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Degradation of cement-based materials by various organic acids in agro-industrial waste-waters

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ABSTRACT

The paper analyses the mechanisms of the degradation of cementitious materials by three organic acids: oxalic, citric and tartaric acids, and evaluates their relative aggressiveness compared to that of acetic acid. These acids have different chemical characteristics in terms of poly-acidity and chemical and physical properties of their calcium salts. The aim was to highlight the links between these properties and the aggressiveness of each acid toward concrete. Degradation mechanisms and kinetics were investigated (using EPMA, XRD and SEM) on cement paste specimens immersed in acid solutions for one year.

The results showed that oxalic acid was not aggressive to the matrix. Citric acid caused the highest kinetics and severe degradations in the paste. Tartaric acid attack developed in two stages: no visible degradation was observed in the first weeks and then damage occurred, the kinetics remaining moderate. Acetic acid had intermediate aggressiveness.

It was confirmed that the solubility of the calcium salts was a major parameter of aggressiveness. It also appeared that, even if salts precipitated, they were not necessarily protective, the protection being correlated with the salt's molar volume. Moreover, poly-acidity seemed, in some cases, to increase the aggressiveness of the acid.

1. Introduction

Concrete in agro-industrial environments may suffer severe degradation, notably linked with attack by waste waters [1–3] such as liquid manure and silage juice produced by stock-rearing activities, whey and white and green waters generated by the dairy industries, or molasses and vinasses from distilleries and the sugar industry. These waste waters contain a broad range of organic acids, which are responsible for acid attacks on concrete [1,4]. The acids can be found in the plants or fruits themselves, or they can come from the metabolism of the microorganisms found in the effluents.

Table 1 gives the composition in acids and the pH of various effluents that are chemically aggressive for concrete.

Acetic and propionic acids and other volatile fatty acids (VFA are carboxylic acids with fewer than 5 carbon atoms), and also lactic, oxalic, succinic and tartaric acids, are found in the effluents. The total concentration may reach several hundreds of millimoles per litre. The resulting pH is between 4 and 7. VFA and lactic acid are found in most effluents. In vinasses and molasses, tartaric, succinic, oxalic, malic, aconitic and fumaric acids are also found. The concentrations of acids in the effluents depend on many factors, among which are the fruit variety, the weather (temperature, humidity), the dilution rate and conditions of storage of the effluents, the way the animals are fed, etc.

Despite containing the highest concentrations of acids, liquid manure is the least aggressive of the effluents listed because of its high pH linked to the presence of the acid–base pair NH_4^+/NH_3.

Attacks by silage juice and liquid manure have been reported in the literature [2,4,15] but attack by molasses or vinasses have been little explored, if at all.

The development of concretes that perform well in such environments requires an understanding of the interaction mechanisms between the acid and the cement-based matrix. These acids have very varied chemical characteristics, which lead to significantly different aggressiveness to concrete [16,17]. Moreover, waste waters generally contain several acids and the resulting attack of the mixture of acids is not necessarily the superposition of the alteration caused by each acid taken separately [4,18,19]. The problem is thus complex and, to adequately understand the phenomenon, each acid should be considered individually with regard to its properties before mixes of acids are studied.

From a general point of view, organic acids, which are weak acids, partly dissociate in water and react with hydrated (notably C-S-H and CH) and anhydrous phases of the cement paste to give mainly calcium salts or complexes. The degradation mechanisms are linked with the characteristics of the acids and their associated salts and complexes. The dissociation constant of an acid and the solubility of a salt are known to directly influence how aggressive the acid is [16–18]. When the calcium salt is soluble (case of acetic and lactic acids), the degradation mechanisms are comparable to those induced by strong acids with soluble calcium salts such as nitric and hydrochloric acids

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Table 1
Predominant acids in some agro-food industries [5–14].

Industry	Waste waters	Acids	Concentration (mmol/L)	pH	Ref.
Wine industry	Vinasses	Tartaric	3.2–8.7	4–6	[5,6]
		Acetic	3.1–5.0		
		Lactic	2.2–5.6		
		Succinic	0.3–6.8		
		Malic	0.5–0.8		
		Total (max.)	26.9		
Sugar industries	Sugar cane vinasses	Lactic	18–80.4	4–7	[7,8]
		Glycolic	12–25		
		Citric	1.7–10.4		
		Trans-Aconitic	0.2–4.8		
		Cis-Aconitic	0.1–2.8		
		Oxalic	0.08–0.8		
		Fumaric	0.1–0.4		
		Total (max.)	124.2		
Dairy industries	Whey	Acetic	14.0	4–6	[9,10]
		Citric	9.2–9.6		
		Lactic	3.4–5.7		
		Propionic	1.0		
		Butyric	0.6		
		Total (max.)	30.9		
Animal rearing	Silage juice	Lactic	55.3–63.7	4–5	[11,12]
		Acetic,	25.3–28.3		
		Butyric	4 3.4		
		Propionic	3.1		
		Total (max.)	99.1		
	Liquid manure	Acetic	31.7–213	5–8	[13,14]
		Butyric	1.1–28.8		
		Propionic	5.4–37.8		
		Totals (max.)	279.6		

[16,18,20]. However, when the calcium salt is slightly soluble to insoluble (case of tartaric, citric, succinic, etc. acids), the degradation mechanisms of the cement paste are not well known as these acids have been little investigated in the literature so far. On the other hand, previous studies suggest that the poly-acidity of the acid and the physical properties of the salts also influence the aggressiveness of the acids [16,17,20–23] but these influences are not well understood.

The work reported here aimed to analyse the mechanisms of the cementitious matrix degradation induced by some acids, the calcium salts of which are slightly soluble to insoluble. The purpose of this study was to help assess the influence of the chemical and physical features of the acids and their salts (pKa, poly-acidity, solubility and density of the salts) on the acid's aggressiveness toward cementitious materials. Three acids with different properties were selected: citric, tartaric and oxalic acids. The degradation mechanisms and kinetics induced on the cement based matrix were compared to those obtained with the reference, acetic acid, which has been thoroughly studied in the literature [4,18,21,22].

Portland cement pastes were exposed to acid solutions with the same concentrations for one year. The degradation kinetics were assessed by mass loss and degraded layer depth measurements. The chemical, mineralogical and microstructural changes were explored by Electron Probe Microanalysis, X-Ray Diffraction and Scanning Electron Microscopy.

2. Materials and methods

2.1. Materials

The specimens were CEM I 52.5 N cement pastes (Table 2) with a water/cement ratio of 0.27. They were cast in cylindrical moulds 75 mm high and 25 mm in diameter. The specimens were taken out of their moulds 24 h after pouring and stored in water at 20 °C for 28 days. They were then immersed in the aggressive solutions for 1 year. In parallel, control specimens were kept in water at 20 °C.

