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Accelerated tests of hardened cement pastes alteration by organic acids: analysis of the pH effect

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Abstract

Effluents, such as liquid manure and silage effluents, stored in silos often made of concrete, contain organic acids that are chemically very aggressive for the cement-based matrix. The pH of liquid manure is comprised between 6 and 8, and the pH of silage effluent is about 4.

There has already been much research done on manure's effect on concrete using aggressive solutions with a pH of or inferior to 4, in order to accelerate alteration kinetics. These studies aimed at simulating liquid manure and silage effluent, equally.

The goal of this article is to validate the use of solutions with a pH of 4 to implement accelerated studies on alterations occurring to structures exposed to the acidic part of liquid manure.

In this study, the alteration mechanisms of the cement-based matrix produced by two solutions of organic acids with pH of 4 and 6 were compared.

At the end of the experiment, carried out on ordinary Portland cement and slag cement pastes, the kinetics of alteration of the cement pastes immersed in the solution with a pH of 4 was ninefold higher than in the solution with a pH of 6.

The chemical and mineralogical modifications of the paste were analyzed by electron microprobe, XRD and BSE mode observations.

It was shown that the alteration mechanisms of the paste are sensibly identical for both solutions: almost complete decalcification, the disappearance of the crystallized or amorphous hydrated phases and the probable formation of a silica gel containing aluminum and iron, mainly. The differences in alteration mechanisms between the two solutions are minor and mainly concern the stability of the anhydrous phases: C_4AF and slag grains.

Keywords: Organic acids; Stability; pH; Electronic microprobe; X-ray diffraction

1. Introduction

Agriculture produces manure (liquid manure, silage effluent, etc.) that causes serious environmental problems: water, soil and air pollution [1]. In order to limit this pollution, manure needs to be stored in water-tight silos often made of concrete.

Manure contains organic acids (acetic, propionic, lactic, etc.) which constitute a severe chemical aggression toward the concrete of agricultural structures. When these acids come into contact with the cement based matrix, the reactions with the hydrates of the cement paste (portlandite, C–S–H and hydrated aluminates) produce mainly calcium and aluminum salts, whose solubility varies from high to very high in water [2–3]. Consequently, the porosity increases, the mechanical strengths drop, and, in the long term, the corrosion of reinforcements can occur in the immersed part of the structures.

The presence of both these acids and the acido–basic couple NH_4^+/NH_3 means the pH of liquid manure is between 6 and 8. However, generally, the pH of silage effluent is about 4 [4–8].

Many studies on manure used aggressive solutions with pH values equal or inferior to 4, in order to accelerate alteration kinetics to simulate liquid manure or silage

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effluent equally [9–12]. In the case of silage effluent aggression, this pH value is suitable. However, when simulating the action of liquid manure within the frame of durability studies, it is necessary to determine if solutions with a pH of 4 produce the same mineralogical and chemical changes to the cement paste as in solutions with a pH between 6 and 8.

It has already been shown that the attack by liquid manure organic acids, at pH 4, results in a well-marked mineralogical and chemical zonation of the immersed specimen [12,13]. The altered zone is progressively and quite totally decalcified, and is made up almost entirely of silicon, aluminum and iron. The crystallized phases (hydrate and anhydrous compounds) are totally dissolved, in the zone in contact with the aggressive solution. Moreover, the external part of the specimen, which is totally amorphous, is composed of a supposed silica gel containing aluminum and iron. It was noticed that slag cements kept their anhydrous grains (amorphous phases) in the external zone. However, to our knowledge, no such study has been carried out at pH value of 6.

This study aims to compare the mineralogical and chemical modifications occurring in the cement-based matrix of ordinary Portland cement and slag cement pastes submitted to organic acids mixes, simulating liquid manure, at pH 4 and 6. The experiment is based on the comparison of the alteration kinetics, assessed by altered depths and mass losses, and of the mineralogical and chemical alteration mechanisms analyzed by X-ray diffraction and electronic microprobe.

2. Experimental process

2.1. Materials

This study was conducted on hardened cement pastes made with two cements: an ordinary Portland cement, designated in French Standard as CEM I 52.5 R [14], and a cement containing 68% blast-furnace slag, or CEM III/B 42.5 N [14]. Compositions are given in Table 1.

2.2. Specimen making and treatment

The water/cement mass ratio of the pastes was 0.27. The hardened cement paste specimens were cylindrical, 75 mm high and 25 mm diameter. The specimens were demolded 24 h after pouring and stored in water at 20 °C for 27 days. Afterwards, the specimens were wiped to eliminate superficial water and immersed in the aggressive solution. Some control specimens are kept in water at 20 °C during the whole experiment.

Table 2
Concentrations and pK_a of the organic acids in the aggressive solutions

Constituents	Acids				
	Acetic ($C_2H_4O_2$)	Propionic ($C_2H_6O_2$)	Butyric ($C_4H_8O_2$)	*Iso*-butyric ($C_4H_8O_2$)	Valeric ($C_5H_{10}O_2$)
Concentration (g/l)	12.8	2.8	1.6	0.6	0.3
pK_a	4.8	4.9	4.8	4.85	4.8

The aggressive solutions are a mix of five organic acids found in liquid manure: acetic, propionic, butyric, *iso*-butyric and valeric acids. The concentrations of these acids in the solution match the maximum values that can occur in real pig slurries (Table 2). The solution is marked synthetic liquid manure (SLM).

2.3. Fixing of the aggressive solutions pH

Fig. 1 shows the curve of the SLM titration by 1 M NaOH. The initial pH was 2.7. The hachured zone matches the solution neutralization. Above pH of 6.5, the pH increases very quickly, for slight soda additions. This zone must be avoided within the frame of pH-maintained studies. In order to limit the number of solution changings, the chosen initial pH of the solution simulating pH 6 was of 5.6, value for which a large amount of the acids is neutralized, and above which a significant part of the acids buffer capacity is preserved.

This SLM solution was added with 2 g/l NaOH in order to bring the pH up to 4 for the SLM1, and 9.6 g/l to bring the pH up to 5.6 for the SLM2. The pHs were maintained, during the experiment, by the changing of the solutions every 5 days during the first 15 days, every 2 weeks during 6 weeks and then every 3 weeks until the end of the experiment, i.e., 18 weeks. Fig. 2 shows the evolution of both pH solutions. Hence, until the 15th day, the pH of the tanks containing SLM1 and SLM2 were between 4 and 4.6, and 5.6 and 7.5, respectively. Then, the values of pH were of 4.25±0.25 for the SLM1, and 6.00±0.3 for the SLM2. The solid/liquid volume ratio was 0.059.

