



# Investigations on stress corrosion of hardened cement pastes

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## Abstract

Test specimens made from “white” Portland cement (WPC), “sulfate resistant” Portland cement (SRPC) and tricalcium silicate were exposed to solutions of ammonium nitrate, sodium sulfate and ammonium sulfate. The interaction between the paste and the dissolved corrosive agents was studied by optical microscopy, back scatter electron imaging, electron microprobe analysis and X-ray diffraction. It was found that a simultaneous exposure of the test specimens to a flexural load accelerated the progress of the corrosion process in the zone under tension and reduced it in the zone under compression in samples that were in contact with ammonium sulfate, whereas it had no noticeable effect on the action of the two other agents. Specimens exposed to ammonium nitrate and ammonium sulfate failed spontaneously if exposed to a simultaneous mechanical loading that was lower than the load needed to produce fracturing of samples not exposed to the corrosive agent, apparently due to a reduced strength of the corroded surface regions. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Stress corrosion is a phenomenon in which a material is exposed to chemical corrosion under a simultaneous exposure to mechanical stresses. It has been observed that in many instances under these conditions the chemical corrosion becomes accelerated and the physicomaterial properties of the material deteriorate more rapidly. Stress corrosion has been observed in a variety of materials, including metals, ceramic materials, glass or polymers. It has been reported that an accelerated strength loss and a spontaneous failure may occur also in Portland cement mortar and concrete test specimens, if exposed simultaneously to a solution of an agent that causes chemical corrosion and to flexural stresses [1–8].

In our work we studied the stress corrosion on plain cement paste specimens made from cements of different composition and exposed to three different corrosive agents. The aim of this investigation was to investigate whether and to what an extent the stress corrosion of the hardened pastes is affected by the selection of the employed binder and corrosive agent. Plain cement pastes,

rather than mortar and concrete mixes, were studied, to eliminate the role of the aggregate–cement matrix interfacial zone and to be better able to study the texture of the corroded samples, in addition to changes of their physicomaterial properties. The work was done both on notched and non-notched test specimens to elucidate the effect of notching on the results obtained.

## 2. Experimental

The following inorganic binders were employed in the study:

- A low-iron (“white”) Portland cement (WPC) with a high tricalcium aluminate content, known to be particularly prone to sulfate attack.
- A high-iron (“sulfate resistant”) Portland cement (abbr. SRPC) which contained no tricalcium aluminate, yet contained increased amounts of the ferrite phase, known to exhibit an increased resistance to sulfate attack.
- Pure tricalcium silicate.

The chemical composition of the two Portland cements and their potential phase composition are given in Table 1.

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Table 1  
Composition of the cements

	WPC	SRPC
CaO	68.4	64.5
SiO <sub>2</sub>	22.3	20.6
Al <sub>2</sub> O <sub>3</sub>	4.89	3.82
Fe <sub>2</sub> O <sub>3</sub>	0.20	6.27
SO <sub>3</sub>	2.25	1.92
MgO	0.70	0.72
K <sub>2</sub> O	0.59	0.51
Na <sub>2</sub> O	0.05	0.09
TiO <sub>2</sub>	0.10	n.d.
L.O.I.	3.09	n.d.
CO <sub>2</sub>	1.79	0.70
C <sub>3</sub> S	72	67
C <sub>2</sub> S	9	10
C <sub>3</sub> A	12	0
C <sub>4</sub> AF	0.6	19

The following corrosive agents were selected to produce chemical corrosion of the hardened cement pastes:

- Ammonium nitrate: Solutions of this compound are known to cause acid corrosion of hardened cement pastes, by dissolving their main constituents. In an attack on hydrated Portland cement the present portlandite and bound CaO are dissolved as well-soluble calcium nitrate, leaving behind a C–S–H phase with a reduced C/S ratio or even amorphous SiO<sub>2</sub> hydrate. As a by-product gaseous ammonia is also liberated.

- Sodium sulfate: This agent was selected to produce a sulfate corrosion of the pastes.
- Ammonium sulfate: This agent produces a combined acid–sulfate corrosion of the cement pastes.

The corrosive solutions were produced by dissolving the pertinent salts in deionized water.

Pastes made from the studied binders with a water–solid (w/s) ratio of 0.35 (w/s=0.45 in the case of C<sub>3</sub>S) were used for producing test specimens 10 × 10 × 60 mm<sup>3</sup>. About one half of the specimens was produced with a notch 2 mm deep, the rest was non-notched. After 24 h the specimens were demolded and subsequently cured in lime-saturated water at 20 ± 2°C for 60 days. At this time, the flexural strength of the hydrated paste was determined in a three-point bending test. The average load required to produce the fracturing of the test specimens (called “load of fracture”) served as a reference which was used in determining the load to be applied on the specimens in subsequent stress-corrosion experiments.