2.2. Organic acid data

2.2.1. Organic acid dissociation constants

The chemical formulas and the dissociation constants of the four acids are given in Table 3.

Acetic acid is a monoacid; it decomposes in water according to one dissociation reaction (1). This reaction is characterised by one dissociation constant Ka and one pKa = −log(Ka) (Table 3).

$$C_2H_4O_2 + H_2O \rightleftharpoons C_2H_3O_2^- + H_3O^+ \qquad (1)$$

$$Ka = \frac{[H_3O^+] * [C_2H_3O_2^-]}{[C_2H_3O_2]} \qquad \mathrm{pKa} = 4.76$$

Tartaric and oxalic acids are bi-acids. These acids are hydrolysed according to two dissociation reactions with two pKa. Reactions (2) and (3) show the dissociation of tartaric acid.

$$C_4H_6O_6 + H_2O \rightleftharpoons C_4H_5O_6^- + H_3O^+ \qquad (2)$$

$$Ka_1 = \frac{[H_3O^+] * [C_4H_5O_6^-]}{[C_4H_6O_6]} \qquad \mathrm{pKa}_1 = 3.04$$

$$C_4H_5O_6^- + H_2O \rightleftharpoons C_4H_4O_6^{2-} + H_3O^+ \qquad (3)$$

$$Ka_2 = \frac{[H_3O^+] * \left[C_4H_4O_6^{2-}\right]}{[C_4H_5O_6^-]} \qquad \mathrm{pKa}_2 = 4.37$$

Citric acid is a tri-acid; it hydrolyses according to three dissociation reactions (4, 5, 6) with three pKa.

$$C_6H_8O_7 + H_2O \rightleftharpoons C_6H_7O_7^- + H_3O^+ \qquad \mathrm{pKa}_1 = 3.14 \qquad (4)$$

$$C_6H_7O_7^- + H_2O \rightleftharpoons C_6H_6O_7^{2-} + H_3O^+ \qquad \mathrm{pKa}_2 = 4.76 \qquad (5)$$

$$C_6H_6O_7^{2-} + H_2O \rightleftharpoons C_6H_5O_7^{3-} + H_3O^+ \qquad \mathrm{pKa}_3 = 6.39 \qquad (6)$$

The structural formulas in Table 3 show the one, two or three carboxyl groups responsible for the release of one, two or three hydronium ions, respectively, for the different acids during the dissociation reactions. During the reaction with the cement-based matrix, oxalic, tartaric and citric acids are likely to release two or three times as much hydronium ion as the mono-acid acetic acid, for the same concentration of acid. It should be noted that oxalic acid has the lowest pKa. This means that, for a given pH, this acid is more dissociated in solution and, consequently, it might be more aggressive.

The predominant species in solution depend on the relative values of the pH and pKa_i as shown in Fig. 1.

2.2.2. Calcium salt data

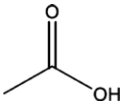
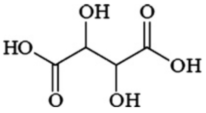
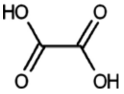
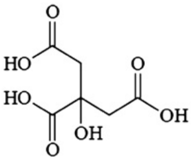
The solubility in water, the density and the molar volume of the calcium salts of the four acids are given in Table 4.

Calcium acetate is soluble in water. Calcium tartrate and citrate are slightly soluble, the solubility of tartrate being slightly lower than that of citrate. Calcium oxalate monohydrate is insoluble.

Table 2
Chemical composition of CEM I 52.5 R cement.

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	Na_2O	K_2O	MnO	SO_3	Ignition loss
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

Table 3
Chemical formulas and dissociation constants of the acids.

Acid	Acetic	Tartaric	Oxalic	Citric
Formula				
pKa (25 °C)	4.76	3.04/4.37	1.25/4.27	3.13/4.76/6.4

Calcium oxalate salts have the highest density and calcium citrate salts the lowest. The salt's molar volume is also important information as the comparison between this volume and that of the original compounds of the cement paste gives information about the possible impact (deleterious or not) of the formation of the salt on the matrix. All the calcium salts considered have higher molar volumes than that of $Ca(OH)_2$ (33.1 cm^3/mole [27]). The molar volume of calcium oxalate is much lower than that of the other acids but it remains 2 times higher than that of $Ca(OH)_2$. The molar volume of calcium citrate is by far the highest among the salts considered. It is at least 4.8 times higher than that of C-S-H ($C_{1.7}SH_z$), the molar volume of which is between 108 and 125 cm^3/mole, depending on the scale of observation of C-S-H and their state of saturation [27,28]. Calcium tartrate has intermediate molar volume (about 143 cm^3/mole).

2.2.3. Composition of the aggressive solutions

The aggressive solutions were made with a concentration of acid of 0.28 M in accordance with our previous investigations [4,18,23] (Table 5). This concentration is the highest total concentration of acids found in the effluents listed in Table 1. Different quantities of sodium hydroxide were added to bring the pH up to 4 (minimum value in the effluents), except for oxalic acid because the reaction between sodium hydroxide and oxalic acid leads to the formation of sodium oxalate salt, which is insoluble in water and disturbs the investigation of degradation mechanisms. The pH of the oxalic acid solution was therefore kept at its initial value of 0.85. Large amounts of sodium hydroxide were added to citric and tartaric acid solutions because of the poly-acidity of these acids. It may be noted that, at a pH of 4, citric acid has two acid functions left ($pKa_1 = 3.14 < pH\ 4 < pKa_2 = 4.76$-$pKa_3$), tartaric acid has one acid function left ($pKa_1 = 3.06 < pH\ 4 < pKa_2 = 4.37$). Oxalic acid solution, with a pH of 0.85, has two acid functions left ($pH\ 0.85 < pKa_1 = 1.25 < pKa_2 = 4.27$).

The specimens were immersed in the aggressive solutions for 350 days in static conditions (no agitation), to recreate the hydraulic conditions occurring in silos, ponds and other effluent storage structures.

Acetic, tartaric, and citric acid solutions were renewed as soon as the pH of one of them reached 4.5. The oxalic acid solution's pH did not change over the time of immersion. However, the solution was renewed at the same time as the others. During the first week, the solutions were renewed every day and then the frequency of the renewals decreased gradually.

The solid/liquid volume ratio was 1/17 (8 cylindrical specimens in 5 L of solution). The solid surface area/liquid volume was thus 102 cm^2/L.

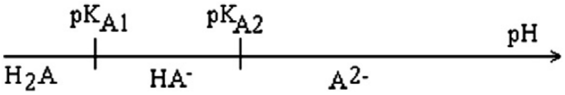


Fig. 1. Diagram of predominant species of a bi-acid H_2A, with dissociation constants pK_{A1} and pK_{A2} according to pH.