2.4. Implemented tests

2.4.1. Kinetics comparative tests

Two comparative parameters of durability were monitored on the paste specimens: altered depth and mass losses

Table 1
Cements chemical composition

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	Na_2O	K_2O	MnO	SO_3	Loss on ignition
CEM I 52,5 R	64.87	21.19	3.94	2.36	2.37	0.21	0.19	0.76	0.10	3.16	1.79
CEM III/B 42,5 N	46.67	30.94	8.92	1.15	5.71	0.39	0.46	0.22	0.06	2.47	1.75

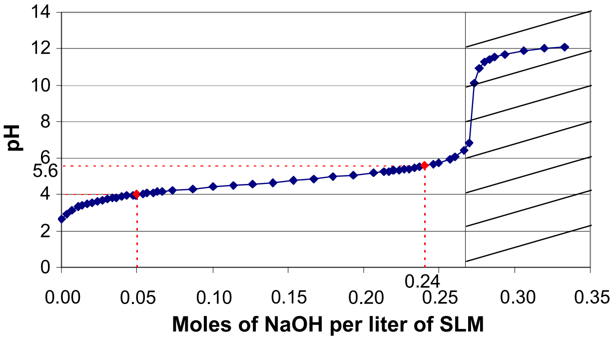

Fig. 1. Titration curve of the synthetic liquid manure (SLM).

variations. Those parameters were measured over the following terms: 0, 1st, 2nd, 4th, 9th, 13th, and 18th week of immersion. To quantify the altered depth, two specimens were sawed perpendicularly to their axes and some phenolphtaleïn was sprayed on the plane sections. The depth of the color change, considered as matching the altered depth, was measured with an optical videomicroscope on 16 points all around the perimeter of the discs. The mass losses measurements were carried out on two immersed specimens, first wiped.

2.4.2. Chemical and mineralogical characterization

In order to characterize chemical modifications of the specimen, analysis with electronic microprobe were carried out. The instrument used was a CAMECA SX 100. The accelerating voltage was 15 kV, the current strength was 20 nA and the scanning area of the beam was 5×5 μm^2. The measurements were led on flat polished sections, according to the distance to the surface of the specimen or depth, in the altered and sound zones. Particular care was given to the choice of the analyzed points in order to get only the hydrated paste and to avoid residual anhydrous grains. Major elements Ca, Si, Al, Fe, Mg, and S were analyzed.

These analyses were carried out on two immersed specimens, for each type of paste, after the 1st, 4th, and 9th week of immersion. Only the results from the 4 weeks of immersion are given here. Two control specimens for each type of paste were analyzed at the rate of 50 points per specimen 5 weeks after pouring. Additionally, some selective analyses associated with observations in backscattered electron mode were carried out in the sound and altered zones of the immersed specimens.

Mineralogical analyses using X-ray diffraction were completed on the specimens with a SIEMENS D5000, fitted with a copper cathode. The anode voltage was 40 kV; the current strength was of 30 mA. The measurements were carried out on two specimens of the same paste in function of depth in the sound and altered zones after 9 weeks of immersion. These analyses were carried out on the plane sides of the cylinders. The altered zone in the radial direction was removed carefully in order to keep the altered zone in the axial direction. The first analysis was carried out on the plane external face of the specimen, which is then abraded and submitted to the next analysis. The last analysis, which matched the core of the specimen, was carried out at a 15 mm depth. A control specimen was also analyzed 5 weeks after pouring.

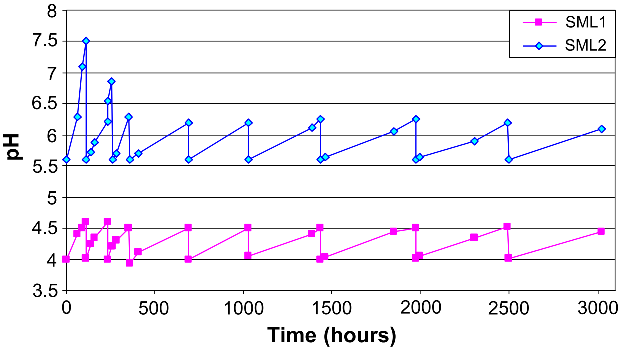

Fig. 2. pH evolution according to time of immersion for SLM1 and SLM2.

3. Results

3.1. Alteration kinetics

Fig. 3a and b shows the evolution of the alteration kinetics of the CEM I and CEM III cement pastes in SLM1

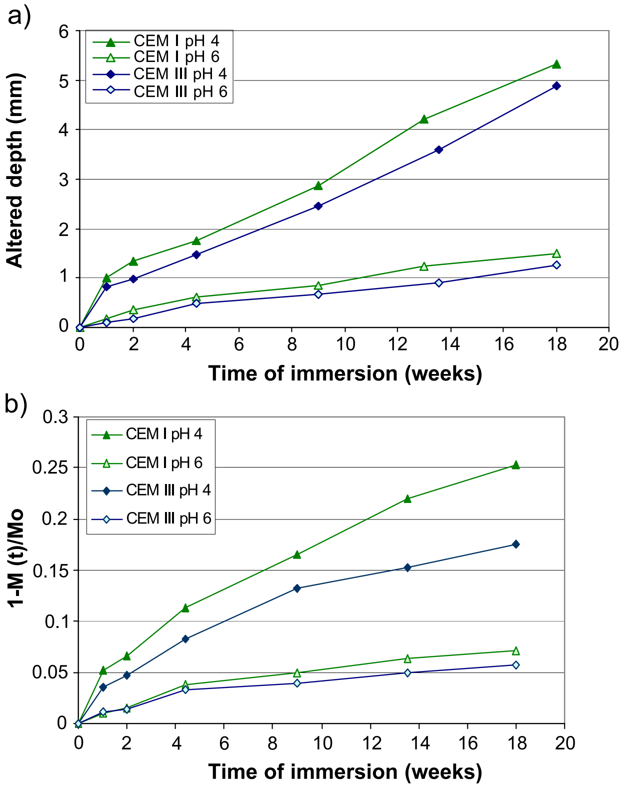

Fig. 3. Evolution of durability criteria: (a) altered depth and (b) mass losses, according to the time of immersion of CEM I and CEM III pastes in SLM1 (pH 4) and SLM2 (pH 6).