To study the behavior of the hardened pastes under stress-corrosion conditions a series of specimens was placed into the corrosive solution and put under a three-point flexural stress in an apparatus shown schematically in Fig. 1. Here, the bending stress was produced by the lever action of a horizontal steel bar loaded at its end by an appropriate load. Another set of specimens was kept in the same corrosive solution without applying any load. Parallel to experiments performed on specimens exposed to the corrosive agent, other specimens, both exposed and

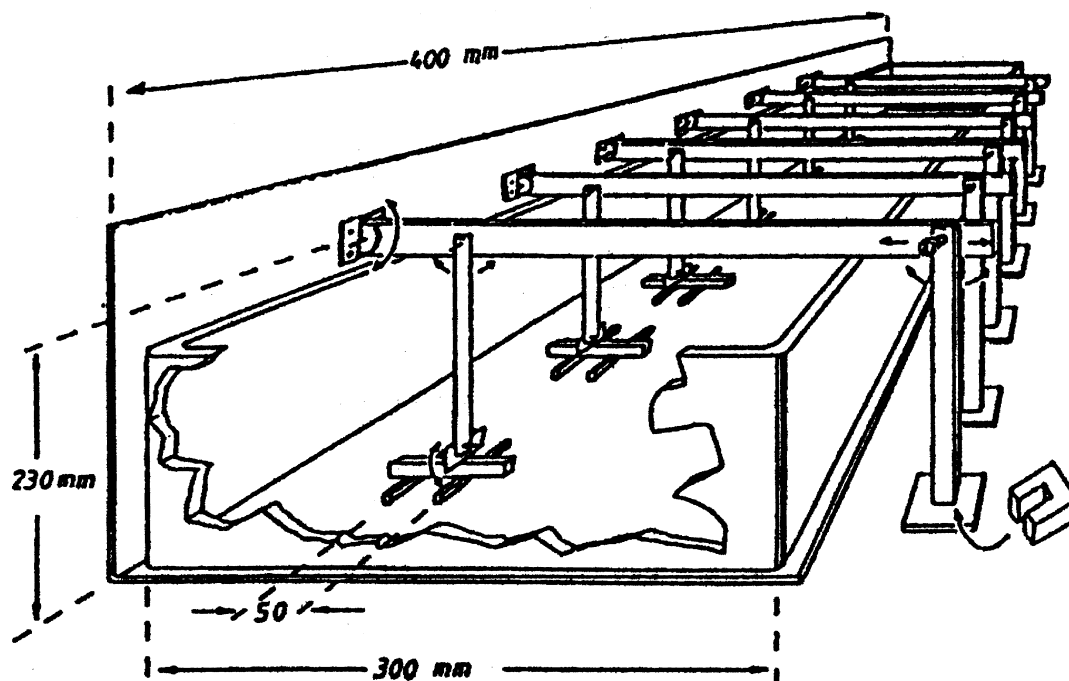


Fig. 1. Apparatus for exposing test specimens to a flexural load.

Table 2  
Flexural strength properties of cement pastes exposed to  $\text{NH}_4\text{NO}_3$  (non-notched test specimens)

Cement	Concentration of $\text{NH}_4\text{NO}_3$ (%/mol)	Applied load (% (N))	Time under load (days)	Load of fracture (N)	Flexural strength (MPa)
WPC	0	–	0	219	16.5
	0	0	60	195	14.7
	0	75 (164)	60	192	14.4
	4/0.5	0	7	190	
	4/0.5	75 (164)	–	failure 2–9 days	
SRPC	0	–	0	154	11.5
	0	0	60	184	13.8
	0	75 (116)	60	206	15.5
	4/0.5	0	7	87	
	4/0.5	75 (116)	–	failure 5–12 days	
C <sub>3</sub> S	0	–	0	37.3	2.80
	0	0	365	36.0	2.68
	0	75 (28)	365	41.3	3.06
	2/0.25	0	5	17.3	
	2/0.25	50 (19)	–	failure 3–5 days	
	4/0.5	0	3	22.7	
	4/0.5	50 (19)	–	failure 2–4 days	
	4/0.5	0	21	9.3	
	4/0.5	25 (9)	–	failure 18–21 days	

non-exposed to a flexural loading, were stored just in plain water to obtain comparative values. In all experiments on non-notched specimens the bending load was applied to the specimens positioned perpendicular to the direction in which the mold had been filled with the fresh cement paste. In experiments with notched samples, the notch was located in the region undergoing tensile stress. The concentration of the corrosive solution, the magnitude of the bending load and the duration of the exposure to such load were selected on the basis of preliminary experiments, to produce a spontaneous fracture of the specimens in a reasonable time and to obtain data that could be mutually compared.

