Leaching of CEM III paste by demineralised or mineralised water at pH 7 in relation with aluminium release in drinking water network

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Abstract

Drinking water pipes can be lined with a cement matrix based on CEM III, which can release aluminium into the water. However, the European Union limits the aluminium concentration in drinking water for public health reasons. In order to study the long-term leaching mechanism of aluminium, semi-dynamic leaching tests using an aggressive solution (demineralised water) or drinking water (mineralised water) were conducted on crushed CEM III pastes maintained at pH 7. They resulted in a very high leaching coefficient, approaching 50 %. However, in spite of this strong leaching, the amount of Al leached remained very low, at less than 1.5 % of the initial amount of Al in the material. Under these conditions, the leaching of Al from a CEM III paste is complex since it involves several steps, where slag (1st and last steps) or cement paste (2nd step) are the main contributors.

Keywords:

Leaching; cement paste; slag; drinking water

1. Introduction

A high consumption of aluminium can be dangerous for humans. For example, it can cause many undesirable effects (encephalitis, bone diseases, anaemia) in dialysis patients, whose treatments are very rich in aluminium [1]. It is also suspected of being related to Alzheimer's disease, even though studies on the subject are currently contradictory and no causal link between aluminium consumption and the onset of the disease has been demonstrated [2]–[7]. This is why the European Union (EU, 98/83/CE) and the World Health Organization (WHO) recommend a concentration of less than 200 µg/L in drinking water for this element. However, trace amounts of aluminium may be

naturally present in water and may come mainly from water treatment (aluminium salts used as coagulant). Thus, the limit of 200 µg/L corresponds to the limit set for the optimization of the coagulation process with aluminium-based coagulants used in drinking water treatment plants, which is lower than the health-based guideline value of 900 µg/L [8].

Some pipelines used for the transport of drinking water consist of a cast iron pipe lined with blast furnace cement mortar (CEM III), which is composed of Portland clinker and blast furnace [9]. The flow of water in the pipe causes leaching of the lining, which leads to the release of chemical elements contained in the mortar, including aluminium, into the drinking water. The presence of blast-furnace slag in CEM III cement promotes the durability of the cementitious material by slowing the leaching kinetics compared to a Portland cement mortar (CEM I), but the aluminium content of the liner is increased [10] – [15]. Studies on the leaching of cementitious materials generally carried out on CEM I-based materials have clearly highlighted the dissolution-precipitation mechanisms involved in relation to kinetics governed by diffusion [16]–[23]. Thus, during the leaching of CEM I-based materials, the departure of cementitious ions and a gradual dissolution of hydrates occurs. In the material, the corresponding dissolution fronts progress in proportion to the square root of the time in the case of a unidirectional geometry [24], [25]. Cementitious ion leaching studies focus mainly on the release of the majority of CEM I ions, i.e. calcium and silicon ions. In addition, they are generally based on fairly short tests leading to moderate leaching of the samples overall. During the leaching of CEM III pastes [11], [13], [25]–[27], the dissolution-precipitation phenomena of the cementitious phases are close to those observed during the leaching of CEM I pastes with, first of all, a dissolution of the portlandite, followed by the sequential dissolution of the AFm and ettringite together with the progressive decalcification of the C-S-H [24], [25], [28]. However, in CEM III-based materials, much of the C-S-H contains aluminium and the leaching mechanisms of C-A-S-H are little detailed in the literature or not at all. In addition, the leaching of aluminium, mainly present in AFm, ettringite, C-A-S-H and residual anhydrous slag, has been little studied in the literature for CEM I and CEM III matrices. The studies carried out by Bertron et al. on the leaching of cement pastes with organic acids and by Müllauer et al. on the leaching of concrete with demineralised water showed a higher relative release of aluminium during the leaching of a CEM III paste than during the leaching of a CEM I paste in the short term [13], [29]. These results indicate that the mechanisms governing the release of aluminium are more complex than those associated with the release of calcium, which are governed by diffusion.

Thus, a specific investigation effort is required with respect to aluminium leaching in order to estimate the impact of the presence of slag in cementitious materials in contact with drinking water. In the light of the particular leaching behaviour of aluminium over time, tests to reach advanced

leaching stages should be carried out to determine the leaching behaviour of aluminium-rich solids. So, to accelerate leaching without modifying the chemical reactions, leaching tests were run on crushed materials. The interest of this type of test, performed on fine grains instead of a monolith, is twofold: on the one hand, it makes it possible to limit the effect of diffusion on the leaching kinetics and, on the other hand, it increases the surface area of the grains in contact with the solution, thus increasing the release kinetics of the chemical elements in solution. However, the various studies on the leaching of crushed cementitious materials were have been conducted under different conditions from those corresponding to the release of chemicals into drinking water - either at an initial pH of 4 [29] or by varying the pH of the leach solution between 2 and 14 [30]–[32]. The purpose of the tests carried out was to study the behaviour and stability of the material at different pH levels and the solubilisation of chemical elements as a function of pH. The leaching tests were based on the standard XP CEN/TS 14429 [33] for the studies by Engelsen et al., Lupsea et al., and Schiopu [30]–[32].

The work reported in this article is intended to provide new data to investigate the mechanisms of aluminium leaching from cementitious materials over the long term under conditions of pH close to 7. To achieve this, leaching tests were carried out at a pH maintained constant at 7, on crushed slag cement pastes (CEM III/B) in the presence of demineralised water or mineralised water under semi-dynamic conditions. Two leaching solutions were used in order to place one paste in aggressive conditions with demineralised water and the other in more realistic conditions with a weakly mineralised water having a composition that was average for a French drinking water. Additional tests were conducted on anhydrous slag and Portland cement paste (CEM I) leaching using demineralised water to estimate the contributions of the two materials in a simplified manner. The amount of chemical elements leached according to the leaching time was calculated from ICP-OES chemical analysis of the resulting leachate. The degraded materials were studied using scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), X-ray diffractometry (XRD) and ^{27}Al nuclear magnetic resonance spectrometry (NMR) analyses to highlight their microstructural, chemical and mineralogical evolution.

2. Materials and methods

2.1. Cementitious materials

Two commercial cements (from Ciments Calcia) were used in this study: one CEM I 52.5 , rated CEM I, and one CEM III/B 32.5, rated CEM III, together with anhydrous blast furnace slag, rated slag

identical to that used to manufacture CEM III. Their chemical compositions are set out in Table 1. Cement CEM III was composed of 94% of binder (71% slag and 29 % clinker) and 6% setting regulator (according to the technical data sheet provided by the cement manufacturer), which corresponds to approximately 67% slag and 27% clinker in the total cement. The blast furnace slag was obtained following a rapid vitrification process which resulted in an essentially amorphous material. Thus, up to 98% of the studied slag was vitrified. The mineralogical analysis of this material revealed the presence of two phases crystallized in very small quantities: quartz and calcite. Specimens of CEM III and CEM I paste were made with a water/cement ratio of 0.31 for the CEM III paste and 0.4 for the CEM I paste, in order to have a sufficient quantity of water to carry out the mixing. The cementitious pastes were made using a standard mortar mixer according to the following mixing protocol: 30 s at low speed (140 rotations per minute), 30 s at high speed (285 rotations per minute), 90 s without rotation and then 60 s at high speed. After mixing, the moulds were half filled and vibrated for 1 minute. They were then completed and vibrated again for 1 minute. The moulds were stored in a room at 20 °C. After 24 hours, the specimens were removed from the moulds and stored at 20 °C in a sealed plastic bag for a minimum of 27 days. The CEM III and CEM I pastes were kept for 16 months and 6 months in plastic bags, respectively, after their manufacture. They were then crushed just before the leaching experiments.

The cementitious pastes and slag used for the leaching tests were manually crushed with an agate mortar and then sieved at 500 µm to zero rejection. Figure 1 shows the particle size distribution and Table 2 shows the particle sizes (D10, D50 and D90) of the various crushed samples measured with a dry laser particle size analyser (Belckman Coulter LS 13 320). Manual grinding explains the differences between the grain sizes of the different samples. Thus, the slag, which is harder, had a coarser grain size than crushed cementitious pastes.

For the sampling of crushed cementitious pastes or anhydrous slag, quartering was performed in order to take 5 grams of powder with characteristics representative of the whole sample.

