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Cement pastes alteration by liquid manure organic acids: Chemical and mineralogical characterization

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Abstract

Liquid manure, stored in silos often made of concrete, contains volatile fatty acids (VFAs) that are chemically very aggressive for the cementitious matrix. Among common cements, blast-furnace slag cements are classically resistant to aggressive environments and particularly to acidic media. However, some standards impose the use of low C_3A content cements when constructing the liquid manure silos. Previous studies showed the poor performance of low-C_3A ordinary Portland cement (OPC). This article aims at clarifying this ambiguity by analyzing mechanisms of organic acid attack on cementitious materials and identifying the cement composition parameters influencing the durability of agricultural concrete. This study concentrated on three types of hardened cement pastes made with OPC, low-C_3A OPC and slag cement, which were immersed in a mixture of several organic acids simulating liquid manure. The chemical and mineralogical modifications were analyzed by electronic microprobe, XRD and BSE mode SEM observations. The attack by the organic acids on liquid manure may be compared with that of strong acids. The alteration translates into a lixiviation, and the organic acid anions have no specific effect since the calcium salts produced are soluble in water. The results show the better durability of slag cement paste and the necessity to limit the amount of CaO, to increase the amount of SiO_2 (i.e., reduction of the Ca/Si ratio of C-S-H is not sufficient) and to favor the presence of secondary elements in cement.

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

1. Introduction

In many countries, excessive manure spreading is the cause of sensitive environmental problems: pollution of soil, air and water natural reserves, particularly in highly concentrated farming areas [1]. To control this pollution, manure needs to be stored in watertight silos often made of concrete.

Liquid manure contains both mineral and organic compounds, in various quantities, among which are volatile fatty acids (VFAs), such as acetic, propionic, butyric, isobutyric and valeric acids. Because of the presence of both these acids and the acidobasic couple NH_4^+/NH_3, the pH of liquid manure is maintained between 6 and 8 [2–5]. Because of the VFAs, liquid manure constitutes a chemically aggressive environment toward the concrete of agricultural structures such as manure pits, cowsheds or milking rooms. Organic acids react with several hydrates of the cement paste (portlandite, C-S-H and hydrated aluminates) to produce calcium and aluminum salts, whose solubility in water varies from high to very high [6–8]. In an immersion situation, those actions on concrete lead to the hydrates' lixiviation, increase in paste porosity and decrease in mechanical resistance, resulting in reinforcement corrosion.

Blast-furnace slag cements are known to offer good resistance to aggressive environments, particularly to acidic media. Furthermore, the French standard [9], among other standards, imposes the use of low C_3A content cement (PM/ES qualification in European designation) when constructing structures intended to contain liquid manure. However, previous studies pointed out the poor performance of mortars designed with low C_3A content ordinary Portland cement (OPC) [10,11]. These elements emphasize the necessity of identifying an effective binder in agricultural environment.

This study aims at analyzing the mechanism of organic acid actions on the cementitious matrix as well as breaking down the cements' composition parameters influencing the durability in acidic environment. Hardened cement paste

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Table 1
Chemical composition of cements

	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 I 52.5 PM/ES	63.56	21.54	2.63	4.34	0.73	0.10	0.21	0.56	0.12	3.06	2.53
CEM III/B 42.5	46.67	30.94	8.92	1.15	5.71	0.39	0.46	0.22	0.06	2.47	1.75

specimens were immersed in a solution composed of a mixture of several organic acids, simulating liquid manure. Three cements were tested: an OPC, designated CEM I in the European standard [12], a low C_3A content OPC, designated CEM I PM/ES, and a blast-furnace slag cement, designated CEM III/B, also qualified as PM/ES. This study is based on both chemical and mineralogical specimen analyses using an electronic microprobe and an X-ray diffractometer. The modifications in the altered specimen were measured taking depth into account. The results of this study allow one to highlight the composition parameters of cement binder favoring durability.

2. Experimental process

2.1. Materials

This study was conducted on pastes made with three different cements: an OPC, designated in European Standard as CEM I 52.5 R [12] (28-day measured compressive strength on mortars, $R_{c,28} = 64.1$ MPa), a low C_3A content OPC, or CEM I PM/ES 52.5 ($R_{c,28} = 67.6$ MPa) and a cement containing 68% blast-furnace slag, or CEM III/B 42.5 ($R_{c,28} = 55.3$ MPa). The cements' compositions are given in Table 1.

2.2. Specimen making and treatment

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

The aggressive solution is a mix of five organic acids found in liquid manure: acetic, propionic, butyric, isobutyric and valeric acids. The concentrations of these acids in the solution match the maximum values that can occur in real pig slurries. To this immersion solution (initial pH 2.7) is added 2 g/l NaOH to bring the pH to 4. Table 2 shows the composition of the aggressive solution as well as the pK_a of the organic acids. During the experiment, a pH value of 4 was maintained by using a mixture of undiluted acids. Every 6 weeks, the solution was renewed. The solid–liquid volume ratio is 0.059.

2.3. Tests implemented

2.3.1. Kinetics comparative tests

Two comparative parameters of durability were monitored on the paste specimens: altered depth and mass variations. These parameters were measured on the following terms: 0, 1st, 2nd, 4th, 9th, 13th, 18th week of immersion. To quantify the altered depth, two specimens were sawn perpendicularly to their axis and a small amount of phenolphthalein was sprayed on the right sections. The depth of the color change, considered as matching the altered depth, was measured with a video microscope on 16 points distributed on the perimeter of the discs.

The mass loss measurements were performed on two immersed specimens after first wiping the specimens.

2.3.2. Chemical and mineralogical characterization

To characterize chemical modifications of the specimen, analyses with a CAMECA SX 50 electron microprobe were done. The accelerating voltage was 15 kV, the current strength was 10 nA and the scanning area of the beam was 5×5 μm^2. The measurements were done on flat, polished sections, according to depth in the altered and healthy zones up to the center of the specimen (about 12.5-mm depth). Particular care was given to the choice of the analyzed points to get only the hydrated paste and to avoid anhydrous grains. The following elements were analyzed: Ca, Si, Al, Fe, Mg, S, K and Na.

