

Attack of cement pastes exposed to organic acids in manure

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Abstract

Manure such as silage effluents and liquid manure contains organic acids which constitute a severe chemical threat toward the concrete of agricultural structures. The purposes of this study were to identify the chemical composition parameters that influence durability by analysing the behaviour of the chemical elements of the cement paste (Ca, Si, Al, Fe and Mg) in organic acid solutions and to compare the intensity of the chemical attack by the different acids found in liquid manure. This study was carried out on cement pastes made from four binders (ordinary Portland cement, slag cement, OPC blended with silica fume and OPC blended with fly ash). The hardened cement pastes were first crushed, then immersed in solutions made of five organic acids with an initial pH of 4 and constantly stirred. The pH and the concentrations of major elements were monitored over time.

The results show that Si, Al, and Fe appear to be favourable elements for the chemical resistance of binders whereas the amount of Ca should be limited. Moreover, it is shown that the four acids found in liquid manure (acetic, propionic, butyric, iso-butyric) are equally aggressive. Lactic acid, present with acetic acid in silage effluent, is more aggressive according to the value of its pK_a .

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1. Introduction

Manure contains organic acids (acetic, propionic, lactic, etc.) in variable quantities. The presence of these acids together with the acid–basic pair $\text{NH}_4^+/\text{NH}_3$, means that the pH of the silage effluents is 4 and that of liquid manure is between 6 and 8 [1–5].

Hence, liquid effluents constitute a severe chemical threat toward the concrete of agricultural structures. Indeed, when these acids come into contact with the cement based matrix, the reactions with the hydrates of the cement paste (in particular portlandite and C–S–H) produce salts, whose solubility is high to very high in water [6], and/or organometallic-associated complexes. Consequently, the porosity increases, the

mechanical strength drops and, in the long term, reinforcement corrosion can occur in the immersed part of the structures.

In order to improve the performance of concrete in agricultural structures, we need to identify the parameters of cement composition that influence its durability. It is therefore necessary to clarify the behaviour of the chemical elements of cement under the effect of manure organic acids. Immersion tests of cement paste monoliths in synthetic liquid manure at pHs maintained at 4 and 6 have already shown that the alteration translates in a well-marked mineralogical and chemical zonation [7–9]. The hydrated and anhydrous phases are progressively dissolved from the unaltered core to the outer zone in contact with the aggressive solution. The altered zone is almost totally decalcified and is made of silica, aluminium and iron. The structure, totally amorphous, is likely to be that of a silico–aluminous gel. In this case

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(immersion of monoliths without stirring), thanks to the stability of the silico–aluminous products and to the electron double-layer phenomenon, the altered zone is not dissolved and thus forms a protective layer which slows down the kinetics of further alteration. In the present study, roughly crushed hardened cement pastes were subjected to dissolution tests in manure organic acids. Constant stirring, causing friction between grains, prevented the formation of the protective layer. The first purpose of the article is to complete our knowledge of the alteration mechanisms of organic acids on cement based matrix and to study the stability of the major elements of the paste (Ca, Si, Al, Fe and Mg).

Moreover, many of the studies simulating the attack of manure on cement-based materials were conducted with the use of acetic acid solutions only [7–15]. However, the pK_a values of these acids, the solubility in water of the calcium, aluminum, iron and magnesium salts and the constants of complex formation in solution do not allow the relative aggressiveness of manure acids to be predicted [16–18]. So it is necessary to determine whether the action of acetic acid is representative of the action of all the manure acids. The second purpose of this work was to compare the chemical aggressiveness of the manure acids (acetic, propionic, butyric, iso-butyric and lactic) on cement based materials.

In order to compare the chemical resistance of several binders, the study was conducted on hardened cement pastes made with four binders: OPC, OPC + slag, OPC + SF, OPC + FA. These hardened cement pastes, first crushed, were immersed in solutions made of the five organic acids with initial pHs adjusted to 4. The pH was not maintained during the experiment. Afterwards, pHs and major element concentrations were monitored over time. X-ray diffraction analyses were also undertaken on the precipitates collected during the filtration of the solutions.

Bibliography on chemical constants of manure acids: Liquid manure contains acetic, propionic, butyric and iso-butyric acids whereas silage effluents contain acetic and lactic acids.

To compare the aggressiveness of the different manure acids, three types of parameters had to be taken into account: the acids' dissociation constants, the solubility of the acid salts in water and the constants of organometallic complexes formed in solution.

The chemical formulas and dissociation constants of the five acids are given in Table 1. The pK_a values of liquid manure acids are very close: 4.81 ± 0.05 , whereas the pK_a of lactic acid, which is found in silage effluent, is lower: 3.86 (Table 1).

Salts of these acids are soluble-to-highly soluble in water [13,14] (Table 2). Given the initial concentrations of this study, salts were unlikely to form in solution. Moreover, complexation phenomena in the solutions of cations, coming from the cement paste dissolution, and

Table 1
 pK_a of the different manure acids

	Acids				
	Acetic (C ₂ H ₄ O ₂)	Propionic (C ₂ H ₆ O ₂)	Butyric (C ₄ H ₈ O ₂)	Iso-butyric (C ₄ H ₈ O ₂)	Lactic (C ₃ H ₅ O ₃)
pK_a (25 °C)	4.76	4.87	4.81	4.85	3.86

anions, from acid dissociation, are governed by complexation constants. Some of these constants are given in Table 3 [15]. It may be noticed that the reactions which lead to the formation of complexes are preponderant over the one leading to formation of salts. Besides, complexation tends to accelerate the kinetics of reactions between acids and the cementitious matrix. These constants vary according to the acid and the chemical element. It is therefore necessary to determine whether the complexation reactions influence the relative aggressiveness of manure acids.

2. Materials and methods

2.1. Materials

This study was conducted on cement pastes made with four cements: 100% ordinary Portland cement (designated in the French Standard NF EN 197-1 as CEM I 52.5 R [19]) referred to as CEM I in this paper, 100% slag cement (CEM III/B 42.5 N [19]) containing 32% OPC and 68% blast furnace slag and referred to as CEM III, a mix of 90% CEM I 52.5 R and 10% silica fume noted CEM I + SF, a mix of 50% OPC and 50% silico–aluminous fly ashes, noted CEM I + FA. The chemical compositions are given in Table 4.

2.2. Specimen making

Cement pastes were made with a water/cement mass ratio of 0.27. The initial hardened cement paste specimens were cylindrical, 75 mm high and 25 mm diameter. The specimens were removed from their moulds 24 h after pouring and stored in water at 20 °C for 27 days. Samples were roughly crushed in a jaw crusher and sieved to eliminate the fraction <2.36 mm which would limit the kinetics of chemical reactions. The coarse grains were immersed in the aggressive solutions described below.