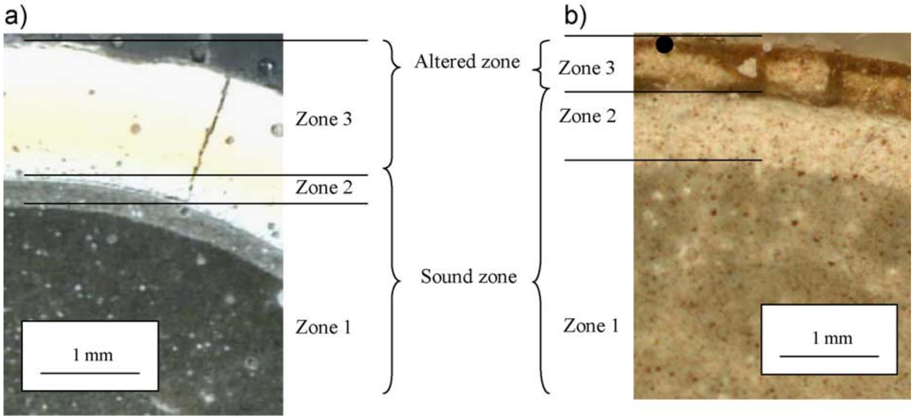

Fig. 4. Observation with videomicroscope of altered hardened CEM I pastes cross sections after 4 weeks of immersion in the aggressive solutions: (a) SLM1 (pH 4) and (b) SLM2 (pH 6).

(pH 4) and SLM2 (pH 6) in terms of altered depths and mass losses of the specimens, respectively. These figures show a usual result: the performances of the slag paste are superior to the ordinary Portland cement ones. The discrepancy between the two pastes is lower at a pH of 6 than at a pH of 4.

After 18 weeks, the immersion in SLM1 induced altered depths 3.5- and 4.1-fold higher and mass losses 3.6- and 2.9-fold higher than in SLM2, for CEM I and CEM III specimens, respectively. SLM1 produced important alteration acceleration: in about 2 weeks of immersion in SLM1, the altered depths and mass losses are equivalent to the one obtained in SLM2 after 18 weeks.

3.2. Observations with optical vidéomicroscope

3.2.1. CEM I paste

Fig. 4a and b shows the cross sections of CEM I paste specimens, after 4 weeks of immersion in the SLM1 and SLM2 aggressive solutions, respectively. The sound zone was considered as the basic area where the color turned violet during the phenolphthalein test. The altered zone showed a very weak mechanical strength and was obviously very porous. Inside the sound zone of the CEM I specimens, two distinct zones were visible: the core, marked zone 1, having the same color pattern as the control specimen, and, next to the altered zone, a light-colored paste layer some several hundred micrometers deep, marked zone 2. The thickness of zone 2 was twofold larger for SLM2 than for SLM1.

The whole zone, where the phenolphthalein does not turn to violet, is marked zone 3. The black point on Fig. 4b indicates the position of the backscattered electron picture, provided on Fig. 12.

3.2.2. CEM III paste

Fig. 5a and b shows the cross sections of CEM III paste specimens after 4 weeks of immersion in SLM1 and SLM2, respectively. Both specimens appeared to have the same alteration aspect. Two distinct zones were visible inward from the sound zone: the core, marked zone 1 (whose blue color is typical of slags), and a darker paste layer, marked zone 2, with a thickness of a hundred micrometers. Zone 2

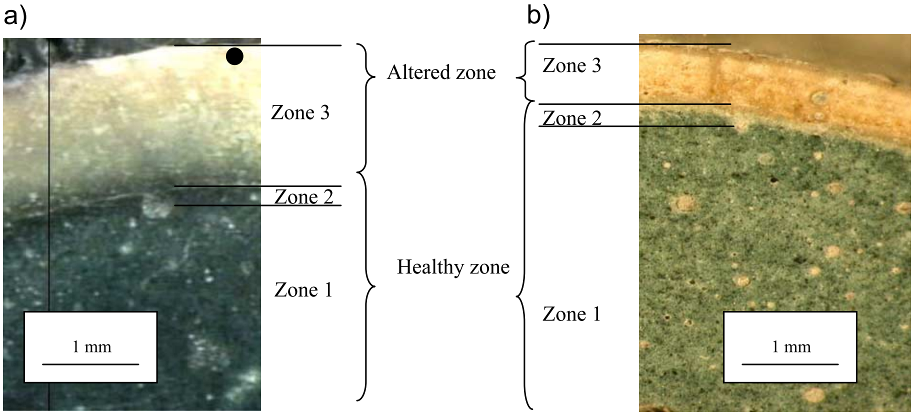

Fig. 5. Observation with vidéomicroscope of altered hardened CEM III pastes cross sections after 4 weeks of immersion in the aggressive solutions: (a) SLM1 (pH 4) and (b) SLM2 (pH 6).

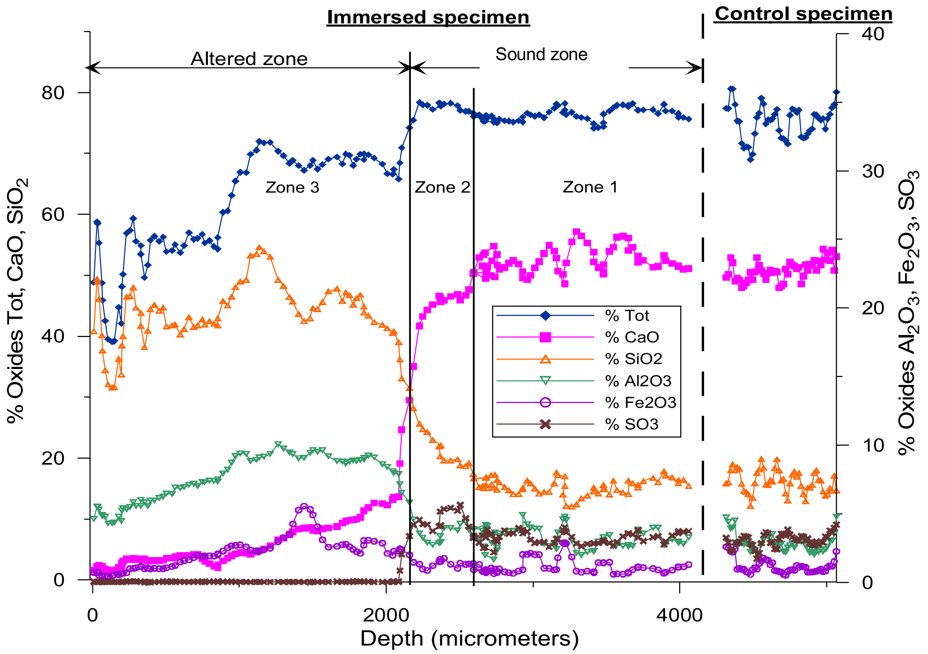

Fig. 6. Chemical analysis with microprobe according to depth of CEM I paste immersed in SLM1 (pH 4) 4 weeks of immersion—Absolutes amounts of oxides: CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3, and total.

was more or less visible from a specimen to another, but was well identified on backscattered electron pictures. The thickness of zone 2 was higher for SLM1 than for SLM2. The altered zone is marked zone 3 for the both specimens immersed in SLM1 and SLM2.