After a preset time of exposure to the corrosive solution, in samples that did not fail spontaneously, the load needed to produce a failure of the specimens was determined in a three-point bending test. From it, the flexural strength of the hardened cement paste could be calculated. All data shown

in the presented tables represent the average value of results obtained in six identical test specimens. In test specimens that failed under the preselected load spontaneously, the duration of the exposure to the corrosive solution until failure was registered.

To determine the effect of the applied mechanical stress on the progress of corrosion, the thickness of the corroded layer was studied in samples exposed for different times to the corrosive solutions, by optical microscopy and backscatter electron imaging. These measurements were made on surfaces that were perpendicular to that exposed to the corrosive agent, and were produced by fracturing the test specimen.

The concentration of selected elements across the specimen, including the surface layer produced in the corrosion process, was determined by quantitative electron microprobe analysis. Parallel to it, the phase composition of the paste at the surface of specimens, both exposed

Table 3  
Flexural strength properties of cement pastes exposed to  $\text{Na}_2\text{SO}_4$  (non-notched test specimens)

Cement	Concentration of $\text{Na}_2\text{SO}_4$ (%/mol)	Applied load (% (N))	Time under load (days)	Load of fracture (N)	Flexural strength (MPa)
WPC	0	no	0	219	16.5
	0	no	60	195	14.7
	0	75 (164)	60	192	14.4
	7/0.5	no	60	264	
	7/0.5	75 (164)	60	242	
SRPC	0	no	0	154	11.5
	0	no	60	184	13.8
	0	75 (116)	60	206	15.5
	7/0.5	75 (116)	60	283	
	7/0.5	75 (116)	60	248	

Table 4

Flexural strength properties of cement pastes exposed to  $(\text{NH}_4)_2\text{SO}_4$  (non-notched test specimens)

Cement	Concentration of $(\text{NH}_4)_2\text{SO}_4$ (%/mol)	Applied load (% (N))	Time under load (days)	Load of fracture (N)	Flexural strength (MPa)
WPC	0	no	–	219	16.5
	0	no	28	186	14.0
	0	75 (164)	28	219	16.5
	6.5/0.5	no	28	114	
	6.5/0.5	50 (110)	–	failure 18–36 days	
	6.5/0.5	no	16	155	
	6.5/0.5	75 (164)	–	failure 6–22 days	

and non-exposed to the corrosive solutions, was determined by X-ray diffraction.

### 3. Results

#### 3.1. Strength properties

Table 2 shows the flexural strength properties of selected non-notched samples stored either in water or in an ammonium nitrate solution. Test specimens that were stored (after a 60 day precuring in saturated  $\text{Ca}(\text{OH})_2$ ) for additional 60 to 365 days in water, showed only minor changes in flexural strength, regardless of whether they were exposed to a flexural load or not. Contrary to that, specimens that were kept in an ammonium nitrate solution exhibited a gradual decline in the load of fracture even if not exposed to flexural forces. At high enough  $\text{NH}_4\text{NO}_3$  concentrations and sufficiently long exposure to the corrosive solution, test specimens exposed to a flexural force exhibited a spontaneous failure even under a load that was well below that needed to cause fracturing of the specimens at the end of the precuring period.

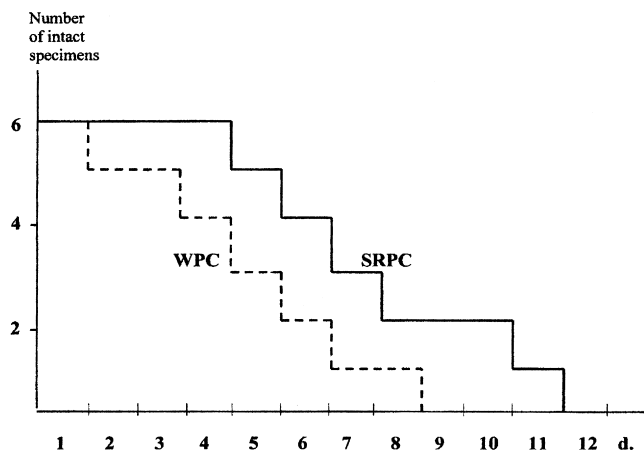


Fig. 2. Timing of the failure of non-notched WPC and SRPC test specimens placed in a 0.5 M  $\text{NH}_4\text{NO}_3$  solution and exposed to a flexural load of 75% of the original load of failure.

Table 3 shows the flexural strength properties of samples stored for up to 60 days in a sodium sulfate solution. Contrary to our expectations, both the WPC and SRPC pastes exhibited an increase of their strength properties under these conditions. A spontaneous failure of test specimens was not observed even under a load corresponding to 75% of the load causing fracture of the specimens right after precuring in a saturated calcium hydroxide solution.