2.3. Test methods

2.3.1. Monitoring of degradation parameters over time

Relative mass losses and depths of the altered layer were monitored versus time during the whole experiment. The mass loss measurements were carried out on two specimens at each solution renewal. Two cement paste cylinders were taken out of the solution, briefly wiped with absorbent paper and then weighed using a weighing device with an accuracy of ± 1 mg.

Degraded layer depths were measured on two slices of specimens sawn perpendicularly to their axes. Phenolphthalein was sprayed on to the plane sections and its change in colour was the criterion used to distinguish the degraded zone from the sound zone. The violet colour of phenolphthalein is characteristic of a pH higher than 9.5. In previous investigations [4,23], the violet zone was not free of chemical and mineralogical changes: a slight decrease of calcium content, related to the dissolution of $Ca(OH)_2$, was notably observed in the outer part of the violet zone. However, these alterations remained minor as compared to those observed in the uncoloured zone. Furthermore, this zone of $Ca(OH)_2$ disappearance was thin in comparison to the total altered thickness of the specimen at pH 4 [23]. The cross sections were scanned, and the images were exploited using the Videomet® software. The altered thicknesses were deduced from the formula: $\frac{\phi_{ini}-\phi_{col}}{2}$ where Φ_{ini} is the initial diameter of the specimen (2.5 cm) and Φ_{col} is the diameter of the area where the phenolphthalein turned violet. The data provided in the paper were obtained from the average of twelve measurements distributed around the circumference of the slices. This procedure is slightly different from that used in previous studies (case of acetic acid and other VFA), where degraded layer depths were measured directly from the thickness of the uncoloured zone [4,23]. In the present study, citric acid and tartaric acid caused partial dissolution of the degraded areas, so this procedure could not be applied.

2.4. Degradation mechanisms

The chemical and mineralogical attacks by the four acids were investigated. The chemical changes caused by the different acids were analysed by electron microprobe (Cameca SX 50, operating conditions: 15 kV, 20 nA), after 1 month of immersion for all the acids and an additional analysis was performed at 10 months of immersion for tartaric acid. Two samples were considered for each acid. Slices were sawn in the cylinders perpendicular to their long axis so that the chemical composition profiles of the specimen could be analysed on the plane surfaces of the slices. These slices were embedded in an epoxy resin (Mecaprex MA2 from Presi) in small moulds open to the air (no penetration of the resin into the porosity of the specimen). After hardening, flat sections of the specimens were prepared by dry polishing and were then coated with carbon. Particular care was taken in the choice of the points analysed with the microprobe in order to study only the hydrated paste and to avoid residual anhydrous grains [29]. Two control specimens were also analysed at the rate of 50 points per specimen 5 weeks after pouring.

Table 4
Properties of the organic acids' calcium salts [24–26].

Acid		Acetic	Tartaric	Oxalic	Citric
Formula		$Ca(C_2H_3O_2)_2$/ $Ca(C_2H_3O_2)_2\cdot H_2O$/ $Ca(C_2H_3O_2)_2\cdot 2H_2O$	(d)$CaC_4H_4O_6\ 4H_2O$/ (dl) $CaC_4H_4O_6\ 4H_2O$/ (Meso) $CaC_4H_4O_6\ 3H_2O$	$CaC_2O_4/CaC_2O\cdot H_2O$	$Ca_3(C_6H_5O_7)_2\cdot 4H_2O$
Solubility (g/100 mL)	Cold water	37.4/ 43.6 (0 °C)/ 34.7 (20 °C)	0.0266 (0 °C)/ 0.0032 (0 °C)/ i	0.00067 (18 °C)/i	0.085 (18 °C)
	Hot water	29.7/ 34.3 (100 °C)/ 33.5 (80 °C)	0.0689 (87,5 °C)/ 0.00078(87,5 °C)/ 0.16 (100 °C)	0.0014 (95 °C)/i	0.096 (23 °C)
Density (g/cm^3)		1.6/no data/no data	No data/1.82/no data	2.02/2.26	1.1
Molar volume (cm^3/mol)		105.44/no data/no data	No data/143.14/no data	63.42/66.41	518.4

i: insoluble.

To explore the mineralogical changes, samples were analysed by XRD (Siemens D5000, 35 kV, 30 nA) after one month of immersion. The measurements were performed according to the distance to the surface in contact with the aggressive solution. They were carried out on the plane sides of the cylinders. The first analysis was on the plane external face of the specimen, which was then abraded and subjected to the next analysis. A control specimen was also analysed 5 weeks after pouring.

Microstructural observations were made using a scanning electron microscope (JEOL JSM-6380LV) fitted with an EDS detector (RONTEC XFlash® 3001).

In what follows, only the results of the mineralogical and chemical investigations on citric, oxalic and tartaric acids are presented, the mechanisms of the attack by acetic acid being well known [4,18–21].

3. Results

3.1. Macroscopic observations

Fig. 2 shows the aspects of the samples immersed in the various solutions after one month of immersion. On the surface of the samples immersed in citric acid, large amounts of white salts had formed. These salts dropped off the cement matrix easily. Moreover, samples in citric acid showed significant and rapid erosion of their outer part.

The samples kept in acetic acid had a somewhat orange colour. The outer layer showed some cracks but this layer adhered to the specimen and was not dissolved during the attack. There was no visible precipitation of salts (in accordance with the solubility of calcium acetate). Thus, cracking was probably due to the shrinkage of the degraded zone resulting from the loss of calcium during the attack [23].

Samples in tartaric acid did not show signs of visible deterioration during the first month. Then, a macroscopic layer of yellowish salts appeared on their surface. The adhesion to the sample surface was quite low and the salts finally accumulated at the bottom of the tank. Then, after two months of immersion, the peripheral zone of the samples gradually dissolved.

Specimens immersed in oxalic acid remained intact; they kept their initial aspect (grey-coloured) and shape. After a year of immersion, the inscriptions made on the samples for identification purposes at the beginning of the immersion test remained clearly visible. Nevertheless, when touched, the sample surface felt quite rough, probably because of some secondary precipitation onto the matrix.

Table 5
Chemical composition of the aggressive solutions.

Acid	Acetic	Tartaric	Citric	Oxalic
Concentration of acids (mol/L)	0.28	0.28	0.28	0.28
Concentration of NaOH (mol/L)	0.06	0.415	0.330	0
pH	4	4	4	0.85

3.2. Degradation measurements over time

Throughout the experiment, the samples immersed in oxalic acid did not show any mass loss and the degraded layer depths were equal to zero (Fig. 3). Acetic acid caused higher degradation kinetics than tartaric acid. Citric acid was the most aggressive: after 100 days of experiment, samples immersed in citric acid had been completely degraded. The kinetics of degradation by tartaric acid was very low in the first 60 days and then increased with time.