The black point on Fig. 5a indicates the position of the backscattered electrons picture provided on Fig. 13.

3.3. *Chemical modification analyzed with electronic microprobe*

The analysis results of the CEM I and CEM III specimens immersed in SLM1 and SLM2, along with the control specimen, are shown in Figs. 6–9. The chemical data are given as absolute percentages of oxide amounts

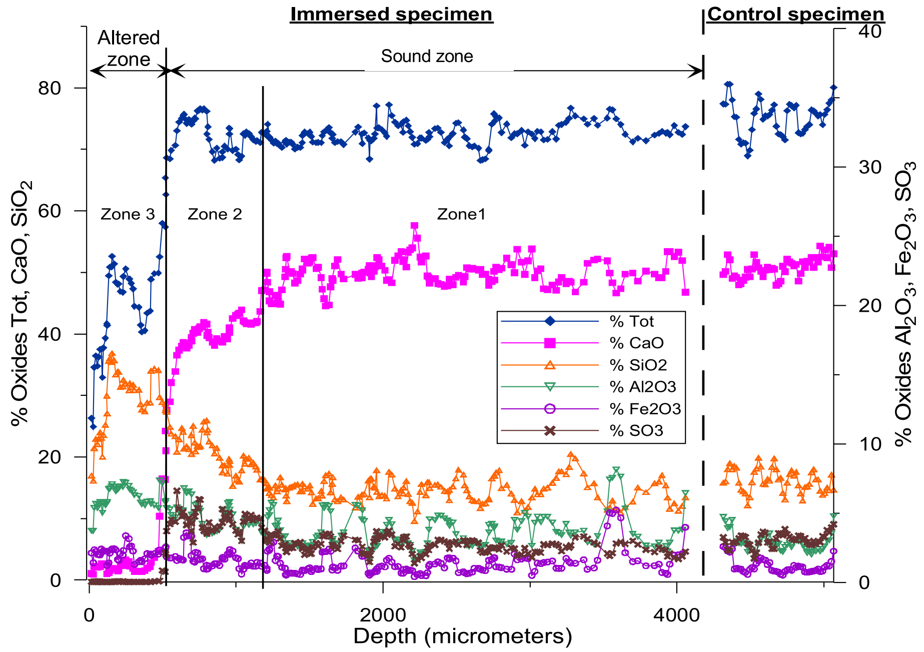

Fig. 7. Chemical analysis with microprobe according to depth of CEM I paste immersed in SLM2 (pH 6) 4 weeks of immersion—Absolutes amounts of oxides: CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3, and total.

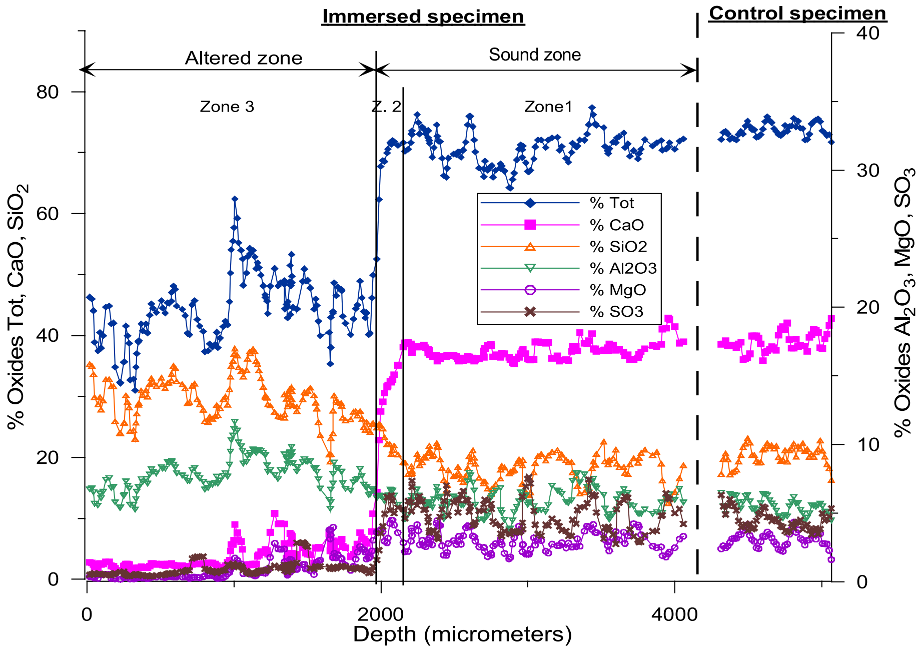

Fig. 8. Chemical analysis with microprobe according to depth of CEM III paste immersed in SLM1 (pH 4) 4 weeks of immersion—Absolutes amounts of oxides: CaO, SiO_2, Al_2O_3, MgO, SO_3, and total.

according to depth. Therefore, the sum of all the oxide amounts gives an indication of the compactness of the cement paste.

The amounts of main oxides CaO, SiO_2, Al_2O_3, Fe_2O_3 or MgO, SO_3, and the sum of all the oxides are given. In order to improve the legibility, the curves were smoothed, each point being the average value of five points in the initial curve.

3.3.1. CEM I paste (Figs. 6 and 7)

On each graph, zones 1, 2 and 3 are defined as reported for Fig. 4a and b. Table 3 provides the average amounts of oxides in each zone.