Finally, Table 4 shows the strength properties of samples stored in an ammonium sulfate solution. Just as with ammonium nitrate and unlike with sodium sulfate, these specimens exhibited a decline of strength and a spontaneous failure if exposed to a flexural load.

Fig. 2 shows the timing of the failures taking place in non-notched test specimens exposed simultaneously to ammonium nitrate and to a flexural load. Here the number of still intact specimens as function of time of exposure to the corrosive solution is shown. In all instances the failing got under way after a short induction period in which the specimens stayed intact, and was completed within a few subsequent days.

Data found in notched test specimens are summarized in Tables 5 and 6 and in Figs. 3 and 4. It may be seen that the

Table 5

Flexural strength properties of cement pastes exposed to  $\text{NH}_4\text{NO}_3$  (notched test specimens)

Cement	Concentration of $\text{NH}_4\text{NO}_3$ (%/mol)	Applied load (% (N))	Time under load (days)	Load of fracture (N)
WPC	0	0	0	79.3
	0	0	60	73.5
	10 (1.25)	0	12	20.8
	10 (1.25)	30 (23.8)	failure	
	10 (1.25)	0	11–13 days	
	10 (1.25)	50 (39.7)	failure	49.0
	10 (1.25)	50 (39.7)	failure	
SRPC	0	0	0	72.2
	0	0	60	69.0
	10 (1.25)	0	12	20.0
	10 (1.25)	30 (21.7)	failure	
	10 (1.25)	0	8–11 days	
	10 (1.25)	50 (36.1)	failure	27.0
	10 (1.25)	50 (36.1)	failure	

Table 6  
Flexural strength properties of cement pastes exposed to  $\text{Na}_2\text{SO}_4$  (notched test specimens)

Cement	Concentration of $\text{Na}_2\text{SO}_4$ (%/mol)	Applied load (% (N))	Time under load (days)	Load of fracture (N)
WPC	0	no	0	79
	0	no	60	74
	10/0.7	no	60	169
	10/0.7	30 (24)	60	173
	10/0.7	no	300	179
	10/0.7	50 (40)	300	174
SRPC	0	no	0	72
	0	no	60	69
	10/0.7	no	60	153
	10/0.7	30 (33)	60	149
	10/0.7	no	300	131
	10/0.7	50 (36)	300	121

results were analogous to those found in non-notched samples. A loss of strength and a spontaneous failure was observed in specimens exposed to ammonium nitrate, whereas the strength increased distinctly in those exposed to sodium sulfate. A comparison of results made with test specimens exposed to flexural loads of different magnitudes revealed that the time for which the specimens sustained the loading before beginning to fail became shortened with an increasing load applied.

### 3.2. Texture of the test specimens

The structural investigations were made on non-notched test specimens stored in the solutions of corrosive agents for different periods of time. All specimens stored in such solutions (with concentrations between 0.05 and 1.25 M) for three or more days possessed a corrosion layer that could be well distinguished visually from the noncorroded core by its brighter color. The thickness of this layer increased with increasing concentration of the

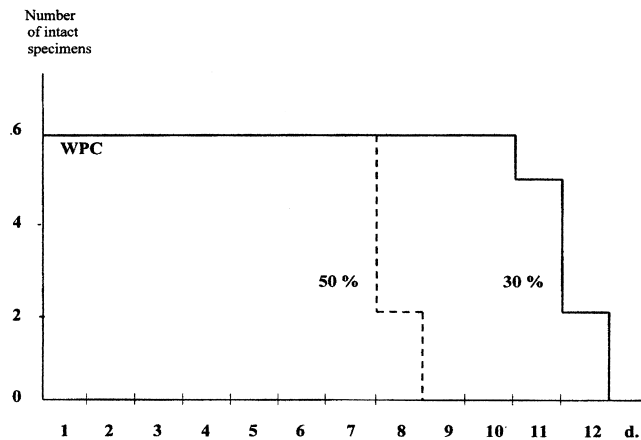


Fig. 3. Timing of the failure of non-notched WPC test specimens placed in a 0.5 M  $\text{NH}_4\text{NO}_3$  solution and exposed to flexural loads of different magnitudes.

