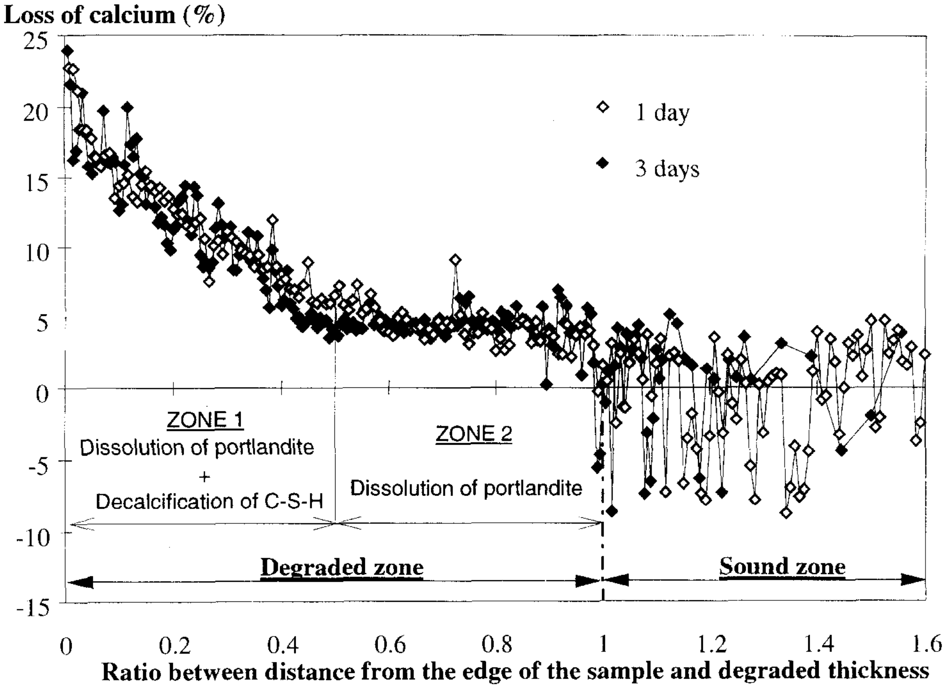


Fig. 1. Profiles of loss of calcium in the solid phase for the pure cement paste present two degraded zones of the same thickness: (1) both dissolution of portlandite and progressive decalcification of C–S–H; (2) only dissolution of portlandite.