These analyses were performed on two immersed specimens, for each type of paste, after the 1st, 4th and 9th week of immersion. Only the results of the 4 weeks of immersion

Table 2
Composition of the aggressive solution and pK_a of the acids

Constituents	Acids					Sodium hydroxide (NaOH)
	Acetic (CH_3COOH)	Propionic ($C_2H_6O_2$)	Butyric ($C_4H_8O_2$)	Isobutyric ($C_4H_8O_2$)	Valeric ($C_5H_{10}O_2$)	
Concentration (g/l)	12.8	2.8	1.6	0.6	0.3	2
pK_a	4.8	4.9	4.8	4.85	4.8	strong base

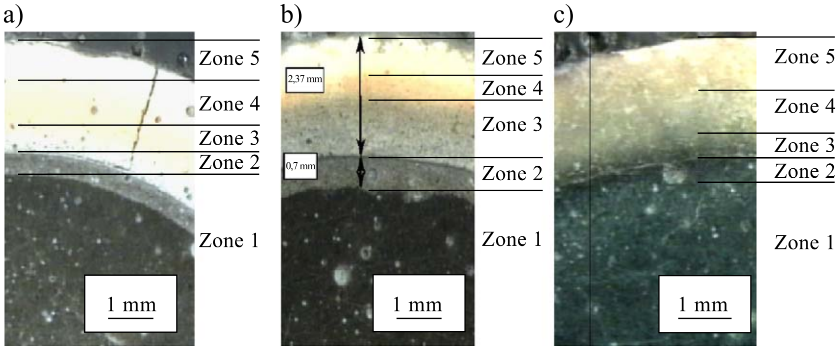

Fig. 1. Altered hardened cement paste cross sections after 4 weeks of immersion in the aggressive solution. (a) CEM I; (b) CEM I PM/ES; (c) CEM III/B.

are presented here. Two control specimens for each type of paste were analyzed, at the rate of 50 points per specimen, 5 weeks after pouring.

Mineralogical analyses using X-ray diffraction were completed on the specimens with a SIEMENS D5000 diffractometer fitted with a cobalt cathode. The anode voltage was 40 kV and the current strength was 30 mA. The measurements were performed on two specimens of the same paste as a function of depth in the healthy and altered zones after 9 weeks of immersion. These analyses

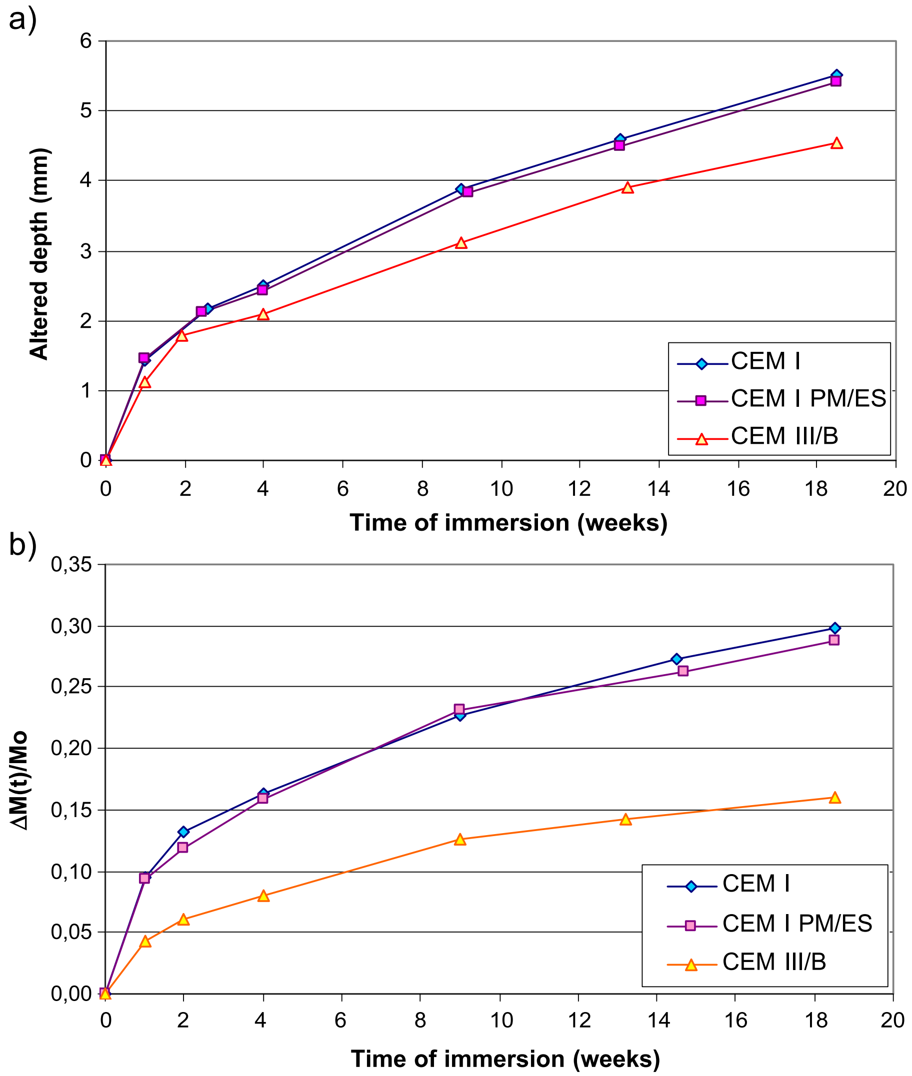

Fig. 2. Evolution of durability parameters for CEM I, CEM I PM/ES and CEM III/B pastes according to the time of immersion. (a) Altered depth; (b) mass relative variation: $\Delta M(t)/M_0=[M(t=0)-M(t)]/M(t=0)$.