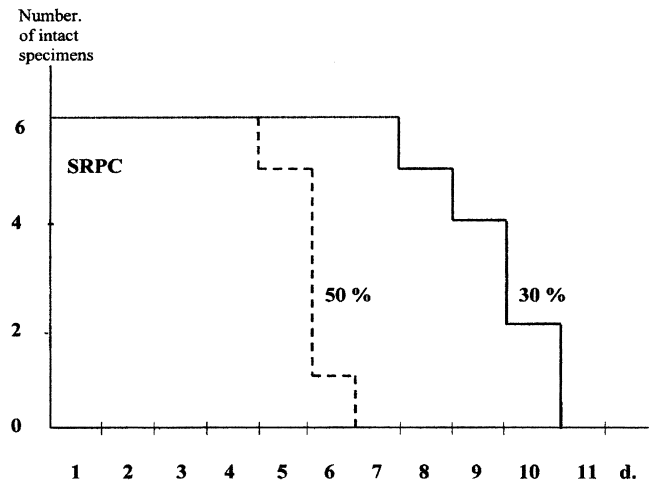


Fig. 4. Timing of the failure of non-notched SRPC test specimens placed in a 0.5 M  $\text{NH}_4\text{NO}_3$  solution and exposed to flexural loads of different magnitudes.

corrosive agent in the solution and the duration of exposure to it. In samples exposed to both ammonium nitrate and ammonium sulfate the corrosion layer was “smeary” if wet and “sandy” when dried, whereas it appeared firm in samples exposed to sodium sulfate. The thickness of the layer that had undergone corrosion was virtually identical in regions of the specimen undergoing tensile and compressive stresses, with the sole exception of specimens exposed to ammonium sulfate. In these the progress of corrosion was accelerated in the region undergoing tensile stress and slowed down in that under compression. Data on the thickness of the corrosion layer are summarized in Table 7.

In addition to the formation of a corrosion layer the test specimens also exhibited changes in their mass as they were kept in the corrosive solutions. Within 28 days the mass decreased to 82%, 96% and 70% of the original value in samples made from WPC, SRPC and  $\text{C}_3\text{S}$ , respectively, and stored in 0.5 M ammonium nitrate. At the same time the mass of the test specimens stored in 0.5 M sodium sulfate increased by about 3–5% in both WPC and SRPC samples. The mass of WPC specimens kept in the 0.5 M ammonium sulfate solution increased by about 3%. A simultaneous exposure to a flexural force did not affect these results noticeably. The length of the test specimens changed only insignificantly in all instances.

Fig. 5 shows the distribution of Ca, Si and Al (expressed as  $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) within an SRPC test specimen that has been cured in a 0.5 M  $\text{NH}_4\text{NO}_3$  solution, while undergoing a flexural stress. It appears that close to the surface the sample was depleted with respect to  $\text{CaO}$  and consequently relatively enriched with respect to  $\text{SiO}_2$  and, in a lesser degree, also with respect to  $\text{Al}_2\text{O}_3$ . The changes caused by corrosion were virtually identical in regions undergoing the tensile and compressive stresses.

Table 7

Thickness of the region undergone corrosion

Corrosive agent	Applied load (%)	Time under load (days)	Thickness of corrosion layer		
			WPC (mm)	SRPC (mm)	C <sub>3</sub> S (mm)
NH <sub>4</sub> NO <sub>3</sub> 0.5 M	50	3	1.0 (N+L)	0.6 (N+L)	1.1 (N+L)
	50	7	1.6 (N+L)	1.4 (N+L)	1.6 (N+L)
	50	28	2.8 (N+L)	2.3 (N+L)	2.5 (N+L)
Na <sub>2</sub> SO <sub>4</sub> 0.5 M	50	3	0.5 (N+L)	0.25 (N+L)	n.d.
	50	28	1.1 (N+L)	0.6 (N+L)	n.d.
	50	100	n.d.	1.15 (N+L)	n.d.
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 0.5 M	75	16	1.15 (N)		
	75	16	0.5 (C)	n.d.	n.d.
	75	16	1.2 (T)		
	50	28	1.2 (N)		
	50	28	0.7 (C)	n.d.	n.d.
	50	28	1.6 (T)		

N: nonloaded test specimens.

L: loaded test specimens, all surfaces.

C: loaded test specimens, region under compressive stress.

T: loaded test specimens, region under tensile stress.

Fig. 6 shows similar results found in a C<sub>3</sub>S specimen. In addition, here the mechanical loading had no significant effect on the progress of the chemical corrosion.

Figs. 7 and 8 show the distribution of CaO, SiO<sub>2</sub> and SO<sub>3</sub> in specimens stored in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution. Here the corrosion zone was depleted with respect to CaO and contained significant amounts of SO<sub>3</sub>. The amount of SiO<sub>2</sub> in this zone was increased only little. In addition, changes in the content of individual elements in the corroded zone were similar in regions undergoing tensile and compressive stresses.

Finally, Figs. 9 and 10 show the distribution of CaO, SiO<sub>2</sub> and SO<sub>3</sub> in specimens that were exposed to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The distribution of these oxides was characterized by a significant reduction of the CaO content and by the presence of high amounts of SO<sub>3</sub> in the corroded regions, with less significant changes in the amount of

present SiO<sub>2</sub>. In samples exposed to a flexural force, unlike in nonloaded samples, the distribution of elements was not symmetrical, as the corroded layer formed in the region under tension was significantly thicker than the one formed in the region under compression.