3.3. Degradation mechanisms

3.3.1. Citric acid

3.3.1.1. Chemical changes. Fig. 4 shows the composition of oxides of a sample immersed in the citric acid solution for 4 weeks, according to the distance to the initial surface in contact with the aggressive solution and the composition of a control sample. The chemical composition data were processed using a method described previously [29]. In particular, in order to display the absolute rather than the relative oxide contents, the composition of oxides in the degraded zone was corrected by using the titanium content of the paste, this element being well preserved during the acid attack. This treatment gave information about the absolute evolution of the different chemical elements and thus allowed a better understanding of the degradation mechanisms.

The figure shows three zones with different chemical compositions:

- Zone 1 or the sound zone, shows no chemical changes; its composition is identical to that of the control sample.
- Zone 2 is a transition zone, characterised by enrichment in sulphur oxide SO_3 and slight decalcification. Zones 1 and 2 caused the phenolphthalein to change colour.

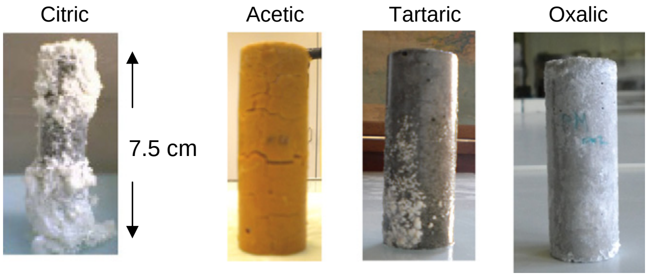


Fig. 2. Aspects of the specimens immersed for 1 month in the various acids.

- Zone 3, or the altered zone, shows very low CaO content – suggesting the complete dissolution of C-S-H – and does not contain any sulphate. The SiO_2 content in this zone is identical to that of the sound zone. The Al_2O_3 and Fe_2O_3 contents are preserved in the inner part of zone 3 and tend towards zero as the distance to the surface decreases.

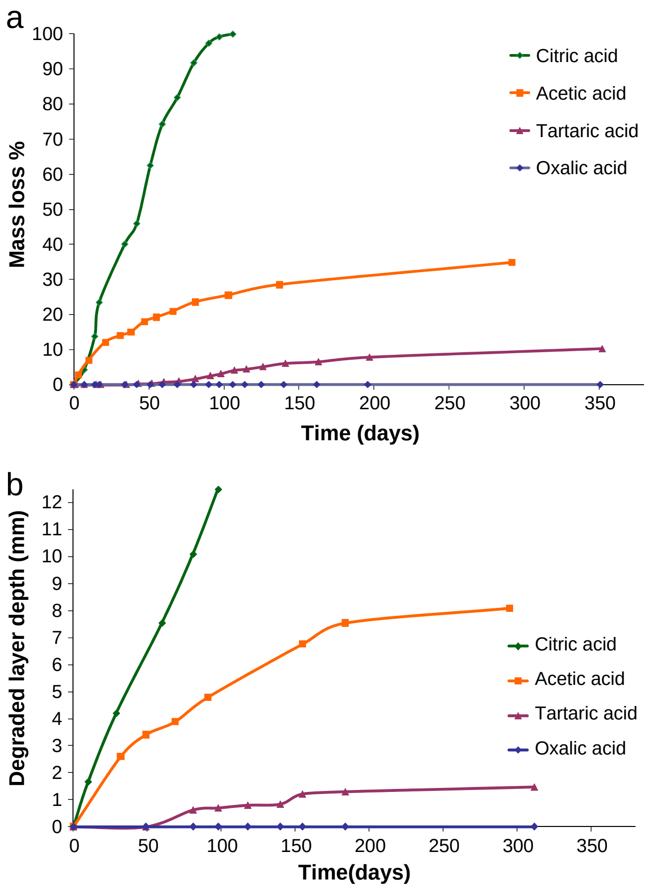


Fig. 3. Degradation kinetics of specimens immersed in organic acids according to time of immersion: a) relative mass losses, b) degraded layer depths.

The thickness of zone 3, 500 μm, is much smaller than the whole altered layer depth (4.2 mm) because much of the degraded area was dissolved during the attack.

3.3.1.2. Mineralogical changes. Fig. 5 provides the mineralogical data collected in the 3 areas distinguished on the chemical profiles obtained by EPMA.

Zone 1 and the control sample have similar mineralogical features. Zone 2 is characterised by (i) the disappearance of the $Ca(OH)_2$ peaks and (ii) higher intensity of ettringite peaks as compared to those of zone 1. These observations can be related to the slight decalcification and the enrichment in sulphate observed in this zone with EPMA. Zone 3 shows clear signs of amorphization: all the crystallised, anhydrous and hydrated phases have disappeared from the degraded zone, except C_4AF. The degraded zone shows no calcium citrate peak (or peak for any other citrate salt), though this salt formed on the surface in a tetrahydrated form, $Ca_3(C_6H_5O_7)_2{\cdot}4H_2O$ (Fig. 6). This absence (i) suggests that this salt is formed outward from the sample and (ii) is correlated with macroscopic observations: the salt did not adhere to the cementitous matrix.

3.3.2. Tartaric acid

3.3.2.1. Chemical changes. The monitoring of mass losses and altered layer depths of the samples exposed to tartaric acid showed two phases in the kinetics of degradation: slight degradation, if any, before 50 days of immersion, then the first mass losses and first in-depth changes, the kinetics of degradation remaining moderate (maximum altered layer depth observed after one year of immersion: 1.5 mm).

Consequently, microprobe chemical analyses were performed for two different dates: 4 weeks (Fig. 7) and 10 months of immersion (Fig. 8).

After 4 weeks of immersion, the chemical profiles showed only 2 zones. Zone 1 had the same chemical composition as the control sample. Zone 2, about 50 μm-thick, showed a slight decalcification. These two zones caused the colour change in phenolphthalein, which explains that no altered layer was observed (Fig. 3).