Table 1: Chemical compositions of CEM I cement, CEM III cement and slag in percent by mass

	CEM I	**CEM III**	**Slag**
CaO	64.31	49.13	42.38
SiO_2	20.12	29.60	37.74
Al_2O_3	5.56	9.41	11.09
Fe_2O_3	2.32	1.21	0.39
MgO	0.93	4.69	6.39

MnO	0.04	0.27	0.39
SO_3	3.82	3.22	0.09
P_2O_5	0.15	0.06	0.02
TiO_2	0.26	0.52	0.73
Na_2O	0.14	0.24	0.29
K_2O	0.95	0.59	0.44
Cl	0.04	0.02	0.01
Cr_2O_3	0.01	0.01	0.01
Ignition loss	1.38	1.02	0.00

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124 *Table 2: Grain sizes (D10, D50 and D90) of crushed samples*

	CEM III paste	**Slag**	**CEM I paste**
D_{10} (µm)	4.3 ± 0.7	93.3 ±3.6	5.1 ± 0.1
D_{50} (µm)	105.2 ± 14.3	348.9 ± 0.9	194.5 ± 4.5
D_{90} (µm)	303.7 ± 14.0	577.4 ± 1.1	507.9 ± 13.3

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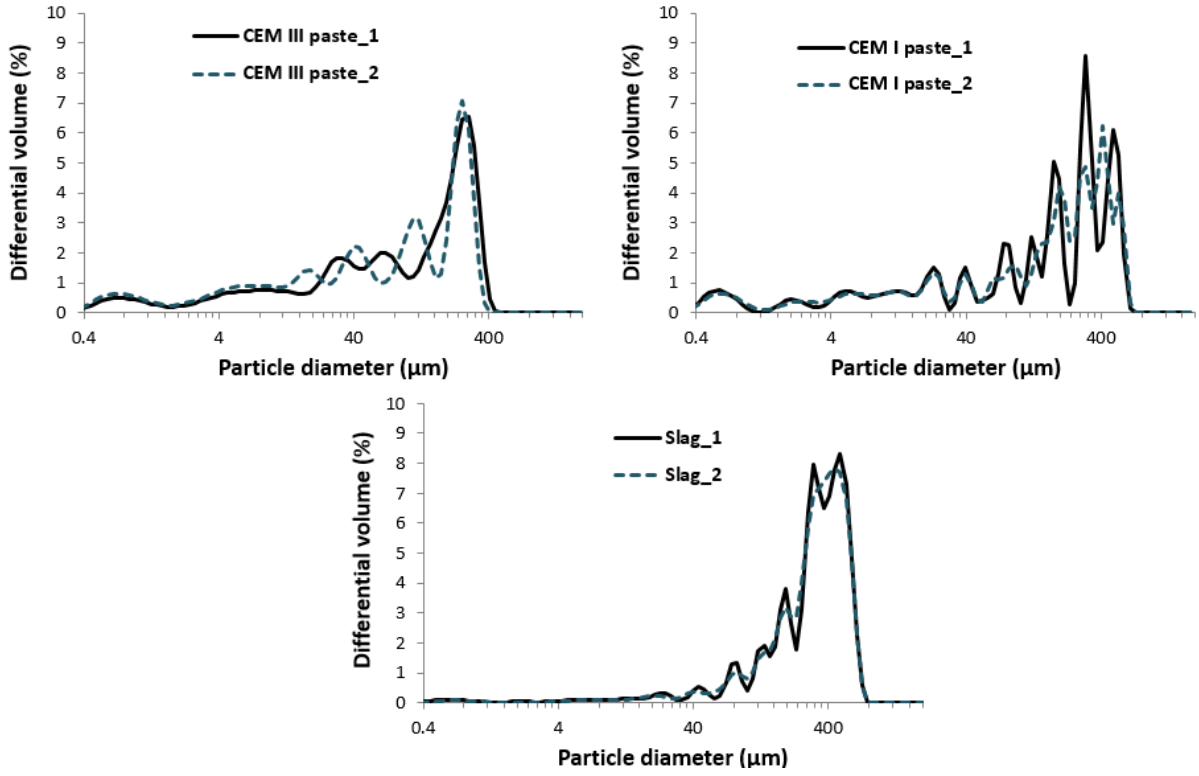

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127 *Figure 1: Particle size distribution of crushed samples*

2.2. Methods

2.2.1. Leaching test

Semi-dynamic leaching tests were carried out on crushed cement paste and slag samples. Adapted from Adenot [34], the principle of the test used was that of an accelerated leaching test characterized by:

- maintaining the pH of the leaching solution by adding concentrated nitric acid at 0.250 mol/L made by diluting nitric acid (HNO3) at 2 mol/L (Fisher Scientific, France)
- regular renewal of the leaching solution (carried out as soon as a given quantity of acid had been added to the solution or at a given time).

The experimental system consisted of a 2 L reactor containing 1 L of leaching solution and 5 g of crushed sample. The reactor was equipped with a pH electrode and a buret connected to a titrator (Radiometer Analytical TitraLab 854), in order to control and measure the pH of the solution continuously (Figure 2). The reactor solution was kept under agitation by a magnetic stirrer. The pH of the leach solution was maintained at 7by adding nitric acid ([HNO_3] = 0.250 mol/L). The pH was chosen in accordance with the European directive UE 98/83/CE that recommends the pH of a drinking water should be comprised in the interval [6.5; 9.5]. The target pH was thus close to the lower value of this interval. Moreover, it should be noted that the speciation of Al is the same on the pH interval [5.5; 8]: $Al(OH)_3$ is the predominant specie [35] Moreover, the possible difference in terms of chemical stability of the cementitious phases between our target pH 7 and the minimal pH of potable water 6.5 should be considered as negligible [36]–[38].

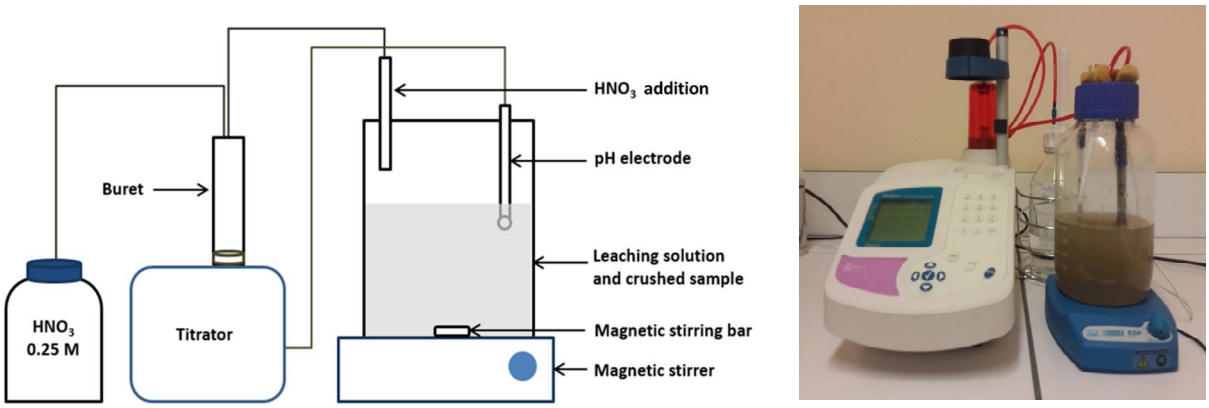

Figure 2: Diagram and photograph of the leaching test carried out on crushed samples

Two types of leaching solutions were used:

- demineralised water (DW) (ELGA labWater purification system)
- weakly mineralised water (Volvic commercial water, pH 6.9). The composition of the mineralised water was analysed by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry, Varian 720-ES) for cation analysis and by ion chromatography (Dionex ICS-3000 with an AG15 pre-column and an AS15 column with a flow rate of 1.2 ml KOH at 38 mM) for anion analysis (Table 3). The aluminium content of this water was below the detection limit of 5 µmol/L.

The tests lasted 1 month and were carried out at a constant temperature of 30 °C. This temperature was chosen to accelerate the diffusion kinetics and also the chemical reactions slightly without changing the stability of the mineral phases present. The CEM III paste was leached with demineralised water and mineralised water, and the slag and paste of CEM I were leached with demineralised water.

Table 3: Composition of mineralised water (mmol/L). DL: detection limit 5 µmol/L

	Ca	**Na**	**K**	**Mg**	**Si**	**Cl**	**SO_3**	**HCO_3**	**NO_3**	**Al**
Concentration (mmol/L)	0.317	0.559	0.179	0.351	0.546	0.421	0.105	1.278	0.113	<DL
Standard deviation	0.011	0.018	0.0057	0.012	0.019	0.003	0.001	0.010	0.003	/

A first renewal was performed after 2.5 hours, followed by a second renewal 16 hours after the first, because of a very high release of chemical elements at the beginning of the test due to the large specific surface of the sample. The following renewals were made every 3.5 days. For the CEM III paste leached with DW, the renewals were spaced over the end of the experiment. Thus the total number of renewals was 8, compared to 10 renewals for the other 3 experimental conditions.

A specific procedure was set up during the renewal of the leaching solution in order to limit the loss of crushed solid sample during this step: the reactor, containing the leachate and the crushed solid, was left to rest for a few minutes after the agitation was stopped, so that the crushed solid could settle. Two hundred millilitres of leachate was then taken from the surface of the reactor and distributed among 4 tubes of 50 mL. These tubes were centrifuged at 7500 RCF (6455 RPM) for 8 minutes (MF20/R Awel Centrifuge). The supernatant was removed and then centrifuged a second time. The first half of the supernatant was collected and acidified to 0.2% HNO_3 at 67% concentration

and filtered through 0.45 µm. The second half was filtered at 0.45 µm and then acidified to 0.2% HNO_3 at 67% concentration. These samples were then analysed by ICP-OES.

In parallel with the centrifugation, the rest of the mixture present in the reactor (mixture of leachate and crushed cement paste) was filtered under vacuum at 0.45 µm in order to recover the solid part, which was then redispersed in a new leaching solution.

2.2.2. Leachate analyses

The chemical composition of the leachate was determined by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry, Varian 720-ES). The concentrations of the elements Ca, Si, Al, Mg were analysed.

The elements were analysed using a nebuliser flow rate of 0.75 L/min and a generator power of 1200 W. In order to increase the analytical accuracy for aluminium in solution, the analytical method was optimised. The optimisation made it possible to analyse, at least, aluminium concentrations (limits of quantification) of 20 µg/L when the analysed solution contained several elements. To achieve this, a standard range of aluminium was produced with a matrix loaded with the following elements: calcium (130 mg/L), silicon (6 mg/L), potassium (40 mg/L) and sodium (5 mg/L) at constant concentrations.

