Cement and Concrete Research 39 (2009) 929–935

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Processing of electron microprobe data from the analysis of altered cementitious materials

A. Bertron [a,*], G. Escadeillas [a], P. de Parseval [b,c,d], J. Duchesne [e]

[a] Université de Toulouse, UPS, INSA, LMDC (Laboratoire Matériaux et Durabilité des Constructions), 135 av de Rangueil, F-31 077 Toulouse Cedex 04, France
[b] Université de Toulouse, UPS (OMP), LMTG, 14 av Edouard Belin, F-31400 Toulouse, France
[c] CNRS, LMTG, F-31400 Toulouse, France
[d] IRD, LMTG, F-31400 Toulouse, France
[e] Centre de Recherche sur les Infrastructures en Béton, Université Laval, Québec, Canada G1K 7P4

ARTICLE INFO

Article history:
Received 1 March 2009
Accepted 11 June 2009

Keywords:
Cement paste
Degradation
Electron microprobe

ABSTRACT

The purpose of this paper is to present a method for processing electron microprobe data coming from the analysis of degraded cementitious materials. The application domain is that of cement matrices exposed to attack by aggressive media inducing the leaching of one or more chemical elements from the cement paste — typically attacked by neutral or acid aqueous environments. As raw data obtained from electron probe microanalysis (EPMA) come in the form of relative quantities of elements, the aim of the processing is to obtain the absolute variation of the specimen's chemical composition in the degraded zone and consequently to allow a better understanding of the degradation mechanisms by the aggressive environment under consideration. This method was designed for degraded specimens in which the porosity was not filled with resin before the EPMA. The method uses the titanium content of the cement matrix as a control, this element being stable during attack by neutral or acidic media. The method is described in detail using the example of the attack of cement pastes by a mix of several organic acids (notably acetic acid) at pH 4. The use of EPMA for sound and altered cement pastes is also validated. The application domain of the correction method is discussed.

1. Introduction

Electron probe microanalysis (EPMA) is a technique for elementary analysis of materials. It consists of bombarding a specimen with a high-energy (typically a few kV: 5–30 kV) focused electron beam, which allows the first micrometres of the specimen to be ionized and induces the emission of characteristic X-rays. These emissions are processed to obtain quantitative analysis using standards allowing the comparison of the concentration of a given element in the specimen to the known concentration of the same element in the standard.

When the electron microprobe is used for cementitious materials, the equipment is operated out of its well known field of applications (bulk samples), the analysis of metallic alloys, minerals, etc. Nevertheless, in porous materials, the electrons penetrate deeper into the sample but the quantity of matter ionized is unchanged, resulting in the same photon absorption as in the bulk materials, so the porosity should not induce a difference in the emerging X-ray intensities, as has been shown by Sorbier et al. [1,2]. However, these authors warn of possible contamination effects (O, C, water…) due to the high specific surface of porous materials.

Yet, the comparison of electron microprobe analysis data with conventional chemical analysis obtained from chemical determination of the solution after total attack is very satisfactory for hardened cement pastes and the use of the electron microprobe for the analysis of cementitious matrices is now widespread [3–11].

The technique is particularly interesting for the analysis of the chemical alteration mechanisms of cementitious matrices by aggressive environments since it can be used to obtain chemical profiles from the surface in contact with the aggressive medium to the core of the specimen [5–10]. However, the concentrations of each element in the probed volume provided by microprobe analyses are in the form of a matter mass percentage (voids excluded). Thus, the real evolution of each element is not visible when the attack causes partial or total leaching of one or more elements (case of pure water, and strong and weak acids, the associated cementitious cation salts which are soluble in water). The loss of an element (calcium for example) leads to an increase in the proportion of a more stable element in the attack (silicon, for example). When the chemical attack results in the loss of an element and the creation of voids, a possible solution to compensate for this phenomenon is to impregnate the porosity of the specimen with resin under vacuum [3,5]. This operation requires the specimen to be dried and impregnated with a fine and sufficiently wetting resin. However, the specimen can be degraded during the impregnation notably when the

---

[*] Corresponding author. Tel.: +33 5 61 55 99 31.
E-mail address: alexandra.bertron@insa-toulouse.fr (A. Bertron).

0008-8846/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2009.06.011

altered zone is fragile. Moreover, the porosity may not be completely impregnated–notably for discontinuous porosity–and thus the chemical analysis may be distorted.

The purpose of this article is to propose a method for processing electron microprobe data obtained from the analysis of degraded cementitious materials when the specimen porosity is not impregnated with resin. The method's frame of application is that of attacks in neutral or acid media generating the leaching of one or more elements of the cement paste. The aim of the processing is to display the absolute variation of the matrix element concentrations from the sound core to the surface in contact with the aggressive solution in order to improve the analysis and the understanding of the mechanisms of alteration by these media. The processing is based on the use of the titanium content of the specimen since this element is known to be stable in acidic media.