After 10 months of immersion, microprobe analyses showed (i) a zone 1 with the same chemical composition as the control sample, (ii) a zone 2, approximately 550 μm-thick, slightly decalcified and enriched in sulphates, and (iii) at the periphery of the sample, a thin layer (approximately 40 μm thick) containing calcium only, among the

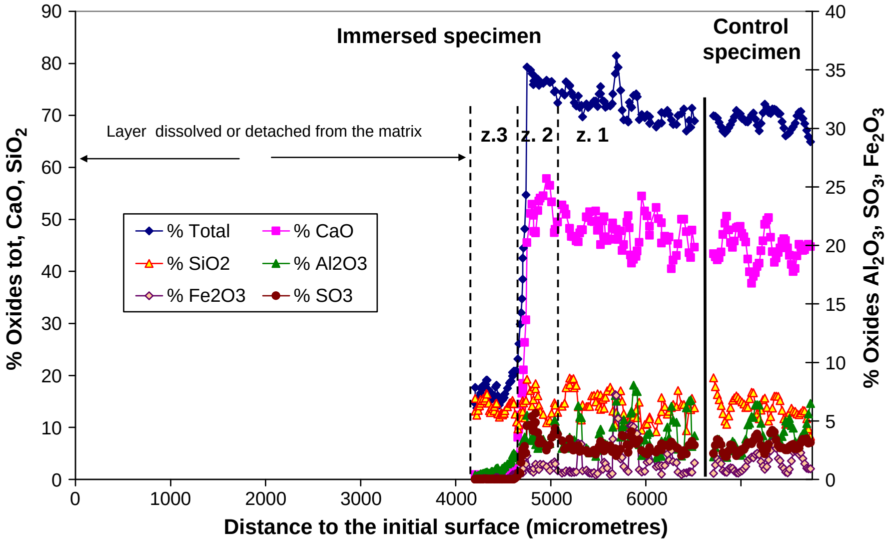


Fig. 4. Chemical composition profile of a cement paste specimen immersed in citric acid for 1 month — Absolute amounts of oxides in sound zone and in altered zone.

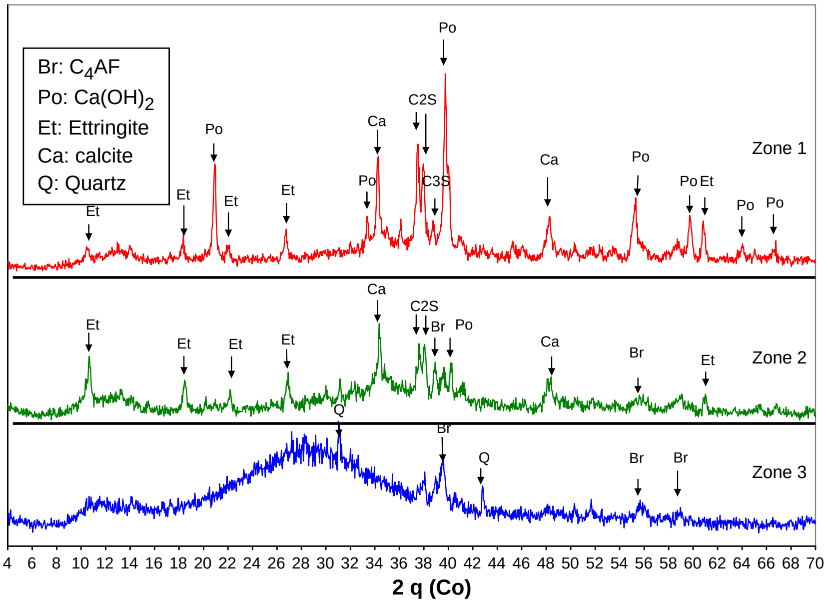


Fig. 5. X-ray traces of a cement paste specimen immersed in citric acid for 1 month.

elements analysed. In zone 2, the localised high content of calcium (at a depth of about 2.1 mm on Fig. 8) can be attributed to a calcium tartrate crystal. Zones 1 and 2 caused phenolphthalein to change colour. The outer zone of the samples was completely dissolved during the attack by tartaric acid, which is why no decalcified zone (such as zone 3 of specimens in citric acid) is observed on Fig. 8.

3.3.2.2. Mineralogical changes. Fig. 9 shows the mineralogical analyses by XRD of the samples immersed in tartaric acid for 10 months. Zone 1 has the same mineralogical characteristics as the control sample. Ca $(OH)_2$ has disappeared from zone 2. The outer layer is made of calcium tartrate ($CaC_4H_4O_6$. $4H_2O$) and contains calcite.

3.3.3. Oxalic acid

3.3.3.1. Microscopic observations. Scanning electron microscope observations (Fig. 10) of the surface of the specimens and of a polished cross section combined with EDS analyses showed that:

- some calcium-bearing salts had precipitated at the surface of the specimens (Fig. 10a),
- in a 300-μm-thick layer in the outer part of the specimen, some calcic compounds had formed in the cementitious matrix. This zone is marked as zone 2 and the inner part of the specimen is marked as zone 1 (Fig. 10b).

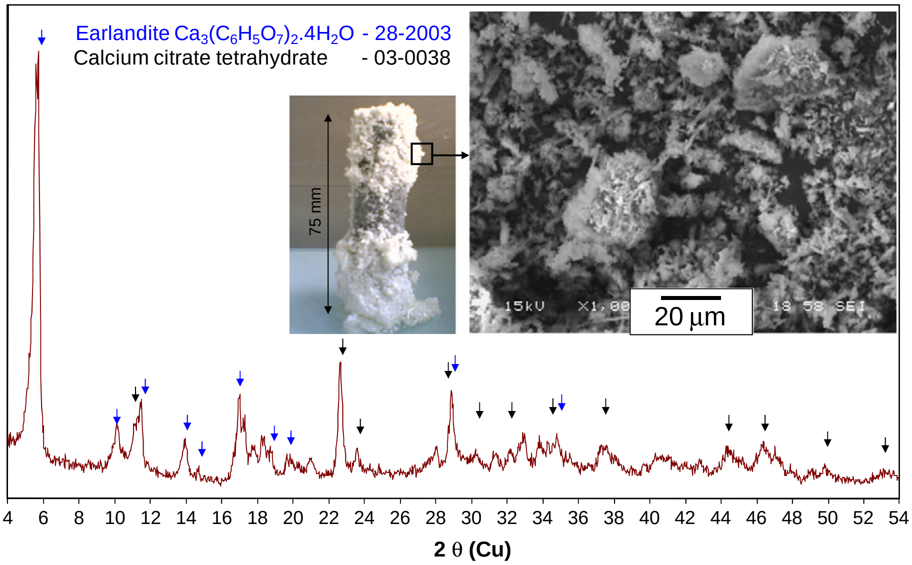


Fig. 6. X-ray trace and observation with SEM of calcium citrate salt collected on the specimens immersed in citric acid.