Figs. 6 and 7 show that zones 1, 2 and 3 match the same chemical modifications for SLM1 and SLM2 solutions. Zone 1 has the same chemical composition as the control specimen. The total amount of oxides, i.e., the compactness

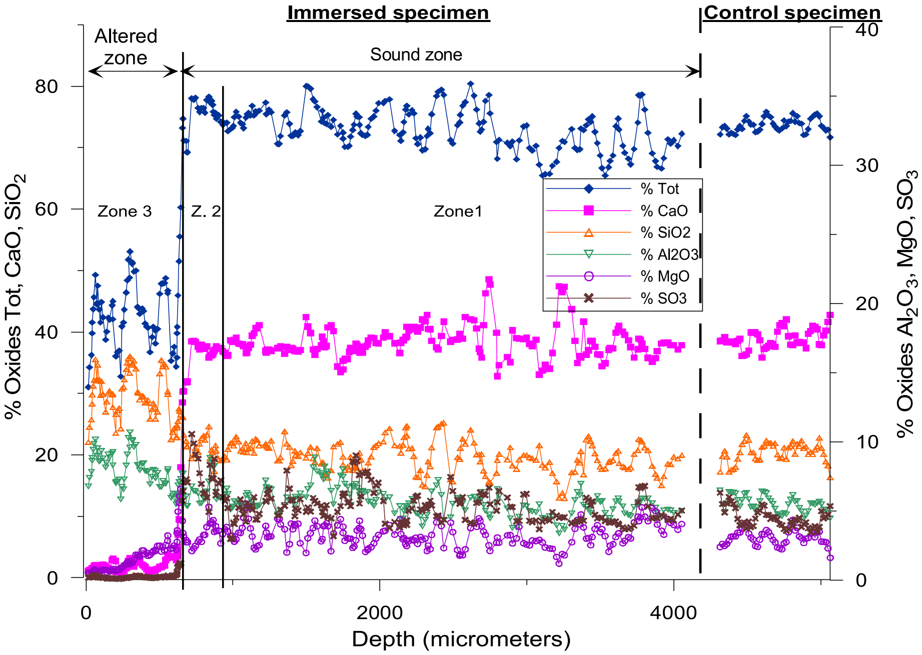

Fig. 9. Chemical analysis with microprobe according to depth of CEM III paste immersed in SLM2 (pH 6) 4 weeks of immersion—Absolutes amounts of oxides: CaO, SiO_2, Al_2O_3, MgO, SO_3, and total.

Table 3
Average amounts of oxides, analyzed with electronic microprobe, in the different zones of the specimen immersed in SLM1 (pH 4) and SLM2 (pH 6)—CEM I paste

	% Tot SLM1/SLM2	% CaO	% SiO_2 SLM1/SLM2	% Al_2O_3 SLM1/SLM2	% Fe_2O_3 SLM1/SLM2	% SO_3
Zone 1	77.5	52	17	3.2	1.1	3.4
Zone 2	78.5	40 to 45	i	i	i	4.5
Zone 3	57 to 64/40 to 50	2 to 9	45/33	9/7	2.7/2.2	0.02

i: progressively increasing from zone 1 to zone 2 amounts.

of the paste, greatly decreases between the sound and the altered zones. The change in color of the phenolphthalein, limit between zones 2 and 3, matches a significant variation of the calcium amount. Zone 2 is slightly decalcified, and the sulfur amount is higher than in zone 1. Zone 3, or altered zone, underwent an important loss in calcium. Zone 3 is constituted with silicon, aluminum, and iron. The calcium amount in the external part of the specimens is the same for both solutions: 2–3%. Sulfur is totally absent of the altered zone (Table 3).

3.3.2. CEM III paste (Figs. 8 and 9)

The nature of the chemical modifications is the same for SLM1 and SLM2 and is identical to CEM I paste. The average amounts of oxides, in the different zones of the specimens immersed in SLM1 and SLM2, are given in Table 4. It may be noticed that, in zone 3, for both aggressive solutions, the amplitude of the decalcification is the same; magnesium is progressively and totally released and the altered zone is made up almost entirely of silicon and aluminum.

3.4. Mineralogical analysis by X-ray diffraction

Figs. 10 and 11show the mineralogical characterization by XRD of CEM I and CEM III pastes immersed in SLM1 and SLM2, for each zone defined on Figs. 4 and 5 and for control specimens. In all cases, zone 1 (i.e., core) and control specimen show identical X-ray patterns.

3.4.1. CEM I paste (Fig. 10)

Zone 2 of specimens immersed in SLM1 show identical X-ray patterns as specimens in SLM2. Only X-ray patterns of zone 3 are different for SLM1 and SLM2. In zone 1, the lines of portlandite, ettringite, C_4AH_x, and of the anhydrous phases C_3S, C_2S, and C_4AF are present. The C–S–H halo, centered on the reticular distance of 3.04 Å, is also visible.

For both treatments, portlandite lines have disappeared in zone 2, whereas the lines of the C_2S and C_4AF grains as well as ettringite are still present, and the C_3S lines are reduced. Additional lines show that some calcite has formed in this zone. The C–S–H halo is preserved. A halo centered on the main line of quartz at 3.35 Å formed in zone 3. A quartz line is also observed. The C–S–H halo is absent from this zone.

In zone 3, the structure is totally amorphous for SLM1, since no line is observed. On the contrary, lines that are typical of C_4AF are present for SLM2, and their intensity is higher than in the control specimen. This may be linked with the quite amorphous nature of the structure, which tends to increase the intensity of the crystallized phases lines. Some lines are also observed in a position lightly displaced from the typical C_2S peaks. Moreover, the amplitude of the halo centered on the quartz main line is higher for SLM1 than for SLM2.

3.4.2. CEM III paste (Fig. 11)

The nature of the mineralogical modifications is identical for specimens immersed in SLM1 and SLM2. For both solutions, the alteration displays by the progressive disappearing from zones 2 and 3 of all the lines of the crystallized phases. In zone 3, a halo centered on the main line of quartz formed; the halos linked with hydrated slag and C–S–H have disappeared.

However, XRD does not enable to account for the evolution of the slag anhydrous grains through the alteration since these phases are essentially amorphous.

3.5. Observations in backscattered electrons mode and punctual analysis of anhydrous compounds with electronic microprobe

3.5.1. CEM I paste

Fig. 12 shows an observation with microprobe of the CEM I paste immersed in SLM2, in BSE mode, of zone 3 periphery, at the position defined on Fig. 4b.