2.2.3. Analyses of cementitious materials

Microstructural observations of the leached crushed materials by scanning electron microscope (SEM, Jeol JSM-6380 LV and Hitachi S 4300 SE/N) were performed, coupled with chemical analysis by EDS (Energy-Dispersive X-ray Spectroscopy, Bruker XFlash® 6/30 and Thermo Electron Ultradry Silicon drift). For this purpose, the leached powder was dispersed in resin (resin and hardener Presi Mecaprex Ma2+ or Araldite 2020), then polished (with silicon carbide discs having a grain size of 26 µm (600), 22 µm (800), 15 µm (1200), and 10 µm (2000), then with 9 µm, 6 µm and 1 µm diamond paste), and metallized. During the chemical analysis of the material by EDS, about 30 points were analysed in the cement paste and slag, in order to obtain an average composition.

X-ray diffraction mineralogical analyses (XRD, Bruker D8 advance with a copper anticathode, 40 kV voltage and 40 mA current or Bruker D8 advance with a cobalt anticathode, 35 kV voltage and 40 mA current) were performed on each of the initial crushed samples and the leached ones.

The analyses in MAS NMR spectroscopy of the 27Al nucleus were performed at 208.48 MHz on a Bruker AVANCE-III spectrometer (18.8 T) equipped with an HX-3.2 mm measuring probe. The recordings were made at a rotational speed of 22 kHz with a pulse time of 0.5 µs and a

radiofrequency field of 30 kHz (measured on a liquid). 8192 accumulations were recorded with a recycling time of 0.5 s. The spectra were corrected for the weak probe signal by subtracting the signal recorded without a sample from the analyses performed.

3. Results

3.1. Leachate analysis

Figure 3 shows the results obtained by leaching the crushed CEM III cement paste with demineralised water (DW) and mineralised water (MW) for one month at 30 °C. Each point represents a renewal. The figure shows very strong leaching of Ca at the beginning of the experiment, since 90 % of the total leached calcium has been released by the 3rd renewal. Thereafter, a small additional amount of calcium is released in solution. For Mg and Si, the total cumulative concentrations are twice the concentration obtained at the 3rd renewal and the curves obtained have a polynomial appearance. A different behaviour is observed for aluminium: only 10% of the total cumulative concentration is leached by the 3rd renewal (5th day of the test). The quantity released is then almost linear according to the number of renewals. A different behaviour is observed for aluminium: only 10% of the total cumulative concentration is leached by the 3rd renewal (5th day of the test).

The test carried out with mineralised water shows results very close to those obtained for demineralised water for Ca and Si, whose concentrations have similar trends. The final cumulative concentrations for Ca are 23.9 mmol/L in the DW and 22.1 mol/L in the MW, and for Si, 4.9 mmol/L in the DW and 5.1 mol/L in the MW. For Mg and Al, on the other hand, the differences between the two solutions are a little more pronounced. On the one hand, the concentration evolution curves are linear for the MW test, from the 3rd renewal for Mg and from the 1st renewal for Al. The difference between the final concentrations is greater. For Mg, concentrations of 1.2 mmol/L for the DW test and 0.8 mmol/L for the MW test were found, and for Al, concentrations were 0.63 mmol/L for the DW test and 0.54 mmol/L for the MW test. Thus, Mg and Al are less leached in the MW.

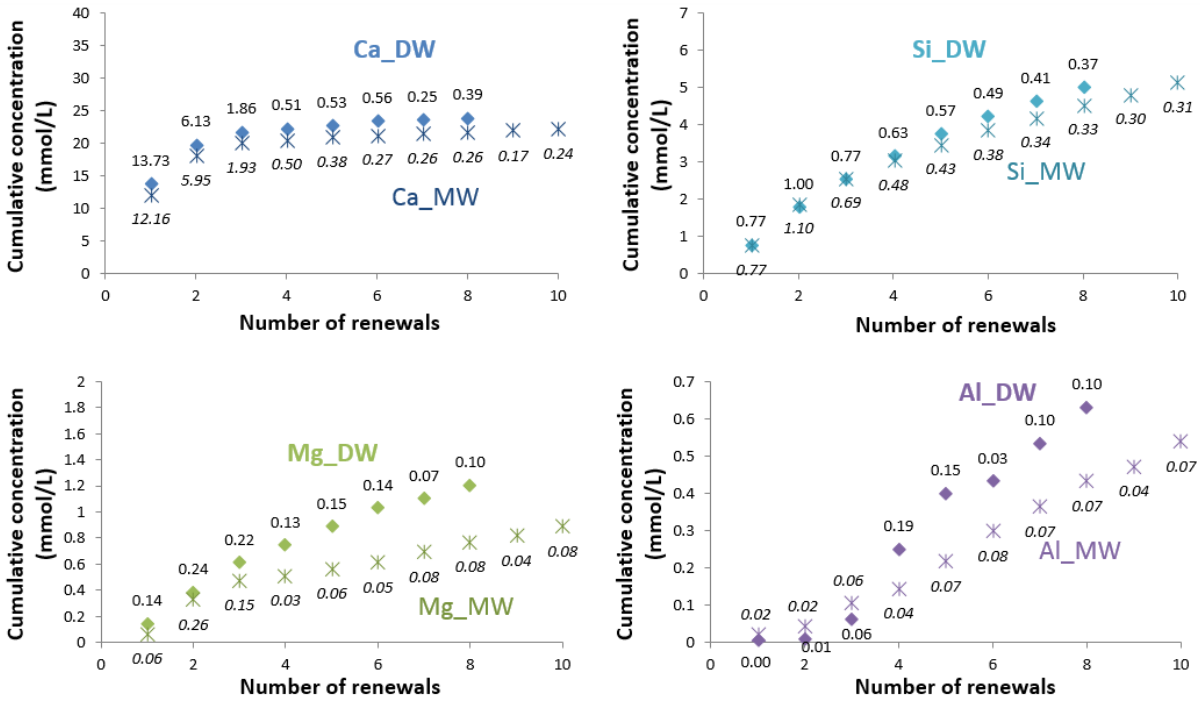

Figure 3: Cumulative concentrations of leached elements during the leaching of the degraded crushed CEM III paste with demineralised water (DW) and mineralised water (MW) for one month at 30 °C according to the number of renewals. Each point represents a renewal of the leachate. The value associated with each point corresponds to the non-cumulative concentrations (mmol/L) analysed for each leachate

Figure 4 shows the results obtained when leaching the crushed CEM I paste and the crushed slag with demineralised water for one month at 30 °C. The leaching of the CEM I paste shows results similar to those of the CEM III paste in terms of the Ca, Si and Al curves. However, the quantities of elements leached are significantly different. For CEM I paste leached with DW, the following concentrations were obtained at the end of the test: Ca = 37.8 mmol/L, Si = 5.8 mmol/L, Mg = 0.4 mmol/L and Al = 0.33 mmol/L. The concentrations released are related to the quantities originally present in the material. Thus, unlike the quantities of Mg and Al, those of Ca and Si are higher for the leaching of CEM I paste than for the leaching of CEM III paste.

For slag, Ca and Mg leaching were almost linear during the number of renewals, with cumulative concentrations of 9.88 mmol/L for Ca and 1.87 mmol/L for Mg at the end of the test (Figure 4). In this test, Si and Al behaved similarly, with slow leaching of these elements during the first 10 days. The release of these elements then increased, to reach 5.21 mmol/L for Si and 0.58 mmol/L for Al at the end of the test.

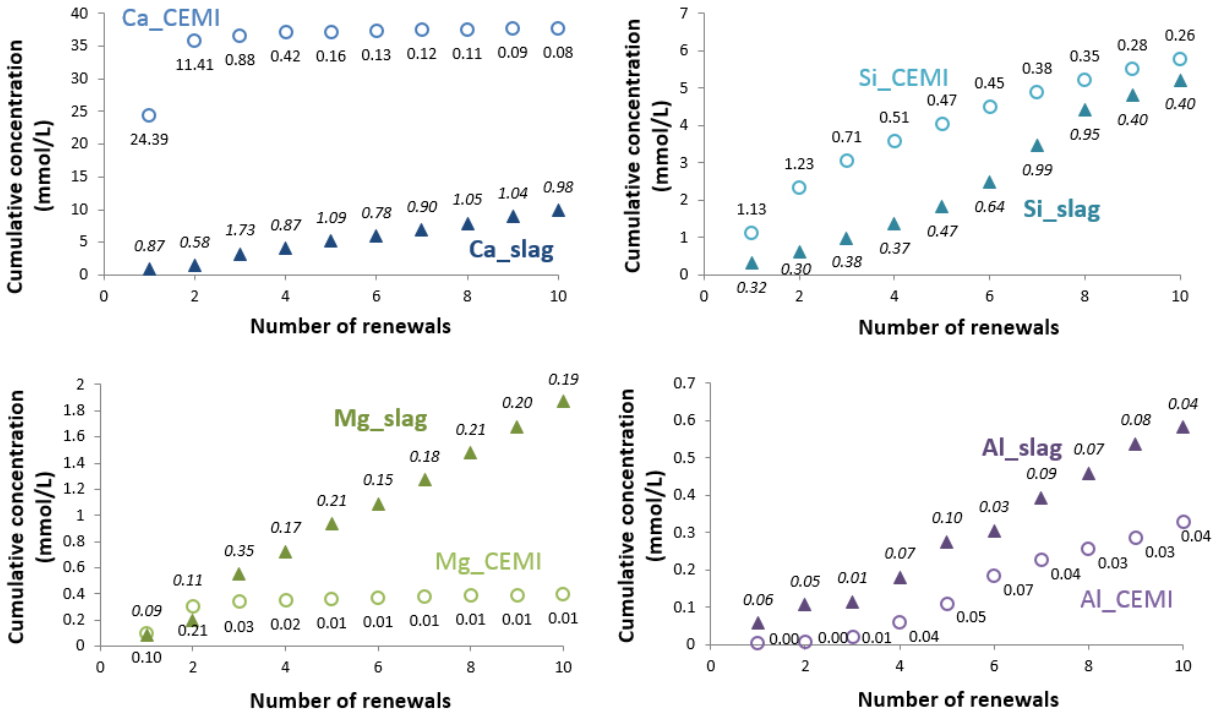

Figure 4: Cumulative concentrations of the leaching elements obtained during the leaching of the slag and of the crushed CEM I paste degraded with demineralised water for one month at 30 °C according to the number of renewals. The values associated with each point correspond to the non-cumulative concentrations (mmol/L) analysed for each leachate.