The use of EPMA is first validated on sound and altered cementitious matrices. Then, the proposed correction method is applied to the analysis of a cementitious matrix altered by a solution of organic acids at pH 4. The correction method is then discussed.

2. Experimental process

2.1. Materials

The study was performed on hardened cement pastes made with a CEM I 52.5 R ordinary Portland cement [12]. The cement chemical composition is given in Table 1.

2.2. Specimen making and treatment

The hardened cement paste specimens, with a water/cement ratio of 0.27, were cylindrical, 75 mm high and 25 mm diameter. The specimens were taken out of their moulds 24 h after pouring and stored in tap water at 20 °C for 27 days. The ‘volume of water/volume of specimens’ ratio was low–about 1.5–to limit the leaching of the specimens during their storage. Twenty-eight days after pouring, the specimens were immersed in the aggressive solution. Control specimens were kept in water at 20 °C during the whole experiment.

The aggressive solution was a mix of 5 organic acids found in liquid manure: acetic, propionic, butyric, iso-butyric and valeric acids. The calcium salts of these acids are soluble to highly soluble in water. The total concentration of the acids was 0.28 mol/l. Two grams/liter of NaOH was added to the solution to bring the pH up to 4. The pH was kept constant by the renewal of the solution during the 18 week-experiment. More details about the aggressive solution are available in previous articles [7,9].

After 4, 9 and 13 weeks of immersion in the aggressive solutions, 2 cylindrical specimens were extracted from the solution. Slices were sawn in the cylinders perpendicularly to their axis so that the chemical composition profiles of the specimen could be analyzed on the plane surfaces of the slices. These slices were then embedded in an epoxy resin (Mecaprex MA2 by Presi) in small moulds for ease of positioning and polishing. The resin used, which was highly viscous, and casting in the open air prevented any intrusion of the resin into the porosity of the specimen. This was checked using microprobe analyses of the outer part of the degraded cement paste (highly porous and thus more likely to be penetrated by the resin than the sound zone) by considering the chlorine content (a Cl-bearing resin was used). The analyses showed that this content was almost equal to zero. After hardening, flat sections of the specimens were prepared by dry polishing using an air gun to avoid the porosity becoming clogged by abrasion dusts as far as possible. The polishing was performed using a series of three silicon carbide polishing disks (by Presi). The references of the abrasive discs and the sizes of the abrasive particles were: P800–22 µm, P1200–15 µm and P4000–5 µm. The time of polishing per specimen with the above mentioned disks was 2 min 30 s, 1 min 30 s, and 30 s, respectively. Other polishing methods–including lubrication–could be used but any solvent employed must not contain water to avoid hydration of the cement paste's remaining anhydrous grains. After polishing, the sections were coated with carbon.

Table 1
Cement chemical composition.

	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 2
Calibration standards, confidence intervals and detection limits for each element analyzed with electron microprobe for hydrated CEM I paste.

Elements	Standard	Confidence interval	Detection limits
Ca	Wollastonite	±0.5%	0.06%
Si	Wollastonite	±0.15%	0.05%
Al	Corumdum	±0.08%	0.05%
Fe	Haematite	±0.16%	0.15%
Mg	Periclase	±0.07%	0.07%
S	Celestine	±0.12%	0.07%
Na	Albite	±0.06%	0.13%
K	Sanidine	±0.05%	0.05%
Ti	Pyrophanite	±0.03%	0.04%
Mn	Pyrophanite	±0.04%	0.05%

2.3. Microprobe analysis

The measurements with the microprobe were made on these flat, polished sections according to the distance to the surface in contact with the aggressive solution in the altered and sound zones. Particular care was paid to the choice of the analysis points in order to measure only the hydrated paste and avoid residual anhydrous grains. Two control specimens were analyzed, at the rate of 50 points per specimen, 5 weeks after pouring. The following elements were analyzed: Ca, Si, Al, Fe, Mg, S, K, Na, Ti and Mn.

The microprobe analysis instrument was a CAMECA SX 50. The accelerating voltage was 15 kV, the current was10 nA and the scanning area of the beam was $2*2\ \mu m^2$. The counting time was 10 s on peak and 5 s on the background on each side of for all elements but titanium. For titanium (minor element used for the correction method) the counting time was 30 s on peak and 10 s on background each side.

Calibration was performed on natural and synthetic standard materials before each series of analyses. These standards are listed in Table 2 with the confidence intervals on the mass percentage of each analyzed element and the corresponding detection limits [13].

3. Validity of electron microprobe analysis applied to sound and altered cementitious materials

3.1. Sound specimen

Microprobe analysis allows concentrations of each element in the probed volume to be expressed as a matter mass percentage (voids excluded). For cementitious materials, these mass percentages are conventionally expressed as mass percentages of associated oxides. Let us consider the case of the analysis of CEM I paste kept in water for

Table 3
Chemical analysis of a cement paste control specimen measured by EPMA (150 points).