2.3. Aggressive solutions

Liquid manure contains acetic, propionic, butyric and iso-butyric acids whereas silage effluents contain lactic and acetic acids. The aggressive solutions were made with these acids. The acid concentrations were the same for all the solutions and fixed at 0.28 mol/l.

Table 2
Solubility of calcium, aluminium, magnesium and iron organic acid salts (g/100 ml) [13,14]

	Acids (formula)	Acetic	Propionic	Butyric	Iso-butyric	Lactic
Ca salts	Formula	$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	$\text{Ca}(\text{C}_3\text{H}_5\text{O}_2)_2 \cdot \text{H}_2\text{O}$	$\text{Ca}(\text{C}_4\text{H}_7\text{O}_2)_2 \cdot \text{H}_2\text{O}$	$\text{Ca}(\text{C}_4\text{H}_7\text{O}_2)_2 \cdot 5\text{H}_2\text{O}$	$\text{Ca}(\text{C}_3\text{H}_5\text{O}_2)_2 \cdot 5\text{H}_2\text{O}$
	Sol. cold water g/cc (T/°C)	37.4 (0 °C)	4.9 (0 °C)	5	20	3.1 (0 °C)
	Sol. hot water g/cc (T/°C)	29.7 (100 °C)	55.8 (100 °C)	sl s	sl s	7.9 (30 °C)
Al salts	Formula	$\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$	—	—	—	$\text{Al}(\text{C}_3\text{H}_5\text{O}_2)_3$
	Sol. cold water g/cc (T/°C)	s sls	—	—	—	vs
	Sol. hot water g/cc (T/°C)	d	—	—	—	—
Mg salts	Formula	$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ or $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$	—	—	—	$\text{Mg}(\text{C}_3\text{H}_5\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$
	Sol. cold water g/cc (T/°C)	vs or 120 (15 °C)	—	—	—	3.3
	Sol. hot water g/cc (T/°C)	vs or ∞	—	—	—	16.7 (100 °C)
Fe salts	Formula	$\text{FeOH}(\text{C}_2\text{H}_3\text{O}_2)_2$	—	—	—	$\text{Fe}(\text{C}_3\text{H}_5\text{O}_2)_3$
	Sol. cold water g/cc (T/°C)	i	—	—	—	s
	Sol. hot water g/cc (T/°C)	—	—	—	—	vs

vs: very soluble; sls: slightly soluble; s: soluble; d: decomposes; i: insoluble.

Table 3

Formation constants of organic acid complexes: $\log(K_i)$ at 20 °C unless specified (near-zero ionic forces or concentrations specified) [15]

Ligands		Cations		
		Ca^{2+}	Mg^{2+}	Fe^{3+}
Acetate anion ($\text{C}_2\text{H}_3\text{O}_2$) ⁻		0.6	0.8	3.2
				(20 °C—1 M)
Lactate anion ($\text{C}_3\text{H}_5\text{O}_3$) ⁻		1.42	1.37	7.1
				u.u.s.

u.u.s.: uni-univalent salt.

The initial pHs of the solutions were raised to 4 by addition of granulated soda.

- The whole experiment, aiming at studying the stability of the major chemical elements in the cements according to the pH of the solution and comparing the durability of the four binders, was performed with an acetic acid solution (0.28 M) with 0.0563 M (2250 mg/l) of soda added.
- Comparison of the aggressiveness of the acids. Two types of solutions were used to compare the aggressiveness of the different acids:
 - Type 1 solution: the same quantity of soda (50.12 mmol/l) was added to each acid solution (0.28 M) to evaluate the effect of the $\text{p}K_a$ value on the intensity of the attack. The pHs obtained were between 3.045 and 4.145 for each solution (Table 5).
 - Type 2 solution: variable quantities of soda were added to bring the pH up to 4 for each acid solution (0.28 M). The aim was to eliminate the effect of pH on the intensity of attack by each acid. The quantities of soda used and the pH obtained are given in Table 5.

2.4. Test methods

The solid/liquid mass ratio of the specimens was 1/20. For every specimen, the mass of coarse grains was 2.50 g and the volume of aggressive solution was 0.05 l. Samples were constantly shaken during the whole experiment. At each sampling period, solid samples were filtrated by gravity. The solutions were recovered for pH measurement and cations (Ca, Si, Al, Fe and Mg) were analysed with a Perkin–Elmer Analyst 100 atomic absorption spectrometer.

For some samples, precipitates were observed and collected on the filters (Fig. 1). These precipitates were analysed by a Siemens D5000 X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation generated at 30 mA and 40 kV. Precipitates were also observed with a JEOL JSM-840A scanning electron microscope equipped with an energy dispersive X-ray analysis system (EDXA).

Table 4
Chemical compositions of the different binders

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	Na ₂ O	K ₂ O	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
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
Fly ashes	1.02	57.68	23.49	5.35	0.43	0.69	0.19	4.22	0.06	0.2	6.65
Silica fume	n.m.	>95	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.

n.m.: not measured.

Table 5
pK_a of the organic acids and compositions of the aggressive solutions

	Acids					
	Acetic (C ₂ H ₄ O ₂)	Propionic (C ₂ H ₆ O ₂)	Butyric (C ₄ H ₈ O ₂)	Iso-butyric (C ₄ H ₈ O ₂)	Lactic (C ₃ H ₅ O ₃)	
pK _a (25 °C)	4.76	4.87	4.81	4.85	3.86	
Acid concentration (mol/l)	0.28	0.28	0.28	0.28	0.28	
Sol. type 1 NaOH: 50.12 mmol/l	Initial pH	4.02	4.15	4.09	4.11	3.05
Sol. type 2 pH = 4	Concentration NaOH (mmol/l)	56.25	43.33	52.50	50.00	170.0
	pH of the solutions	4.04	4.07	4.05	4.03	4.00

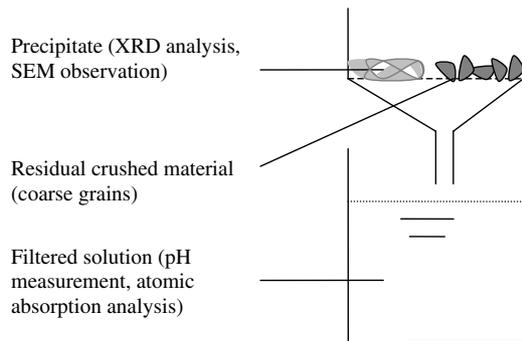


Fig. 1. Tests performed on the specimens.