Figure 5 shows the cumulative amount of added nitric acid at each renewal. As in previous results, the curves obtained for the cementitious pastes have similar patterns, with 95% of the amount of added HNO_3 being reached at the 2nd renewal for the test conducted on the CEM I paste. From the 3rd renewal, the amount of HNO_3 added in the rest of the test is very small. For the CEM III paste, the two curves are almost identical until the 4th renewal. At this point, for DW leaching, the amount of HNO_3 added is very small. For the MW test, the amount of HNO_3 added increases linearly until the end of the test. For slag leaching, the amount of HNO_3 added is almost linear throughout the test.

The monitoring of the addition of HNO_3 between the 1st, 3rd, 5th and last renewals is available in the supplementary material (Fig. sm1) for the 4 tests conducted.

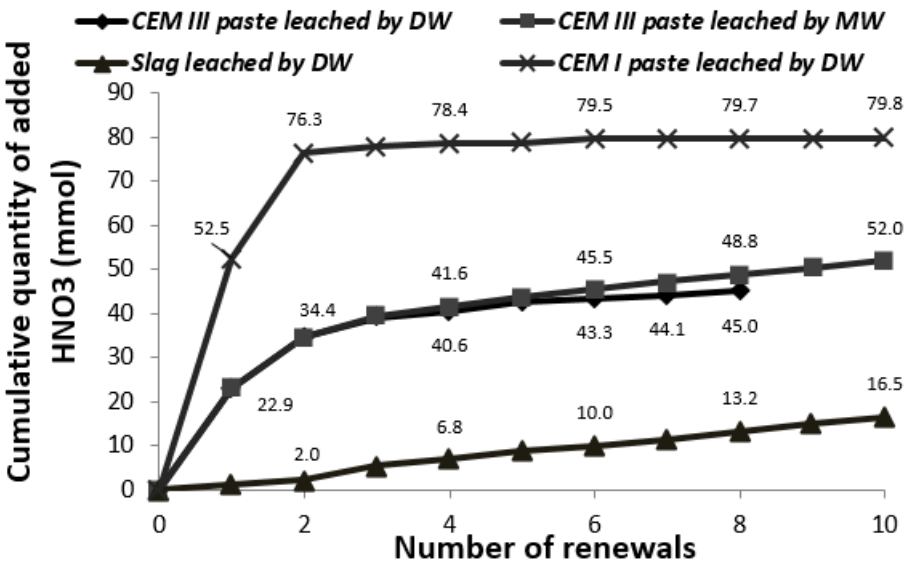

Figure 5: Cumulative amount of nitric acid added in the one-month leaching tests according to the number of renewals. The values indicated are the cumulated amounts of nitric acid added.

3.2. Analysis of degraded materials

Figure 6 shows a SEM backscattered electron mode image of the materials after leaching and Table 4 shows the relative chemical compositions obtained by EDS pointing. The SEM images show a strongly degraded CEM III paste still containing unreacted slag grains (Figures 6b and 6c). Any clinker grains observed before leaching (Figure 6a) do not appear to be present after leaching.

The EDS analysis of CEM III paste leached with the DW or MW shows a significant degradation compared to non-leached materials, with a consequent decrease of Ca and S in the cement paste: the chemical composition decreases from 55.44% to 8.69% for CaO and from 6.37% to 0.50% for SO_3. This decrease leads to a relative increase in the percentages of SiO_2, Al_2O_3 and MgO due to the 100% normalization of the quantity of chemical elements analysed. Chemical analysis of the residual slag present in the CEM III paste also shows a slight loss of calcium and a loss of sulfur. However, the chemical composition remains very close to that of the unleached slag.

XRD mineralogical analyses of the CEM III paste (Figure 7a) show the complete dissolution of the portlandite, ettringite, C_2S and C_3S initially identified in the unleached paste. Some brownmillerite (C_4AF) in the clinker is still detected after leaching with DW and MW. In the case of DW leaching, quartz, originally present in the slag, and hydrotalcite are also identified. A low intensity peak is observed at 18° but is not identified among the mineral phases of the CEM III cementitious paste. It was attributed to Teflon (PTFE - Polytetrafluoroethylene), as the Teflon magnet bar used for stirring was severely degraded due to its abrasion during the test. There was therefore a potential pollution

of the cementitious paste by Teflon, as can be seen from the EDS points in areas composed of 98% fluorine. This polymer has a semi-crystalline structure that allows it to be identified by XRD [39], [40].

The ^{27}Al NMR analysis, in Figure 8, of the CEM III paste before leaching shows the presence of Al in tetrahedral coordination (100/50 ppm range) noted Al^{IV} and Al in octahedral coordination (20/-10 ppm range) noted Al^{VI}. The wide signal centred around 60 ppm indicates the presence of Al^{IV} in an amorphous compound. It is characteristic of C-A-S-H and slag. Peaks at 10 and 13 ppm are attributed to AFm and ettringite, respectively [41]. The 5 ppm peak could be attributed to TAH (Third Aluminate Hydrate), a calcium aluminate hydrate or amorphous aluminium hydroxide linked to the formation of C-A-S-H, according to studies conducted by Andersen et al. [42], [43]. The analysis of the CEM III paste after leaching shows a dissolution of the ettringite during leaching in the DW or MW and a change in the shape of the Al^{IV} peak. A peak around 6 ppm is observed for the DW test, which would indicate an increase in the amount of TAH in relation with the increase in the amount of C-A-S-H demonstrated by the displacement of the maximum of the Al^{IV} peak from 65 to 60 ppm. The XRD results obtained also suggest that the peak analysed at 6 ppm could be related to the hydrotalcite observed in XRD, which was poorly crystallized and could have led to a broader NMR peak.

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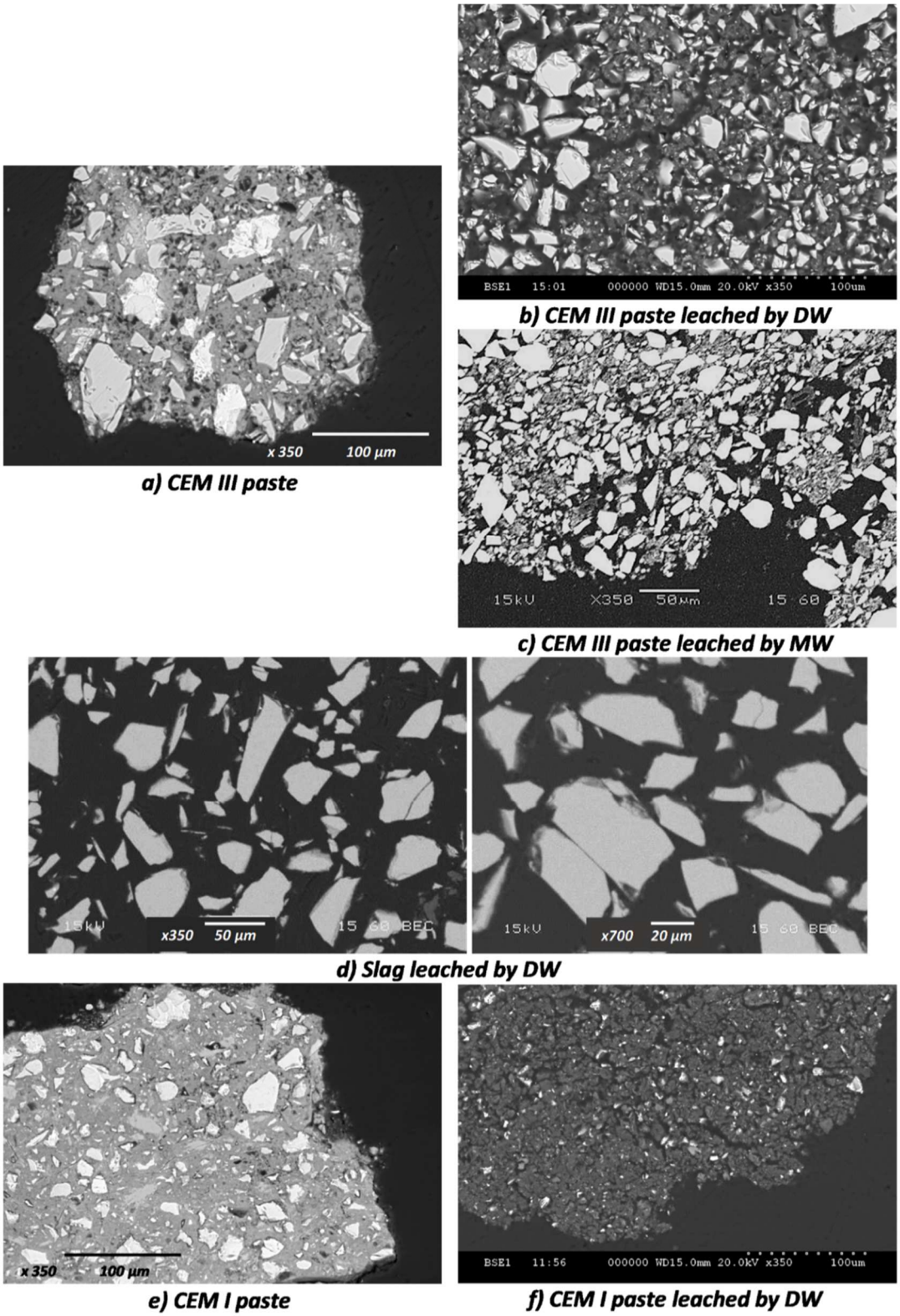
311 *Table 4: Chemical compositions of crushed CEM III pulp leached with demineralised water and*
312 *mineralised water, crushed CEM I pulp and slag grains leached with demineralised water for one*
313 *month. The compositions were obtained by EDS pointing.*