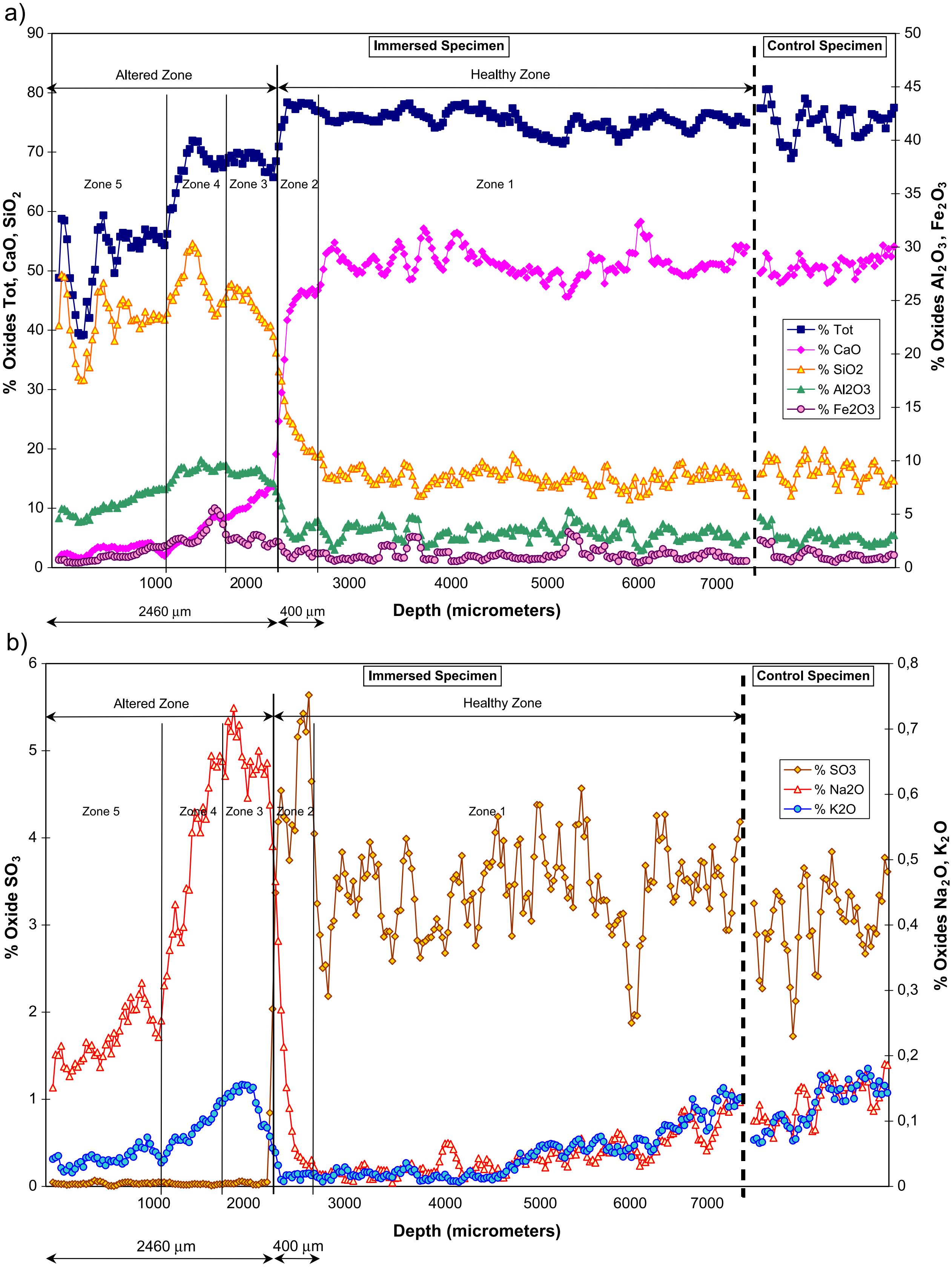

Fig. 3. CEM I paste chemical analysis with microprobe according to depth after 4 weeks of immersion. Absolute amounts of oxides (a) CaO, SiO_2, Al_2O_3, Fe_2O_3, total; (b) SO_3, Na_2O, K_2O.

Table 3
Average amounts of oxides, analyzed with electronic microprobe, in the different zones of the CEM I paste specimen immersed in synthetic liquid manure

Zone	% Total	% CaO	% SiO_2	% Al_2O_3	% Fe_2O_3	% SO_3	% Na_2O	% K_2O
1	75	51	15	3.3	1.2	3.4	0.02–0.14	0.01–0.13
2	78	44–48	i	i	i	4.7	i	i
3	69	9.3–14	45	8.8	2.6	0.02	0.66	0.14
4	65	3.6–9.2	47	8.8	3.0	0.02	0.28–0.66	0.07–0.13
5	52	3.0	41	4.6–7.9	0.70–2.0	0.02	0.15–0.28	0.02–0.06

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

were performed on the plane sides of the cylinders. The altered zone in the radial direction was carefully removed to keep the altered zone in the axial direction. The first analysis was done on the plane external face of the specimen, which was then abraded and submitted to the next analysis. The last analysis, which corresponded to the healthy zone of the specimen, was done at a 15-mm depth. A control specimen was also analyzed 5 weeks after pouring. The specimen holder that was used during the XRD measurement was made of aluminum.

The previous results have been collated to scanning electron microscopy observations in backscattered electron mode on polished sections.

3. Results

3.1. Observations with video microscope

Fig. 1a, b and c shows a cross section of CEM I, CEM I PM/ES and CEM III/B paste specimens, respectively, after 4 weeks of immersion in the aggressive solution.

The healthy zone was considered as being the basic zone where the color turns violet during the phenolphthalein test. The altered zone had very weak mechanical resistance and was very porous.

Inside the healthy zone of the CEM I and CEM I PM/ES pastes, two distinct zones were visible: the heart, marked Zone 1, having the same color pattern as the control specimen and, next to the altered zone, a light-colored paste layer of some hundreds of micrometers deep, marked Zone 2.

The altered zone of the CEM I and CEM I PM/ES cement pastes showed three zones colored differently: a gray-brown layer inside the altered zone (Zone 3), a yellowish layer on the outside of the altered zone (Zone 5) and, in the middle zone, an orangey layer (Zone 4).

Two distinct zones were visible inward from the healthy zone of CEM III/B: the core, marked Zone 1 (the blue color of which is characteristic of slags), and a darker paste layer, marked Zone 2, with a thickness of 100 µm. Zone 2 was more or less visible from one specimen to another, but was well identified on backscattered electron pictures.

The altered zone of the CEM III/B pastes showed three different zones: the inside layer was dark blue (Zone 3), the outside layer (Zone 5) was whitish and the middle zone (Zone 4) had an intermediate color.

3.2. Altered depths and mass loss evolution

Fig. 2a and b represents the evolution of the specimen's altered depths and mass losses according to the time of immersion for the three types of hardened cement pastes.

The graphs showed the same tendency: CEM I and CEM I PM/ES behaved markedly in the same way and had alteration kinetics more important than CEM III/B paste, although CEM III/B cement had the lowest normal strength.

After 4 weeks of immersion, the altered depths for CEM I, CEM I PM/ES and CEM III/B pastes were 2.5, 2.4 and 2.1 mm, respectively. The mass losses were 16%, 16% and 8%, respectively.

3.3. Chemical analysis with electronic microprobe

3.3.1. CEM I and CEM I PM/ES pastes

The results of the analysis of the CEM I pastes that were immersed in the aggressive solution, according to depth, and of the control specimen are shown in Fig. 3a and b. The chemical analysis data are given as absolute percentages of the oxide amounts. Therefore, the sum of all the oxide amounts gives an indication of the compactness of the cement paste.

