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EFFECT OF ITZ LEACHING ON DURABILITY OF CEMENT-BASED MATERIALS

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ABSTRACT

The results obtained on both cement paste samples with and without silica fumes and mortars with and without silica fumes, show that there is an Interfacial Transition Zone (ITZ) effect on the alteration of the mechanical properties due to leaching. © *1997 Elsevier Science Ltd*

Introduction

Leaching of cement-based materials by de-ionized waters leads to an increase in porosity and a decrease of mechanical properties. This chemical attack induces a total leaching of the portlandite and a progressive decalcification of the C-S-H (1). Because of the slow leaching kinetics obtained by using de-ionized waters, an accelerated method (using NH_4NO_3 solution) was performed. A physical and chemical model of the leaching process has been proposed by Adenot and Buil (2), and a prediction model of the decrease of mechanical performances established by Carde et al. (3). These models were validated on cement pastes only, whereas the final aim of the research program is to forecast the concrete's behavior during the leaching process. By using mortar instead of cement paste, two additional phases are introduced: aggregate and ITZ defined by Farran (4). Indeed, the presence of aggregates tends to modify the microstructure of cement paste at the interface. From a theoretical point of view, higher porosity and higher portlandite content of the ITZ should facilitate the penetration of external aggressive agents and increase calcium leaching. However, recent data tends to show that the effect of the ITZ on the leaching kinetics is limited (5). Furthermore, the use of silica fumes to produce mortars and concretes leads to a resorption of the ITZ (6). This paper presents the results of an investigation carried out in order to define better the effect of the ITZ leaching on the mechanical properties of mortars in contact with an aggressive solution of NH_4NO_3 and thus with de-ionized waters. The results thus obtained on mortars with and without silica fume were compared to those of a previous work (3) dealing with cement pastes with and without silica fume.

Materials and Sampling

The cement used is an OPC CEM I 42.5 whose chemical composition is provided in Table 1.

TABLE 1

Chemical Composition of OPC CEM I 42.5 Cement

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3
% mass	20.18	4.93	3.04	63.44	3.18

To compare the results with those obtained on the cement pastes (3) two different types of mortars were investigated. In the first one, the binder was only the same OPC cement (M_1) than the one used for cement paste, whereas in the second one the binder was a mixture of the same OPC cement and silica fumes (M_2). The silica fume used is 30% substituted of the cement weight. This high content of silica fume used is to be sure that all the calcium hydroxide is consumed in order to modify the mineralogical and microstructural properties of the ITZ. The aggregate used was a siliceous sand. Compositions of the two mortars are reported in Table 2.

The samples used were cylinders whose diameters are 10, 14 and 30 mm with a ratio $h/\phi = 2$ (h height of the sample). After curing, the samples were extracted from the test pieces by means of a diamond-tipped core lubricated with water. For each sample size, two series of samples were made, the first one was immersed in the aggressive solution (treated series), the other one kept in an endogenous environment (control series).

Experimental Program

Leaching Process. Because of the slow leaching kinetics obtained by using de-ionized water, an ammonium nitrate solution was used in order to degrade the samples. The similarity of these two aggressive environments was established mineralogically, chemically and mechanically in a previous work (7). In the case of pure cement based material, the action of these two solutions leads to a total dissolution of the portlandite and to a progressive decalcification of the C-S-H in the first half of the degraded thickness (3). In the case of cement-based material which contains enough silica fumes to consume all the portlandite by pozzolanic reaction, the degradation leads only to a progressive decalcification of the C-S-H in the whole degraded thickness (3). The use of the NH_4NO_3 solution allows the leaching kinetics to be accelerated a hundred fold, and thus to obtain degraded ratios ranging from 0 to 1. For cylindrical samples, the degraded ratio was defined by dividing the leaching area of the cross section (A_d) by the total area of this section (A_t). This ratio is equal to 0 when the leaching has not started, and to 1 when the sound zone has disappeared. The degraded thickness was measured by optical microscopy.