To analyse the relative aggressiveness of the acids, the tests were conducted on the CEM I paste after 6 hours and 7 days of immersion. Two specimens were analysed for each acid and at each sampling period.

Acetic acid solution was used to compare the dissolution of the four binders according to the pH of the solutions. Analyses were run in duplicate after 2, 4, 6, 10, 15, 20 h, and 1, 4, 9, 13 weeks of immersion.

3. Results

3.1. Element by element analysis and comparisons between binders

3.1.1. Variation of pH according to time

Fig. 2 shows the pH variations with time of the acetic acid solutions containing the four binders.

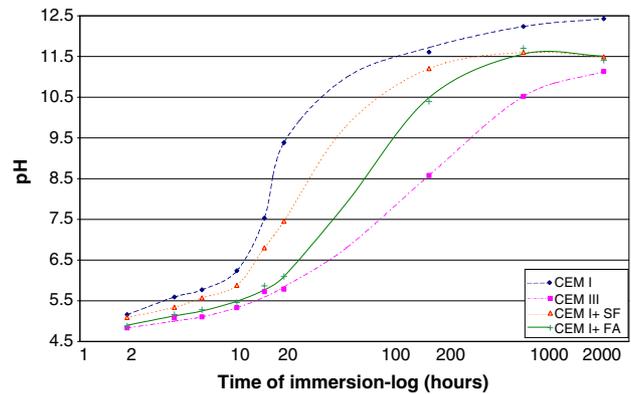


Fig. 2. pH variation of the acetic acid solutions containing the four tested binders versus time.

In the short term (time of immersion less than or equal to 15 h), pHs of the solutions were between 4.8 and 7.6, an interval matching the pH of real liquid manure and silage effluents. The pH variations were very slow at the end of the experiment (13 weeks or 2200 h), indicating that the kinetics of the reactions were largely reduced. Moreover, the pH values were high in solutions, with pHs of 11.1 for the slag cement paste (CEM III) and 12.4 for the OPC paste (CEM I).

The criteria considered for global chemical resistance of binders were the kinetics of pH increase in the short term. Fig. 2 shows that the increasing order of chemical resistance was the following: CEM I, CEM I + 10% silica fume, CEM I + 50% fly ash and then CEM III. The addition of silica fume offered a slight gain in

chemical resistance with performance close to that of CEM I. CEM III kinetics for pH increase was a third that of CEM I, on average, before 15 h of immersion.

3.1.2. Variation of the chemical elements concentrations with time

Figs. 3–7 present the variation of the concentrations of the major elements (Ca, Si, Al, Fe and Mg) with time

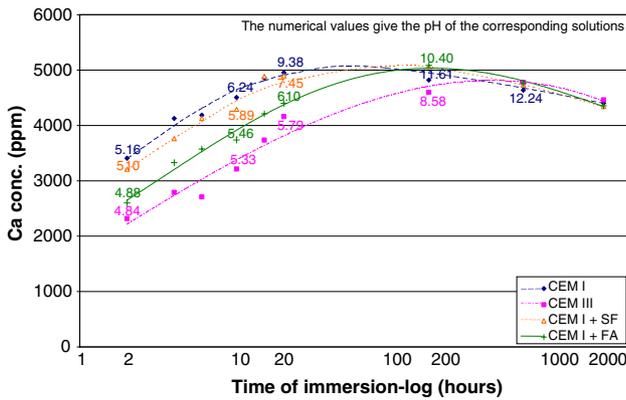


Fig. 3. Calcium concentration in acetic acid solution for the four binders according to time of immersion.

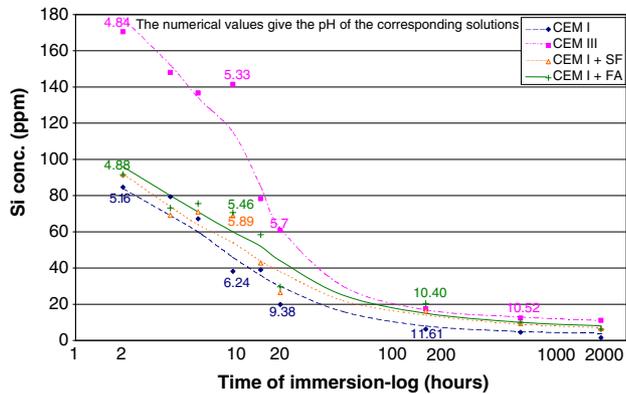


Fig. 4. Silicon concentration in acetic acid solution for the four binders according to time of immersion.

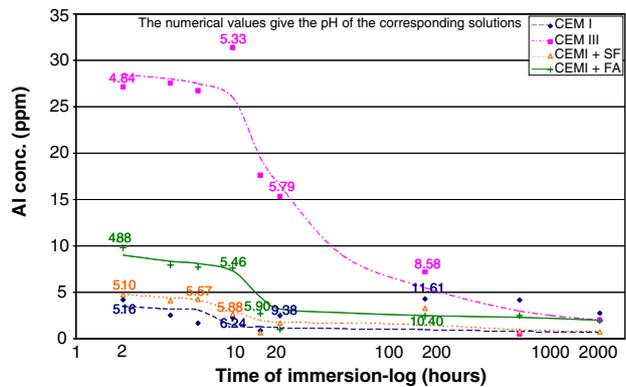


Fig. 5. Aluminium concentration in acetic acid solution for the four binders according to time of immersion.

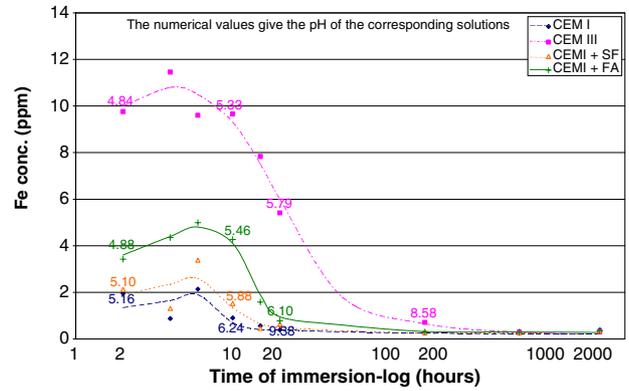


Fig. 6. Iron concentration in acetic acid solution for the four binders according to time of immersion.