Results of the performed X-ray diffraction studies are summarized in Table 8. They revealed great differences in the phase composition of the corroded surface layers compared to the noncorroded cores. In surface layers of pastes exposed to ammonium nitrate, calcium carbonate in the form of calcite, and in to lesser extent also vaterite, were the only crystalline reaction products detectable, indicating a carbonation of that fraction of primarily formed portlandite that had not been dissolved in the liquid phase. It may be assumed that at the same time the C–S–H phase was converted into a product with a lower C/S ratio and/or into a hydrous amorphous

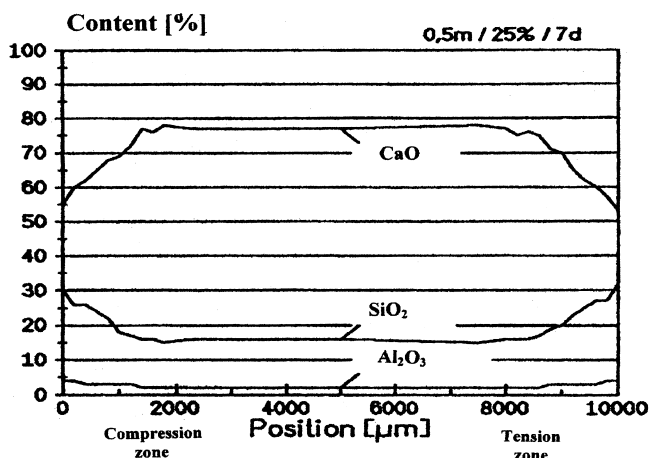


Fig. 5. Distribution of CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> within an SRPC test specimen cured 7 days in a 0.5 M NH<sub>4</sub>NO<sub>3</sub> solution and exposed to a flexural load equal to 25% of the original load of failure.

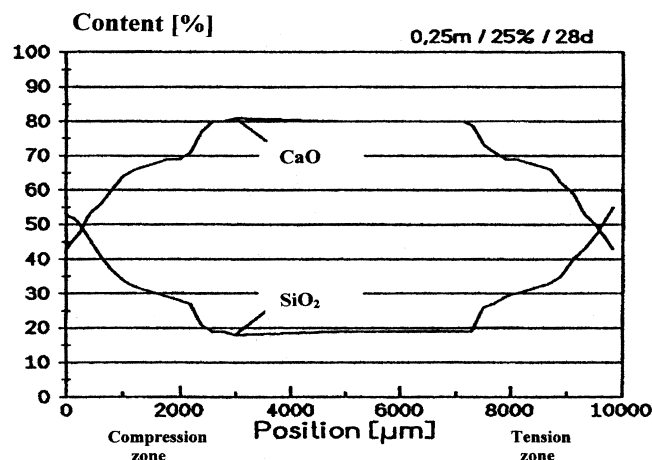


Fig. 6. Distribution of CaO and SiO<sub>2</sub> within a C<sub>3</sub>S test specimen cured 28 days in a 0.25 M NH<sub>4</sub>NO<sub>3</sub> solution and exposed to a flexural load equal to 25% of the original load of failure.

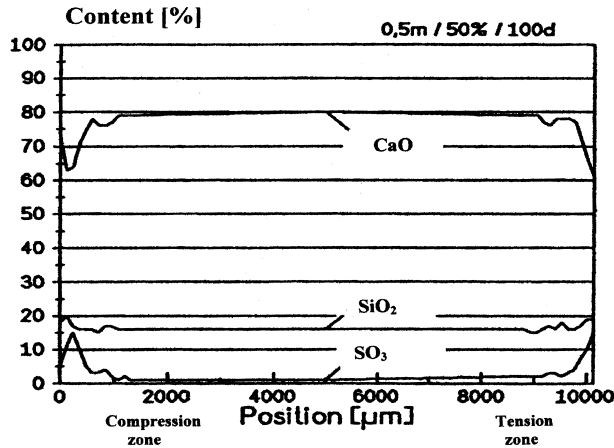


Fig. 7. Distribution of CaO, SiO<sub>2</sub> and SO<sub>3</sub> within a WPC test specimen cured 100 days in 0.25 M Na<sub>2</sub>SO<sub>4</sub> solution and exposed to a flexural load equal to 25% of the original load of failure.

SiO<sub>2</sub> gel doped with Al<sub>2</sub>O<sub>3</sub> and other oxides present, not detectable by X-ray diffraction. A simultaneous exposure of the test specimens to flexural forces had no noticeable effect on the phase composition of the corrosion layer.

In pastes exposed to sodium sulfate significant amounts of calcite were also formed, but portlandite was usually also present in SRPC samples. The SO<sub>3</sub> was present in the form of gypsum and only in WPC samples, also in the form of ettringite.