TABLE 2

Composition of the Mortars Experimented

	Cement	Sand 0.6/1.2 mm	Sand 1.2/2.5 mm	Silica fume	Water
M_1 (kg/m^3)	673	942	404	0	269
M_2 (kg/m^3)	402	804	345	172	230

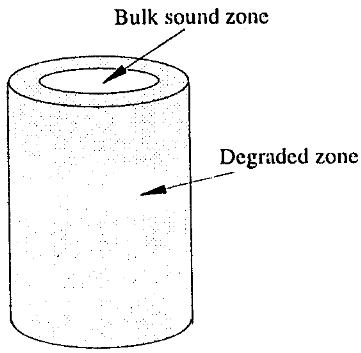

FIG. 1.
Cement pastes and mortars samples partially leached.

Mechanical Tests. Both treated and control samples were subjected to a compressive load to measure their compressive strengths. The displacement speed was checked during the load. The force applied on the sample was measured during the test. The compressive strength was evaluated by dividing the maximal load F_{ult} by the area of the sample S.

Experimental Results

Bourdette (5) has shown that there are no effects of ITZ on leaching front and kinetics. As a result, the leaching of cement paste and mortar samples is characterized by a peripheral degraded zone and a bulk sound zone (Fig. 1).

Tables 3 and 4 present the experimental results obtained on mortar without silica fumes and mortars with silica fumes respectively. To compare the alteration in mechanical properties between the different series of samples, the results were expressed in relative values as follows:

TABLE 3

Compressive Strength in Relation to the Degraded Ratio for the Mortar Without Silica Fumes

ϕ (mm)	A_d/A_t	σ_T control (MPa)	Deviation (MPa)	σ_d degraded (MPa)	Deviation (MPa)	$\Delta\sigma/\sigma$
10	0.46	52.5	2.6	29.8	2.7	0.432
	0.76	52.5	2.6	15.7	1.7	0.700
	0.92	50.8	2.6	6.5	1.0	0.872
	1.00	50.8	2.6	4.7	0.9	0.907
14	0.53	58.5	2.8	32.0	2.1	0.453
	0.68	58.5	2.8	25.0	2.6	0.573
	1.00	52.7	2.9	7.4	1.4	0.860
30	0.41	55.2	2.5	35.2	1.5	0.362
	0.56	55.2	2.5	30.6	1.3	0.446
	0.66	63.7	2.3	26.7	0.3	0.581
	0.94	66.0	2.8	14.8	0.6	0.776

TABLE 4

Compressive Strength in Relation to the Degraded Ratio for the Mortar With Silica Fumes

ϕ (mm)	A_d/A_t	σ_T control (MPa)	Deviation (MPa)	σ_d degraded (MPa)	Deviation (MPa)	$\Delta\sigma/\sigma$
10	0.37	57.8	2.2	49.6	2.9	0.142
	0.58	57.8	2.2	48.7	2.5	0.157
	0.76	56.9	3.0	43.8	2.1	0.230
	0.96	56.9	3.0	35.1	2.6	0.383
14	0.27	54.9	2.7	51.2	2.5	0.067
	0.80	53.0	2.5	38.3	2.4	0.277
30	0.36	74.4	1.9	63.5	2.5	0.147
	0.49	74.4	1.9	61.1	3.0	0.179
	0.57	71.5	2.6	58.6	0.8	0.180
	0.70	73.1	3.1	54.9	2.4	0.249

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

where σ_T is the average compressive stress of the control group, and σ_d is the average compressive stress of the degraded group.

Like those obtained on the cement pastes (3), these results show that the leaching process leads to a decrease in the compressive strength which is less significant in the case of the mortar containing silica fumes.

Modeling

To compare these results with those obtained on the cement pastes, the model of stresses distribution at the rupture proposed by Carde et al. (3) was applied. This model is based on three assumptions.

1.) the stress at rupture is directly linked to the solid calcium content present in the material, determined by a microprobe analysis. This hypothesis is illustrated in Figure 2 (e is the degraded thickness, and r is the radius of the sample). The removal of the calcium hydroxide leads to a sharp loss of stress whereas the progressive decalcification of the C-S-H induces a progressive loss of strength. Since experimental results show that there is a residual strength after total degradation and as the calcium content remains constant at the edge of the sample, the minimal stresses reached in the leaching zone $\sigma_{T\text{-}c}$ (Fig. 2a) or $\sigma_{T\text{-}p}$ and $\sigma_{T\text{-}p}$ (Fig. 2b) are assumed to be constant.
2.) 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 assumption is expressed as follows:

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

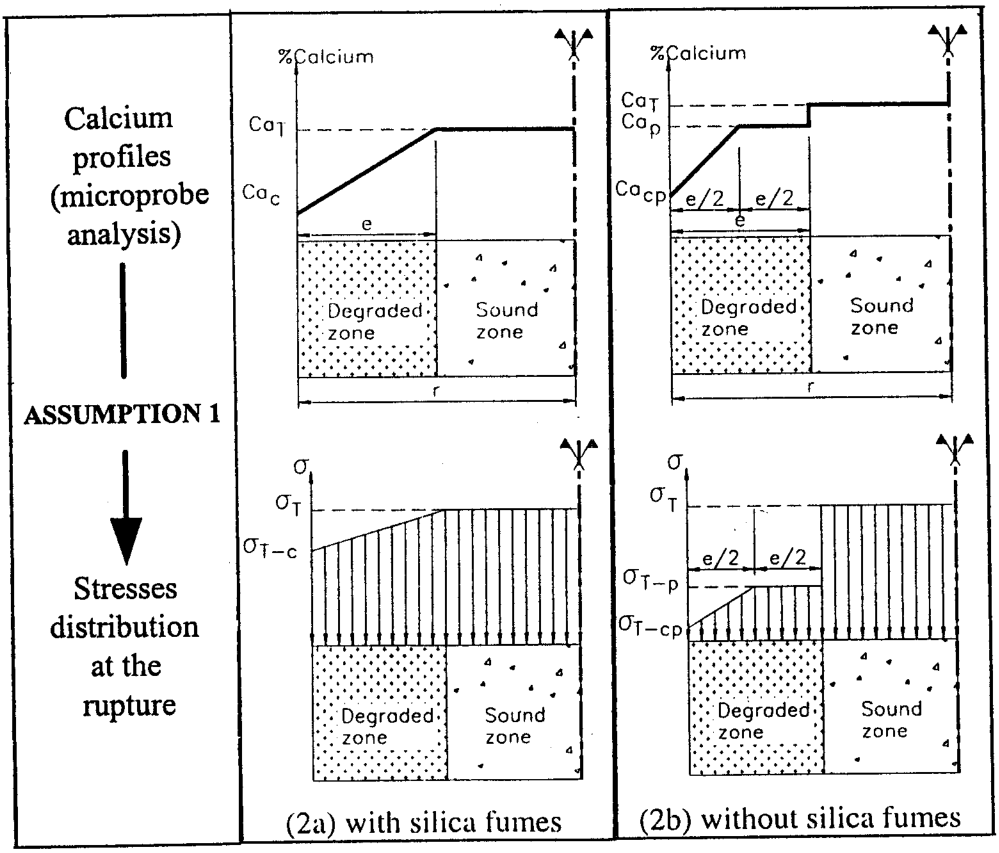

FIG. 2.
Modeling of stress distribution for both sound and leaching zone for a cement based material without calcium hydroxide (1a) and with calcium hydroxide (1b).

3.) The sample behavior is close to a perfect elasto-plastic behavior. 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.

To simplify the calculation, the ratios R_T, R_c, R_p et R_{cp} are defined as follows:

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

By comparing this model with the experimental results it is possible to determine the parameter R_c in the case of cement-based materials without calcium hydroxide, and the parameters R_p and R_{cp} in the case of cement-based materials with calcium hydroxide.

The results obtained on both mortars are presented in Fig. 3, and those obtained on cement pastes (3) are also recalled in this figure.

Characteristic parameters of stress profiles obtained with the model proposed are presented in the Table 5 for both cement pastes and mortars.