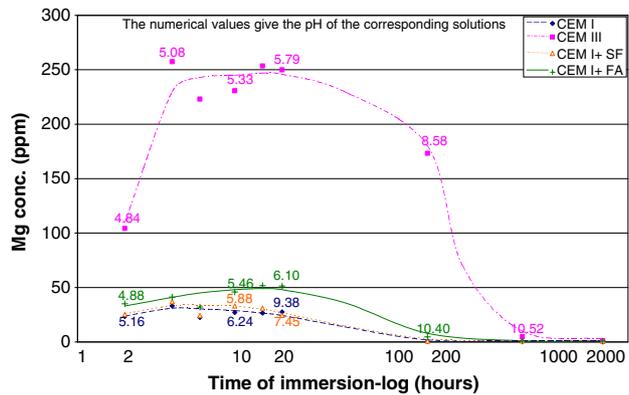


Fig. 7. Magnesium concentration in acetic acid solution for the four binders according to time of immersion.

for each binder. The pH values measured are also mentioned on the graphs.

3.1.2.1. Calcium. The variation of the concentrations of Ca in solution, for every binder, comprised three phases (Fig. 3):

- (1) Ca concentrations increased almost linearly with the logarithm of time from about 3000 ppm (75 mmol/l) up to 4800 ppm (120 mmol/l) in the first part of the experiment. This phase lasted 15 h for CEM I binder and 50 h for the CEM III cement. pHs were between 4.8 and 7.6.
- (2) Then, the increase was much slower, maximum concentrations were reached and were between 4800 and 5100 ppm for the different binders. At the maximum, pHs were about 11 for all the solutions.
- (3) Ca concentrations decreased slightly from the maximum down to 4700 ppm at the end of the experiments for all the solutions.

Solutions containing CEM III pastes had concentrations consistently 20–35% lower than CEM I pastes, the discrepancy decreasing with increasing pH.

For CEM I, CEM I + SF and CEM I + FA binders, the Ca concentrations were equivalent.

3.1.2.2. Silicon. The curves of Si concentration comprised two phases for all the binders (Fig. 4):

- (1) Concentrations of Si decreased strongly from the beginning of the experiment (this decrease indicates that the concentration of Si first increased and went through a maximum before the first term of the experiment, which was 2 h). Si concentration in solution was about twice as high for CEM III binder (180 ppm or 6.4 mmol/l) as for the other binders after 2 h.
- (2) Then, the Si concentrations stabilised when the values became as low as 20 ppm (after 20–100 h in terms of binder function) or for a pH of about 9.5 for every solution.

3.1.2.3. Aluminium. The concentrations of Al (Fig. 5) in CEM III and CEM I + FA solutions:

- were quite stable at the beginning of the experiment, with highest values for CEM III binder (30 ppm, about 1 mmol/l) and intermediary values for CEM I + FA binder (8 ppm, 300 μ mol/l) (as for silicon, the short-term variation of aluminium concentration indicates that it went through an maximum before the first term of the experiment);
- decreased from pH of about 5.5 until Al was reduced to traces in solution.

For CEM I and CEM I + SF binders, the amounts of Al were as low as 5 ppm during the whole experiment.

3.1.2.4. Iron. The amounts of Fe in the solutions of CEM III and CEM I + FA increased slightly at the beginning of the experiment, up to about 10 h or a pH of 5.3, then decreased rapidly to be reduced to traces in solution (Fig. 6). The maximum amounts reached were 12 ppm (214 μ mol/l) for CEM III binder and 4.3 ppm (77 μ mol/l) for CEM I + FA binder. For CEM I and CEM I + SF, the amounts of Fe were low at the beginning of the experiment (2 ppm or 36 μ mol/l).

3.1.2.5. Magnesium. The concentrations of Mg (Fig. 7) for CEM III binder increased strongly until the fourth hour of immersion while the pH reached 5.1. Then, the Mg concentrations stabilised, the plateau extending to 7 days of immersion and a pH of about 9. The Mg amounts decreased afterwards to reach negligible amounts. For the other binders, the amounts of Mg in-

creased slightly after the first measurement and then stabilised, the plateau extending beyond 20 h or pH estimated at about 9. In this case, the amounts of Mg also decreased to traces in solution from this pH.

Highest amounts of Mg (250 ppm, 10 mmol/l) were found in the CEM III solutions. Maximum Mg concentration in the CEM I + FA solutions was about 50 ppm. CEM I and CEM I + SF showed Mg concentrations of 35 ppm (1.4 mmol/l) on average for pHs between 5.2 and 10.

3.1.3. Quantitative comparison of the chemical stabilities

The comparison of the concentrations of elements leached into solution from the different binders and the analysis of the stability of each element required the initial content of each element in each binder to be taken into account.

The ratio of the element mass in solution and the initial mass of the element in the specimen is marked DR or “dissolution rate”. The element mass in solution is the product of the element concentration in solution and the solution volume (0.050 l). The initial mass of the element in the specimen is the product of three terms: the mass percentage in the binder, the binder ratio in the hardened pastes ($1/(1 + 0.27)$) and the mass of coarse grains in a specimen (2.50 g).

Table 6 gives these values for each binder and each element measured at 6 h of immersion. This time was chosen because the chemical reactions were advanced and the solutions pHs were still acidic. Indeed, the pHs of the CEM I and CEM III solutions were 5.7 and 5.2, respectively, after 6 h of immersion.

Calcium was the element with the highest DR ratios, the values lying between 13.3% and 20.9% depending on the binder. Magnesium gave DR between 3.6% and 11.8%. Silicon, aluminium and iron had the lowest DR with values between 0.28% and 1.65%, 0.18% and 0.94%, and 0.14% and 1.9%, respectively.

CEM III and CEM I binders gave Ca dissolution rates weaker than those of CEM I + SF and CEM I + FA. CEM III had the highest DR values for Si and secondary elements. Indeed, for Al, Fe and Mg, the DR values of CEM III were two to sevenfold those of other binders.

CEM I + FA was the binder with the lowest initial amount of Ca but presented the highest DR value. CEM I + SF was the binder with the lowest DR for Si.

DR values for Fe and Al were equivalent for CEM I alone or substituted with silica fume or fly ash.