Oxides	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	TiO_2	Na_2O	K_2O	MnO	Total
Mean (%)	49.3	15.9	3.3	1.2	3.4	0.59	0.13	0.12	0.09	0.03	74.1
Standard deviation (%)	4.1	3.7	1.2	0.7	1.1	0.37	0.08	0.07	0.06	0.04	3.3

35 days. Table 3 gives the average composition of oxides obtained from 150 analyses distributed over a representative specimen together with the standard deviation linked with the heterogeneity of the matrix.

The sum of the oxide percentages was 74%. The compliment to 100 of this sum (26%) covered non-analyzed species, such as hydrogen, carbon and phosphorus, and elements in small quantities that were not included in the analysis programme. Carbon in CO_2 form, phosphorus in P_2O_5 form, and heavy metals represented 1 or 2% of the total of the oxides. The remaining percentage (about 24%) can be attributed to bound water in the hydrated phases of the cementitious matrix: C–S–H, calcium hydroxide, ettringite, etc.

The electron beam focusing can have an influence on the volume of solid analyzed and on the sum of oxides. For previously analyzed cementitious matrices, the sum of oxides could vary by ±2% depending on the EPMA electron beam focusing, probably because of the partial inclusion of residual anhydrous grains in the sounded volume. Even if the analysis points are chosen on the hydrated phase, when the focusing of the beam decreases, the volume analysed increases and it is more likely to contain residual anhydrous grains, thus increasing the sum of oxides.

3.2. Altered specimen

Fig. 1 shows the raw chemical composition profiles obtained with electron microprobe for a CEM I cement paste specimen immersed in the aggressive solution for 4 weeks. The amounts of CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO_3 are given according to the distance to the surface in contact with the aggressive solution. The Na_2O, K_2O, TiO_2 and MnO contents are not provided on the graph since their influence on the total oxides is quite negligible. The sum of all oxides is also represented, as is the analysis of a control specimen. In order to improve the readability, the curves have been smoothed using a moving average calculated from 5 points of the initial curve.

Sound and degraded zones are reported on the graph. The zones were identified visually by the change in colour of phenolphthalein on another slice of the same specimen. The thickness of the degraded zone was measured using a video microscope. The distinction between zones 1 and 2, and 3 to 5, sub-divisions of the two main zones, was linked to differently coloured layers as described elsewhere [7].

The chemical composition of zone 1 in the sound zone was equivalent to that of the control specimen. The chemical compositions of each zone in the degraded zone are given in Table 4 (Na_2O, K_2O, TiO_2 and MnO do not appear but they are taken into account in the total of oxides). The table also provides mean values in the whole degraded zone and the composition normalized to 100%.

Table 4
Average oxide contents in the altered zone and mean values normalized to 100%.

	Oxide contents (%)					
	Total	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3
Zone 3	68	9.3 to 14	43	8.4	2.5	0.03
Zone 4	67	3.6 to 9.2	46	9.2	3.3	0.03
Zone 5	52	3.0	40	4.6 to 7.85	0.70 to 2.0	0.03
Average of AZ	**60**	**6.0**	**44**	**7.4**	**2.0**	**0.03**
$\frac{\%\ \text{Oxide}_k}{\sum_i \%\ \text{Oxide}_i}$	**100**	**10**	**73**	**12.3**	**3.3**	**0.05**

Data set in bold indicates the average of altered zone.

Fig. 1 shows that the altered zone was strongly decalcified. The degradation mechanisms of cementitious matrices by acetic, propionic, butyric, etc. acids, the calcium salts of which are soluble to highly soluble in water, have been thoroughly described in previous papers [7–9].

Moreover, Table 4 shows that:

- the total of oxides in the altered zone was about 60%, which indicates that the material contained about 40% water. This estimation was confirmed with DTA/DTG analysis of the degraded zone. At the end of the test, the specimen mass loss–mainly matching the strongly- and weakly-bound water release–was 40% (Fig. 2). Fig. 2 also shows that the water release for the sound zone was between 20 and 25%, which matches the compliment to the total amount of oxide given in Table 3.
- SiO_2 and Al_2O_3 contents in the altered zone were sensibly higher than those found in the core. Al and Si being stable in an acidic medium, these increases may be linked with the relative character of the quantification. Moreover, as the sound zone showed SiO_2 and Al_2O_3 contents that were constant and identical to those of the control specimen, no migration of silicon or aluminium from solid phases of the sound zone to the degraded zone could have generated these increases.

These results raise two questions. The first issue concerns the validity of the results obtained from the analysis of the degraded zone: the characteristics of this zone (very porous and amorphous [9]) do not match the usual field of application for the electron microprobe. The second issue concerns the relevance of representing the results in element or oxide relative amounts.