In pastes exposed to ammonium sulfate, calcite and gypsum were found as the sole crystalline reaction products.

#### 4. Discussion

Expectedly, an exposure of the studied cement pastes to ammonium nitrate caused a corrosion at the surface of the

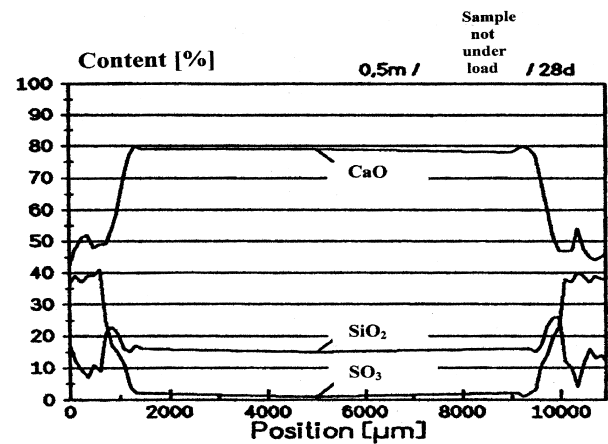


Fig. 9. Distribution of CaO, SiO<sub>2</sub> and SO<sub>3</sub> within a WPC test specimen cured 28 days in a 0.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution, not being under a flexural load.

test specimens, associated with a dissolution of calcium hydroxide and an increase of porosity within the region undergoing corrosion. Contrary to that, the absence of a damaging corrosion of test specimens exposed to sodium sulfate was rather unexpected. It suggests the precipitation of all the formed gypsum and ettringite within the existing pores, without damaging the cohesion of the material, while lowering its porosity and increasing its strength. The absence of ettringite in SRPC pastes is due to the absence of tricalcium aluminate in clinkers of this type. In samples exposed to ammonium sulfate a dissolution of calcium hydroxide and a simultaneous precipitation of gypsum in the pore system of the corrosion layer were the characteristic features of the corrosion process. Ettringite was not formed in the corrosion by this agent, obviously due to a too low pH of the liquid phase.

Internal stresses in the hardened paste generated by placing the test specimen under a flexural load did have

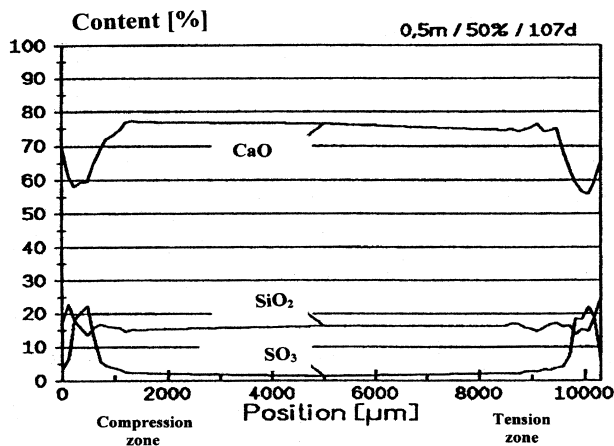


Fig. 8. Distribution of CaO, SiO<sub>2</sub> and SO<sub>3</sub> within an SRPC test specimen cured 107 days in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution and exposed to a flexural load equal to 25% of the original load of failure.

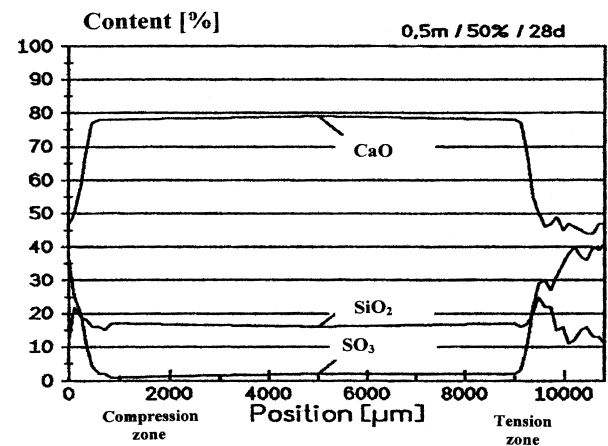


Fig. 10. Distribution of CaO, SiO<sub>2</sub> and SO<sub>3</sub> within a WPC test specimen cured 28 days in a 0.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution and exposed to a flexural load equal to 50% of the original load of failure.