The amounts of main oxides CaO and SiO_2, secondary oxides Al_2O_3, Fe_2O_3, SO_3, Na_2O and K_2O and the sum of all the oxides are given. To improve legibility, the curves were smoothed, each point being the average value of five points in the initial curve.

On each graph, Zones 1 to 5, as defined in Fig. 1a, are reported. Table 3 provides the average amounts of oxides in each zone. From the inside to the outside of the specimens, Fig. 3a and b shows that:

- Zone 1 has the same chemical composition as the control specimen, except for Na_2O and K_2O, the amounts of which decrease in Zone 1 until about 0 next to Zone 2 (Table 3).
- The change in color of the phenolphthalein, limit between Zones 2 and 3, matches a substantial variation of the CaO amount and a great decrease of the total amount of oxides, i.e., the compactness of the paste.

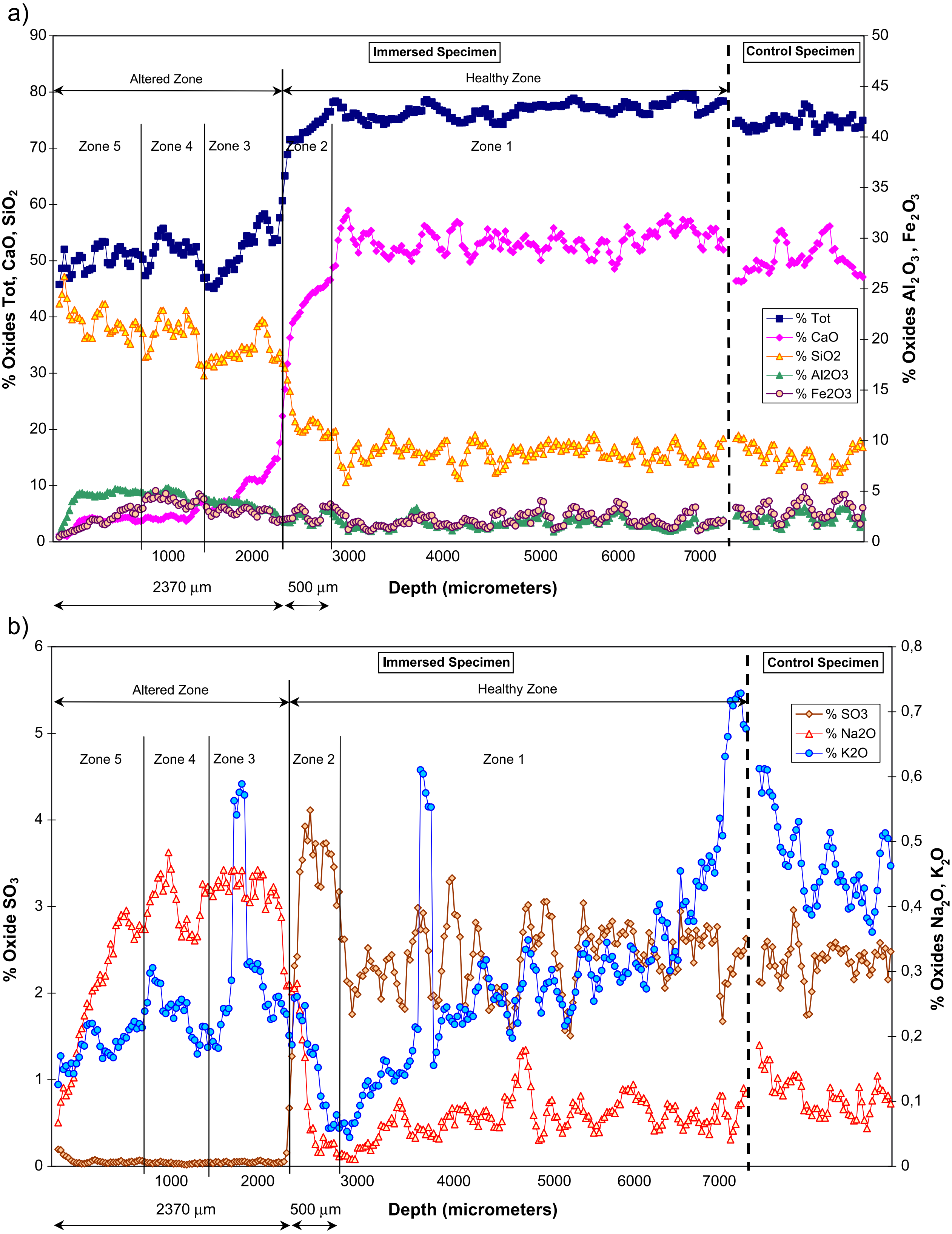

Fig. 4. CEM I PM/ES paste chemical analysis with microprobe according to depth after 4 weeks of immersion. Absolutes amounts of oxides (a) CaO, SiO_2, Al_2O_3, Fe_2O_3, total; (b) SO_3, Na_2O, K_2O.

Table 4
Average amounts of oxides, analyzed with electronic microprobe, in the different zones of the CEM I PM/ES paste specimen immersed in the synthetic liquid manure

Zone	% Total	% CaO	% SiO_2	% Al_2O_3	% Fe_2O_3	% SO_3	% Na_2O	% K_2O
1	77	53.4	16	1.8	2.2	2.4	0.02–.11	0.06–0.60
2	72–76	39–45	i	i	i	3.5	i	i
3	52	8.0–15	35	3.6	2.9	0.05	0.42	0.32
4	51	3.9–7.5	37	4.6	4.0	0.05	0.41	0.24
5	50	3.9	39	4.8	0.48–3.18	0.06	0.07–0.39	0.15–0.24

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

- Zone 2 is slightly decalcified, although Zones 3 to 5 underwent an important loss in calcium (Table 3). The amount of CaO in Zone 5 is 2–3%. In Zone 2, the SO_3 amount is higher than in Zone 1 (Table 3), and the amounts of SiO_2, Al_2O_3 and Fe_2O_3 increased.
- The altered zone shows enrichments occurring mainly in Zones 3 and 4. They are important for SiO_2, significant for Al_2O_3 and slight for Fe_2O_3. SO_3 is totally absent from the altered zone.
- The amount of Na_2O is severalfold higher in Zones 3 and 4 than its maximum in Zone 1. The range of the K_2O higher amount in Zones 3 and 4 is the same as the maximum value in Zone 1 (Table 3). The amounts of alkaline oxides decrease when approaching the surface of the specimen (Zone 5).