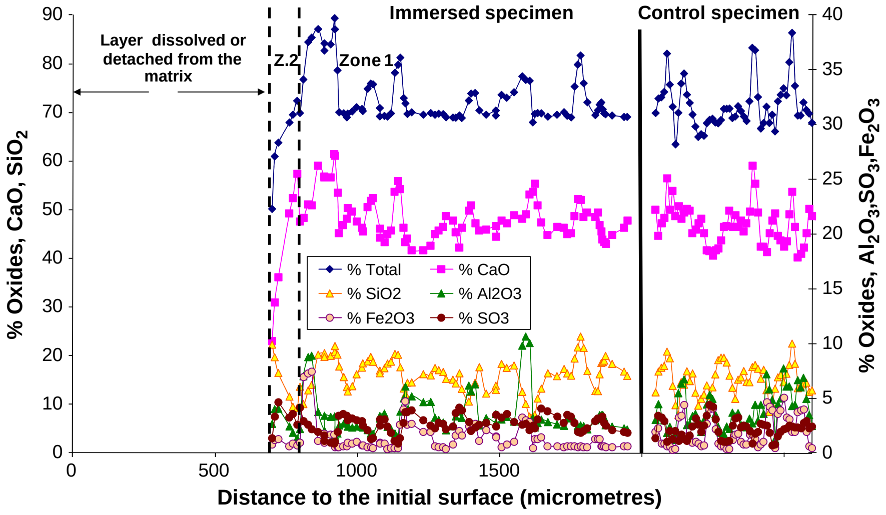


Fig. 7. Chemical composition profile of a cement paste immersed in tartaric acid for one month.

3.3.3.2. Chemical changes. Electron microprobe analyses (Fig. 11) showed that there was no noticeable change in the chemical composition of the cementitious matrix according to the distance to the surface in contact with the aggressive solution. Zone 1 and zone 2 had the same oxide contents. There was no detectable release of calcium from the specimen.

3.3.3.3. Mineralogical changes. XRD analyses (Fig. 12) showed that calcium hydroxide had disappeared from zone 2 and that calcium oxalate mono-hydrate $CaC_2O_4 \cdot H_2O$, or whewellite, had formed in this zone as well as on the surface of the specimen. This means that calcium released by the dissolution of $Ca(OH)_2$, and maybe a part of C-S-H, directly combined inside the cementitious matrix with oxalate acid anion to form calcium oxalate salt.

4. Discussion

The relative aggressiveness of the acids was determined from the kinetics of degradation. It is possible to classify the acids tested in decreasing order of aggressiveness: citric acid >acetic acid >tartaric acid >oxalic acid.

The aggressiveness of oxalic acid toward the cement matrices was null: altered layer depths and weight losses remained zero despite a much lower pH than in the other solutions.

Tartaric acid showed some similarities with oxalic acid during the first few weeks: neither mass loss nor degraded layer was observed. However, after 60 days, the first mass losses were observed.

Citric acid and acetic acid were much more aggressive for the cement paste; the changes began in the early days of immersion. Citric acid was by far the most aggressive. The outer zone of the sample was progressively and rapidly dissolved (samples had dissolved completely after two months of immersion).

The citric acid attack on the cementitious matrices generated the precipitation of large amounts of calcium citrate tetra-hydrate salt. This salt did not adhere to the surface of the sample and the formation of the salt was strongly deleterious to the matrix, the outer layer of which was very rapidly broken up and then dissolved. Actually, the break-up of the periphery of the samples was probably due to the precipitation of the citrate salt, the molar volume of which, 518 cm^3/mol, is very high compared to the hydrates at the expense of which it formed ($Ca(OH)_2$ and C-S-H, mainly — 33.1 cm^3/mol and 108 to 125 cm^3/mol respectively). Within the cement matrix, the attack

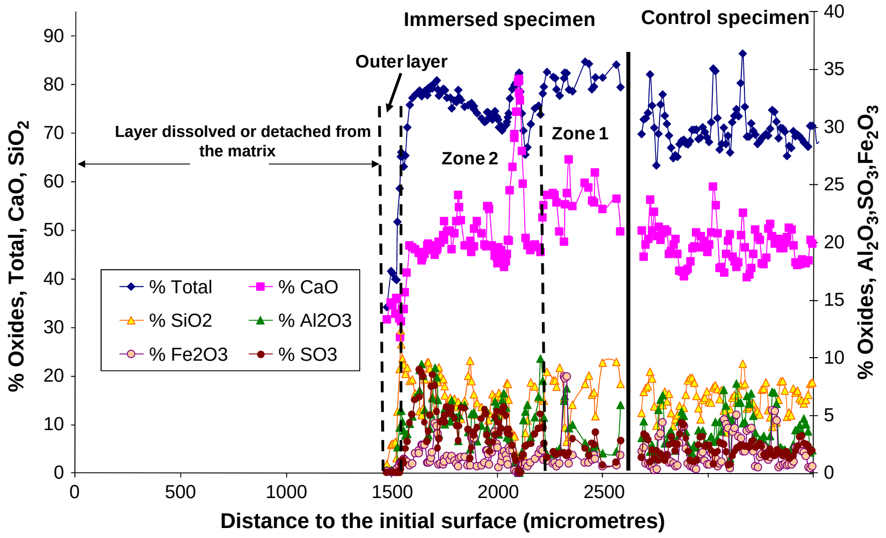


Fig. 8. Chemical composition profile of a cement paste immersed in tartaric acid for 10 months.

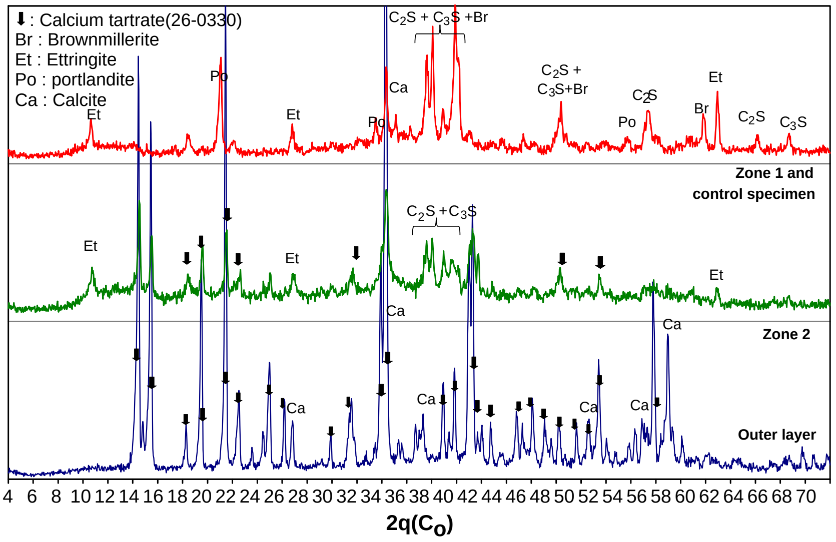


Fig. 9. X-ray traces of cement paste specimen immersed in tartaric acid for 10 months.

resulted in a well-marked mineralogical and chemical zonation. Three zones were observed. Zone 1 or the sound zone did not suffer any damage; its composition was the same as that of the control sample. Zone 2 was a so-called "transition zone". It was slightly decalcified and enriched in sulphates because of the dissolution of calcium hydroxide and of the precipitation of non-expansive secondary ettringite respectively. Zone 3 was severely damaged: this zone was quasi-amorphous and completely decalcified, which revealed the dissolution of the C-S-H and the other cementitious hydrated phases.