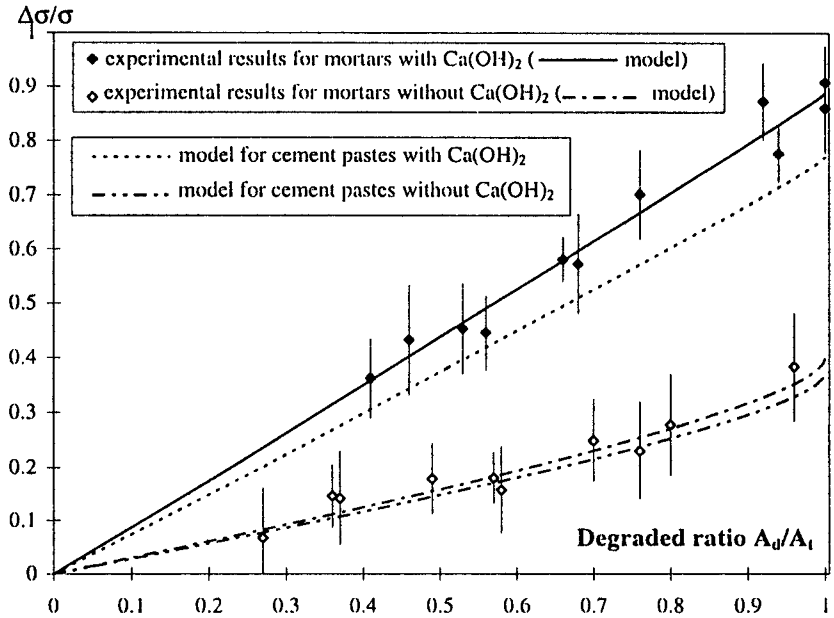

FIG. 3.
Comparison between model and experimental results for mortars with and without silica fumes.

On one hand, these results show that the parameter R_c is similar for mortar and cement paste with silica fumes. On the other hand, in the case of materials without silica fumes, the parameters R_p and R_{cp} are significantly different between the two materials.

Discussion

Leaching of cement pastes and mortars causes a total dissolution of calcium hydroxide and a progressive decalcification of C-S-H. The main difference between these two materials is the presence of ITZ in mortars. Furthermore, the use of silica fume allows two different ITZ to be studied. The results obtained can be explained as follows:

— in the case of materials containing enough silica fumes to consume all the calcium hydroxide by pozzolanic reaction, there is no difference between the paste and the mor-

TABLE 5

Parameters of the Stress Profiles Obtained With the Model Proposed

	Cement paste without silica fumes	Mortars without silica fumes	Cement paste with silica fumes	Mortars with silica fumes
R_c	-	-	0.44	0.40
R_p	0.30	0.15	-	-
R_{cp}	0.13	0.06	-	-

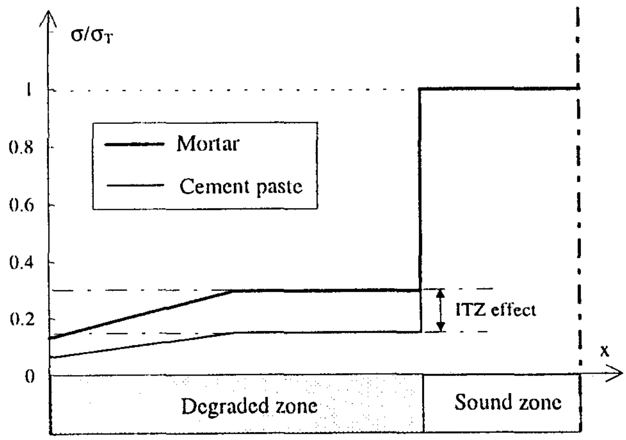

FIG. 4.
Comparison of stress distribution profiles at rupture between a pure cement paste and a mortar.

tar. This result can be explained because, in that case, ITZ properties are modified and are close to those of the bulk paste (8). As a result, the leaching does not lead to a loss of cohesion of interfacial zones.

— in the case of materials without silica fumes, the loss in compressive strength is more significant for mortars than for the paste, because the ITZ contains more calcium hydroxide than the rest of the material (9). As a result, the preferential leaching of this hydrate in the ITZ causes a loss of cohesion of the interfacial zone between the paste and the aggregate, and then a more significant decrease of mechanical properties. The part of ITZ leaching, obtained with the model proposed, is illustrated in the Fig. 4.

Conclusion

To characterize the effect of ITZ leaching on mechanical properties of cement-based materials, the experimental program was carried out on cement pastes and mortars with and without silica fumes. As previously stated (7), there is no difference in leaching kinetics and leaching front between cement paste and mortar samples. But there is an ITZ effect on the alteration of mechanical properties. As a result, the residual strength of the degraded zone of mortar represents half of that for the paste. This difference could be attributed to the ITZ which contains more portlandite in the case of the mortars. Furthermore, silica fumes used to obtain the resorption of the ITZ induce the same mechanical properties of the degraded zone for mortars and paste.

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