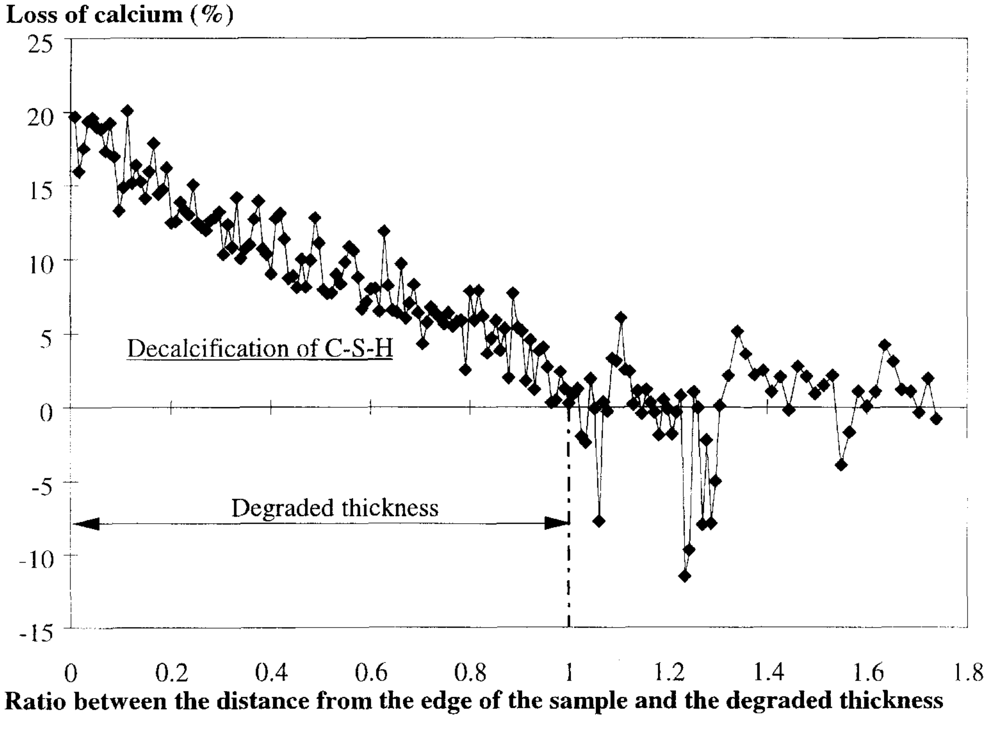


Fig. 2. Profile of loss of calcium in the solid phase for the paste containing silica fume shows the progressive decalcification of C–S–H in the degraded zone.

water, and degraded samples, kept in the aggressive solution, until they reach constant mass. The water evaporated at the temperature selected (80°C) is equated to the free water contained in the porous system.

Finally, the degraded thickness was evaluated by optical microscopy by means of a displacement control device of the microscope platen which has a precision of ±50 μm.

The degraded ratio is defined by reporting the degraded area of the cross-section of the cylinder (A_d) and the total area (A_t). This ratio is equal to 0 initially, and to 1 when the sound zone has disappeared.

5. Experimental results and modelling

5.1. Model of stress distribution at rupture

The model of stress distribution has already been presented in a previous paper [5], therefore we only recall the synthesis here. Three hypotheses were used to build the model:

Hypothesis 1: the sample behaviour is close to perfect elasto-plastic behaviour when the strain increase is due to a constant load.

Hypothesis 2: the stress rupture in a point is directly linked to the amount of calcium present in the solid phase of the material. This second hypothesis is illustrated in Fig. 4 for the mixture containing silica fume as well as for the pure cement paste.

σ_T corresponds to the rupture stress of the sound zone (control group), and $\sigma_{T\text{-}c}$ is the minimal stress in the zone of constant gradient linked to the C–S–H decalcification in the degraded thickness in the case of the mixture containing silica fumes.

$\sigma_{T\text{-}p}$ is the residual stress after total dissolution of the calcium hydroxide, and $\sigma_{T\text{-}cp}$ is the minimal stress in the zone of constant gradient due to the C–S–H decalcification in the first half of the degraded thickness in the case of a pure cement paste.

These parameters are constant as the sound zone exists because the contents of calcium to which they are linked are in chemical balance with the aggressive solution. This second hypothesis allows for determination of the equation of the stress distribution at rupture for the two mixtures. The unknown parameters are $\sigma_{T\text{-}c}$ for the paste containing silica fume, and $\sigma_{T\text{-}p}$ and $\sigma_{T\text{-}cp}$ for the pure cement paste.

Hypothesis 3: 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 cement paste and in the paste with silica fume. This simplifying hypothesis leads to the following relation:

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

These three hypotheses allows one to calculate the relative loss of average stress $\Delta\sigma/\sigma$ and to compare it to experimental results (Fig. 3).