		CaO	**SiO_2**	**Al_2O_3**	**SO_3**	**MgO**	**Fe_2O_3**
CEM III paste leached by demineralised water	**Composition of the leached crushed paste (%mass)**	8.69 ± 3.70	53.37 ± 3.59	27.89 ± 2.47	0.50 ± 0.19	7.38 ±3.14	/
	Composition of the degraded slag (%mass)	39.93 ± 1.09	38.31 ± 0.79	12.06 ± 0.56	1.63 ± 0.74	7.32 ± 0.50	/
CEM III paste leached by mineralised water	**Composition of the leached crushed paste (%mass)**	8.42 ± 3.25	64.72 ± 3.61	19.25 ± 1.02	0.35 ± 0.22	4.76 ± 1.23	/
	Composition of the degraded slag (%mass)	39.06 ± 1.05	38.21 ± 1.30	12.40 ±1.00	1.85 ± 0.27	7.23 ± 0.37	/
Slag leached by demineralised water	**Composition of the degraded slag (%mass)**	38.62 ± 4.15	40.26 ± 3.82	11.64 ± 1.21	1.84 ± 0.29	6.44 ± 0.94	/
CEM I paste leached by demineralised water	**Composition of the leached crushed paste (%mass)**	9.70 ± 3.65	53.30 ± 7.96	22.36 ± 3.60	0.28 ± 0.17	1.29 ± 0.51	13.06 ± 4.66
Control materials	**Composition of the anhydrous slag (%mass)**	43.63 ± 0.76	35.00 ± 0.79	11.58 ± 0.77	2.21 ± 0.68	6.43 ± 0.55	/
	Composition of CEM III paste (%mass)	55.44 ± 2.82	28.91 ± 4.05	4.83 ± 1.53	6.37 ± 2.50	1.29 ± 0.76	/
	Composition of CEM I (%mass)	63.67 ± 5.70	22.99 ± 4.04	4.29 ± 1.82	0.52 ± 0.19	7.06 ± 1.72	1.44 ± 0.69



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315 *Figure 6: Backscattered electron mode SEM image of sound crushed CEM III paste (a), crushed CEM III*
316 *paste after leaching with demineralised water (b), and after leaching with mineralised water (c);*
317 *crushed slag leached with demineralised water (d); sound crushed CEM I paste (e), after leaching with*
318 *demineralised water (f).*

The SEM images of the leached anhydrous slag (Figure 6d) do not allow any alteration of the slag to be identified via density variations, as the grey level of the grain is homogeneous. As a reminder, the grey level in a back-scattered electron microscopy image reflects density (here, the lighter the grey level, the higher the density of the material). Nevertheless, chemical analysis of the grains by EDS shows a slight decalcification of the slag. In addition, the analysis of the leach solutions showed a calcium release which, considering the initial amount of slag, corresponds to a loss of about 4% of CaO. These results indicate that the variation in the chemical composition of the leached slag analysed by EDS was indeed due to the leaching of the sample and not to the measurement error related to the analytical technique used.

The mineralogical analyses performed by XRD on the crushed anhydrous slag before and after demineralised water leaching are shown in Figure 7b. The mineralogical analysis shows essentially the presence of an amorphous phase and a crystallized phase previously identified as Teflon and already observed during the leaching of CEM III cementitious pastes [39], [40]. NMR analysis of ^{27}Al slag before and after leaching seems to show the formation of C-A-S-H (weak displacement of the Al^{IV} peak) but no hydrotalcite (no noticeable peak at the Al^{VI} level).

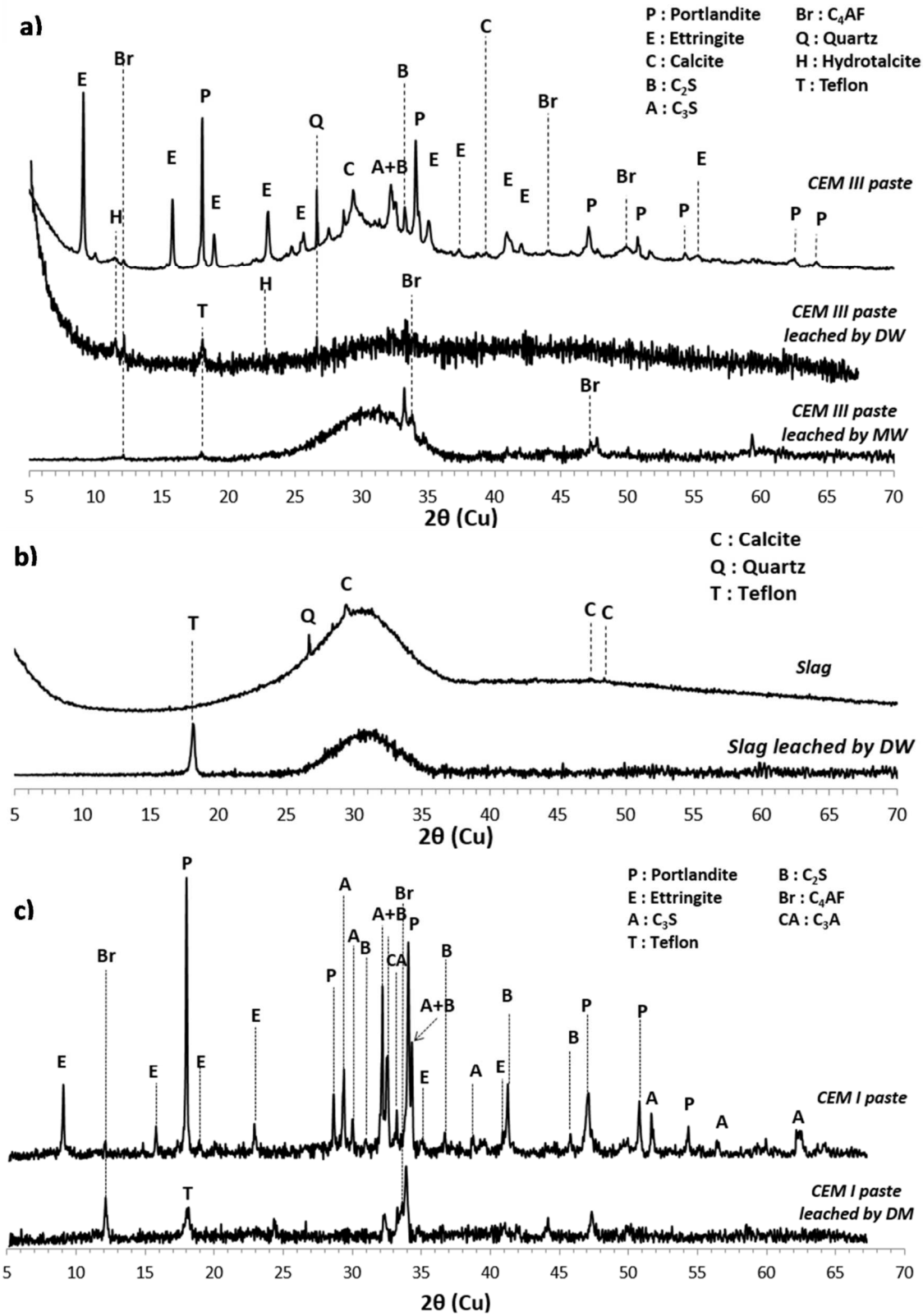


Figure 1 : Mineralogical analyses of crushed CEM III paste leached by demineralised and mineralised water (a), crushed slag leached by demineralised water (b), and crushed CEM I paste leached by demineralised water for one month at 30 °C (c) compared to the control samples.

338 The SEM images presented in Figures 6e and 6f show a backscattered electron mode SEM
339 observation of the crushed CEM I cementitious paste before and after one month of leaching with
340 demineralised water at 30 °C. Unlike the CEM III paste samples, the leached CEM I paste still contains
341 visible clinker grains.

342 EDS chemical analyses performed on the CEM I paste leached by DW showed similar results to those
343 obtained for the CEM III paste leached by DW and MW (Table 4). These results show a strong
344 leaching of calcium and sulfur. Due to the relative nature of chemical analysis, the low percentage of
345 calcium is accompanied by an increase in the percentage of silicon, iron and aluminium. Thus, the
346 composition changes from 63.67% CaO and 7.06% SiO2 in the unleached CEM I paste to 9.70% CaO
347 and 0.28% SO_3 after leaching.