In order to determine whether the porous and amorphous character of the degraded zone could induce perturbations in the analysis, beads

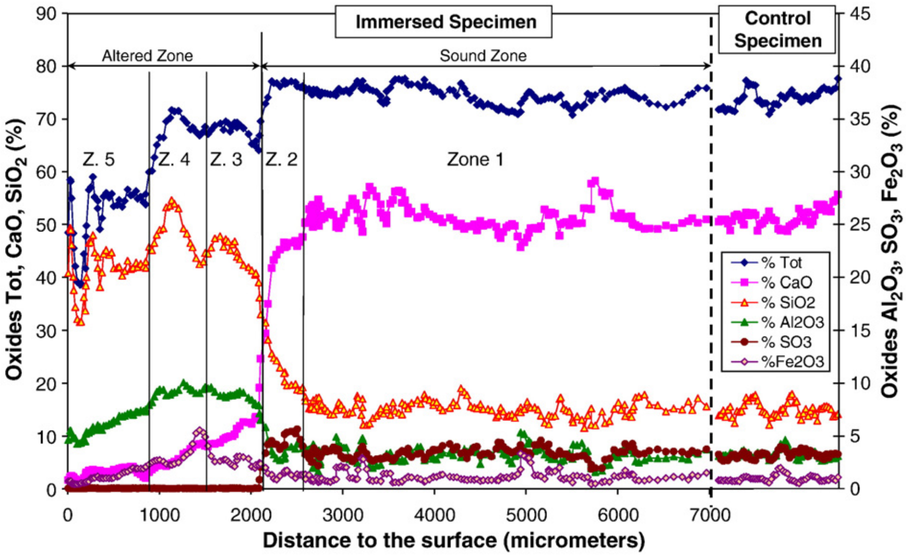

Fig. 1. Chemical composition of oxides of a CEM I paste immersed in a solution of organic acids at pH 4 for 4 weeks according to the distance to the surface of the specimen.

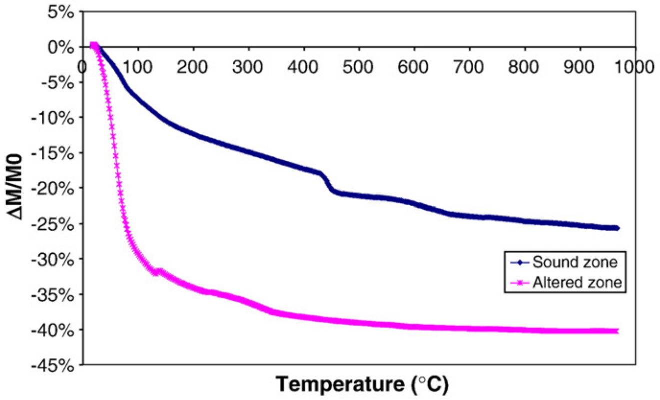

Fig. 2. TG analysis of sound and degraded zones.

made from ground specimens sampled in the degraded and in the sound zones were analyzed chemically (Table 5) and the results were compared to the previous ones. The material was dried at 50 °C, heated to 1100 °C to form beads, ground to reduce the size to under 80 µm and mixed with 50% of lithium tetraborate. This process destroyed the material structure and the porosity of the beads was zero.

The comparison of the last lines of Tables 4 and 5 shows that the amounts of CaO, SiO_2 and Al_2O_3 obtained from the two types of analysis are quite similar. However, a great difference appears in the percentage of Fe_2O_3, which is 7.1% for the beads whereas it is 3.9% for profiles.

This difference may be linked with the integration of residual anhydrous grains during the analysis of the bead. As mentioned previously, the microprobe profiles were drawn up from the analysis of the hydrated cement paste monoliths only: particular care was paid to the location of the analyses on the specimen in order to avoid residual anhydrous grains, whose chemical changes are quite different from those of the paste [8,9]. In contrast, beads were made by sampling the whole degraded or sound zone, including residual anhydrous grains. Now, it has been shown that C_4AF residual anhydrous grains are the only ones to be preserved in the degraded zone: they are found at least in zone 3 at pH 4 and in the whole degraded zone at pH 6 [8]. In hydrated cement pastes, iron is essentially contained in anhydrous grains since Fe-bearing phases are not very mobile [14]. Thus, the large difference observed for iron may be linked with the analysis of residual anhydrous grains.

Table 5
Chemical analysis of beads made from ground samples of altered and sound zones.

	Chemical composition in oxides (%)				
	Tot	CaO	SiO_2	Al_2O_3	Fe_2O_3
Sound zone	100	64.0	21.3	5.55	2.30
Altered zone	100	8.53	64.7	15.7	7.10

It may be concluded from this comparative study that microprobe analyses in the altered zone–almost amorphous and very porous–seem to be consistent with analyses of beads made from the same material. The use of the microprobe for the characterization of degraded monoliths is thus validated.