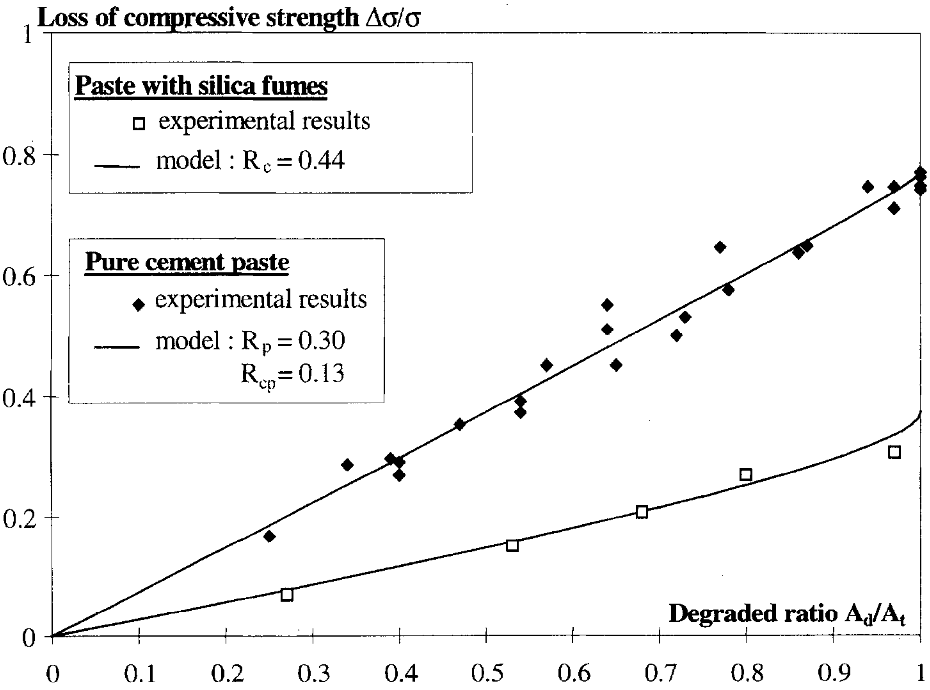


Fig. 3. Comparison between model and experimental results for the two mixtures.

The parameters defining the profiles of the stress distribution at rupture are:

paste with silica fumes: $\sigma_{\text{T-c}} = 0.44\ \sigma_{\text{T}}$
pure cement paste: $\sigma_{\text{T-p}} = 0.30\ \sigma_{\text{T}}$
$\sigma_{\text{T-cp}} = 0.13\ \sigma_{\text{T}}$

5.2. Model of calculation of the porosity increase

5.2.1. Hypotheses

The same hypotheses as those of the model of stress distribution at rupture are used, except for the mechanical behaviour.

Hypothesis 1: the local porosity is directly linked to the quantity of calcium present in the solid phase of the material. This hypothesis is illustrated in Fig. 4 for the two cement pastes.

P_{T} corresponds to the porosity of the sound zone (control group), and P_{C} is the residual porosity for the constant gradient zone, linked to the C–S–H decalcification in the degraded thickness in the case of the mixture containing silica fumes.

P_{P} is the new porosity after total dissolution of the calcium hydroxide, and P_{CP} is the new porosity for the constant gradient of porosity due to the C–S–H decalcification in the first half of the degraded thickness in the case of a pure cement paste.

As in the model of stress distribution at rupture, P_{C}, P_{P} and P_{CP} are constant because these parameters correspond to contents of calcium in chemical balance with the aggressive solution. This hypothesis allows determination of the equation of the porosity distribution for the two mixtures. The unknown parameters are P_{C} for the added silica fumes paste, and P_{P} and P_{CP} for the pure cement paste.

Hypothesis 2: the porosity increase of the C–S–H due to the leaching process is the same for both C–S–H in the pure cement paste and in the paste with silica fume. This simplifying hypothesis leads to the following relation:

$$\frac{P_{\text{C}}}{P_{\text{T}}} = \frac{P_{\text{CP}}}{P_{\text{P}}}$$

5.2.2. Equations and resolution

The total porosity P_{d} resulting from the integration of the local porosity plotted in Fig. 4(a) in the case of the paste containing silica fumes is (h is the height of the sample):

$$P_{\text{d}} = \frac{1}{\pi r^2 h}\left[\int_0^e \left(\frac{P_{\text{T}} - P_{\text{C}}}{e}\right) x 2\pi h(r - x)\mathrm{d}x + \int_0^e P_{\text{C}} 2\pi h(r - x)\mathrm{d}x + \int_r^e P_{\text{T}} 2\pi h(r - x)\mathrm{d}x\right]$$