348 The mineralogical analyses performed on the CEM I paste before and after leaching are shown in
349 Figure 7. They complete the chemical analysis carried out previously and show significant
350 degradation of the material, with the dissolution of ettringite and portlandite and the presence of
351 residual clinker phases after leaching of the material (C_2S, C_3S, C_4AF and C_3A). As in the previous tests,
352 Teflon from the degraded bar magnet was observed [39], [40].

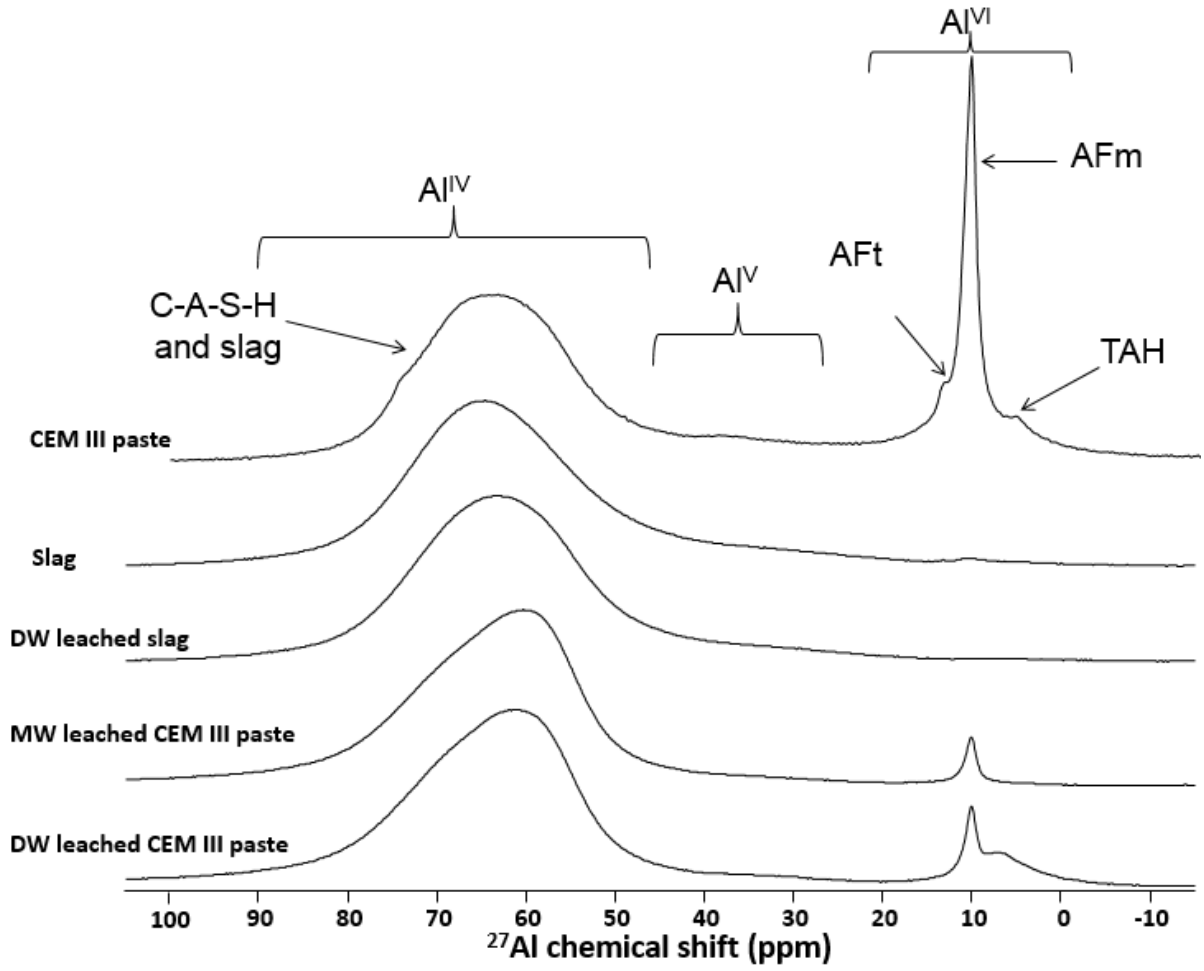


Figure 2 : NMR results obtained for crushed CEM III paste leached by demineralised water and demineralised water, and for slag leached by demineralised water. Controls for CEM III paste and slag are also presented.

4. Discussion

It is always difficult to compare leaching tests carried out at constant pH because the amounts of acid added are usually not the same, due to different chemical compositions of the leaching material or solution. However, it is possible to compare the degree of leaching of the different samples by using a Leaching Coefficient (LC) (Equation 1) [44].

$$LC(t) = \sum_{i=Ca,Al,Si,Mg} \left[\frac{amount\ of\ element\ i\ leached\ (mmole)\ at\ time\ t}{initial\ amount\ of\ element\ i\ in\ cement\ paste\ (mmole)} \times \frac{molar\ \%\ of\ element\ i}{\sum molar\ \%\ of\ Ca, Al, Si, Mg} \times 100 \right] \quad \text{Eq. 1}$$

The coefficient is equal to 0 when the cementitious paste is not leached and is equal to 100 when the cementitious paste is completely leached. In the work presented here, the leaching coefficients of calcium, aluminium, silicon and magnesium were taken into account when calculating the leaching coefficient. For leaching tests conducted with mineralised water, the concentrations corrected from initial concentrations in mineral water are used to calculate the leaching coefficient. For tests conducted on crushed samples, the term "*initial amount of element i in the cement paste*" takes a linear loss of mass of the sample throughout the renewals into account according to the following approximation: considering the final mass of the sample after leaching, the loss of mass of the total sample is known and is divided by the number of renewals. Thus, a constant and linear loss of mass at each renewal is assumed.

Table 5 presents leaching coefficients obtained at the end of the leaching test for the different elements studied (Ca, Al, Si and Mg). Calcium was found to be the most leached element in all the tests performed. Therefore, for the demineralised water leaching of CEM III, 32.4% of the calcium in the sample was leached, as were 9.2% of the silicon, 2.2% of the magnesium and 1.4% of the aluminium. The percentages obtained for the test carried out with mineralised water follow the same trend but are slightly lower than those obtained with demineralised water. They are 29.1% for calcium, 8.6% for silicon, 1.1% for aluminium and 1.5% for magnesium. The global leaching coefficient is 45% for demineralised water leaching and 40% for mineralised water leaching. On the one hand, this indicates that the CEM III cementitious pastes were strongly degraded under both conditions. On the other hand, the slightly lower leaching coefficients found with mineralised water are probably related to the influence of ions in solution from the mineralised water that modify the chemical conditions in the solution. This difference was also observed by Kamali et al. [11], Hartwich and Vollpracht [20], and Guillon [22] on monolithic cement pastes, in terms of both altered depth and concentrations of released elements. The difference between DW and MW attacks could also be due to the precipitation of secondary phases as a result of chemical reactions between chemical elements of the leachate and those contained in the mineralised water.

The slag has a lower percentage of calcium leached by demineralised water (14.9 %) than that obtained for CEM III cementitious paste (32.4 %). The amounts of silicon (8.1 %) and aluminium (0.9 %) leached are also slightly lower than for CEM III cementitious paste (9.2 % and 1.4 %, respectively). However, the orders of magnitude are the same for these two chemical elements. The percentage of leached magnesium, in contrast, is higher (2.8% vs. 2.2 %). Overall, the leaching coefficient of the slag

leached by demineralised water (26.7%) is lower than that obtained for CEM III cementitious paste under the same conditions (45%).

For CEM I cementitious paste leached with demineralised water, magnesium is the least leached element (0.6 %). This contrasts with the situation for CEM III paste and slag. 11.8% of silicon and 1% of aluminium are leached from CEM I in this test. The alteration of the CEM I cementitious paste is the strongest as shown by its leaching coefficient of 62.6%, which is consistent with a better durability of the CEM III cementitious matrices than CEM I cementitious matrices [11]–[15], [27].

Table 5: Leaching coefficients obtained for each element (Ca, Al, Mg and Si) at the end of the test for CEM III paste leached by demineralised water and mineralised water, and for slag and CEM I paste leached by demineralised water

Leaching coefficient	Ca	Si	Al	Mg	Total
CEM III paste leached by DW	32.4	9.2	1.4	2.2	45.2
CEM III paste leached by MW	29.1	8.6	1.1	1.5	40.3
Slag leached by DW	14.9	8.1	0.9	2.8	26.7
CEM I paste leached by DW	49.2	11.8	1.0	0.6	62.6
CEM III paste leached by DW estimated by eq. 1 with y=31	25.6	9.3	0.9	2.1	37.9

Schiopu studied the leaching of crushed concrete slabs and the influence of pH on the release of elements [32]. These tests were carried out according to the draft standard on the characterisation of construction waste, CEN/TS 14429 [33]. Samples of concrete slabs made of CEM I and silico-calcareous aggregates were crushed to 1 mm and brought into contact with an aqueous acid or basic solution for 48 hours. The percentage of elements released during the test was determined by considering the amount released in relation to the initial total content according to the pH. This quantity can be compared to the calculated leaching coefficients. For a pH of 7.1, the author reports aluminium, calcium, and silicon leaching rates of 0.07%, 31%, and 3.3%, respectively (magnesium was not studied). The fact that the percentages are lower than those obtained in this study may be explained by the shorter test time and coarser particle size of the leached material. However, both studies show high leaching of calcium followed by that of silicon and, finally, low leaching of aluminium.