The second question was about the relevance of representing the profiles in relative quantities, which masks the real variation of each element. The drastic drop in calcium content induces increases of elements which are leached in relatively lower quantities. A correction method using titanium as a control element is proposed below.

4. Correction method

4.1. Bibliography on titanium in cement

Clinker raw materials–limestone and clay–contain traces of transition metallic elements such as titanium, manganese, phosphorus, etc. Corresponding metallic oxides are thus found in cements and make up 1–2% of the material. They are found in substitution in anhydrous phases [15]. Trace elements can also be introduced during concrete mixing, in the form of soluble salts. These elements may modify some properties such as the formation of clinker and its grindability [15,16], the hydration processes [17] or the microstructure of hardened cement paste [18]. In this case, they can be found: incorporated in the structure of some hydrates (ettringite and C–S–H mainly), adsorbed at their surface, or present in residual anhydrous phases [19–21]. The leaching of trace elements depends on the stability of the hydrated or anhydrous phases they are part of and on the chemical solubility of the trace element in the conditions of leaching. For cement paste attacked by acids whose calcium salts are soluble in water, all the hydrated and most of the anhydrous phases are dissolved in the cement paste at pH below 6 [7–9]. The leaching of trace elements will thus depend on the chemical speciation of the species in the conditions of the attack.

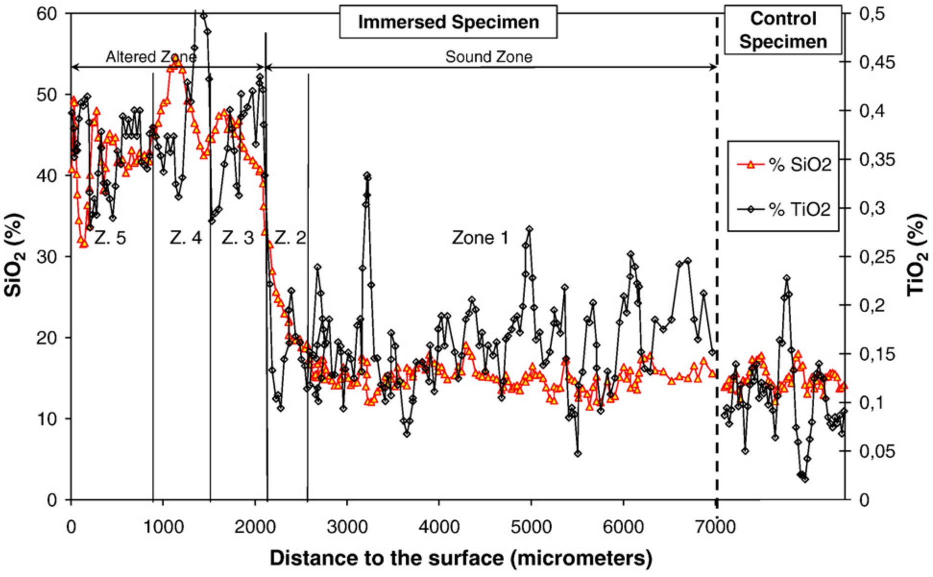

Fig. 3. Raw profiles of TiO_2 and SiO_2 amounts for a CEM I paste specimen immersed in the aggressive solution for 4 weeks and for a control specimen.

Table 6
Mean amounts of TiO_2 and standard deviations in the different zones of the immersed specimen and in the control specimen.

Zone		Altered zone				Sound zone		Control
		Zone 5	Zone 4	Zone 3	Mean DZ	Zone 2	Zone 1	
% TiO_2	Mean	0.356	0.393	0.370	0.371	0.151	0.160	0.147
	Standard deviation	0.0374	0.075	0.053	0.053	0.037	0.045	0.042

Among the trace elements, titanium present in the form of rutile titanium oxide is known to be very stable. Knauss et al. have measured the solubility product of Ti(IV) in aqueous solution at pH between 1 and 13 [22]. They have shown that rutile has a minimal and constant solubility of $10^{-7.72 \pm 0.15}$ at 100 °C for pH between 3 and 9.5. The solubility product decreases with temperature following the same law. Titanium is thus very stable over the pH interval [4; 9.5], which includes the pH interval of the degraded zone since:

- the pH of the aggressive solution in contact with the surface of the specimens was 4 or more,
- the pH at the limit between the degraded and sound zones was 9.5 since the change in colour of phenolphthalein, the indicator used to distinguish the two zones, occurs at pH 9.5.

So, titanium was used as a control element between the degraded and sound zones in order to correct the chemical data of the degraded zone.

It should be noted that some other authors have already used titanium as a control element, as, for example Faucon et al., for cement pastes exposed to leaching by demineralized and weakly acidified waters [23].