The curves of the amount of oxides in the CEM I PM/ES pastes had the same tendency as CEM I pastes (Fig. 4a and b). The amount of oxides for this binder in the different zones defined in Fig. 1b is given in Table 4.

3.3.2. CEM III/B paste (Fig. 5)

Analysis results of the specimens that were immersed in the aggressive solution, according to depth, and of the control specimen are given in Fig. 5a and b. The amount of main oxides CaO and SiO_2, of secondary oxides Al_2O_3, MgO, SO_3, Na_2O, K_2O and the sum of all the oxides amount are given. The average amounts of oxides in the different zones of the specimens are given in Table 5.

The nature of the chemical modifications for the analyzed elements is quite identical to that of CEM I and CEM I PM/ES pastes.

In Zones 3 to 5, the amplitude of the decalcification is the same as CEM I paste, MgO is progressively and totally dissolved and SiO_2 and Al_2O_3 amounts are more significant as compared to Zone 1.

3.4. Mineralogical analysis by X-ray diffraction

Figs. 6 and 7 show the mineralogical characterization by XRD of CEM I and CEM III/B pastes, respectively, according to depth. The X-ray patterns of CEM I PM/ES paste, which were markedly the same as that of CEM I paste, are not reported.

Each figure presents the X-ray patterns of the immersed specimen in each zone described previously, as well as the X-ray pattern of the corresponding control specimen.

For each type of paste, Zone 1, constituting the bulk of the altered zone, showed markedly the same X-ray patterns as the control specimen.

3.4.1. CEM I paste (Fig. 6)

- In Zone 1, the peaks of the following crystals were present: portlandite, ettringite, C_4AH_x, the anhydrous phases C_3S and C_2S, and brownmillerite (C_4AF). The C-S-H halo, centered on a reticular distance of 3.04 Å, was visible in the central part of the graph. A slight halo was visible in aluminate zones (reticular distance of about 8 Å); which might be linked with a measurement artifact caused by the use of a specimen holder in alumina.
- In Zone 2, portlandite peaks had disappeared, whereas the peaks of the C_3S, C_2S and anhydrous C_4AF as well as ettringite were still present, and those of C_3S and C_2S being slightly decreased. Additional peaks showed that some calcite has formed in this zone. The C-S-H halo was preserved.
- In Zone 3, crystallization of gismondite, eventually substituted by sodium $(Ca,Na_2)O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}4H_2O$, occurred. C_4AF was still present but was partly dissolved, and other crystals had disappeared. The C-S-H halo was largely reduced and another one had formed, centered on the main peak of quartz at 3.35 Å, which might be attributed to a silica gel.
- For the X-ray patterns of Zones 4 and 5, the structure was completely amorphous. The halo centered on the main ray of quartz silica gel was far more pronounced. A large part of the C-S-H was dissolved. The halo centered around 2 Å seemed to have developed. This may be the contribution of the artifact mentioned earlier and of the formation of an alumina gel in this zone.

3.4.2. CEM III/B paste

Fig. 7 shows the mineralogical characterization by XRD, according to depth, of the CEM III pastes immersed in the aggressive solution. The graph provides the X-ray patterns of the altered specimens for each zone defined in Fig. 1c and

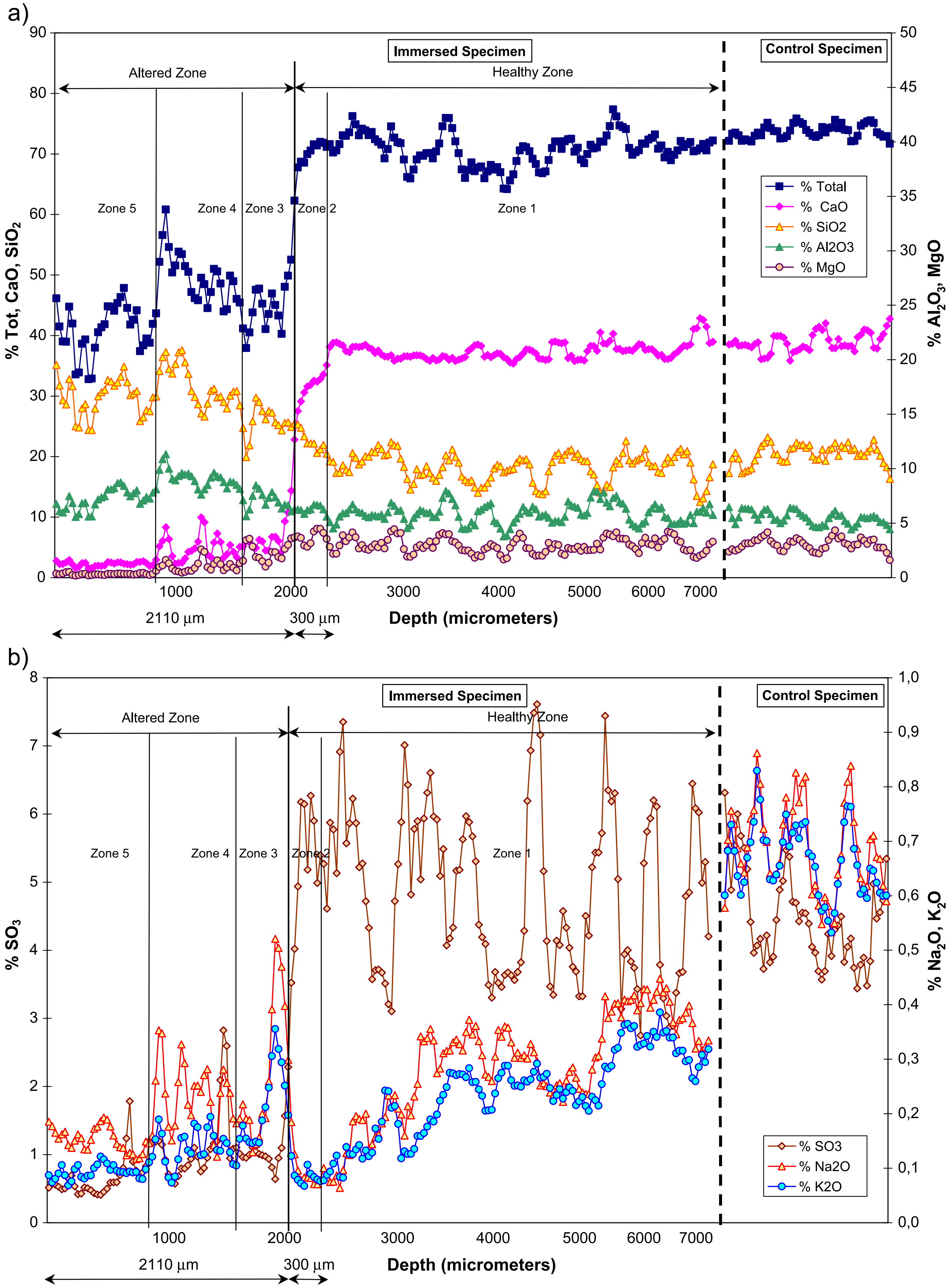

Fig. 5. CEM III/B paste chemical analysis with microprobe according to depth after 4 weeks of immersion. Absolutes amounts of oxides (a) CaO, SiO_2, Al_2O_3, MgO, total; (b) SO_3, Na_2O, K_2O.