Table 8

Phase composition of noncorroded and corroded cement pastes

Cement	Noncorroded paste	Corroded paste		
	Phases	Corrosive agent	Time (days)	Phases
WPC	portlandite +++ clinker phases ( $C_2S + C_3S$ ) + ettringite +	$NH_4NO_3$ 0.5 M	28	calcite +++ vaterite +
		$Na_2SO_4$ 0.5 M	28	calcite +++ gypsum +++ ettringite ++
		$(NH_4)_2SO_4$ 0.5 M	28	calcite +++ gypsum +++
SRPC	portlandite +++ $C_4AF$ ++ clinker phases ( $C_2S + C_3S$ ) +	$NH_4NO_3$ 0.5 M	28	calcite ++ $C_4AF$ ++ clinker phases ( $C_2S + C_3S$ ) + vaterite +
		$Na_2SO_4$ 0.5 M	28	calcite ++ portlandite ++ gypsum ++ $C_4AF$ ++
$C_3S$	portlandite +++ $C_3S$ +	$NH_4NO_3$ 0.5 M	28	calcite +++

Intensities of the XRD peaks: (+) weak, (++) medium, (+++) strong.

no effect on the progress of corrosion of specimens exposed to ammonium nitrate and sodium sulfate, but affected the progress of corrosion caused by ammonium sulfate. We assume that in the case of ammonium sulfate the higher porosity of the paste in the region undergoing tensile stress, and a reduced porosity in the region under compression caused differences in the rate of migration of the corrosive medium towards the noncorroded core and that of the dissolved species into the bulk liquid, thus influencing the rate of corrosion. Contrary to that, in samples exposed to ammonium nitrate the porosity, and thus the permeability of the corrosive layer, became increased by the existing dissolution of calcium hydroxide to such a degree at which the changes in permeability generated by the applied bending force became negligible. In the case of sodium sulfate the filling of the pore

system with reaction products seems to eliminate or reduce the effect of deflection of the test specimen on the permeability of the hardened paste. It must be stressed, however, in this context that conditions found by us on flat surfaces of pure cement pastes may or may not reflect also conditions existing on the tip of a notch in notched test specimens, or in mortar/concrete samples.

The changes in the magnitude of the load needed to fracture the test specimens seen in samples exposed to the corrosive solutions are the consequence of structural changes that have taken place in the corrosion layer. In samples exposed to ammonium nitrate and ammonium sulfate the gradual decline of the load of fracture appears to be due to a loss of strength of the paste that had undergone corrosion and to a decrease of the cross section of the noncorroded core of the test specimen. Such loss of

Table 9

Comparison of the load of fracture in nonloaded samples and the applied load in loaded samples

		Nonloaded test specimens		Loaded test specimens	
Corrosive agent	Cement	Curing time (days)	Load of fracture (N)	Applied load (N)	Time of failure (days)
<i>Non-notched test specimens</i>					
NH <sub>4</sub> NO <sub>3</sub> 0.5 M	WPC	7	190	164	2–9
	SRPC	7	87	116	5–12
	C <sub>3</sub> S	3	23	19	2–4
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 0.5 M	C <sub>3</sub> S	21	9	9	18–21
	WPC	28	114	110	18–36
		16	155	164	6–22
<i>Notched test specimens</i>					
NH <sub>4</sub> NO <sub>3</sub> 0.5 M	WPC	12	21	24	10–12
	WPC	7	49	40	6–8
	SRPC	12	20	22	8–11
	SRPC	7	27	36	5–7

strength was most probably due to the degradation of the present C–S–H phase by the corrosive agent and, in the case of  $\text{NH}_4\text{NO}_3$ , also to an increase of the porosity of the corrosion layer. The increase in strength in samples exposed to sodium sulfate appears to be mainly due to a reduction of porosity as the pore system became filled with gypsum and/or ettringite. Table 9 compares the loads of fracture of a series of nonloaded test specimens with the applied loads to identical specimens exposed to flexural loading, both exposed to the same corrosive solution. The obtained results indicate that the load of fracture in samples not exposed to a bending force was not too different from the applied load in samples under flexural loading, if compared at similar times of exposure to the corrosive liquid. This suggests a roughly identical cross section of the noncorroded core in both sets of test specimens and thus a similar overall rate of their corrosion.

## 5. Conclusions

Hardened Portland cement and tricalcium silicate pastes exposed to ammonium nitrate undergo surface corrosion associated with leaching of calcium hydroxide, increase of porosity and loss of strength. The corrosion process is not accelerated in test specimens simultaneously undergoing a flexural load.

Test specimens made from Portland cement pastes exposed to sodium sulfate for up to 60 days exhibited an increase of strength, apparently due to precipitation of gypsum and ettringite in the pore system close to the surface. The thickness of this region is not altered in test specimens simultaneously undergoing a flexural load.

The corrosion of hardened Portland cement pastes by ammonium sulfate is characterized by leaching of calcium hydroxide and precipitation of gypsum in the pore system, resulting in a gradual loss of strength. In test specimens exposed to a flexural load the progress of corrosion is accelerated at the surface undergoing tensile stress and is reduced at that undergoing compression.

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