4.2. Principle and validity of the processing method

Average amounts of titanium in the degraded zone (DZ) and in the sound zone (SZ) are calculated from microprobe analysis data — about 150 punctual analyses are performed in each zone. The ratio of these amounts $C = \frac{TiO_2 \text{ amount in SZ (\%)}}{TiO_2 \text{ amount in DZ (\%)}}$, smaller than 1, is used as a correction coefficient for the data on chemical composition in oxides in the degraded zone.

Fig. 3 shows the raw profiles of TiO_2 and SiO_2 amounts for a CEM I paste specimen immersed in the aggressive solution for 4 weeks and for a control specimen. It can be observed that the amounts of both elements evolve in the same way. They have similar behaviours toward the attack. This result was found for all the types of cement that were tested: CEM I, CEM I PM/ES, CEM III and CEM V.

Mean amounts of TiO_2 and standard deviations in the different zones of the immersed specimen and in the control specimen are given in Table 6.

In the conditions of our analyses (current 10 nA, accelerating voltage 15 keV), the element detection limit was 500 ppm. Concentrations of titanium in CEM I and CEM I PM/ES pastes were about 3000 ppm in the altered zone and 1500 ppm in the sound zone. They were about 4500 ppm and 2200 ppm in the altered and sound zones, respectively, of CEM III hydrated pastes. Confidence intervals for titanium were ±0.05% and ±0.06% in the sound and altered zones respectively. Hence, for a TiO_2 amount of 0.16% in the sound zone, for example, the confidence interval was [0.11%; 0.21%] and for a TiO_2 amount of 0.37% in the altered zone, the confidence interval was [0.31%; 0.43%]. These intervals are quite wide. However the large number analyses in each zone allowed clear trends to be obtained on the graphs.

4.3. Choice of correction coefficient

It is noteworthy that the use of a single correction factor is sufficient for the whole altered zone exposed at pH 4 since the amounts of TiO_2 in zones 3, 4 and 5 were equivalent (Table 6). The same result was obtained at pH 6. This may be explained by the fact that (i) the solubility of rutile is minimal and constant at pH between 3 and 9.5, so the TiO_2 content remains constant in the whole altered zone and (ii) the contents in other major elements of the cement paste remain quite constant in the altered zone.

The correction factor *C* used in the degraded zone of CEM I paste was 0.160/0.371 = 0.431.

Zone 2 was corrected with a factor varying progressively from 1 at the limit with zone 1 to the value of the correction factor *C* at the limit with zone 3. The variation of this factor was proportional to the number of punctual analyses performed in zone 2.

The result of the correction of the curves is given on Fig. 4 and the amounts of oxides in each zone are provided in Table 7.

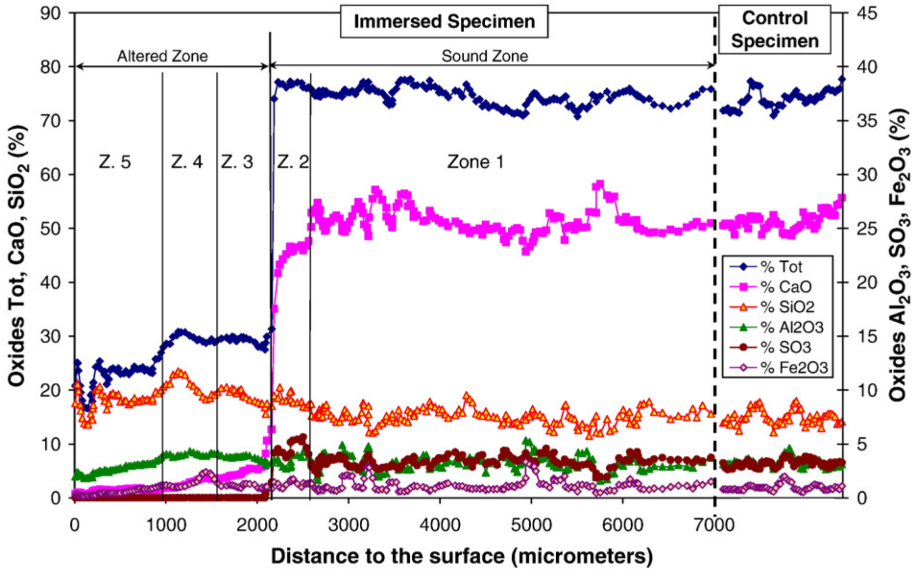

Fig. 4. Chemical composition of oxides of a CEM I paste immersed in a solution of organic acids at pH 4 for 4 weeks according to the distance to the surface of the specimen (analysis by electron microprobe, corrected).

The correction allows the amounts of silicon, aluminium and iron in the degraded zone and in zone 2 to be made consistent with those of zone 1.