Bertron et al. also studied the leaching of crushed CEM I and CEM III cementitious pastes (particle size greater than 2.36 mm) leached with acetic acid solution at an initial pH of 4 [29]. The mechanisms of alteration of the cementitious paste by acetic acid were similar to those observed with a strong acid such as HNO_3 [29]. A leaching percentage was calculated after 6 hours of testing. For CEM I paste, the results showed 14.2% for calcium, 1.1% for silicon, 0.19% for aluminium and 3.6% for magnesium. For CEM III cementitious paste, they were respectively 13.3%, 1.65%, 0.94% and 11.8%. Calcium remained the most leached element in the test and aluminium the one with the lowest leaching percentage. Magnesium, however, was strongly leached at pH 4, in contrast to the results obtained in the present study at pH 7.

The two leaching tests, conducted by Schiopu and Bertron et al. [29, 32], showed low percentages of leached aluminium. For a CEM III paste, the leaching percentage obtained by Bertron et al. was of 0.94 % after 6 hours of testing at pH 4, whereas, in the work reported here, the leaching coefficient obtained for aluminium at pH 7 was 0.008 % after 24 hours of testing, despite a less favourable particle size distribution in the case of Bertron et al.'s tests. This gap can be explained by the difference between the pH values of the tests performed, as found in Lors et al. [44]. Numerous studies, carried out in accordance with CEN/TS 14429, have investigated the variation in the concentration of different leached elements at different pH values (between 3 and 12) [30]–[33], [46]. These tests have shown that concentrations of leached aluminium are high in acidic media, pass through a minimum in neutral media and then increase again in basic media. This phenomenon could thus explain the differences in the percentage leaching obtained for aluminium, which are related to its stability range. This element is in ionic (soluble) form for pH < 6 (Al^{3+} for pH < 4, $Al(OH)^{2+}$ and $Al(OH)_2^{+}$ for pH between 4 and 6), in solid form $Al(OH)_3$ for pH between 5 and 8, and in ionic form for pH > 8, ($Al(OH)_4^{-}$ for pH between 8 and 11, and $Al(OH)_5^{2-}$ for pH > 11) [46]). This discrepancy may also have been due to the leaching solution used: complexation phenomena between acetate and aluminium could occur and increase aluminium leaching [35], [47], [48]. Magnesium leaching according to pH was also studied by van der Sloot et al. [49], who showed a slightly higher leaching of magnesium at acidic pH than at pH 7, which may explain the difference between Bertron's results [29] and those obtained in the present study for magnesium.

The leaching observed for CEM III paste comes from the contribution of cement paste from clinker and slag with a thin layer of hydrates on its surface. These two contributions, which are different, are important for understanding the different stages of the leaching of chemical elements over time. Since the tests carried out do not allow us to trace the origin of the leaching of chemical elements, hypotheses have been used in the aim of determining general trends in the role of cement paste and hydrated slag on the surface. These hypotheses are also based on the use of finely crushed samples,

thus reducing the limited influence of diffusion on the leaching kinetics. Thus, as a first approximation, it is considered that the leaching coefficient of the chemical elements of the crushed CEM III paste corresponds to a linear combination of the leaching coefficient of the chemical elements of the crushed CEM I paste and the leaching coefficient of the chemical elements of the crushed slag:

$$LC\ CEM\ III = y \times LC\ CEM\ I + (100 - y) \times LC\ Slag \quad \text{Eq. 2}$$

with y the percentage of clinker in CEM III and LC the total leaching coefficient or that of a chemical element.

As the slag in the CEM III paste hydrates on a thin surface layer, the amount of chemical elements released should not exceed that of the slag alone. A CEM III/B contains between 20 and 34 % of clinker, between 80 and 65 % of slag, and between 0 and 5 % of secondary constituents (calcium sulfate). Thus, when CEM III is leached by demineralised water, Equation 2 indicates that the leaching coefficient of a chemical element for CEM III should be between that of slag and that of CEM I, corresponding to y = 0 and y = 100, respectively. The CEM III leaching coefficients for Ca, Si and Mg are well within the range of leaching coefficients of these elements for CEM I and slag but, for Al, the leaching coefficient is higher than that of slag and also higher than that of CEM I, thus reflecting a more intense Al release mechanism.

The MgO content is a good tracer for estimating the respective quantities of clinker (estimated by CEM I) and slag from the CEM III used. Thus, considering the leaching coefficient of Mg (LC Mg Table 5), the value of y (clinker content estimated by CEM I) obtained with equation 2 is 27 %. The same value calculated from the leaching coefficient of Si is 30 %. These values of y are well within the range of 20 to 34 %. Furthermore, the composition of CEM III estimated with the chemical compositions of Table 1 gives a value of y equal to 31 % CEM I and 69 % slag, which is a possible composition for a CEM III/B. There is thus an acceptable consistency of these results in view of the approximations made.

If we consider the value y = 31 % in equation 2, the values of LC Ca, LC Si, LC Al and LC Mg are 25.5, 9.3, 0.9 and 2.1 % respectively (Table 5). Thus, Ca is released much more than expected (experimental LC Ca was 32.4 %), Al is released to a lesser extent, and Si and Mg show the expected behaviour (Table 5). The higher Ca release could be due to a higher contribution from the cement paste, indicating higher leaching in the case of CEM III compared to CEM I. This may be the consequence of the smaller amount of clinker and therefore of hydrated cement paste in the CEM III sample, which is nevertheless subject to leaching of similar intensity. This hypothesis is also compatible with an acceleration of Al release. A different reactivity of the residual slag anhydride due

485 to the co-grinding could be another explanation. The slag in CEM III cement is probably finer than the
486 leaching anhydrous slag, and is thus more reactive, i.e. it is more hydrated (more paste available than
487 in the theoretical 70-30 superposition). There are therefore more hydrated phases potentially
488 available for leaching. In addition, if the residual anhydrous slag were to react a little (as the leaching
489 results suggest), their reactivity would be stronger, due to the fineness of the grains.

490 In the case of CEM I and CEM III cement pastes, the leaching coefficient increases very strongly
491 during the first two leachings, then increases much more slowly and almost identically for all other
492 renewals (Figure 9). Thus, it is only after the majority of the calcium contained in the most soluble
493 phases has been leached that the leaching of the other chemical elements becomes significant
494 (Figure 10, Ca leaching coefficient of about 25 % for the leaching of CEM III paste at the second
495 renewal when added to the value of the first renewal). It is therefore imperative to reach a high
496 leaching coefficient to highlight the release of Al. In leaching tests on CEM I cementitious paste,
497 aluminium leaching is not immediate despite the large specific surface area of the crushed sample. A
498 latency time is observed before a higher aluminium leaching rate. At the beginning of the test, Al is
499 leached very little into solution because the Al-containing phases are less soluble than the other
500 phases present, particularly the portlandite. The contribution of these phases to Al leaching becomes
501 visible when their amount in the sample reaches a sufficiently high level, once the more soluble
502 phases have been partially or even completely dissolved. This corresponds to LC values of 50 and 30
503 for CEM I and CEM III respectively. The higher LC value for CEM I has to be related to the higher
504 amount of Ca in this cement compared to CEM III (Table 1) since part of the Ca is associated with the
505 most soluble phases. The Al enrichment of the solid during leaching is well demonstrated by the
506 evolution of the chemical composition of the solid measured by EDS. In the case of the CEM III
507 cementitious paste, this behaviour persists but the latency time is less marked, certainly because of
508 the contribution to leaching of the hydrated slag on its surface, which is present from the beginning
509 of leaching. No latency time is observed for the leaching of Al during the leaching of anhydrous slag
510 (Figure 4).

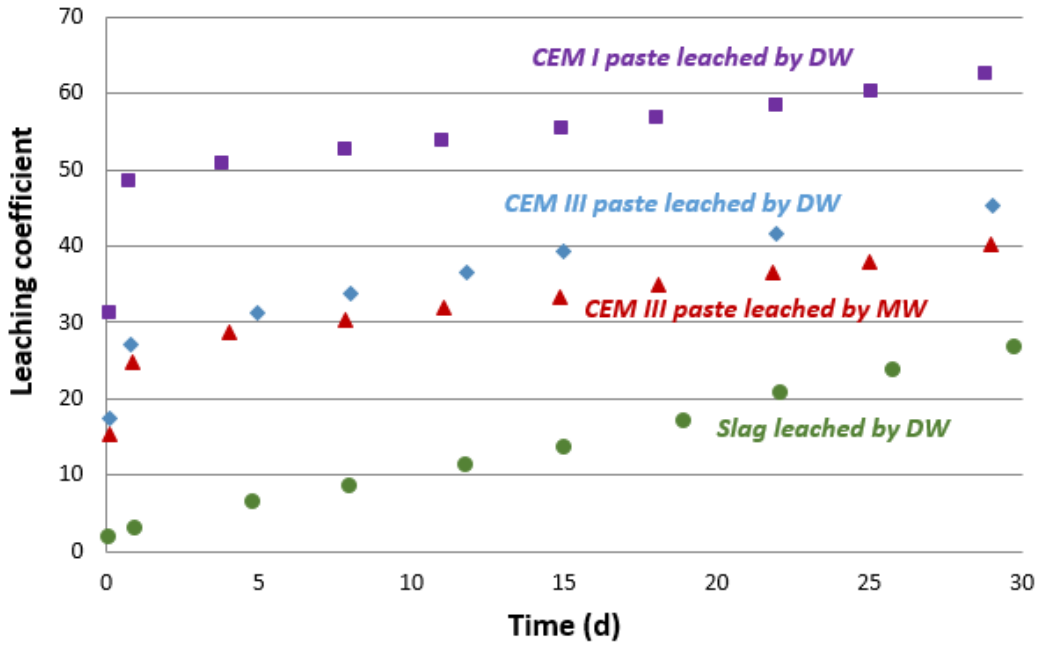
511 The use of a crushed sample in a smaller quantity than the monolithic sample allows a high leaching
512 coefficient to be obtained quickly and thus reduces the latency time before the leaching of Al is
513 observed. The use of a leaching solution having an acidic pH is another way of reducing the latency
514 time for monolithic samples because, apart from AH_3, the solubility of Al-containing phases increases
515 at lower and lower pH values. Thus, an LC Al of 1.46 is obtained for a CEM I cement-based mortar
516 monolith leached at a constant pH of 2 [45]. This LC Al value is comparable to that obtained for the
517 CEM III but lower: 26.46 instead of the 45.2 obtained in this study. This highlights the increase in the
518 amount of Al leached (as well as the other elements) compared to the amount of Ca leached when