3.1.4. X-ray diffraction analysis of the precipitates

Fig. 8 presents the XRD analysis of the precipitates collected from CEM I and CEM III pastes immersed

Table 6

Masses of elements in each binder specimen, masses of elements in solution after 6 h of immersion and corresponding dissolution rate

Element		Binder			
		CEM I	CEM III	CEM I + SF	CEM I + FA
Ca	Mass in specimen (mg)	913	657	822	529
	Mass in sol. after 6 h (mg)	209	141	208	179
	Dissolution rate (%)	14.2	13.3	15.7	20.9
Si	Mass in specimen (mg)	196	285	372	285
	Mass in sol. after 6 h (mg)	3.36	7.47	3.55	3.78
	Dissolution rate (%)	1.10	1.65	0.28	0.79
Al	Mass in specimen (mg)	41	93	37	131
	Mass in sol. after 6 h (mg)	0.127	1.378	0.151	0.377
	Dissolution rate (%)	0.19	0.94	0.25	0.18
Fe	Mass in specimen (mg)	32	16	47	72
	Mass in sol. after 6 h (mg)	0.075	0.483	0.076	0.210
	Dissolution rate (%)	0.14	1.9	0.17	0.18
Mg	Mass in specimen (mg)	28	68	25	26
	Mass in sol. after 6 h (mg)	1.66	12.9	1.85	2.29
	Dissolution rate (%)	3.6	11.8	4.6	5.5

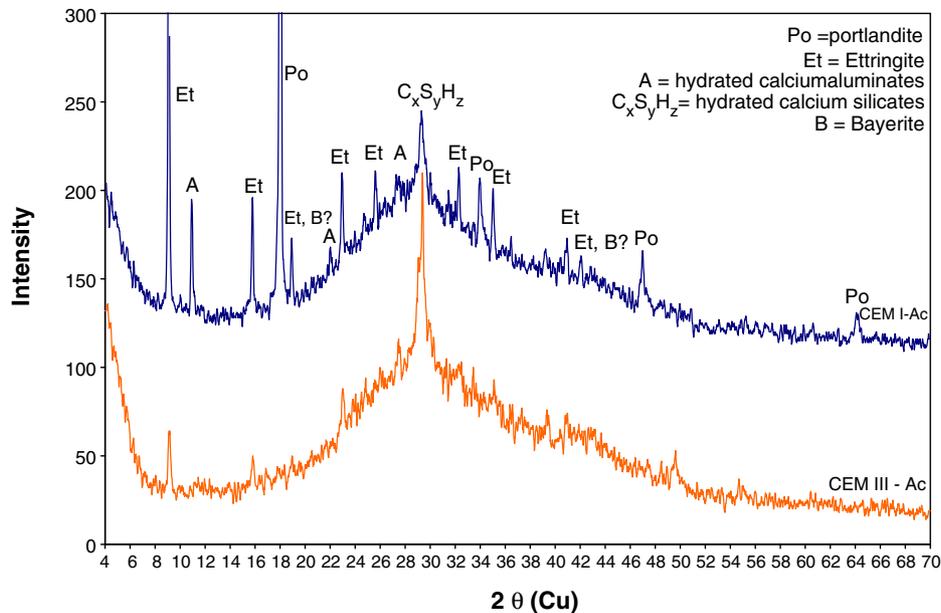


Fig. 8. XRD diagrams of the filtrates for CEM I and CEM III pastes immersed in acetic acid after 13 weeks of experiment.

in acetic acid solution at the end of the experiment. These diagrams are representative of the overall mineralogical characteristics of the precipitates collected for each binder.

These diagrams do not show the formation of acid salts. In every solution and for every binder, ettringite and hydrated calcium silicates lines are present. Moreover, each diagram shows a wide halo extending from 1.8 to 4.7 Å. This halo might result from the superposition of signals of several amorphous species. The largest halo is centred on the hydrated calcium silicates main line.

Portlandite lines were identified for the CEM I binder whatever the acid. Portlandite had either not or not

significantly precipitated for other binders. For CEM I and CEM I + FA immersed in acetic acid, some typical hydrated calcium aluminate lines were found.

3.2. Analyses of the acids' relative aggressiveness

3.2.1. Analysis for the same addition of soda

Fig. 9 shows the results of the immersion experiment of CEM I paste in type 1 solution.

Fig. 9a presents the acids' pK_a values, the initial pH of the solutions and the pH at 6 h and 7 days. On the one hand, the pHs of the solutions at 6 h and 7 days were markedly the same for the acids of liquid manure:

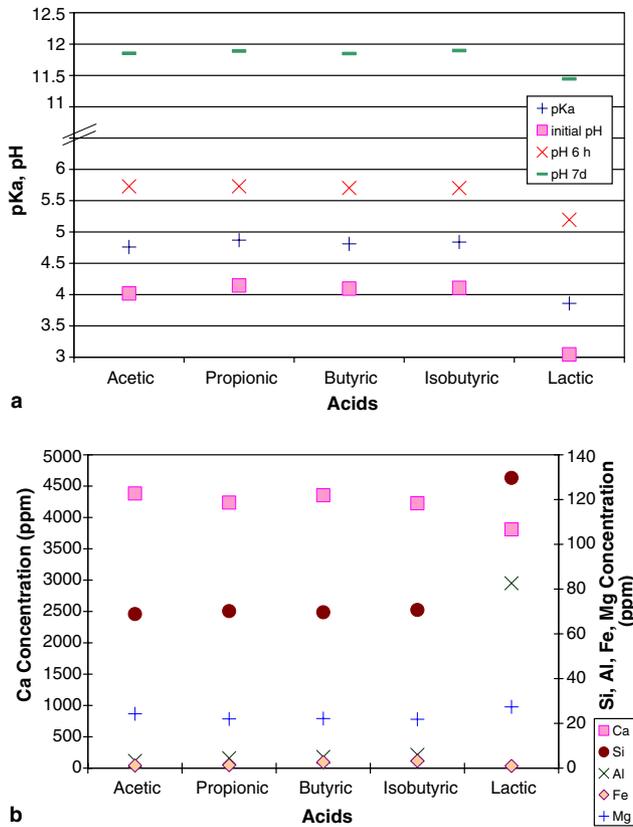


Fig. 9. (a) Organic acid pK_a , and pH initially, at 6 h and 7 days, (b) amounts of Ca, Si, Fe, Al, Mg at 6 h, of the organic acid solutions with 50.12 mM NaOH added.

acetic, propionic, butyric and iso-butyric. All the pH values were between 5.72 ± 0.01 at 6 h and 11.87 ± 0.02 at 7 days. The increasing order of pH of each acidic solution does not match the increasing order of the corresponding pK_a values. It indicates that the experimental error influencing the pH values is higher than the difference between the pK_a values. On the other hand, lactic acid gave the lowest pH at 6 h and 7 days (5.20 and 11.45) in accordance with its pK_a value and the initial pH of the solution.