5. Discussion: Generalization/limits of the method

The application of the correction method based on the use of titanium content shows that, in the aggressive conditions (pH 4), the amount of silicon in the altered zone is globally constant and equal to that in the sound zone. This result was obtained for all the types of pastes that were studied (CEM I, CEM I PM/ES, CEM III/B and CEM/V). This means that silicon is little, if at all, leached from the specimen during the attack. This can be checked by using the results of the chemical determination of an aggressive solution (Table 8).

Table 7 shows that 95% of the calcium initially contained in the cement paste is leached from the degraded zone. Considering the cement paste initial silicon content, Table 8 shows that only 3% of silicon is eliminated from this zone. Taking into account the errors associated with the different chemical determination methods, it is valid to state that silicon is globally well preserved in the altered zone.

This leads us to propose the use of the silicon content as a correction criterion for microprobe data in addition to or in replacement of the use of titanium. The advantage is to consider a major element of the matrix with which a more satisfactory confidence interval is associated: ±0.15% for absolute average amounts of about 12%. It may be relevant to use the titanium content in an initial step of the correction method in order to first check the evolution of silicon.

The use of aluminium or iron is less relevant for the pH interval considered (pH between 4 and 6). These two elements are leached from the external part of the specimens and the initial amounts are smaller than that of silicon. In all cases, the method should be applied to a great number of punctual analyses (a typical 10 µm-step between two successive analyses is recommended) in order (i) to compensate for the high variability of cement paste chemical composition and (ii) to clearly identify the different zones of the altered specimen.

The correction method was also validated on data taken from the analysis of cement pastes altered at pH 6 by the same mix of acids, the calcium salts of which are soluble in water. The results of the correction method are given in [8].

This method could be used for all types of aqueous attacks where the stability of TiO_2 is maintained i.e. with pH between 3.5 and 9. The validity of the method must then be checked by using, for example, the same type of tests as those presented in this paper. The reliability of the method depends greatly on the stability of the hydrated phases to which Ti is bound (Si-bearing phases, probably). If silicon leaching occurred (long exposure to aggressive solution, highly aggressive aqueous environment such as citric acid [24], etc.), Ti would be leached as well. But, in this case, the degraded zone would dissolve and it would no longer be possible to perform microprobe analysis in the zone concerned.

Moreover, in the present case, a single correction coefficient was used for the whole degraded zone because the major element contents remained quite constant throughout the zone. In other cases of attack, the use of several coefficients may be necessary.

Table 7
Average chemical composition in oxides in the different zones of CEM I paste specimen immersed at pH 4 (analysis by electron microprobe, corrected).

Zone	% Tot	% CaO	% SiO_2	% Al_2O_3	% Fe_2O_3	% SO_3
Z. 1	74.6	51.4	15.2	3.26	1.16	3.38
Z. 2	76.5	44.8	16.2	3.60	1.33	4.62
Z. 3	29.3	3.7–12.7	18.1	3.31	1.08	0.15
Z. 4	29.0	2.6	19.6	3.95	1.42	0.01
Z. 5	22.4	1.2	17.8	2.35–3.20	0.47	0.01

Table 8
Element concentrations in an aggressive solution at 2 weeks of immersion (CEM I paste specimens, solid/liquid ratio = 1/18).

	Ca	Si	Al	Fe
Concentration (mg/l)	5956	40	33	25

6. Conclusion

A method for processing microprobe data from the analysis of degraded cementitious materials has been presented. This method is particularly well suited to degraded specimens, the porosity of which is not filled with resin. As raw data obtained from EPMA are in the form of relative quantities of elements, the aim was to obtain the absolute variation of the specimen's chemical composition in the altered zone and thus to allow a better understanding of the mechanisms of degradation by the aqueous environment considered. The method was applied and validated on cement pastes exposed to the attack of organic acids, the calcium salts of which are soluble in water, at pH 4 and 6. The principle of the method lies in the use of the titanium content of the cementitious specimen, titanium being well preserved during the acid attack. This method could be applicable, after validation, to all kinds of aqueous attack that maintain (i) the stability of titanium contained in the cement paste (pH of the degraded zone between 3.5 and 9) and (ii) the integrity of the altered zone so that it can be analyzed with the microprobe.

Regarding the attacks by organic acids at pH 4 and 6, it was observed that the silicon content could also be used for the correction method, in addition to or in replacement of the titanium content, as this element is also well preserved during the attack. It allows better confidence intervals to be obtained for the final graphs.