Table 4
Average amounts of oxides, analyzed with electronic microprobe, in the different zones of the specimen immersed in SLM1 (pH 4) and SLM2 (pH 6)—CEM III paste

	% Tot SLM1/SLM2	% CaO	% SiO_2 SLM1/SLM2	% Al_2O_3 SLM1/SLM2	% MgO SLM1/SLM2	% SO_3 SLM1/SLM2
Z. 1	75.4	37.4	21.3	6.3	3.3	5.5
Z. 2	76.5	33 to 36	i	i	3.3	5.5/7.3
Z. 3	42 à 48/44	2 to 9	33/29	6.5 to 9.2/6 to 8.5	0 à 3	0.05

i: increasing.

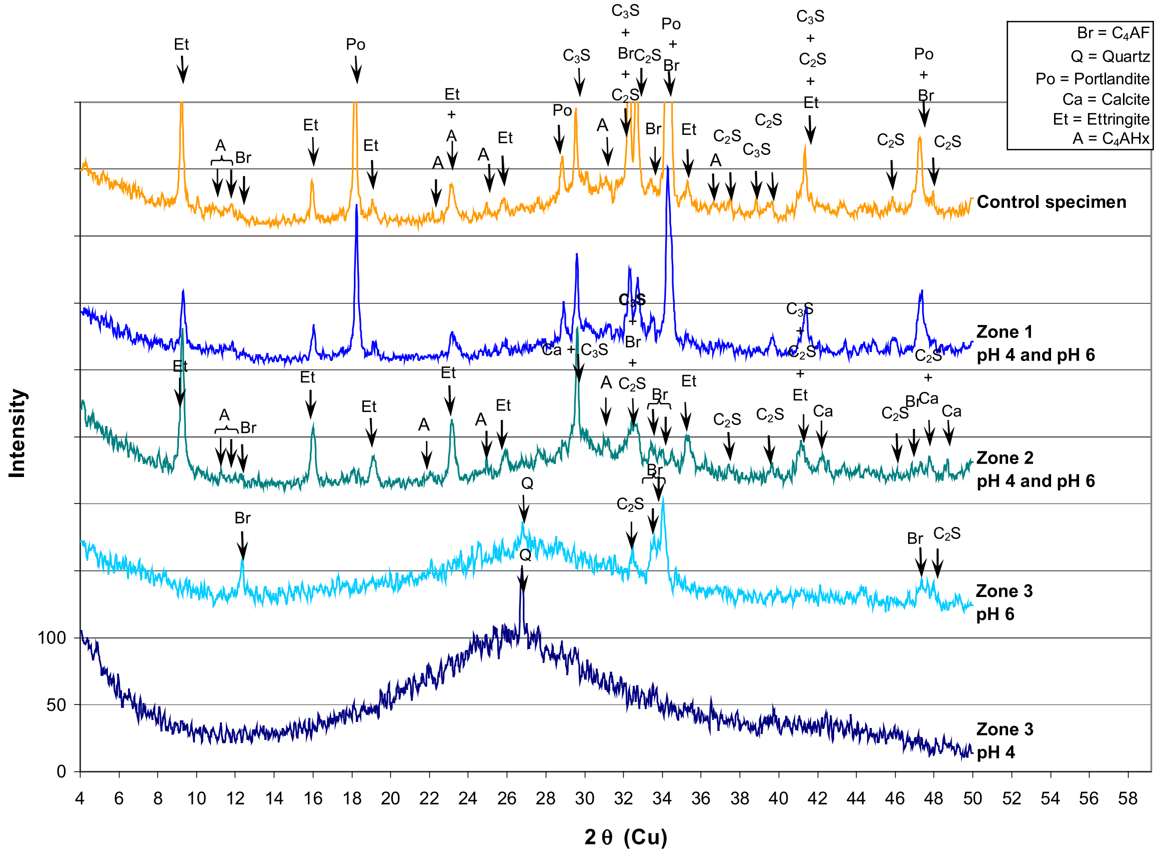

Fig. 10. X-ray patterns of the three zones of the specimen immersed in SLM1 (pH 4) and SLM2 (pH 6) after 9 weeks of immersion and of the control specimen—CEM I paste.

The analyses on light-colored compounds showed that they are residual C_4AF grains. The darker grains match anhydrous phases, probably silico-calcic phases, which underwent chemical modifications. The typical composition of these grains is given in Table 5. It may be noticed that it matches the average chemical composition of the hydrated surrounding paste.

Additionally, some little quartz grains, supposedly a small pollution of the cement, were observed and analyzed in the cement paste. It may explain the presence of the main quartz line in the diffractogram of zone 3 on Fig. 10.

Observations of zone 3 on the CEM I paste immersed in SLM1 showed the presence of C_4AF in the area next to zone 2 but its absolute absence in the external part.

3.5.2. CEM III paste

Fig. 13 shows a BSE mode observation of the CEM III paste immersed in SLM1, in the periphery of zone 3, at the position defined on Fig. 5a.

A high density of anhydrous slag grains is present in zone 3. Table 6 gives the typical compositions of slag grains in zone 3 and in zone 1 (core). The slag grains of zone 3 underwent a slight decalcification while keeping a CaO amount markedly superior to the surrounding hydrated paste. As for CEM I paste, the darker grains are likely to be silico-calcic anhydrous grains that were submitted to chemical modifications. Their composition is the same as the one provided in Table 5.

The observations realized in zone 3 of CEM III pastes immersed in SLM2 showed also a high density of slag grains. The chemical analyses proved that these grains kept their initial composition (Table 6).

4. Discussion

4.1. Comparison of the alteration kinetics at pH 4 and 6

The immersion at a pH of 4 produced a significant acceleration of the alteration kinetics observed at a pH of 6 on cement pastes monoliths. Indeed, specimens immersed in SLM1 (pH 4) showed altered depths more than 3.5-fold higher and mass losses more than 2.9-fold higher than specimens immersed in SLM2 (pH 6) at the end of the 18 weeks of the experiment. Alteration kinetics was ninefold higher in SLM1 than in SLM2. As a matter of fact, the final alteration obtained in SLM2 was achieved in just 2 weeks with SLM1.