As noted in previous studies, the samples attacked by acetic acid also showed a 3-zone mineralogical and chemical profile [23]. Zones 1 to 3 had features similar to those described for citric acid attack. However, in the case of acetic acid, acetate salt did not precipitate (according to the solubility of the corresponding salts). In addition, the attack by acetic acid was less aggressive than by citric acid and the peripheral area of samples was not dissolved during the attack. The degradation mechanisms are similar to those of strong acids, the calcium salts of which are soluble (HNO_3, HCl) [20,22].

The attack by tartaric acid led to the precipitation of calcium tartrate tetrahydrate, which seemed to efficiently protect the sample during the first two months of the experiment, limiting the attack to microscopic changes. Then, macroscopic degradations began. The attack took the form of (i) the precipitation of a thin layer of calcium tartrate salts adhering to the matrix and (ii) the break-up and dissolution of the cement matrix periphery. Within the matrix, 2 zones were observed with similar features to those observed on the samples in citric and acetic acids (non-altered core and transition zone).

The calcium tartrate layer in the periphery of the samples seemed to protect the matrix, at least partially, as the kinetics of degradation remained moderate during the whole experiment. This phenomenon was comparable to a process used in the wine industry. This process, consisting of brushing the inside walls of tanks with a solution of tartaric acid, helps protect the cement matrix against attack by the acids in wine. However, this protective role is of limited duration since, as observed in this study, despite the precipitation of calcium tartrate at the periphery of the matrix, the degradation front progresses over time.

The presence of calcite in the outer layer might be attributed to the decomposition of carbonate-bearing AFm phases such as mono- or hemi-carboaluminate hydrates [30] which have been shown to be the second cementitious hydrated phase to dissolve, right after $Ca(OH)_2$, during leaching of CEM I paste [31]. The dissolution of these phases releases carbonate anions which can recombine with calcium cations released by the dissolution of Ca-bearing phases of the cement paste. The precipitation of calcite as a secondary product of the leaching of the cement was also observed in the transition zones of cementitious specimens immersed in acetic acid [23].

The attack by oxalic acid led to the formation of calcium oxalate salts on the surface, which fully protected the cement matrix throughout the experiment. After several months, calcium oxalate still adhered strongly to the matrix and could not be removed even by vigorous scraping. At

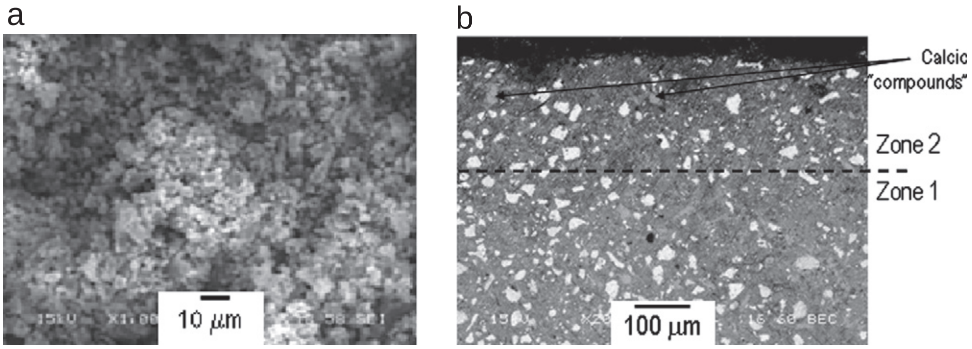


Fig. 10. Observations with SEM of a specimen immersed in oxalic acid for on month: a) salt precipitated at the surface in SE mode, b) polished cross-section in BSE mode.

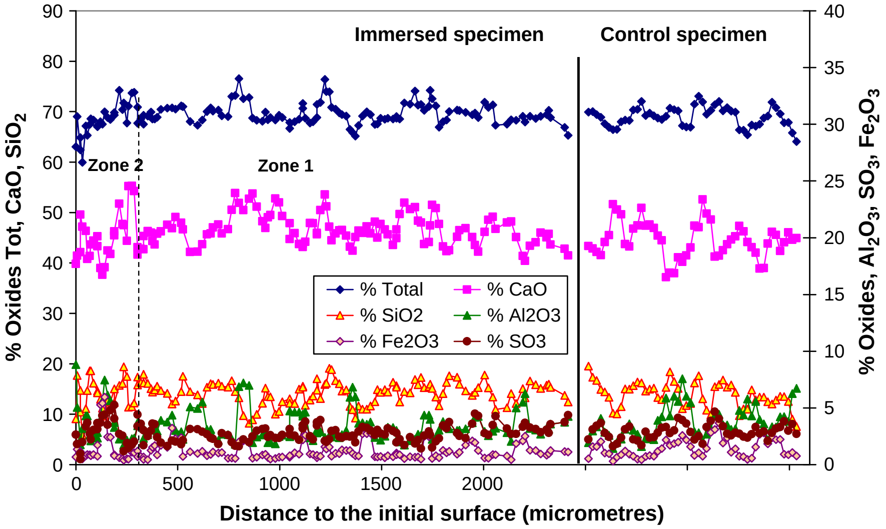


Fig. 11. Chemical composition of a cement paste immersed in oxalic acid for one month.

the periphery of the matrix, calcium oxalate was formed from $Ca(OH)_2$ and, as a first approach, at least a part of the C-S-H, without any loss of calcium from the matrix.

Other experiments were performed using CEM III/C pastes immersed in oxalic acid. CEM III/C are clinker cements with high substitution rates of slag (>81%) [32]. The specimens were severely attacked right from the beginning of the experiment. This proves the key role of $Ca(OH)_2$ in the protective action of calcium oxalate monohydrate salt. Slag cement pastes are known to be more resistant than ordinary Portland cement paste in acidic conditions, obtained with acetic acid for example [33]. However, in the case of the attack by oxalic acid, the absence of $Ca(OH)_2$ is prejudicial to the matrix.

The chemical stability of the hydrated phases of the solid is of prime importance in the determination of the impact of the oxalic acid attack on the matrix (and not only the chemical nature of the cation combining with the oxalate anion to form an insoluble salt). For the oxalate salt to have the most beneficial effect, its formation should occur at as high a pH as possible, so that further hydrolysis of the matrix can be prevented. In cement paste, $Ca(OH)_2$ is the least stable hydrated phase of the cement paste, its dissolution occurring from a pH of 12.5 in the interstitial solution [31]. Hence, it may be assumed that the good resistance of CEM I paste toward the attack of oxalic acid is linked with the sacrificial behaviour of $Ca(OH)_2$, on the one hand, and with the preservation of C-S-H, the main hydrated phase of the cement paste, responsible for the mechanical strength of the matrix, on the other hand.