References

[1] L. Sorbier, E. Rosenberg, C. Merlet, X. Llovet, EPMA of porous media: a Monte Carlo approach, Microchim. Acta 132 (2000) 189–199.
[2] L. Sorbier, E. Rosenberg, C. Merlet, Microanalysis of porous materials, Microsc. Microanal. 10 (2004) 745–752.
[3] O. Mejlhede Jensen, A.M. Coats, F.P. Glasser, Chloride ingress profiles measured by electron probe micro analysis, Cem. Concr. Res. 26 (11) (1996) 1695–1705.
[4] M. Paul, F.P. Glasser, Impact of prolonged warm (85 °C) moist cure on Portland cement paste, Cem. Concr. Res. 30 (12) (2000) 1869–1877.
[5] Y. Maltais, E. Samson, J. Marchand, Predicting the durability of Portland cement systems in aggressive environments—Laboratory validation, Cem. Concr. Res. 34 (9) (2004) 1579–1589.
[6] C. Carde, R. François, Aging damage model of concrete behavior during the leaching process, Mater. Struct. 30 (8) (1997) 465–472.
[7] A. Bertron, G. Escadeillas, J. Duchesne, Cement pastes alteration by liquid manure organic acids: chemical and mineralogical characterization, Cem. Concr. Res. 34 (10) (2004) 1823–1835.
[8] A. Bertron, J. Duchesne, G. Escadeillas, Accelerated tests of hardened cement pastes alteration by organic acids: analysis of the pH effect, Cem. Concr. Res. 35 (1) (2005) 155–166.
[9] A. Bertron, J. Duchesne, G. Escadeillas, Degradation of cement pastes by organic acids, Mater. Struct. 40 (3) (2007) 1061–1071.
[10] B. Gérard, C. Le Bellego, O. Bernard, Simplified modelling of calcium leaching of concrete in various environments, Mater. Struct. 35 (10) (2002) 632–640.
[11] K. Haga, S. Sutou, M. Hironaga, S. Tanaka, S. Nagasaki, Effects of porosity on leaching of Ca from hardened ordinary Portland cement paste, Cem. Concr. Res. 35 (9) (2005) 1764–1775.
[12] European Standard EN 197-1, Cement, Composition, Specifications and Conformity Criteria for Common Cements, AFNOR, Paris, 2000, 35 pp.
[13] M. Ancey, F. Bastenaire, R. Tixier, in: F. Maurice, L. Meny, R. Tixier (Eds.), Applications des méthodes statistiques en microanalyse. Microanalyse et Microscopie Electronique à Balayage, Les éditions de Physique, Orsay, France, 1978, pp. 323–344.
[14] H.F.W. Taylor, D.E. Newbury, An electron microprobe study of a mature cement paste, Cem. Concr. Res. 14 (4) (1984) 565–573.
[15] M.B. Marinho, F.P. Glasser, Polymorphism and phase changes in the ferrite phase of cements induced by titanium substitution, Cem. Concr. Res. 14 (3) (1984) 360–368.
[16] R. Bucci, Influence de la nature et de la préparation des matières premières sur la réactivité des crus, 7th International Congress on the Chemistry of Cement, vol. 1, 1980, p. I-1/3, Paris.

[17] G. Kakali, S. Tsivilis, A. Tsialtas, Hydration of ordinary Portland cements made from raw mix containing transition element oxides, Cem. Concr. Res. 28 (3) (1998) 335–340.
[18] S. Tsivilis, G. Kakali, A study on the grindability of Portland cement clinker containing transition metal oxides, Cem. Concr. Res. 27 (5) (1997) 673–678.
[19] M.L.D. Gougar, B.E. Scheetz, D.M. Roy, Ettringite and C–S–H Portland cement phases for waste ion immobilization: a review, Waste Manage. 16 (4) (1996) 295–303.
[20] F. Ziegler, A. Johnson, R. Giere, Heavy Metals Binding Mechanisms in Cement-Based Waste Materials: Incorporation of Zinc in Calcium Silicate Hydrates (CSH), Stabilisation des Déchets et Environnement 99, Lyon Villeurbane, France, 1999, pp. 36–40.
[21] C. Le Callonnec, C. Richet, R. Ayache, The Uptake of Cs, Cl, I, Co, Pu by C–S–H and Ettringite, STAB & ENV 99, Stabilisation des Déchets et Environnement 99, Lyon Villeurbane, France, 1999, pp. 365–369.
[22] K.G. Knauss, M.J. Dibley, W.L. Bourcier, H.F. Shaw, Ti(IV) hydrolysis constants derived from rutile solubility measurements made from 100 to 300 °C, Appl. Geochem. 16 (9–10) (2001) 1115–1128.
[23] P. Faucon, Durabilité du béton: Physico-chimie de l'altération par l'eau, PhD Thesis, Université de Cergy Pontoise, Spécialité Génie Civil, 1997.
[24] A. Bertron, S. Larreur-Cayol, T. Le, G. Escadeillas, Degradation of cementitious materials by some organic acids found in agroindustrial effluents, in: M.G. Alexander, A. Bertron (Eds.), Proceedings of RILEM TC 211-PAE Final Conference, Toulouse, France, 3–5 June 2009, vol. 1, 2009, pp. 96–107.