519 the environment is more acidic. The origin of this behaviour is certainly associated with the solubility
520 increase of the Al-containing phases when the pH of the leaching solution decreases. Thus, the LC
521 value necessary to obtain a sizeable release of Al decreases with decreasing pH.

522 These results show that leaching tests leading to low LC only partially describe the mechanism of Al
523 leaching from a cement paste and underestimate leaching. In the case of a CEM I cement paste
524 leached at a constant pH of 7, very little Al is leached in a first step until an LC of 50 for CEM I is
525 reached. This value is 30 for a CEM III paste. This first step can be very long since leaching 50% of a
526 monolithic sample can take a very long time. Nevertheless, once this LC value is exceeded, the
527 release of Al will become much more noteworthy during a second step, which lasts until the phases
528 containing Al have disappeared. In the case of a CEM III paste leached under the same conditions, the
529 contribution of the partially hydrated slag on its surface will be added to the contribution of the
530 cement paste, which can be assimilated to a CEM I paste as a first approximation. Moreover, the
531 presence of slag leads to a lower quantity of Ca in the CEM III. Thus, the Al leaching mechanism for a
532 CEM III paste at pH 7 can be considered to take place in 3 stages. Slag would be the largest
533 contributor to Al leaching for the first and third stages, where LC is less than 30 or very high -
534 corresponding to the total leaching of Al from the cement paste, which then contains only Si,
535 certainly in the form of silica gel with slag certainly still present. In the second step, the main
536 contributor would be the cement paste.

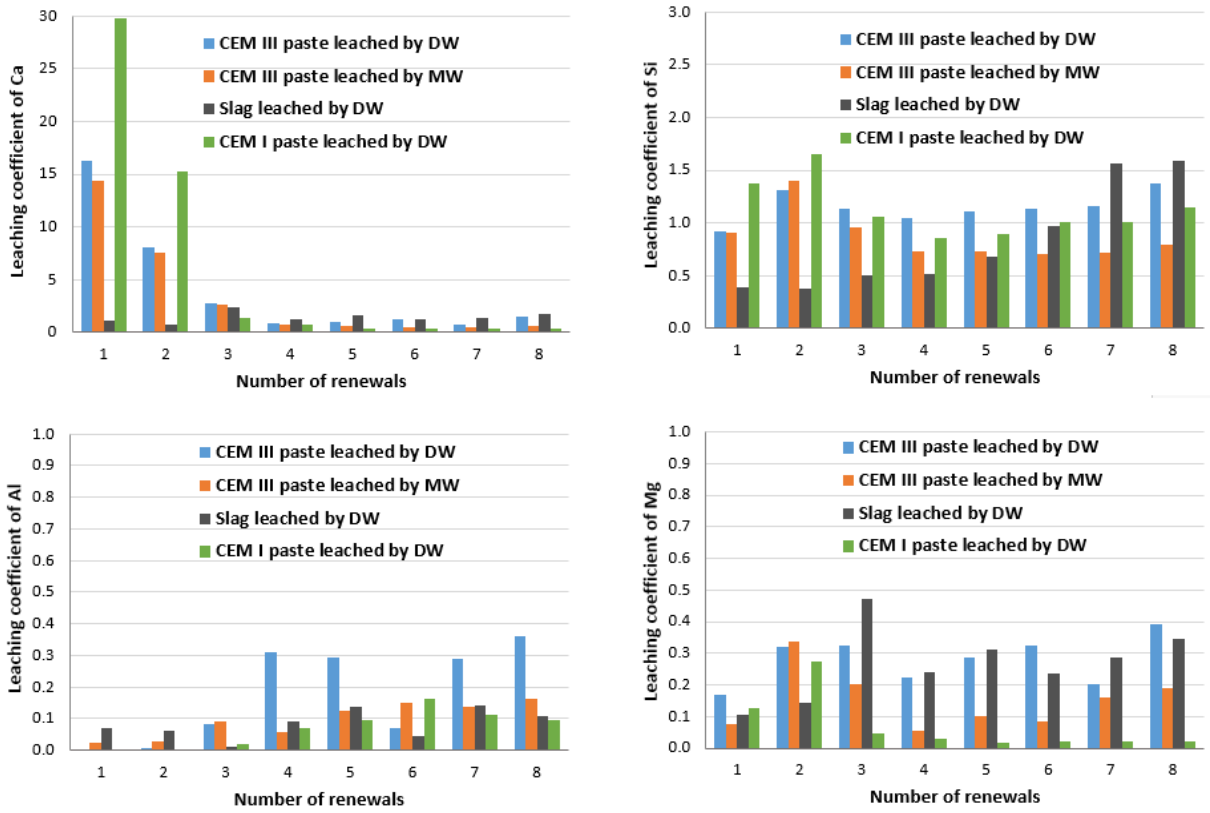
537 However, this Al leaching mechanism must be viewed in the context of a cementitious material used
538 in a drinking water supply pipe. On the one hand, obtaining an LC greater than 30 certainly requires
539 very long exposure times, especially considering the low diffusion coefficient of a CEM III paste and
540 the presence of mineralised water. Practice shows that, in most cases, the very dense microstructure
541 of the CEM III-based cementitious material covering the inside of a cast iron pipe [50] will strongly
542 reduce the leaching kinetics by slowing down diffusion and promoting the formation of a dense layer
543 of mineral phases blocking the porosity [51], especially in the presence of mineralised water. On the
544 other hand, if LC values above 30 were reached, these would certainly be associated with a loss of
545 physical integrity of the cementitious material, leading to a loss of material transported by the water
546 flow, which may lead to other release mechanisms.

547



548

549 *Figure 3 : Leaching coefficients for tests carried out on crushed CEM III cementitious paste leached by*
550 *demineralised water and mineralised water according to time*



551

552 *Figure 10: Leaching coefficients for Ca, Si, Al and Mg for each leachate renewal, obtained during tests*
553 *of CEM III cementitious paste leaching with demineralised water and mineralised water, and also for*
554 *slag and CEM I cementitious paste leached with demineralised water*

5. Conclusion

Tests conducted on crushed CEM III pastes maintained at pH 7, in the low pH range of potable water in accordance with the European directive UE 98/83/CE, led to a very high leaching coefficient approaching 50 %. However, despite this high leaching, the amount of Al leached remained very low, i.e. less than 1.5 % of the initial amount of Al in the material. In these experiments, the hydrated slag on the surface, which was rich in Al, tended to release its Al continuously over time, but with slower kinetics than the crushed cement paste. The cement paste released very little Al before the majority of the Ca contained in the most soluble phases had been leached. Then its leaching made a more significant contribution than that of the slag. When the cement paste was almost completely leached, its contribution again became smaller. The leaching of Al from a crushed CEM III paste maintained at pH 7 thus involves 3 steps: (i) a first stage during which the leaching of Al is very slow (LC Al < 0. 1 %) and mainly concerns the slag as long as the LC remains below 30 % (value associated with the experimental protocol), (ii) a second stage of significant leaching where the majority contribution comes from the cement paste until its Al is totally consumed, and (iii) a third and final stage (very high LC) during which the leaching of Al is governed by the residual slag and only Si remains present in the cement paste. Thus, a cementitious material that contains a larger amount of Al will not necessarily lead to higher leaching kinetics even if the total amount of Al likely to be leached is initially greater.

Despite the use of a crushed material and a high water/material ratio in the leaching tests, the leaching coefficient of Al remains very low here (around 1.4 %). Obtaining a higher leaching coefficient for Al would require a very high number of solution renewals, which is very difficult to achieve experimentally, either on crushed samples or on monoliths. In addition, the impact of the material microstructure on leaching kinetics is greatly reduced with crushed material. The very dense microstructure of a cementitious material based on CEM III will strongly reduce the leaching kinetics by slowing down diffusion and by promoting the formation of a dense layer of mineral phases blocking the porosity in the presence of mineralised water. It is therefore very difficult to perform leaching tests to obtain a high leaching coefficient for Al. Reactive transport modelling would certainly provide additional information on the leaching mechanism if the effect of the microstructure, which is essential to estimate the time needed to reach a given LC value, were associated with it. Further stages of the study consisted in exposing slag cement-based monolithic mortars to leaching tests under close-to-real conditions in order to assess the range of aluminum concentration in the leachate in relation to regulatory limits.

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