Table 5
Average amounts of oxides, analyzed with electronic microprobe, in the different zones of the specimen immersed in the synthetic liquid manure—CEM III paste

Zone	% Total	% CaO	% SiO_2	% Al_2O_3	% MgO	% SO_3	% Na_2O	% K_2O
1	71	37	18	5.9	3.0	4.8	0.10–0.36	0.10–0.44
2	68–71	28–34	i	i	3.5	4.3	0.13	0.17
3	43	5.0–9.3	26	7.2	2.1	0.97	0.19	0.23
4	50	5.0	32	9.1	1.1	1.1	0.14	0.24
5	41	2.3	30	7.2	0.33	0.66	0.09	0.15

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

also the X-ray pattern of the control specimen. The alteration is shown by the progressive disappearing of the peaks of all the crystallized phases (anhydrous and hydrated compounds) in Zones 2 to 5: portlandite, ettringite, carbonated hydrotalcite $Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$, C_4AH_x, and the anhydrous phases C_3S, C_2S, merwinite $3CaO\cdot MgO\cdot SiO_2$ and melilite $4CaO\cdot Al_2O_3\cdot MgO\cdot SiO_2$.

In Zones 3 to 5, a halo centered on the main peak of quartz formed, whereas the C-S-H halo and the halo that is characteristic of the phases coming from the slag hydration have disappeared.

Because the anhydrous slag is essentially amorphous, XRD does not allow the determination of the anhydrous grains evolution in the different zones of the specimens.

3.5. SEM observations in backscattered electron mode

Fig. 8 shows the areas next to the limit between the altered and healthy zones for CEM I (Fig. 8a) and CEM III (Fig. 8b) pastes after 4 weeks of immersion.

For both pastes, the healthy zone was visibly denser than the altered zone. The alteration front appeared markedly between Zones 2 and 3. The cracks in Zone 3 stem from shrinkage occurring in the altered zone during the specimen drying.

For CEM I paste, Zone 2 is composed of dense anhydrous grains (black colored) slightly less important than Zone 1; however, the number of grains is still very large. In the altered zone, some of the anhydrous grains were dissolved, most of them having changed shade:

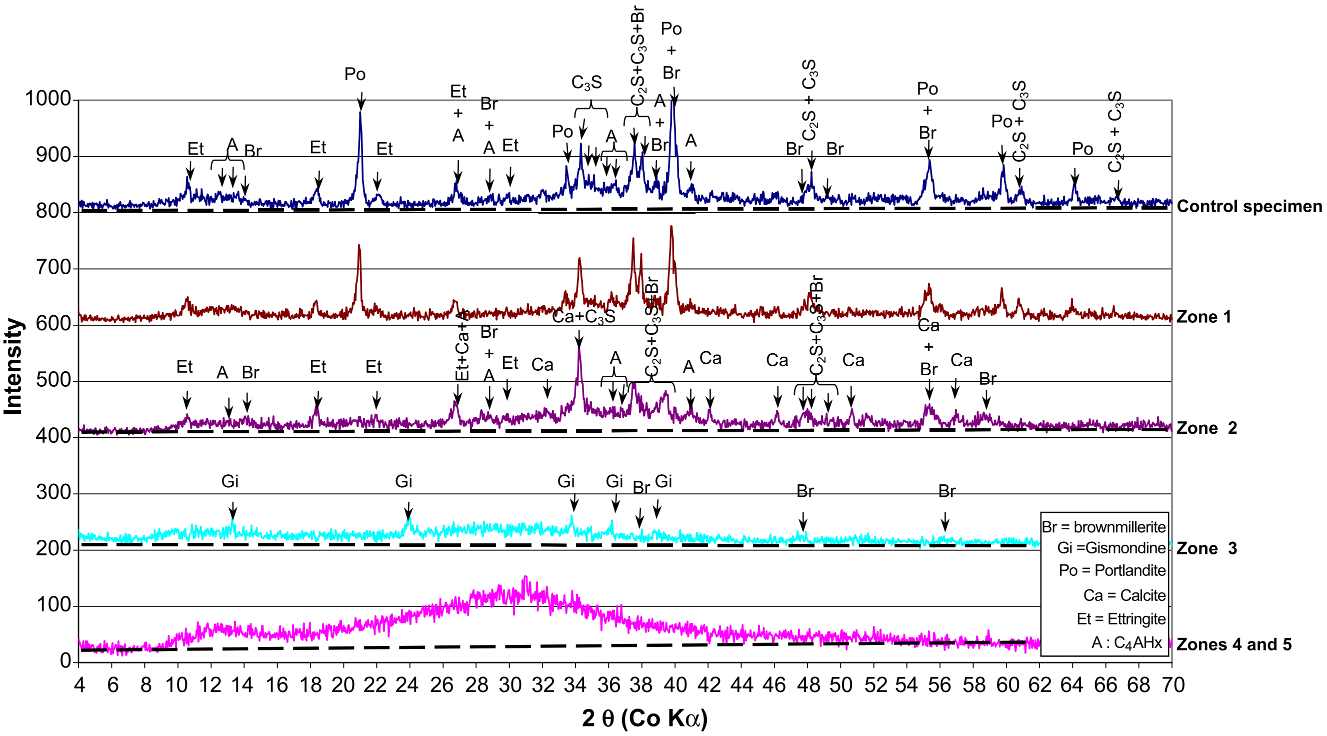

Fig. 6. Mineralogical analysis by XRD of the CEM I paste after 9 weeks of immersion—five zones of the immersed specimen and control specimen X-ray patterns.