Fig. 9b shows the quantities of the major elements in solution after 6 h of immersion. The quantities of Ca, Si and Mg were very close for the 4 manure acids with average amounts of: 4300 ± 78 ppm, 69.8 ± 0.9 ppm, and 22.6 ± 1.2 ppm, respectively. After 6 h, traces of Al and Fe were found in solution (4.69 ± 1.36 ppm and 2.09 ± 1.03 ppm, respectively). In the lactic acid solution, the concentrations of Si and Al were much higher than in liquid manure acids: 129 ppm and 83 ppm, respectively. The concentration of Mg was slightly higher (27.5 ppm). Finally, the amount of Ca was 11% lower than in liquid manure acids. Analyses at 7 days revealed the same tendency, traces of Fe, Mg and Al being found in solution.

3.2.2. Analysis at identical pH

Fig. 10 shows the experimental results for the immersion of the crushed CEM I paste in type 2 solutions. Fig. 10a presents the acid pK_a values, the initial pH of the solutions and the pH at 6 h and 7 days.

The pH values of the solutions at 6 h and 7 days were markedly the same for the acids of liquid manure with values of 5.75 ± 0.07 and 11.62 ± 0.04 respectively. The pH of the lactic acid solution was at least one order of magnitude higher than the previous values. This is linked with the discrepancy between its pK_a and that of the manure acids: for a given pH, lactic acid is more dissociated in solution than other acids; the kinetics of pH increase is higher.

In this case, the pHs obtained for manure acids do not obey the increasing order of soda additions which change the dissociation level of the acid in solution. The same comment as Section 2.1 can be made concerning the experimental dispersion.

Fig. 10b shows the amounts of the major elements in solution after 6 h of immersion. The concentrations of Ca, Si, Mg were very close for the 4 manure acids with average values of: 4187 ± 144 ppm, 67.2 ± 5.1 ppm, and 22.5 ± 0.6 ppm, respectively. After 6 h, traces of Al and Fe were found, with concentrations of 1.67 ± 1.87 ppm and 2.14 ± 1.95 ppm, respectively. In lactic acid solution, the amounts of Ca, Si and Mg were lower with

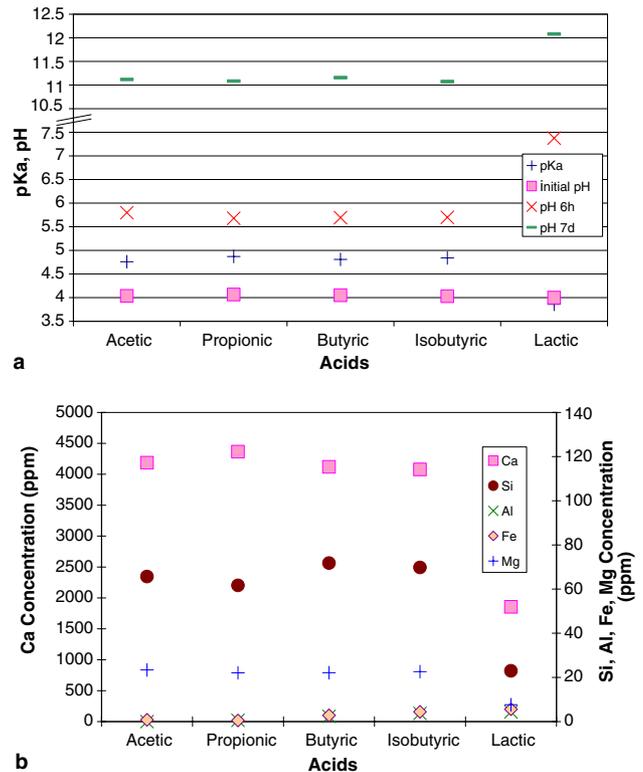


Fig. 10. (a) Organic acid pK_a , and pH initially, at 6 h and 7 days, (b) amounts of Ca, Si, Fe, Al, Mg at 6 h, of the organic acid solutions with an initial pH of 4.

values of 1856 ppm, 23.0 ppm and 7.63 ppm, respectively. Traces of Fe and Al were also found in these solutions. Analyses at 7 days showed the same trend,, traces of Fe, Mg, Al and Si having been found in solution.

4. Discussion

4.1. Cement paste alteration mechanisms, concentration of elements and pH according to time of immersion

The variation of concentrations of elements in solution versus time is the result of the competition between the releases of elements linked with the cement paste phases dissolution and the precipitation of secondary phases when pH and concentrations of elements reach adequate values.

4.1.1. Dissolution of elements

Chemical analysis of the solutions at the beginning of the experiment showed the release of all the elements under the effect of a total dissolution reaction of most of the cement paste phases. Afterwards, when pH increased but was still acid, the hydrated phases continued to react with the acids, but some phases such as anhydrous grains were no further dissolved.

Indeed, as established in previous studies [7–9], the attack by a simulated solution of liquid manure at a pH maintained at 4 or 6 causes the dissolution of all the hydrated phases of OPC or slag cement paste monoliths. Moreover, microprobe punctual analyses on anhydrous grains showed that, in these experimental conditions:

- (a) Slag grains were the only anhydrous phases to be preserved at a pH of 4, although they were slightly decalcified.
- (b) The pH for C_4AF stability was between 4 and 6, since C_4AF was absent from the external part of the specimens immersed in pH 4 solutions, but was still present at pH 6.
- (c) C_2S was still present in the internal part of the altered zone at a pH of 6. The pH value for C_2S stability was presumed to be between 6 and 9.

4.1.2. Precipitation of secondary phases

The decrease in concentrations of elements in solution with time indicates the precipitation of secondary phases. The precipitations are enhanced by the increase of the pH conditions and the concentrations of certain elements. These precipitations may be presented in increasing order of pH whatever the binder. Indeed, Si precipitation had already started in the first sampling period for pHs below 5, and then Al and Fe precipitated

for pHs between 5 and 6, Mg at a pH estimated to be about 9, and Ca at a pH of about 11.

Si precipitation in solution started for pHs below 5. XRD analyses showed that amorphous phases had precipitated in all the solutions at the end of the experiment. The wide halo may be the superposition of several amorphous phase signals, the major halo being centred on the hydrated calcium silicates main line. However, precipitation of hydrated calcium silicates is not conceivable at this range of pH. Hence, it may be assumed that Si first precipitated under the form of silica gel [20], whose signal on XRD diagrams, centred at 4.05 Å, may be masked by the CSH gel.