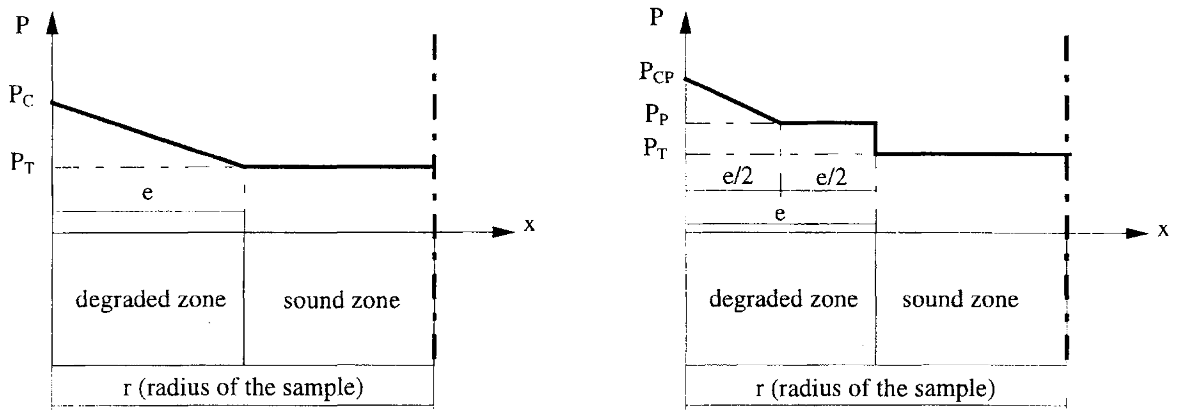
The increase in porosity is then:

$$\Delta P = P_{\text{d}} - P_{\text{c}} = \left(\frac{P_{\text{C}} - P_{\text{T}}}{3}\right)\left[\frac{V_{\text{d}}}{V_{\text{t}}} - \left(1 - \frac{V_{\text{d}}}{V_{\text{t}}}\right)^{1/2} + 1\right]$$

where

$$\frac{V_{\text{d}}}{V_{\text{t}}} = \frac{A_{\text{d}}}{A_{\text{t}}} = \frac{2e}{r} - \frac{e^2}{r^2}$$

In the case of the pure cement paste, the total porosity P_{d} resulting from the integration of the local porosity plotted in Fig. 4(b) is:


(6a) : cement paste with 30% of silica fumes

(6b) : pure cement paste

Fig. 4. Profiles of local porosity for the mixture containing silica fume (a) and for the pure paste cement (b). These profiles have the same shape as the profiles of loss of calcium presented in Figs. 1 and 2.

$$P_d = \frac{1}{\pi r^2 h}\left[\int_0^{e/2}\left(\frac{1-P_C}{e/2}\right)P_P x 2\pi h(r-x)\mathrm{d}x + \int_0^{e/2} P_C P_P 2\pi h(r-x)\mathrm{d}x + \int_{e/2}^{e} P_P 2\pi h(r-x)\mathrm{d}x + \int_e^r P_T 2\pi h(r-x)\mathrm{d}x\right]$$

Then the increase in porosity is:

$$\Delta P = \left(\frac{P_C P_P}{12P_T} - \frac{11P_P}{12} - P_T\right)\frac{V_d}{V_t} + \left(\frac{P_P}{3} - \frac{P_P P_C}{3P_T}\right) \times \left(1-\frac{V_d}{V_t}\right)^{1/2} + \left(\frac{P_P(P_C-P_T)}{3P_T}\right)$$

For the two mixtures, the comparison of ΔP with the experimental results allows for calculation of the parameters P_C and P_P. Then the second hypothesis allows for calculation of P_{CP}. The porosity of the control group is, for both cases, experimentally equal to 0.42. The results are presented in Fig. 5.