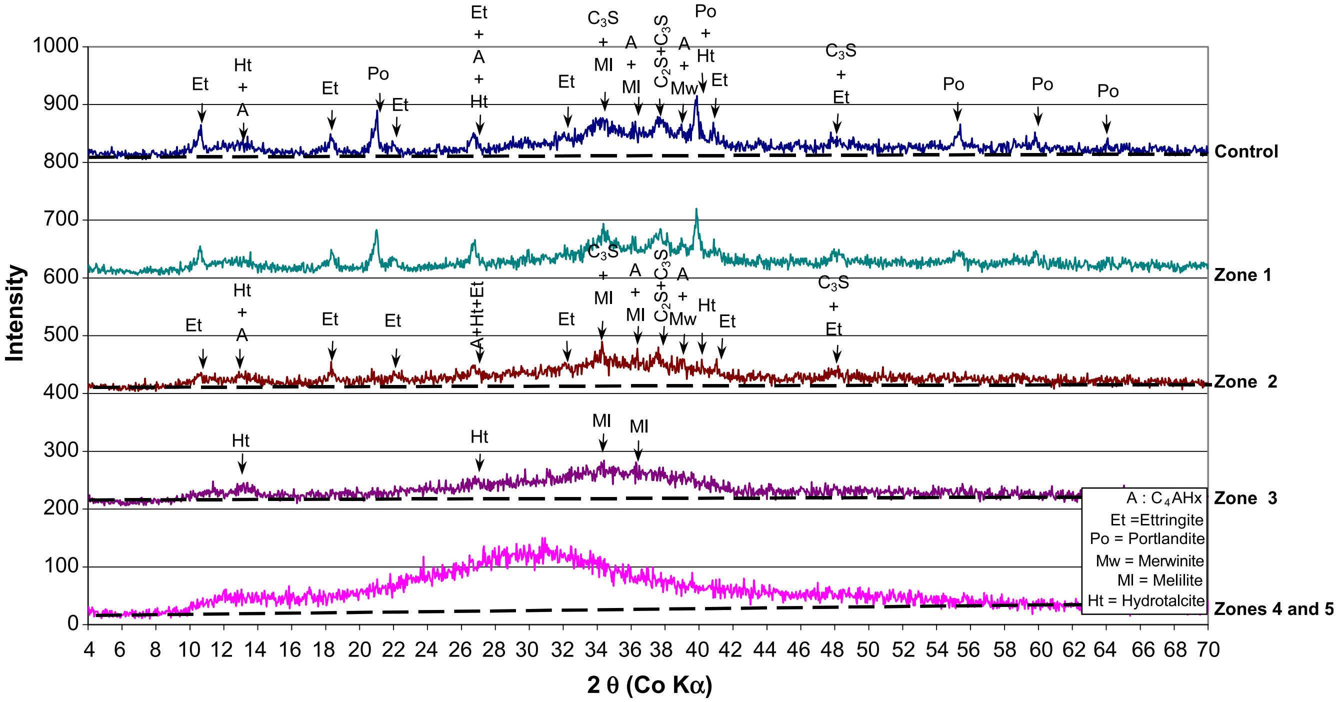

Fig. 7. Mineralogical analysis by XRD of the CEM III/B paste after 9 weeks of immersion—five zones of the immersed specimen and control specimen X-ray patterns.

their density seemed to be intermediary between that of the altered zone paste and the healthy zone paste. In Zone 3, only the C_4AF was clearly visible and kept its shade.

Observation of the CEM III/B specimen shows that the quantity of anhydrous grains present in the heart, mainly blast-furnace slag grains, was higher than in CEM I and CEM I PM/ES pastes. There was no significant difference between Zone 1 and 2. The amount of nondissolved anhydrous grains in Zone 3 and 4 is much higher. They were blast-furnace slag grains. Between Zonez 3 and 4, the shade difference of the hydrate paste indicated the decrease in compactness.

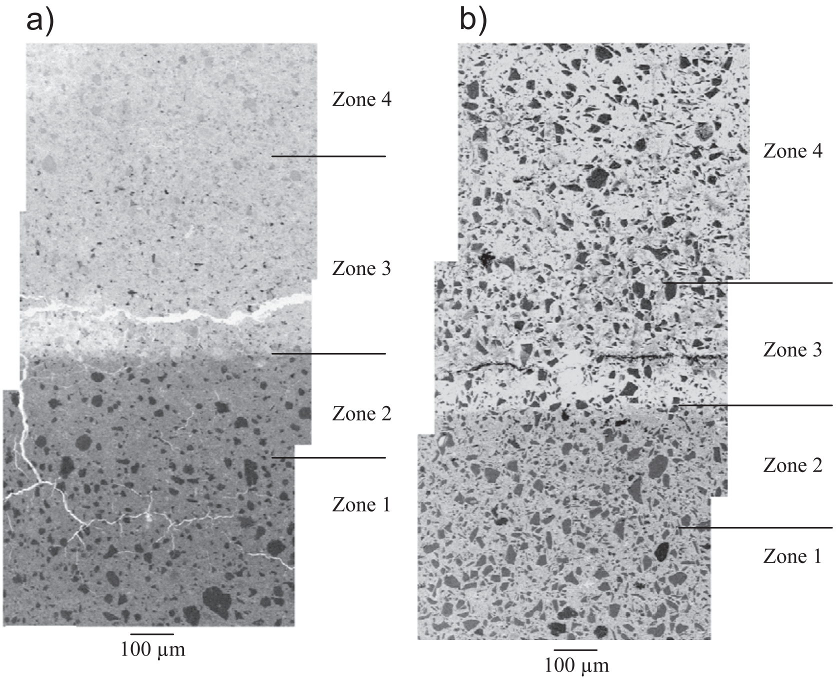

Fig. 8. SEM observation in BSE mode of the area next to the limit between healthy and altered zone: (a) CEM I paste; (b) CEM III paste after 4 weeks of immersion.

4. Discussion

4.1. Analysis of alteration mechanisms by organic acids

The chemical reactions between the cementitious matrix and the organic acids produce calcium and aluminum salts soluble to highly soluble in water [7,8]. Hence, they have no protective effect on the matrix, and the organic acid anions have no specific effect compared to that of the lixiviation enhanced by the acidobasic reaction. The attack by the organic acids of liquid manure may then be compared with that of strong acids.

The altered zone, distinguished from the healthy zone by the change in color of the phenolphthalein, shows very high porosity and very weak strength. The cement paste undergoes a chemical and mineralogical zonation. The matrix alteration occurs mainly by a progressive and almost complete decalcification and by the dissolution of all the crystallized phases (hydrated and anhydrous compounds) for CEM I, CEM I PM/ES and CEM III pastes.

For all the pastes, the alteration mechanisms were quite the same and are the following.