Al precipitation occurred in solution at pHs between 5 and 6. At this range of pH, Al^{3+} , released by the cement paste, might react in solution to form aluminium hydroxide such as bayerite $Al(OH)_3$. Indeed, Verdes performed experiments on the rehydration of Al_2O_3 amorphous oxides at 21 °C [21]. Amorphous oxides were immersed in a diluted HCl solution with an initial pH of 4. The solid/liquid ratio was 0.05%. In these conditions, Verdes observed the rapid precipitation of bayerite at a pH of 5.1.

However, XRD diagrams do not guarantee the presence of bayerite in the precipitates since both main lines of bayerite are superposed on the ettringite reflections (1 0 4) and (2 2 6) (Fig. 8). Supplementary studies will clarify this point.

The kinetics of Ca dissolution decreased for pH between 7.5 and 11. Some hydrated calcium silicates may have formed in solution and/or C–S–H(α) of the paste may have been preserved [22,23]. The decrease of Ca concentration in solution from pH 11 may be linked with the formation of both hydrated calcium silicates and aluminates, ettringite, and then portlandite, whose lines were identified on XRD diagrams [22–25].

4.2. Comparative analysis of binder durability

The increasing order of alteration kinetics, evaluated by the increase in pH, was the following: CEM III, CEM I + FA, CEM I + SF and then CEM I. The kinetics of CEM III binder was about three times lower than the kinetics of CEM I until the 15th hour of experimentation, when the pHs of all the solutions were below 7.5.

CEM I and CEM III binders presented equivalent stability toward Ca. However, it was noticeable that the stability of the CEM III binder was the lowest toward Si, Al and Mg, compared to the other binders.

The CEM III binder contained 68% blast furnace slag and 32% ordinary Portland cement. Table 7 shows the origin of oxides between OPC and slag for CEM III. It may be noted that, for Si, Al and Fe, more than 79% come from slag, which suggests that the behaviour of slag causes the low stability of CEM III binder toward secondary elements.

Table 7
Origin and amounts of oxides in CEM III binder

Oxides	Composition of CEM III binder (%)	Composition of slag (%)	Composition of OPC (%)	Origin (%)	
				Slag	OPC
CaO	46.67	41.53	64.87	57.63	42.37
SiO ₂	30.94	37.80	21.19	79.13	20.87
Al ₂ O ₃	8.92	10.57	3.94	85.09	14.91
Fe ₂ O ₃	1.15	0.36	2.36	24.00	76.00
MgO	5.71	8.61	2.37	88.64	11.36

Moreover, the pH of CEM III and CEM I solutions were 5.2 and 5.8, respectively, at 6 h of experiment. At these pHs, no hydrated cement phase is stable. Hence, the difference in stability between the two binders may not be linked to the stability of the initial hydrated phases. Two factors might be at the origin of the CEM III binder behaviour toward Si, Al and Mg:

- the low stability of the anhydrous slag grains in acidic media,
- the differences in kinetics of secondary species formation in solution (see Section 4.1) between binders.

However, the first hypothesis is not in accordance with previous results obtained on cement paste monoliths immersed in organic acids without stirring at pH 4 and 6 [8]. Slag grains were stable toward the aggression as observed by SEM in backscattered electron mode and by punctual microprobe analyses. The stability of slag

grains in the previous experiment might be due to the congruent behaviour of that phase: chemical reactions take place at the surface of the slag grain and form products with chemical compositions close to that of the initial anhydrous grain (Fig. 11). This secondary phase layer remains dense and protects the rest of the anhydrous grain during diffusion of the aggressive solution in the pores and the progression of the dissolution front. In monoliths, this layer keeps its integrity due to the presence of a porous zone, rich in Si and Al, formed from the reaction between the hydrated phases of the paste and the acidic solution [7].

In the present experiment, the constant stirring of the containers caused this layer to disintegrate, because of friction between grains of the crushed hardened pastes. Slag grains are not very stable due to their glassy structure. Hence, slag grains may have dissolved. This might explain that the CEM III cement released the same quantity of secondary elements as other binders, relative to its initial amounts.

Moreover, the kinetics of increasing pH, illustrating also the kinetics of secondary phase (such as silica gel) formation, is lower for CEM III binder. This might explain that dissolution rates of Si and Al were higher for CEM III. The same argument might be used to account for the behaviour of CEM III toward Mg even though the Mg-containing secondary phase was not identified.

The lowest Si dissolution rate was found for CEM I + SF binder. This might be linked with the stability of silica fume in acidic media. The lowest Fe dissolution rate was associated with CEM I which contains the

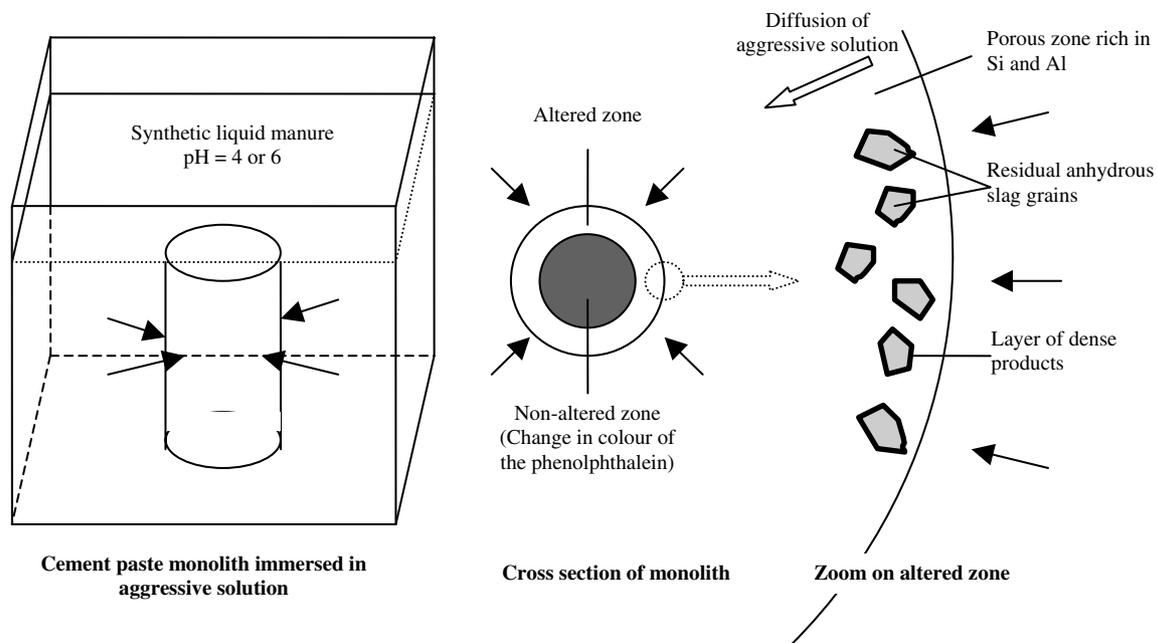


Fig. 11. Experiment of immersion of slag cement paste monoliths in synthetic liquid manure. Hypothesis on the origin of the stability of residual anhydrous slag grains.

highest proportion of C_4AF . C_4AF is the most stable anhydrous phase for ordinary Portland cement paste in acidic media [7–9].