The parameters which define the porosity distribution profiles are:

paste with silica fumes: $P_C = 0.56$

pure cement paste: $P_P = 0.55$

$$P_{CP} = \frac{P_C P_P}{P_T} = 0.74$$

6. Discussion

In the case of a pure cement paste, the model of stress distribution at rupture shows that the dissolution of the calcium hydroxide leads to a loss of strength of about 70% ($R_P = 0.3$), while the global loss for $A_L/A_T = 1$ is equal to 76%. Then the loss of strength due to the decalcification of the C–S–H is only of the order of 6% which means that the dissolution of the calcium hydroxide is the main parameter which determine the loss of strength. Thus, the loss of strength linked to the decalcification of the C–S–H represents only 1/12 of the total loss.

The calculation model of the porosity increase also shows that the total leaching of the calcium hydroxide leads to a porosity increase of about 0.13 ($P_P = 0.55$) while the increase due to the decalcification of the C–S–H is 0.08. As a result, the gain of porosity linked to the decalcification of the C–S–H represents 1/3 of the total gain.

Thus, there is an apparent contradiction between these two results (C–S–H represents only 1/12 of the strength loss but 1/3 of porosity increase). Nevertheless, if we plot the porosity increase in relation to the relative loss of strength, we note that there is a good correlation (Fig. 6) between the porosity increase and the compressive strength loss. This result shows the coherence of both models proposed.

Thus, the apparent contradiction can be explained because the total leaching of massive crystals of calcium

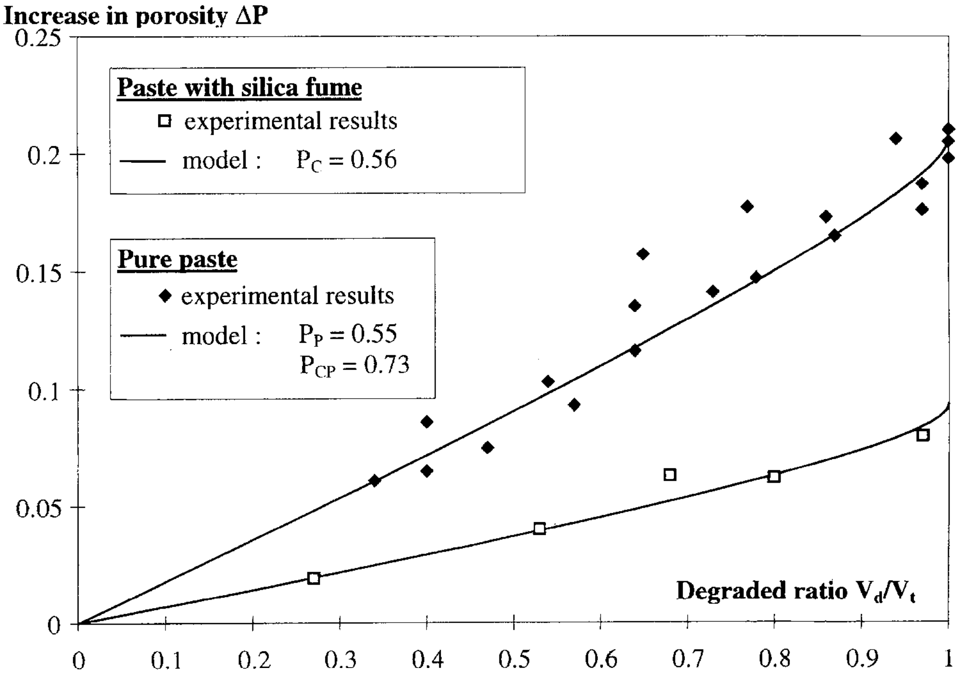


Fig. 5. Comparison between model and experimental results for the two mixtures.