Moreover, as no evolution of the thickness was observed over time at the outer part of the specimen where Ca-oxalate precipitated, it may be assumed that the formation of this salt prevented the penetration of the aggressive species deeper into the sample and that the salt acted as a sealant of the capillary porosity of the outer layer of the matrix. In a CEM I paste with $E/C = 0.27$, it can be calculated, following Bejaoui and Bary [34], that $Ca(OH)_2$ occupies about 15% of the total volume of the paste. The total porosity of the paste, measured by water intrusion, is about 28–30% [4]. The capillary porosity (pore diameter >10 nm), measured by mercury intrusion porosimetry, is 10% (original data). The volume of calcium oxalate being 2-fold that of $Ca(OH)_2$ (66.4 cm^3/mole versus 33.1 cm^3/mol), it may be assumed that the formation of the salt enabled (i) the initial volume of the dissolved $Ca(OH)_2$, (ii) the capillary porosity and, maybe (iii) a small part of the hydrates porosity to be filled, without any damage to the matrix.

The action of oxalic acid on the cementitious matrix can be compared to that on calcareous rocks. Many natural rocks: sandstone, granitic rock, basalt, calcareous rocks etc. are affected in quite different ways by oxalic acid produced by lichens [35,36], combining

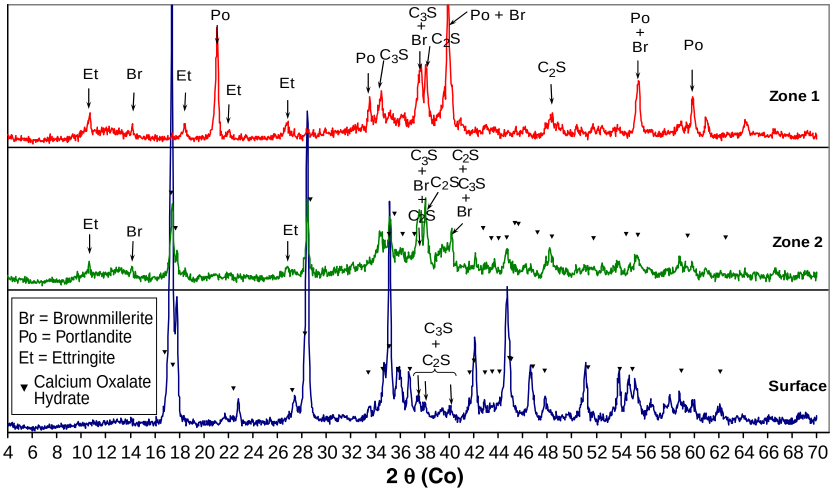


Fig. 12. X-ray traces of cement paste specimen immersed in oxalic acid for one month.

the mechanical effect of the penetration of lichens' hyphae inside the rock and chemical effect of the acid production. Depending on the rock composition, Ca, Mg, Al and Fe are released and/or combined into secondary products, these elements being sensitive to the strong chelating effect of oxalic acid [35,37,38]. The action of oxalic acid on calcareous sandstones leads to the dissolution of calcite and the formation of Ca-oxalate, which seems to protect the rock against further ageing [39,40].

The formation of Ca-tartrate salt was less protective to the matrix than that of oxalic acid. This is probably, and at least partially, due to its higher molar volume (143.1 cm^3/mol versus 66.4 cm^3/mol). Assuming that the formation of this salt is only linked to the dissolution of calcium hydroxide, the molar volume of the salt is too high to replace the reactive phase and seal the porosity without generating internal stresses. It may be thought that, during the first two months of the experiment, the formation of calcium tartrate generated micro-cracks that were not sufficient to allow great quantities of aggressive agents to penetrate further into the cement matrix. After 2 months, propagation of micro-cracks in the matrix may have generated macro-cracks and macroscopic degradations were then observed.

The mesoscopic shape of the salt may also be considered as another important parameter determining the protective effect of the salt. Calcium tartrate tetrahydrate precipitates in a prismatic form [41] whereas calcium oxalate monohydrate precipitates in a hexagonal form [42], which covers a surface more easily (Honeycomb conjecture [43]). It should be noted that the calcium salt form is variable and depends on many different chemical parameters. It has been found that calcium oxalate monohydrate salt may precipitate in a prismatic form, too [44,45]. The data on the shape of the salts and on and their affinity toward the cement matrix should be analysed in further studies.

When calcium salts are soluble or when they are slightly soluble but non-protective, the poly-acidity seems to influence the aggressiveness of the acids toward the cementitious matrix. The very high aggressiveness of citric acid, which dissolves the specimen's degraded zone and causes very high degradation kinetics as compared to the other acids studied, could be related to its poly-acidity. For one mole of acid in solution, at pH 4, citric acid generates 2 moles of hydronium ions versus 1 for acetic acid. Its reserve of conjugated base at pH 4 is very large.

5. Conclusion

In this paper, the mechanisms of cement paste degradation by tartaric, oxalic and citric acids have been analysed and compared to those by acetic acid. The increasing order of aggressiveness of the four acids on the cement matrix is as follows: oxalic acid <tartaric acid <acetic acid <citric acid.

The low or null aggressiveness of oxalic acid is linked with the formation, in a thin outer layer of the cement matrix, of calcium oxalate from calcium hydroxide and, presumably, at least a part of calcium silicate hydrates. It is assumed that, thanks to a low solubility and a suitable molar volume, the formation if this salt acts to seal the capillary porosity.

Tartaric acid is not very aggressive for the cement matrix. The degradation kinetics is moderate and the damage to the cement matrix appears later (after 60 days) and is observed as a decalcification and a dissolution of the outer layer. The delay in the degradation may be correlated with the tartaric acid treatment applied to concrete tanks used in the wine industry.

Acetic acid has an intermediate aggressiveness. The attack results in almost complete decalcification of the matrix and in the dissolution of hydrated and anhydrous phases of the cement matrix.

Citric acid is the most aggressive for the cement pastes. The slightly soluble citrate salt precipitates but, first, it is expansive (high molar volume as compared to that of $Ca(OH)_2$ or C-S-H) and, second, it does not adhere to the cement matrix and thus is not protective.

This study points out that the first parameter to be considered to evaluate the aggressiveness of acids is the solubility of their salts. When the salt is soluble, it does not protect the cement matrix. However, when the salts are poorly soluble or insoluble, they are not necessarily protective. The study shows a correlation between the molar volume and the protective effect of the salts. The way the salt precipitates on the matrix, particularly its mesoscopic shape, and the salt's affinity for the matrix are also influential parameters, which should be investigated in further studies. Moreover, when the salts are not protective, the poly-acidity seems to promote aggressiveness on the cement matrix.

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