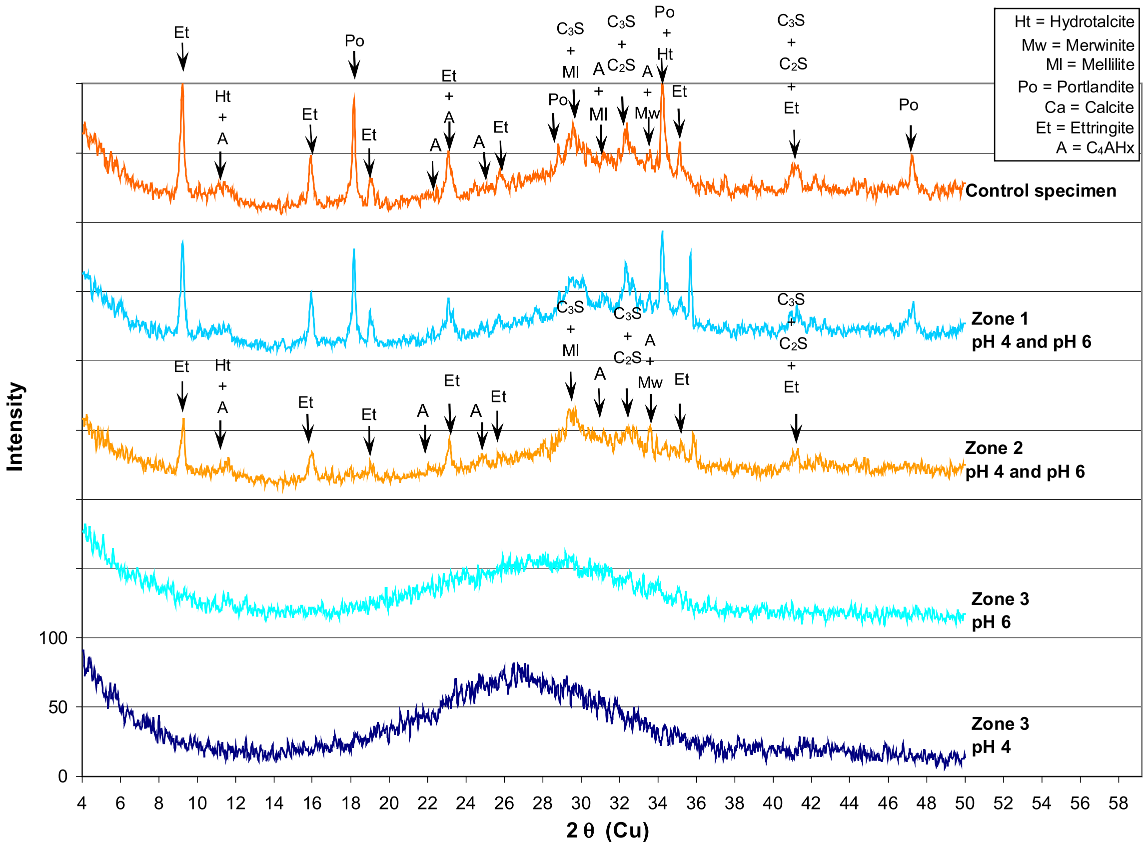

Fig. 11. X-ray patterns of the three zones of the specimen immersed in SLM1 (pH 4) and SLM2 (pH 6) after 9 weeks of immersion and of the control specimen—CEM III paste.

4.2. Comparison of the alteration mechanisms at pH 4 and 6

Calcium salts produced by the reaction of the liquid manure organic acids and the hydrates of the cement pastes are soluble to highly soluble in water [2]. Hence, they have no protective effect on the matrix, and the organic acid anions have no specific effect compared to that of the leaching enhanced by the acid/base reaction. Finally, the attack by these organic acids may be compared with the one of strong acids.

For both solutions, the altered zone shows very high porosity and very weak mechanical strength. The cement paste undergoes a chemical and mineralogical zonation: the attack occurs mainly by a progressive and almost complete decalcification of the paste and by the dissolution

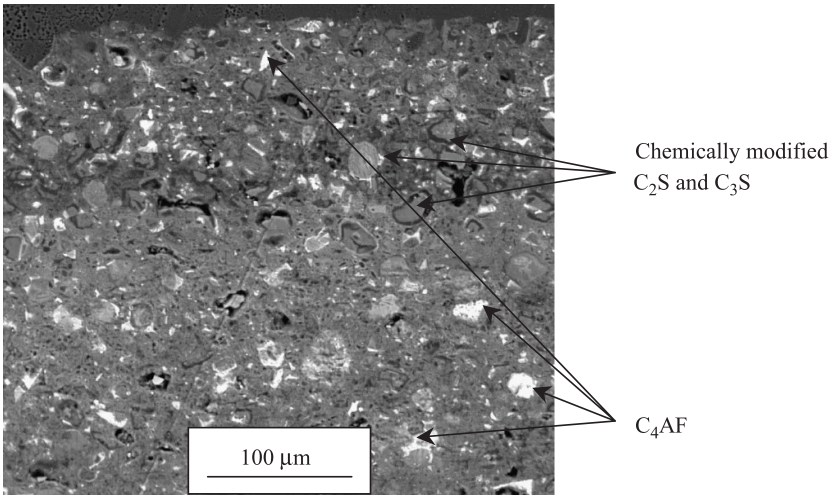

Fig. 12. Zone 3 of the CEM I paste immersed in SLM2 (pH 6)—Observation with electronic microprobe in BSE mode.

Table 5
Typical composition of anhydrous grains chemically modified in zone 3—CEM I paste

Oxides	% Tot	% CaO	% SiO_2	% Al_2O_3	% Fe_2O_3	% SO_3
Amount	46.2	1.9	33.0	6.1	2.2	0.0

Table 6
Typical composition of anhydrous grains chemically modified in zone 3—CEM III paste

Oxides	% Tot	% CaO	% SiO_2	% Al_2O_3	% MgO	% SO_3
Zone 1 (pH 4/ pH 6)	88.1	34.7	32.6	10.6	7.9	2.2
Zone 3 (pH 4)	76.3	26.6	30.0	10.3	7.5	2.1
Zone 3 (pH 6)	88.0	33.5	33.1	10.9	7.9	1.5

of all the crystallized phases for CEM I and CEM III pastes.

The alteration mechanisms are globally the same for SLM1 and SLM2. For CEM I and CEM III pastes immersed in both aggressive solutions, three zones may be observed.