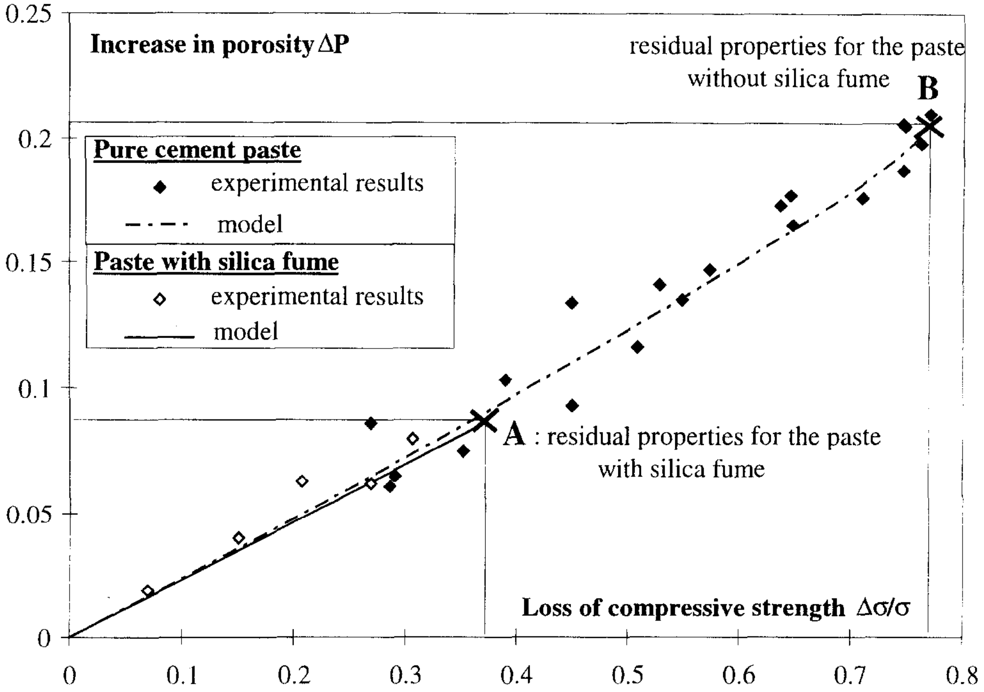


Fig. 6. Evolution of the increase in porosity as a function of the compressive strength decrease for the two mixtures.

hydroxide creates a macroporosity (capillary porosity) and the decalcification of the C–S–H creates a microporosity. In the case of pure cement paste this macroporosity is responsible for almost all compressive strength loss, while the microporosity has little effect on this porosity. Some authors have already demonstrated that the compressive strength is more influenced by the capillary porosity [9].

Furthermore, the same work can be done with both experimental results and the model obtained in the case of the paste with silica fume (without $Ca(OH)_2$). As a result, Fig. 6 shows that both experimental and model behaviours governing the porosity increase in relation to the loss of strength are the same as those obtained with pure cement paste samples. However, the field of validity is shorter (only between 0 and **A**), which means that there is a single law between the porosity increase and the loss of strength whatever the initial amount of $Ca(OH)_2$, but the residual properties are governed by the amount of calcium hydroxide initially present in the material.

As a result, the initial amount of calcium hydroxide is the main parameter governing the decrease of mechanical performances and thus the durability of the degraded materials. For a given initial amount of calcium hydroxide between 0 and about 20% (pure Portland cement paste), the representative point of the residual properties after total leaching is located between **A** and **B** in Fig. 6.

7. Conclusion

Leaching of massive crystals of the calcium hydroxide creates a macroporosity which has a greater effect on the loss of strength than on the porosity increase. On the contrary, the decalcification of C–S–H creates a microporosity which has less influence on the loss of strength than on the porosity increase. Modelling taking into account the nature of degraded hydrates was performed. A good correlation between the stress distribution model [5] and the calculation porosity model was established. In both models, the loss of calcium in the solid state was the state variable. Its main originality lies in the prediction of both loss of strength and porosity increase according to the initial content of portlandite in the cement-based materials. The modelling confirms that the durability of cement-based materials, subject to the action of an ammonium nitrate solution and then to the action of demineralised water, depends essentially on the initial amount of calcium hydroxide. The use of mineral additions to consume a part of this calcium hydroxide by pozzolanic reaction is then clearly demonstrated.

Acknowledgements

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