- In Zone 1, the mineralogical structure and the average chemical composition are the same as that of control specimens, except for the alkaline oxides. The binding forces of these ions to the paste are weak since they are adsorbed on the surface of some hydrates and they progressively diffuse from Zone 1 to Zones 3 to 5 (see below).
- Zone 2 or transition zone between the core and the altered zone shows a slight decalcification linked with the portlandite dissolution as shown by XRD and microprobe analysis.

  For the CEM I paste, some ettringite precipitated, since sulfates diffused from Zones 3 to 5, where this phase is dissolved. This result was validated by other works on alteration of Portland cement pastes by demineralised water [13]. A part of C_3S is dissolved in Zone 2.

  Calcite formation in Zone 2, where pH is greater than 9.5 (phenolphthalein color change), may be linked to the precipitation of the Ca^{2+} and $CO_3{}^{2-}$ ions, stemmed with the portlandite dissolution, and the dissolved CO_2 in solution, respectively.

  For CEM I paste, BSE mode observations and analysis by XRD showed that some C_3S grains were partly modified in this zone.
- Limit between Zones 2 and 3 corresponds with a considerable drop of the CaO amount, which may be linked with the dissolution of the most calcic C-S-H [14] (C-S-H (β) and C-S-H (γ) [15]). Indeed, CaO/SiO_2 ratio is >2 in Zone 2, and <1 in Zone 3. C-S-H (γ) and (β) have CaO/SiO_2 ratios >1.5 and >1, respectively. Hence, it may be concluded that these forms of C-S-H were dissolved. This limit matches also the dissolution front of ettringite and C_3S and C_2S grains.
- Zones 3 to 5 (altered zone). These zones have undergone enrichments: important in silicon, significant in aluminum and slight in iron.

Considering the amount of CaO in Zone 3, it may be supposed that C-S-H (α), less soluble since less calcic [14], is preserved. Indeed, assuming that the silica enrichment in Zone 2 to 5 largely results in silica gel precipitation (as shown by XRD), the CaO/SiO_2 mass ratio of the remaining C-S-H is between 0.71 and 0.89. Other enrichments may partly be linked to the incorporation of aluminum and iron in this less calcic C-S-H, as many authors have shown [16–19].

In Zones 4 and 5, structure is completely amorphous and is made up almost entirely of silicon, aluminum and iron. The X-ray patterns indicated that this zone may contain a silica gel. It might be supposed that this gel is enriched with aluminum and iron. This gel, although weakly mechanically resistant, is important for the durability since it constitutes a semipermeable membrane that limits the alteration kinetics.

The silica, aluminum and iron enrichments of the paste may be linked with the diffusion of the corresponding ions from Zones 1 and 2. Indeed, silica activity is minimal and constant for pH <9.5, and aluminum and iron ion activities are minimal for pH of 6 and 8.5, respectively, and increase below and beyond these pH values. Hence, these ions in interstitial solution diffuse from the healthy zone to the altered zone, and precipitate in the altered zone.

The enrichment in alkaline ions may be linked with the interaction between alkaline ions and C-S-H [20–23], among others. The negative surface charge of the C-S-H at low Ca/Si provokes the alkaline ion adsorption on C-S-H. Alkali retention increases when Ca/Si of the C-S-H decreases [20,21,23]. Hence, it might be assumed that part of the alkaline ions are adsorbed on the remaining C-S-H (α). The amounts of alkaline ions decrease in Zones 4 and 5, which might be linked with the dissolution of the C-S-H (α). The remaining amount of alkaline may be bound by adsorption on the surface to the silica gel that might have formed in the altered zone.

The differences, in the altered zone, between the CEM I and CEM III binders are minor and mainly concern the residual anhydrous grains. In OPCs, the most stable anhydrous grains in acidic medium being C_4AF, only those are observed in Zone 3; no anhydrous grain is observed in Zones 4 and 5. For CEM III paste, a large amount of slag grains are observed in Zones 3 to 5.

For CEM III paste, with 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.

4.2. Analysis of cement composition parameters influencing the durability of the porosity pastes in acidic environment

On the basis of the previous considerations, it may be concluded that:

- The amount of calcium is the first unfavorable composition parameter. Decreasing the C-S-H Ca/Si ratio is not sufficient, as a study, done at the same time on CEM I added with 10% silica fume pastes, showed an intermediary behavior of this binder between CEM I and CEM III pastes. The amount of CaO has to be limited in cement-based materials submitted to acidic environments.
- The amount of silicon in the binder is a positive parameter since reducing of the C-S-H Ca/Si ratio allows the precipitation of more stable C-S-H in acidic environment.
- The amount of aluminum and iron is also a favorable parameter: the incorporation of aluminum in a C_3S paste allows one to improve the charges balancing in the C-S-H structure but does not stabilize on its own the superficial layer [18]. However, iron can substitute for calcium in C-S-H and helps to avoid their total dissolution when the paste is largely decalcified [19,20].

These elements are confirmed by the results of the comparative study of the three pastes (Section 2.2). The CEM III/B pastes, which are more resistant to the aggression than the CEM I pastes, contain a lower amount of calcium and a higher amount of silicon. As indicated by SEM observations, CEM III/B pastes also contain more anhydrous grains.

5. Conclusion

During this study, the alteration mechanisms of the cementitious matrix by the organic acids were analyzed using electronic microprobe and X-ray diffraction. The attack by the organic acids of liquid manure may be compared with that of strong acids. The alteration translates into a lixiviation, and the organic acid anions have no specific effect, since the calcium salts produced are soluble in water. The results show that the alteration is translated into a decalcification of the altered zone, and a modification of the microstructure manifesting itself by the progressive dissolution of all the crystallized phases and the formation of a probable silica gel enriched with silicon, aluminum and iron in the superficial layer.

The altered zone thus constituted has poor mechanical resistance but is not dissolved and then constitutes a semi-permeable membrane that slows down the alteration kinetics.

Previous results show the necessity to limit the amount of CaO, to increase the amount of SiO_2 and to favor the presence of secondary elements such as iron and aluminum in cement, to improve durability in acidic environment. The quantity of residual anhydrous grains seems to be a favorable parameter: some complementary studies are necessary to clearly identify their role.

For this type of aggression, it clearly appears that C_3A amount limitation in cement is not a major composition parameter. This is notably confirmed by the equivalent behavior of CEM I and CEM I PM/ES pastes against organic acid attack. Hence, the strict observance of the French standard prescriptions concerning the choice of cements used for the manufacturing of manure pits is not sufficient. The composition of an effective binder is not determined yet, since the CEM III/B kinetics alteration, which was the slowest among tested binders, remains very high.

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