4.3. Stability of the chemical elements

In order to quantify the apparent chemical stability of major elements in the cement paste, a dissolution rate, marked DR, was introduced. DR was defined for a given element and a given binder. It was the ratio between the mass of an element in solution after 6 h of immersion and the initial mass of this element in the specimen. After 6 h of experiment, the pHs of the solutions were between 5.1 and 5.8, depending on the binder, and thus were lower than the pH of real liquid manure.

The dissolution rate enables two phenomena to be taken into account: the release of the elements, linked with the dissolution reactions of the cement paste phases, and the capacity of some elements to react in acidic media and form secondary solid phases. In the case of immersion of monoliths without stirring, these secondary solid phases may precipitate in the altered zone and create a protective membrane which helps to limit the kinetics of further alteration [7–9].

Dissolution rate is hence a significant parameter of the durability of binders.

Whatever the binder, Ca and Mg have the highest DR, whereas Si, Al and Fe have the lowest DR.

- (a) High values of Ca DR may be linked to the presence of Ca in major phases such as portlandite and C–S–H which are dissolved at pH 4 and may form only at high pH and in specific concentrations of elements in solution [22–25].
- (b) The release of Mg may be linked with the dissolution of Mg-bearing slag and OPC hydrated phases. Elevated values of Mg DR were linked with the fact that Mg precipitated in solution only from pH 9. The Mg-bearing secondary phase was not identified.
- (c) Low values of Si DR may be linked with its capacity to react in acidic media, at pH less than or equal to 5, probably to form a silica gel as suggested by XRD diagrams run on the precipitates.
- (d) Secondary elements Al and Fe had the lowest DR among the major cement elements. Figs. 7 and 8 show that Al and Fe precipitated in solution from about 6–10 h of immersion. It may be thought that Al and Fe reactions form an Al and Fe-hydroxide gel as stable phases of these elements at low pH.

Low DR of Fe may equally be linked to the low occurrence of Fe in hydrated phases. Indeed, the low mobility of the Fe bearing phases in cement paste (Fe oxides or hydroxide gels) implies that these phases may be situated in the original confined space of the

Fe anhydrous phase [26]. Hence, Fe is mainly contained in the C_4AF phase which is the late phase of hydration and is stable from pH values between 4 and 6 [8].

4.4. Comparative analyses of the aggressiveness of the different acids

Three parameters are likely to influence the relative aggressiveness of the different organic acids:

- (a) The solubility of the organic acid salts: available values show that these salts are soluble-to-highly soluble in water, except for aluminium acetate and calcium butyrate and iso-butyrate which are slightly soluble at high temperature.
- (b) The dissociation constants of the acids: pK_a of liquid manure acids are very close and are between 4.76 for acetic acid and 4.87 for propionic acid; pK_a of lactic acid which is found in silage effluent is of 3.86.
- (c) The formation constants of organometallic complexes, which strongly depend on the organic acid under consideration and on the cation freed by the cement paste.

Immersion experiments were conducted with two types of solutions: same initial pH, and same quantity of added soda.

Results showed that reactions with the different liquid manure acids released equivalent quantities of each element analysed at the both sampling periods (6 h and 7 days). In both cases, the differences between acids were linked with experimental dispersions (crushing and specific surface area of the materials, pH-meter accuracy, etc.) and did not match the increasing order of solubility and/or pK_a values.

Hence, the differences in salt solubility values and complexation phenomenon in solution did not have a detectable influence on the quantities of major elements released from the cement paste. This indicates that the aggressiveness of the different acids found in liquid manure is equivalent toward cement paste dissolution.

Lactic acid presents a higher aggressiveness as regards pH increasing kinetics and release of elements, in accordance with its pK_a .

5. Conclusion

Hardened cement pastes, made with four binders, were roughly crushed and were then immersed in solutions of five organic acids present in manure.

The comparison of pH variation showed that the decreasing order of binder chemical resistance was: slag cement, 50% ordinary Portland cement blended with 50% fly ashes, 90% OPC with 10% silica fume, and then

OPC. The kinetics of pH increase were three times higher for the less resistant binder than for the most resistant one, for pH lower than 7.5.

The variation of major element concentrations in solution showed that all the elements are released in solution at the beginning of the experiment due to the dissolution of the initial phases of the cement paste and then some of them (Si, Al and Fe) may rapidly combine and precipitate in solution when pH and concentrations increase.

In order to identify the compositional parameters of cements which influence the durability, apparent chemical stability of the major elements was evaluated by introducing a dissolution rate. This rate was defined for a given element and a given binder. It divided the mass ratio of released element in solution after 6 h by the initial mass of the element in the specimen. Results showed lowest dissolution rates for Si, Al and Fe according to the composition of the altered zone of monoliths immersed in aggressive solution without stirring. This confirms that the Si, Al and Fe contents are favourable parameters for assessing the chemical resistance of binders. Measurements also confirmed a well-known result: Ca presented the highest dissolution rate of all the elements. Moreover, the results showed a high dissolution rate for Mg, whose amounts are already limited in cements.

In order to compare the relative aggressiveness of the acids toward cement based matrixes, the pH variations of each solution were measured and the major elements of cement paste (Ca, Si, Al, Fe and Mg) were analysed in solution. Results showed that the aggressiveness of the different acids essentially depended on the dissociation constants. Then, the main acids of liquid manure (acetic, propionic, butyric and iso-butyric acids), whose pK_a are close, are equally aggressive. Parameters such as solubility values of organic acids salts and constants of formation of organo-metallic complexes in solution do not have detectable influence on the attack intensity by each acid.

Besides, lactic acid, which is found in silage effluents with acetic acid, presents a higher aggressiveness, in accordance with its pK_a value.

Hence, in the case of a simulated attack by liquid manure, an aggressive solution made solely of acetic acid, at an adequate concentration, is equivalent to a mix of the different acids found in liquid manure. However, in the case of an attack by silage effluent, the use of a solution of acetic acid showed a milder attack than the real one.

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