– Zone 1 did not undergo any mineralogical and chemical modification for the major elements of the cement paste.
– Zone 2 is part of the sound zone, since it provokes a change in color of the phenolphthalein. Its physical and mechanical properties are markedly the same as those of zone 1, the chemical and mineralogical changes are minor. The slight decrease in the calcium amount is linked to the portlandite dissolution, confirmed by the XRD tests. For the CEM I paste, some ettringite precipitated, since sulfates diffused from the altered zone where this phase is dissolved. A part of C_3S is dissolved.
– Zone 3: the limit between zone 2 and zone 3 corresponds with a sudden drop of the CaO amount, probably linked with the dissolution of the most calcic C–S–H [C–S–H (β) and C–S–H (γ)], and the dissolution front of ettringite and C_3S and C_2S grains. For CEM III paste, the amount of magnesium, converging to 0 to the periphery of the specimens, let us suppose that the slag hydrated amorphous phases have been dissolved. Zone 3 is made up almost entirely of silicon, aluminum, and iron. Considering the CaO/SiO_2 ratio of the paste in the beginning of zone 3, it may be supposed that C–S–H (α) are preserved [12], because they are less soluble since less calcic [15]. Moreover, aluminum and iron may have incorporated in the less calcic C–S–H during hydration [16–20]. The amorphous structure of the external part of zone 3 may contain a silica gel, and eventually an Al-bearing gel, as indicated by X-ray patterns, aluminum issued from the dissolution of Al-bearing hydrated phases. This gel, although weakly mechanically resistant, is important for the durability since it constitutes a semipermeable membrane that limits the alteration kinetics. Analyses with microprobe underlined that the C_3S and C_2S grains had undergone chemical modifications; their composition matches that of the surrounding paste.

Minor differences were found between the alteration mechanisms in SLM1 and SLM2.

– The behavior of C_4AF, C_2S, and of slag anhydrous grains is different at a pH of 4 and 6. Indeed, some nonaltered C_4AF was found out in the periphery of the specimens immersed in SLM2 but not in the one immersed in SLM1. At a pH of 6, the slag grains were stable and kept their chemical composition, and in particular, their initial amounts of calcium and magnesium. The density of the anhydrous slag grains is

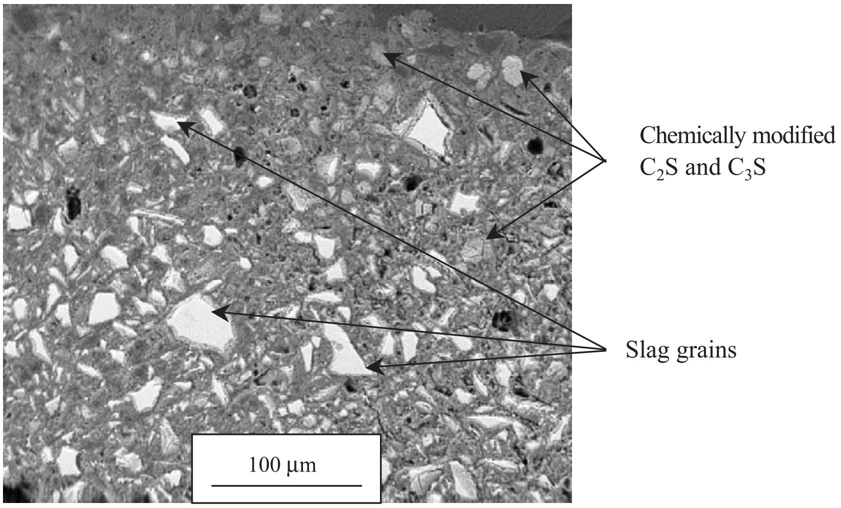

Fig. 13. Zone 3 of the CEM III paste immersed in SLM1 (pH 4)—Observation with electronic microprobe in BSE mode.

equally important at a pH of 4, but they underwent a slight decalcification. At last, some XRD lines, slightly moved from C_2S typical lines, appear on the X-ray patterns of CEM I paste at pH 6. However, analyses with microprobe showed that the silico-calcic anhydrous phases had been submitted to important chemical modifications. It might be supposed that, in spite of these modifications, C_2S phases have kept a crystallized structure during the immersion at a pH of 6 contrary to immersion at a pH of 4.

- Zone 2, transition zone between the core (zone 1) and the dissolution front of the altered zone, show a higher thickness in the case of pH 6 than in the case of pH 4. It may be assumed that, the pH difference between the core and the aggressive solution being less important at a pH of 6, the kinetics of the chemical reactions leading to the phase's dissolution are lower. Then, the diffusion phenomenon of the aggressive solution through the porosity of the paste, without being most prominent, becomes more marked. Hence, the transition zone is larger at a pH of 6 than at a pH of 4.
- At last, the amplitude of the halo centered on the quartz main line, attributed to the formation of a silica gel, is less important at a pH of 6 than at a pH of 4. This may be correlated with the mass attenuation coefficients of silicon (and aluminum) weaker compared to iron [21]. A higher proportion of silicon in the structure leads to a lower attenuation of the X-ray intensity during the measurement and hence increases the amplitude of the signal.

5. Conclusion

During this study, the alteration mechanisms of the cement-based matrix produced by two solutions of organic acids at pH values of 4 and 6 were compared. The aim was to validate the use of solutions at a pH of 4 for accelerated tests on alterations occurring to structures which come in contact with liquid manure.

At the end of the experiment, carried out on ordinary Portland cement and slag cement pastes, the immersion of hardened pastes in the solution with a pH of 4 showed kinetics of alteration (mass losses and altered depths) ninefold higher than the immersion at a pH of 6.

The analysis with electronic microprobe, by XRD and BSE mode observations, showed that the alteration mechanisms are sensibly identical. The alteration of the cement paste occurs in both cases by an almost complete decalcification, the disappearance of the crystallized or amorphous hydrated phases and the probable formation of a silica gel containing aluminum and iron, which enables to limit the kinetics of further alteration. The intensity of the alteration, in terms of decalcification and loss of magnesium, is identical for both solutions. The alteration mechanism differences between the two solutions are minor and mainly concern the stability of the anhydrous phases. Indeed, C_4AF is preserved in the periphery of the specimens immersed in the solution at a pH of 6 for CEM I paste, and is not at a pH of 4. Besides, the slag anhydrous phases, globally stable in both solutions, show, however, a light decalcification when CEM III pastes are immersed in the solution with a pH of 4.

It may be assumed that the disappearance of the C_4AF, minor phase of OPC, in the external zone of the specimen at a pH of 4 does not have a great influence on the alteration of the CEM I paste. Hence, it can be considered that the use of solutions at a pH of 4 to carry out accelerated studies of the organic acids aggression on the cement-based matrix allows suitable simulation of the alteration mechanisms of liquid manure on concretes.

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